SPECIATION OF CHROMIUM IN SOILS BY SPECTROMETRIC METHODS

By

Naveed Zafar Ali

DEPARTMENT OF CHEMISTRY
QUAID-I-AZAM UNIVERSITY
ISLAMABAD
JANUARY 2003

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A dissertation submitted to the Department of Chemistry, Quaid-I-Azam University, Islamabad, in the partial fulfillment of the requirement for the degree of

MASTER OF PHILOSOPHY
IN
INORGANIC/ANALYTICAL CHEMISTRY
BY

NAVEED ZAFAR ALI

UNDER THE SUPERVISION OF
DR. M. JAFFAR

DEPARTMENT OF CHEMISTRY
QUAID-I-AZAM UNIVERSITY
ISLAMABAD
JANUARY 2003

DEDICATED TO

MY ADORABLE FATHER

WALI UR REHMAN

Who gave me the sheen of confidence and encouraged me to achieve success in every sphere of life and led me to the destination.

DECLARATION

This is to certify that this dissertation submitted by *Naveed Zafar Ali* *is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, as satisfying the dissertation requirements for the degree of Master of Philosophy in Analytical/Inorganic Chemistry.*

Prof.Dr.M.Jaffar
Supervisor
Department of Chemistry,
Quaid-i-Azam University,
Islamabad.

Prof.Dr.A.Y.Khan
Chairman
Department of Chemistry,
Quaid-i-Azam University,
Islamabad.

External Examiner

ACKNOWLEDGEMENT

All commendations to Almighty ***Allah****, who imparted me resoluteness and fortitude for the accomplishment of this dissertation successfully. I pay my tribute to the* ***Holy Prophet Muhammad*** *(Exalted is He), who is forever a torch of guidance and knowledge for humanity.*

I offer my gratitude to ***Prof.Dr.A.Y.Khan****, Chairman, Department of Chemistry, for providing access to facilities that ensured successful completion of this work. I am also grateful to all the respected teachers of the department for their exemplary attitude and valuable technical advices.*

I am indebted to my supervisor, ***Prof.Dr.M.Jaffar****, for his supervision, guidance, and suggestions at all stage, during the completion of this work.*

I express my special thanks to all my amicable friends and class-fellows for their discussions, comments and collaboration, especially to members of ***AAS*** *research group for the congenial atmosphere of cooperation and mutual support. I cannot forget the contribution of my parents whose endless prayers and continuous moral support enabled me to attain the targets of my entire academic career. I am extremely indebted to my loving and venerable brothers,* ***Mr.Asif Ur Rehman*** *and* ***Mr.Mujeeb Ur Rehman****, whose constant encouragement and endless prayers ever remained with me throughout the period of my academic journey.*

(Naveed Zafar Ali)

ABSTRACT

The speciation of chromium was done in thirty two soil samples procured from areas in close vicinity of tanneries in Punjab as well as from background suburbs of Rawalpindi and Islamabad, the latter being considered as typical background samples, while the former as typical chromium-contaminated samples. Total chromium in the samples was estimated by the atomic absorption method using the HCl-based wet digestion procedure and the Cr(VI) by the DPC complexation based spectrometric method, employing 540.0 nm λ_{max} *line. The difference between the two levels yielded the trivalent chromium content of given sample. The relationship between chromium speciation and relevant physical parameters of the soils, such as moisture and water related* $pH(pH_w)$ *were also studied. The moisture content in the soil samples varied between 0.81%(w/w) and 13.50%(w/w) in soil samples taken from Samrial, Sialkot and G-6/1-4, Islamabad, respectively. The* pH_w *values also showed quite divergent levels with the minimum at 7.28 in the soil sample of the Sialkot and the maximum at 11.24 for a soil sample from Lahore. For background soil samples, however, the* pH_w *values showed consistently close values falling between 8.11 to 8.95. The results of the study showed no correlation between* pH_w *and the moisture content. The estimated levels of total chromium ranged from a minimum of 32.18 mg/kg to a maximum of 310.12 mg/kg in soil samples affected by tanneries taken from Niaz Nagar, Kasur and Samrial, Sialkot respectively, showing and almost ten-fold enhanced level of the metal in the tannery affected area. The background soil samples from Rawalpindi and Islamabad were found to contain the minimum Cr(VI) levels running from 27.24 to 46.00 mg/kg. The study showed that in case of soil samples from close to the work place the Cr(VI) levels are substantially higher reaching to a peak value of about 230 mg/kg. On the whole, the hexavalent chromium content of these soils remained three-fold to seven-fold in case of effluent contaminated soil. For the background soils the Cr(VI) to Cr(III) ratio was found to be between 1-2, but in contrast this ratio went high by four-fold in case of the contaminated soils. The study thus evidenced enhanced levels of Cr(VI) in local tannery effluent contaminated soils, a situation that requires strict effluent quality control and it's implementation.*

CHAPTER 1

INTRODUCTION

1.1 CHROMIUM-AN OVERVIEW

Chromium occurs principally as the mineral chromite, having the composition $FeCr_2O_4$. This composition has been found in nature only in meteorites, and the natural mineral is usually of the formula $(Fe,Mg)(Cr,Al,Fe)_2O_4$ with lesser replacement of the divalent elements by manganese. The lattice may also contain some excess of the tervalent elements. The various chromites form the only commercial source of the element. The gems ruby and emerald owe their color to small quantities of chromium. In spite of the large number of chromium minerals known, chromite occurs characteristically in ultrabasic rocks such as pyroxenites or peridotites. Chromium ranks twentieth in abundance in the earth's crust. Chromium was discovered in 1797,by Vauquelin, in Siberian mineral (crocoisite), and was named after the beautiful colours which characterizes it's compounds. Vauquelin succeeded in reducing the oxide to metal by reduction with carbon.

$$FeCr_2O_4 + 4C \longrightarrow 4CO + Fe + 2Cr$$

The inertness of the principal mineral chromite makes it unlikely that large quantities of chromium will be found in other natural materials. Chromium is rare in natural waters which may contain 0.04 ppm. Cr.Traces of chromium occurs in plants; it is not definitely established whether the chromium plays any part in plant economy generally, although sugar cane, cotton and cucurbits are evidently benefited by the presence of chromium. Conversely, adverse effects have been ascribed to the presence of chromium. Chromium does not appear to play a useful part in human and animal chemistry. Traces are present in various organs and in excreta; the amounts are increased in the case of workers manufacturing chromium compounds. In normal soil and in infertile, high chromium soils the chromium contents found to be 0.017% to 3.4%

respectively. Chromium is an essential ingredient of many yellow, orange, red and green pigments. In general the chromium content, which may range from a trace in tints to 68.4% in pure chromic oxide, is less important than the physical qualities of the pigment.

Chrome-tanned leathers contain appreciable quantities of chromium, from 3.5 to 6% Cr_2O_3 on the basis of the hide substance. Again, however, the chromium content is not usually specified by the purchaser of leather, although chromium determinations have played an important part in tanning research. Many formulations for plating and finishing metals contains chromium compound usually a dichromate or chromium (VI) oxide. The conversion coatings formed also frequently contain chromium, and their corrosion-resisting properties depend on this fact. Industrial circulation-water systems frequently contain a regulated amount of chromate's (from 50 to 3000 ppm. of Na_2CrO_4) to inhibit corrosion. Nearly all inorganic preservatives used in the treating of wood to combat fire, decay, and termites contain chromium. The chromium is present in the treated wood to the extent of 0.15 to 0.7% Cr. In the textile industry, dichromates are used for mordanting of wool, dyeing nylon and wool. Chromium also is used to impart color to glass, ceramics, roofing granules, and similar products, and may be present in amounts between 0.1 and 5% Cr_2O_3.

1.2 PROPERTIES OF CHROMIUM AND ITS COMPOUNDS

Physical and Chemical properties.

Chromium (atomic number 24, relative atomic mass 51.996) occurs in each of the oxidation states from –2 to +6, but only the 0 (elemental), +2, +3, and +6 states are common. Divalent chromium is unstable in most compounds, as it is easily oxidized to the trivalent form by air. Only the trivalent and hexavalent oxidation states are important for human health. It is of great importance to realize that these two oxidation states have very different properties and biological effects on living organisms, including man. Therefore, they must always be examined separately: a valid generalization of the biological effects of chromium as an element cannot be made. The relation between the hexavalent and trivalent states of chromium is described by the equation:

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \xrightarrow{\hspace{3em}} 2Cr(III) + 7H_2O + 1.33v$$

The difference electric potential between these two states reflects the strong oxidizing properties of hexavalent chromium and the substantial energy needed to oxidize the trivalent to the hexavalent form. For practical purposes, it can be stated that this oxidation never occurs in biological systems. The reduction of hexavalent chromium occurs spontaneously in the organism, unless present in an insoluble form. A gradual reduction of hexavalent chromium to the trivalent state is demonstrated by the colour change of the conventional chromate cleaning solution in the laboratory from bright orange to green, in the presence of organic matter. In blood, chromate is reduced to the trivalent state, once it has penetrated the red cell membrane and becomes bound to the haemoglobin and other constituents of the cell and therefore unable to leave the cell again. As a rule, its coordination number is 6, the complexes being generally octahedral.

A large number of complexes and chelates of chromium have been investigated, ranging from simple hexa- or tetra-aquo complexes to those with organic acids, vitamins, amino acids and others. The rate of ligand exchange of chromium complexes is slow in comparison with other transition elements, with the exception of the even slower rate of cobalt complexes; most of the Cr(III)-complexes are kinetically stable in solution. This property adds to the relative inertness of trivalent compounds, in addition to the electrochemical stability of the trivalent state. However, at near neutral or alkaline pH, the milieu of the animal organism, the simple chromium compounds to which the organism is exposed in the environment or through supplementation, rapidly become insoluble, because hydroxyl ions replace the coordinated water molecules from the metal and form bridges, linking the chromium atoms into very large, insoluble complexes. Coordination of trivalent chromium to biological ligands is the prerequisite for its solubility at physiological pH and therefore for its biological function and for its availability for intestinal absorption.

Common chromium compounds

Poorly soluble “sandwich complexes” of metallic chromium (oxidation state =0) are known, e.g., $Cr(C_6H_6)_2$; these have little practical application. Divalent compounds, such as chromium (II) chloride ($CrCI_2$) are used as strong reducing agents in the laboratory, but have little industrial use. Of the many hundreds of trivalent chromium compounds known, chromic oxide ($Cr_2 O_3.nH_20$), is used as a pigment in paints and as a faecal marker in digestive studies. It dissolves in acids and forms the hexa-aquo or tetra-aquo complex, e.g.,

$$Cr_2 O_3.9H_{2}0 + 6HCl \longrightarrow 2[Cr\ (H_{2}0)_6]\ Cl_3$$

Violet Color

$$\longrightarrow 2[Cr\ (H_{2}0)_4Cl_2]\ Cl + 4H_2O$$

Dark Green Color

Chromium chloride $[Cr(H_{2}0)_6]Cl_3$ or $[Cr(H_{2}0)_4Cl_2]Cl$ is used in basic solution for leather tanning. The fluoride is used industrially in printing and dyeing, and chromium sulfates and nitrates are used as colouring and printing dyes.

The earth's most important deposits of chromium are in either the elemental or the trivalent oxidation state. Hexavalent compounds of chromium in the biosphere are predominantly man-made, and experience with hexavalent chromium is relatively short. Chromates and dichromates are produced from chromite ore by roasting in the presence of soda ash. From these, chromium (VI) oxide, (CrO_3), is precipitated out by the addition of sulfuric acid. Sodium and potassium dichromates are widely used industrially as sources of other chromium compounds, particularly of chromium (VI)oxide, and these processes are a major source of hexavalent chromium pollution.

The physical properties of chromium and its compounds are of secondary analytical importance. However, a brief summary of some of the more important properties of the element and principal compounds may prove useful. Because chromium is a transition element, it may have compounds in which any number of the readily dissociable 3d and 4s electrons are used; thus it may have an electrovalence of from zero to +6. Only a few of these compounds are important analytically; in most of these chromium has a valence of +3 or +6. Chromium also forms peroxy compounds having formulas such as Na_3CrO_8,$CrO_4.3NH_3$, and CrO_5. These compounds are varied in color and are unstable except at low temperatures. For this reason little is known of the valence of chromium in these compounds or of their physical properties, although valences of +5 and +6 seem most likely.

1.2-1 Electrochemical Properties

The following standard potentials involving chromium have been published.

Sr.#	**Electrode Reaction**	**E° , v**
1.	$Cr(OH)_3+3\bar{e}\square\ Cr+3OH^{-}$	-1.3
2.	$CrO_2^{-}+2H_2O+3\bar{e}\ \square\ Cr+4OH^{-}$	-1.2
3.	$Cr^{+2}+2\bar{e}\ \square\ Cr$	-0.91
4.	$Cr^{+3}+3\bar{e}\square Cr$	-0.74
5.	$Cr_2O_7^{-2}+14H^{-}+6\bar{e}\ \square\ 2Cr^{+3}+7H_2O$	+1.33

Because of the complexity of ions formed by chromium, there is little information on transference numbers and specific ion conductance. Conductometric methods are used more for study of ion species than for analysis of chromium compounds.

1.2-2 Optical Properties

1. Infrared Absorption

There are limited references to the infrared absorption of chromium compounds. A compilation of inorganic salt spectra lists values and absorption curves for $CrPO_4.H_2O$,$KCr(SO_4)_2.12H_2O$,$(NH_4)_2CrO_4$,Na_2CrO_4,K_2CrO_4,$MgCrO_4.7H_2O$,$K_2Cr_2O_7$, $CaCr_2O_7.3H_2O$, and $CuCr_2O_7.2H_2O$. The curves for chromates and dichromates show strong resemblances: a sharp, strong absorbance in the 3.6-μ, region, a weak , sharp pair of absorbances on each side of 7-μ and a strong absorption in the 12-μ, region. In addition, some dichromates show a characteristic doublet at 11-μ. Spectra of various chromic complexes have been examined and the results interpreted in terms of structure. The liquid chromyl compounds CrO_2CI_2, CrO_2FCI, and $CrO_2(NO_3)_2$ have been studied in the gas phase. The characteristic absorption is at 10μ. The halides have a simple spectrum, but that of the nitrate is complex . In addition, the infrared and Raman spectra of liquid chromyl chloride have been measured.

2. Absorption in the visible range

As has been noted, virtually all chromium compounds are strongly colored. The color of chromates is detectable at 1 ppm., and this is a convenient way of determining Cr^{+6} in the absence of other colored materials. Care must be taken to adjust the pH so that only single ion species is present, otherwise it will be found that the solutions do not obey Beer's Law. Usually this is done by converting the solution to chromate at pH 9, where it may be shown that CrO_4^{-2} is virtually the only ion present. Under these conditions, maximum absorption is obtained at 366 mμ. The maximum absorption for dichromate is at 525 and 545 mμ. Measurements should be made near this maximum to obtain Beer's Law linearity; for chromate, the variation is then less than 1% up to 10% concentration.

Chromic ion also may be measured colorimetrically, but care must be taken that conditions are identical in all measurements because of the large number of ion species. In acid solution the absorption peak is at 580mμ. Trivalent chromium may be converted to a violet trioxalate complex that may be read at 420 or 560mμ.

Other methods depend on colored complex or oxidation products formed with organic reagents. The most important of these is with s-diphenyl carbazide, which has maximum absorption at 540mμ. This reaction is very sensitive, having a molar extinction coefficient, based on dichromate ion, of 3.14 X 10^4 at 540mμ. Other workers give 2.60 to 4.17 X 10^4. This color reaction is the best for traces of chromium; only iron, vanadium, molybdenum, and mercury give interferences. Other color reactions adaptable to visual absorption measurements are with sodium 1,8-dihydroxynaphthalene-3,6-disulfonate, benzidine, diphenylamine, Serichrome Blue R, and aniline .

3 Ultraviolet Absorption.

Since chromium is commonly determined in aqueous solution and possesses so many color reactions, there is little need for study of absorption in the ultraviolet, and no data are available on methods based on such absorption.

4 Emission Spectroscopy

Chromium emits a number of lines and it can be determined readily on the spectrograph. Arc lines at 425.4 mμ. are sensitive. Flame photometry also is feasible, using the band at 357.9 mμ.

5 X-ray Spectroscopy

Chromium compounds can be characterized readily by x-ray diffraction, and excellent results can be obtained using x-ray fluorescence analysis in determining chromium content of metals and ores.

6 Polarized Light

Chromium complexes can exist in d- and l-forms, and these can rotate the plane of polarized light. The molar rotations are height and vary greatly with temperature. No analytical use has been reported for this property to date, although it is of obvious use in studies of racemization and resolution of complex ions.

1.2-3 Chromium Compounds As Analytical Standards, Reagents, & Indicators.

There is an extensive use of chromium compounds in the analytical laboratory as reagents, indicators, and standards, and a brief discussion of their use in this way appears pertinent. The principal materials used in this manner are potassium dichromate, chromous salts, and potassium chromate; of these, the first is by far the most important.

1.2.4 Metallurgy

The largest use of chromium is in the metallurgical field. Chromium ores frequently are classed according to their end use as metallurgical, refractory, or chemical ores. High – grade metallurgical chrome ore should contain at least 48% $Cr_2 O_3$ mμ and have a Cr:Fe weight ratio of 3:1 or more. It also is desirable that the percentage of $A1_2O_3$ exceeds that of MgO. To achieve this, ores frequently are blended before use.

The chrome ore is reduced in a submerged-arc furnace to produce ferrochome. This alloy is made in a wide variety of grades, with different carbon and silicon contents. While at least one process yields chromium alloys, such as stainless steels, directly from the ore, in general ferrochrome is the preferred material for the addition of chromium to ferrous alloys. About 60% of the metallurgical use of chromium is in the stainless steels, 20% in low-alloy steels, 10% in high temperature alloys, and 10% in high-speed steels. Manufacture of chromium as the pure metal involves first the preparation of a chromium chemical, although in the electrowinning of chromium the electrolyte is prepared from ferrochrome.

1.2.5 Chemicals

About 15% of the consumption of chromium is used in the production of chromium chemicals. So-called “chemical” ore from the Transvaal is almost exclusively used, and the primary chemical manufactured is sodium dichromate.

This chemical is produced by sintering chrome ore in rotary kilns with sodium carbonate and lime or leached residues, and then leaching the sinter to yield a sodium chromate solution, which is then acidified with sulfuric acid to produce sodium dichromate solution and sodium sulfate by-product. The sodium dichromate solution is concentrated and crystallized as the dihydrate, $Na_2Cr_2O_7.2H_2O$.From sodium dichromate are manufactured sodium chromate, potassium dichromate, chromium (VI) oxide ("chromic acid"), chromic sulfates of various compositions, and a variety of less important chromium compounds. About 25% of the production are used in the manufacture of chrome pigments, such as chrome yellow, chrome green, chromic oxide green, and molybdate orange. A further 35% is consumed by the metal finishing industry in such uses as chromium plating, brass pickling, anodizing, conversion coating, and as a corrosion inhibitor, Twenty per cent is used in the tanning of leather and about 5% in the textile industry in mordanting of dyes. The remainder is consumed in smaller uses, such as the manufacture of catalysts, wood preservation, and the manufacture of dyes and organic chemicals, or is sold outside the United States or through distributors from whom the end use cannot be traced.

The sampling of commercial chemicals has been vastly simplified by the gradual disappearance of large crystals from the scene. The granular products now encountered are quite uniform and present no major sampling problems. Many commercial chromium chemicals such as "chromic acid" and sodium dichromate are deliquescent; therefore, samples from a large container should be obtained rapidly, using a thief, rather than by pro-longed coning and quartering. For the various determinations, a sufficiently large sample should be taken to allow for segregation and nonuniformity, using aliquots if needed.

1.3 SAMPLING OF PRINCIPAL CHROMIUM CONTAINING MATERIALS

It is axiomatic that no analysis of a large quantity of material can be any better than the sample taken. The usual sampling techniques apply with force to chromium-containing materials.

1.3.1 Ores

Chromite ores vary in sampling difficulty with their source. Some ores are essentially pure chromite mineral; others are composed of particles of chromite interspersed with or disseminated in relatively barren gangue. There also is wide variation in particle size. As a result of long experience between buyers and sellers of ore, procedures have been evolved that are mutually satisfactory and that reduce sampling errors to the same order of magnitude as observed in the chemical analysis. Care is of course taken that the original 3000-Ib bulk sample reflects the cargo in ratio of fines to lump, and in ore quality. After the 23-Ib. sample is delivered to the laboratory, it is dried and run through a disc pulverizer with alloy plates to produce a sample pulp that can pass completely through 100-mesh and 50 to 75% through 200-mesh screens.
If moisture samples are required, they are obtained quickly from the bulk sample and sealed.

1.3.2 Solution Procedures

Perchloric acid is the principal reagent used for the attack of chromium containing materials that do not respond to simple acid solution. Chrome ores may be slowly but completely dissolved by digestion in boiling perchloric acid; the action may be accelerated by the use of sulfuric or phosphoric acids, but at the risk of producing insoluble chromic sulfates or complicating the subsequent analysis for alkaline earths. Perchloric phosphoric acid mixtures are recommended for the determination of chromium in stainless steels and similar alloys.

The action of perchloric acid depends on the oxidation of chromium to chromium (VI). The oxidation is nearly quantitative in hot solution (fumes of $HClO_4$); in the cold solution, the chromium (VI) oxide separates out nearly quantitatively as CrO_3 crystals. At intermediate temperatures, however, some reduction of Cr(VI) takes place, possibly due to the formation and decomposition of peroxide like compounds. Therefore, the perchloric acid solution, after dilution, cannot be relied on to have all the chromium in the sexivalent condition. With substantial amounts of Cr, the oxidation may be sufficient for routine use; with microgram amounts, the method is completely unsatisfactory. If silver ion is present, the results are more nearly quantitative. If chloride or fluoride ions are present in the sample, there is risk of loss of Cr as CrO_2CI_2 or CrO_2F_2. This loss has been recovered by the use of a condenser .

The usual precautions in the use of perchloric acid must be observed. Sulfides and other reducing ores should receive a preliminary attack with nitric acid. Perchloric acid also does attack many silicates; the silicate residue from a perchloric acid digestion always should be treated with hydrofluoric and sulfuric acids, and any residue returned to the analysis. Many ferrochromes do not dissolve easily in acids, and fusion procedures are preferred.

1.4 DETECTION AND IDENTIFICATION OF CHROMIUM COMPOUNDS

1.4.1 Precipitation Reactions

The principal reactions used involve the precipitation of slightly soluble chromates, especially those of barium and lead, both of which precipitate in weakly acid solution. Barium chromate is pale lemon yellow in color. A definite precipitate forms at 30 ppm. of chromate, but a haze is detectable at 4 ppm.; the reaction is thus somewhat less sensitive than the color of chromate ion itself, but it may be useful to determine whether a yellow color is due to chromate. Sulfate, and larger amounts of oxalate and fluoride, interfere. Lead chromate is a much deeper yellow in color, and its precipitation is noticeable at 4 ppm, with turbidity detectable at 0.5 ppm. of CrO_4^{-2} . Its precipitation is thus quite a sensitive reaction. Sulfate and large quantities of fluoride interfere.

There are no sensitive precipitation reactions of trivalent chromium, and those reported are not specific. Precipitation of the hydrous oxide is noticeable as a green to violet precipitate at 30 ppm. of Cr^{+3}, but a haze or floc unidentifiable as to color can be detected at 8 ppm. Phosphate ion at neutral or faintly acid pH forms a green precipitate of similar sensitivity.

Under the microscope, the formation of characteristic crystals of silver chromate, lead chromate, or cesium chromium sulfate are employed to detect the presence of chromium in a solution. The gray – violet octahedral of the cesium chromium alum are slow to form but are characteristic of the presence of chromium(III) ion. By fusion of a soluble chromium(III) salt in 8-hydroxyquinoline, the chromium(III) is converted into characteristic bluntly terminated needles on the hot stage.

1.4.2 Colour Reactions

A Large number of color reactions have been proposed for the detection of chromium. Many of the organic reagents suggested give a color reaction with chromium(VI) because of the oxidizing characteristics of the chromate ion. The reaction is thus not specific for chromium. Still other organic reagents, of which alizarin is a common example, give chromium lakes in the presence of chromium(III) ions. Since many other elements, notably aluminum, form such lakes, the test is not particularly helpful unless the chromium lake happens to possess a characteristic color. The important methods of detection are those based on chromium compounds themselves. In the first place, the existence of a colorless solid or solution is reasonable assurance of absence of large amounts of chromium. The only colorless chromium compound is the carbony1, $Cr(CO)_6$. Chromium (VI) as the chromate may be detected visually in a 50-ml. Nessler tube at about 1 ppm. of chromium. The color of chromium(II) is comparable to that of chromium(III).

The outstanding color reaction is that of chromium (VI) with s-dipheny1 carbazide (1,5-dipheny1 carbohydrazide) in acid solution, giving a distinctive red-violet color that is detectable at 0.01 ppm. of Cr, provided freshly prepared reagent is used, or stable reagent is prepared. The color has maximum absorption at 540 mμ and the best color stability is at about 0.2N acidity, preferably as sulfuric acid. The mechanism of the color formation is not unequivocally established, but apparently a Cr(III) complex of dipheny1 carbazone forms. This cannot be obtained directly but can be formed by reduction of Cr(VI) by dipheny1 carbazide or by oxidation of Cr(II) in the presence of dipheny1 carbazone. If Cr(VI) is present in excess, the dipheny1 carbazide color will be further oxidized and destroyed.

In many cases, the yellow color of the chromate ion in alkaline solution suffices for detection. As noted above, the test is sensitive (1 ppm. of chromium) and it is also quite specific. Maximum absorption is at 370 nm. Whereas iron, cerium, vanadium, and uranium all yield yellow colors in oxidized acid solution, only uranium interferes in alkaline solution, since cerium and iron usually precipitate and the monovanadate ion is colorless. In the presence of silica, traces of iron may remain in colloidal solution and color the solution. Occasionally a faint color may be derived from filter paper or other organic materials. It is, therefore, well to confirm the test with dipheny1 carbazide.

In acid solution, hydrogen peroxide produces a violet-blue color with either chromic ion or chromate. The color is due to perchromic acid and can be extracted with ether or ethyl acetate. The sensitivity is of about the same order as that of the chromate ion color
(~2 ppm.). The color is transitory and is not suitable for quantitative measurement. Since the discovery of the diphenyl carbazide reaction, the perchromic acid test has been little used as a sensitive test or confirmation of chromium.

In alkaline solution, peroxide produces a transitory red color with chromate solution, forming the $(CrO_8)^{-3}$ ion. Chromotropic acid (1,8-dihydroxynaphthalene-3, 6-disulfonic acid), as a 1% solution of the sodium salt, gives a red color with chromium (VI) in acid solution, The reaction is capable of detecting 0.02 mg. of chromium. Ferric iron gives a green color, and vanadium and titanium give brown colors with this reagent.

1.4.3 Physical Methods

1 Emission Spectroscopy

Detection of 0.0001% chromium is possible using the 425.435nm. line. The sensitivity is estimated by some as 0.00001 mg., and others have claimed detection of 0.002 mg. in a 1-g. sample using the ultraviolet lines at 272.6, 278.0, 291.1, and 305.4nm. The triplet 357.87, 359.35, and 360.54nm. has a lower sensitivity, and may be obscured by the cyanogen band headed at 359.0nm. The line 302.15nm., (e.p. 5.13 v., intensity 300) is located in a frequently photographed region, although the iron lines at 302.06 and 302.10nm. may interfere if dispersion is insufficient. Detection of 0.002% chromium is possible with this line. The triplets 357.9, 359.4, and 360.5 and 425.4, 427.5, and 429.0nm. are useful in flame photometry.

Metal or alloy samples are used as fine drillings, small chips, flat disks, or rods. The counter electrode is graphite or metal. Sensitivity is about 0.005 to 0.01% chromium. A porous-cup electrode is used for liquid samples. From 0.2 to 0.3 ml. of sample is sufficient, with a detection of 1 to 10 ppm. possible. The quantitative techniques of a graphite disc rotating in a boat of liquid and the rotating platform are equally satisfactory. A cobalt internal standard has been recommended for this technique. A detection limit of approximately 10 mg/L can be attained by absorbing the liquid into a flat top electrode and using alternating current.

2 X-Ray Spectroscopy

As a result of excitation with a suitable source of x-radiation, materials containing chromium emit the characteristic radiation of the element in amounts proportional to the chromium content. A lithium fluoride crystal is suitable for diffraction of the emitted radiation, which is then measured with a scintillation or proportional counter. Under ideal conditions, as little as 50 ppm. of chromium can be detected, but in a routine qualitative examination for several elements. 0.05% may be the practical limit. The Cr K∝1 line is the most sensitive, at 0.2290nm; other wavelengths are κ∝2 0.230nm., and κβ 0.2085nm

3 Absorption Spectroscopy

The characteristic absorption bands in the visible and infrared, regions have been described for various chromium compounds and ions, measurement of absorption or identification of the bands is rarely used as a means of qualitative detection of the element or of identification of a specific compound.

1.5 TOXICOLOGY AND HYGIENE

Biological activity of chromium compound is generally considered to be concentrated in the hexavalent compounds of the element: the toxicity of soluble chromic salts is of a low order and the insoluble chromic oxide and phosphate are nontoxic. The acute oral toxicity of chromates to humans is apparently quite moderate. There is a reported instance of the use of drinking water containing 1 to 25 ppm. of chromate without ill effect. Toxicity tests on mice, rabbits, and fish also support this conclusion. However, fatalities have been reported from the ingestion by humans of quantities of the order of 10g. Chromate dusts are irritating and protection against them is desirable. Cr(VI) is highly toxic (MAC value 50μg/L only). Ulceration and perforation of the nasal system may result from exposure to mists or dusts containing hexavalent chromium. To protect against this hazard, a maximum allowable concentration of 0.1 mg. of CrO_3/ cubic meter of air has been set. Cuts and open wounds may fail to heal readily if contaminated with chromate. Ulcers may form, and consequently all open wounds should be protected from access of chromate.

A more than normal incidence of lung cancer has been noted among workers in plants where chromates have been produced for many years. It has not yet been established what class of compounds may be responsible. Close control of hygiene in modern plants is believed to have either eliminated this hazard or reduced it to a point of minor concern.

An occasional individual exhibits a typical allergic reaction to chromates and may show dermatitis as a result of working with these compounds. In this event, the affected individual should be removed from the contact with chromate, in which case the dermatitis usually is quickly relieved. To protect against these hazards, safety data sheets have been issued by the Manufacturing Chemists Association for the principal industrial compounds. Use of respirators, gloves, and goggles in handling bulk quantities is advised, as well as the usual recommendations for cleanliness. The kinetics of chromium depends on its oxidation state and the chemical and physical form within the oxidation state. Most of the daily chromium intake (50-200 μg) is ingested with food and is in the trivalent form. About 0.5 – 3% of the total intake of trivalent chromium is absorbed in the body. It is possible, but it has not yet been proved, that chromium in the form of some complexes, such as a dinicotinic-acid-complex, glucose tolerance factor, is better available for absorption. The gastrointestinal absorption of 3- 6% of the total intake of hexavalent chromium has been reported. Once absorbed, chromium is almost entirely excreted with the urine: the daily urinary-chromium loss of 0.5 – 1.5 μg is approximately equal to the amount absorbed from the average diet. However, dermal losses, losses by desquamation of intestinal cells and by perspiration have not been quantified. Ingested or injected chromium leaves that blood rapidly. Blood-chromium levels do not reflect the overall chromium content of tissues, except after a glucose load, which induces an immediate increase in the plasma- and urine-chromium levels of chromium-sufficient subjects. Trivalent chromium inhaled from the air is trapped in the lung tissues, if in the form of small particles within the respirable range. The chromium concentrations in lungs increase with age. Larger particles (greater than 5 μm), regardless of oxidation state, are moved to the larynx by ciliary action and become part of the dietary intake.

1.6 CHROMIUM SOURCES. ENVIRONMENTAL LEVELS & EXPOSURE

Chromium occurs ubiquitously in nature (< 0.1 $\mu g/m^3$ in air). Natural levels in uncontaminated waters range from fractions of 1 μg to a few μg/litre. The concentration of chromium in rocks varies from an average of 5 mg/kg (granitic rocks) to 1800 mg/kg (ultramafic/basic and serpentine rocks). The earth's most important deposits are either in the elemental or the trivalent oxidation state.

In most soils, chromium occurs in low concentrations (2-60 mg/kg), but values of up to 4 g/kg have been reported in some uncontaminated soils. Only a fraction of this chromium is available to plants. It is not known whether chromium is an essential nutrient for plants, but all plants contain the element (up to 0.19 mg/kg on a wet weight basis). Almost all the hexavalent chromium in the environment arises from human activities. It is derived from the industrial oxidation of mined chromium deposits and possibly from the combustion of fossil fuels, wood, paper, etc. In this oxidation state, chromium is relatively stable in air and pure water, but it is reduced to the trivalent state, when it comes into contact with organic matter in biota, soil, and water. There is an environmental cycle for chromium, from rocks and soils to water, biota, air, and back to the soil. However, a substantial amount (estimated at 6.7×10^6 kg per year) is diverted from this cycle by discharge into streams, and by runoff and dumping into the sea. The ultimate repository is ocean sediment.

Chromium compounds are used in ferrochrome production, electroplating, pigment production and tanning. These industries, the burning of fossil fuels, and water incinerations are sources of chromium in air and water. Most of the liquid effluent from the chromium industries is trapped and disposed of in land fills and sewage sledges, the chromium being in the form of the insoluble trivalent hydroxide.

In chromium ore mines, the concentration of chromium in dust ranges from 1.3 to 16.9 mg/m^3 . During the production of refined ferrochromium, the air in the work-place may contain large, amounts of dust (0.03 –3.2 mg/m^3). In chromium plating factories, concentrations of 1 µg/m^3 up to 1.4 mg/m^3 have been measured. In Portland cement from 9 European countries, the contents of chromium (VI), extractable with sodium sulfate, varied from 1 to 83 g/kg cement.

Today, it is generally accepted that only the zero-, di-, tri-, and hexavalent oxidation states have biological importance. The effects of the last 2 oxidation states are so fundamentally different that they must always be considered separately. The trivalent form is an essential nutrient for man. In amounts of l50-200 µg/day.

Chromium can be detected in all matter in concentration ranging from less than 0.1 µg/m3 in air to 4 g/kg in soils. Naturally occurring chromium is almost always present in the trivalent state: hexavalent chromium in the environment is almost totally derived from human activities.

1.6.1. Soils

The weathering of rocks produces chromium complexes that are almost exclusively in the trivalent state. In most soils, chromium complexes that chromium occurs in low concentrations; an average of 863 soil samples from the USA contained 53 mg/kg . The highest concentrations, as high as 3.5 g/kg are always found in serpentine soils. In a small area in Maryland, USA, with soil infertility, the chromium concentration (as Cr_2O_3) was as high as 27.4 g/kg. Conversely, low chromium concentrations (10 –40 mg/kg) have been detected in soils derived from granite or sandstone. Only a fraction of the chromium in soil is available to the plant; thus, it is important to determine "available" soil-chromium. A rough approximation of this available chromium fraction can be made by extracting soil with acids or chelating agents and by measuring the chromium in the extract. Though the amount of extractable chromium is not identical with that truly available to the plant, it is a much better measure of availability than the total chromium. The amount of chromium extracted from the soil with acetic acid varied much less than the total soil content, and was not correlated with the latter. It indicates that the amount of chromium available to the plant is relatively independent of the total concentration. The complex principles determining the availability of chromium for plants are poorly understood.

1.6.2. Water

It is now generally agreed that, except in areas with substantial chromium deposits, high chromium levels in water arise from industrial sources. With the exception of areas bearing chromium deposits or in highly industrialized areas, most surface waters contain very low levels of chromium. Although modern methods of water treatment remove much of the naturally present chromium, it should be noted that chlorinated drinking water usually contains traces of hexavalent chromium. The mean level in the drinking-water supplies in 100 cities in the USA was only 0.43 μg/litre, with a range from barely detectable to 35 μg/litre.

Sea water contains less than 1 μg chromium/litre but the exact chemical forms in which chromium is present in the ocean, and surface water are not known. Theoretically, chromium can persist in the hexavalent state in water with a low organic matter content. In the trivalent form, chromium will form insoluble compounds at the natural pH of water, unless protected by complex formation. The exact distribution between the trivalent and hexavalent state is unknown.

1.6.3 Air

Chromium occurs in the air of non-industrialized areas in concentrations of less that 0.1 μg/m3. The natural sources of air-chromium are forest fires and, perhaps, volcanic eruptions). Man-made sources include all types of combustion and emissions by the chromium industry). The chemical forms of chromium in the air are not known, but it should be assumed that part of the air-chromium exists in the hexavalent form, especially that derived from high-temperature combustion. Chromium trioxide (CrO_3) may be the most important compound in the air.

1.6.4. Plants And Wildlife

It is not known whether chromium is an essential nutrient for plants, but all plants contain the element in concentrations detectable by modern methods.
Chromium concentrations in food plants growing on normal soils range from not detectable to 0.19 mg/kg wet weight. In addition, chromium of vegetable origin has a relatively low biological activity.

Much higher concentrations have been reported in plants growing on chromium deposits. Plants grown in the vicinity of chromium-emitting industries or those fertilized by sewage sludge are exposed to substantial amounts of chromium. The chromium contents of plants growing were determined near cooling towers, where chromates were present as corrosion inhibitors. It was shown that chromium levels in grasses, trees, and litter, decreased with increasing distance from the towers. No information was given as to whether the variations in chromium concentrations were the result of surface contamination or of true absorption by the roots of the plant.

Sewage sludge can contain chromium levels as high as 9000 mg/kg. Application of sewage sludge to soils, which increased the chromium levels from 36.1 to 61 mg/kg on a dry weight basis, increased the contents of chromium in plants growing in the soil from, e.g., 2.6 to 4.1 mg/kg in fodder rape. However, most of the increased uptake in plants is retained in the roots, and only a small fraction appears in the edible part. Other elements within the sludge, e.g., cadmium or nickel, pose a greater problem for human health. Of particular importance is the chromium concentration in the forage of meat animals. Strong seasonal variations in the chromium levels in 3 different kinds of grasses; the highest level found was 590 μg/kg dry weight in hay.

Higher levels of chromium in vegetation not used for human consumption may account for the generally higher chromium contents in the organs of wild animals, compared with man. The chromium concentrations in different organs and muscles of wild animals and found that they ranged from 0.04 to 0.48 mg/kg on a wet weight basis. Chromium concentrations in the hair of several wild-animal species, ranged from 640 mg/kg in a pronghorn antelope.

1.6.5. Environmental Contamination From Natural Sources

No data have been found that indicate any significant contamination of the environment from natural sources, though major catastrophic events, such as large forest fires or volcanic eruption, could conceivably contribute to the concentration of chromium in air. Water supplies originating in areas with chromium deposits may contain elevated chromium concentrations).However, none of these natural sources contributes enough chromium to pose a hazard for human or animal health.

1.7 ENVIRONMENTAL TRANSPORT AND DISTRIBUTION

Industrial effluents containing chromium, some of which is in the hexavalent form, are emitted into streams and the air. Whether the chromium remains hexavalent until it reaches the ocean depends on the amount of organic matter present in the water. If it is present in large quantities, the hexavalent chromium may be reduced by, and the trivalent chromium adsorbed on, the particulate matter. If it is not adsorbed, the trivalent chromium will form large, polynucleate complexes that are no longer soluble. These may remain in colloidal suspension and be transported to the ocean as such, or they may precipitate and become part of the stream sediment. Similar processes occur in the oceans: hexavalent chromium is reduced and settles on the ocean bed. It is replaced by an estimated 6.7×10^6 kg of chromium from rivers. In a study of the oxidation state of chromium in ocean water, detected an increased proportion of the trivalent form with increasing depth. Chromium is emitted into the air, not only by the chromium industries, but also by every combustion process, including forest fires. The oxidation state of chromium emissions is not well defined quantitatively, but it can be assumed that the heat of combustion may oxidize an unknown proportion of the element to the hexavalent state. While suspended in the air, this state is probably stable, until it settles down and comes into contact with organic matter, which will eventually reduce it to the trivalent form. Living plants and animals absorb the hexavalent form in preference to the trivalent, but once absorbed, it is reduced to the stable, trivalent state.

The transport of chromium in the environment is summarized in Fig. below. It should be noted that there is a complete cycle from rocks or soil to plants, animals, and man, and back to soil. Only part of the chromium is diverted to a second pathway leading to the repository, the ocean floor. This part consists of chromium from rocks and soil carried by water (concentrations, a few µg/litre) and animal and human excreta, a small part of which may find their way into water (e.g., runoff from sewage sludge). Another cycle consists of airborne chromium from natural sources, such as fires, and from the chromate industry. This cycle also contains some hexavalent chromium, with by products going into the water and air. Part of the air-chromium completes the cycle by setting on the land, but a very significant portion goes into the repository, the ocean, where it ends up as sediment on the ocean floor.

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Low levels of chromium are omnipresent in the environment. Under normal conditions, human exposure to chromium does not represent a toxicological risk, but it should be pointed out that too low an intake of chromium may lead to deficiency. Airborne concentrations of chromium, predominantly as trivalent chromium, are usually below 0.1 $\mu g/m^3$ and there are many places where the concentration is below the detection limit. Concentrations in river water are typically in the range of 1 - 10 µg/litre and do not constitute a health threat. Drinking-water from municipal water supplies does not contribute more than a few micrograms of chromium to the daily human intake, but untreated water in certain areas may be contaminated by runoff or effluents from industrial sources and may contribute significant amounts of chromium. The oceans contain less than 1 µg/litre.

The daily human intake through food varies considerably between regions. Typical values range from 50 to 200 µg/day. They do not represent a toxicity problem. However, significant exposures exist in the occupational field. In the past, chromium-ore mining generated chromium containing dusts, levels of which ranged up to 20 mg/m^3 in different work-places. Other exposures ranged up to 150 mg/m3 and consisted of dust containing as much as 48% chromium (Cr_20_3). In production plants, hexavalent chromium can Occur in the airborne state. However, implementation of protective measures at ferrochromium production sites reduced the airborne hexavalent chromium to levels of 30 60 $\mu g/m^3$.The health effects of the two common oxidation states of chromium are so fundamentally different that they must be considered separately. In the form of trivalent compounds chromium is an essential nutrient and is relatively non-toxic for man and other mammalian species. The hexavalent form is man-made by oxidation of naturally-occurring trivalent chromium minerals and is widely used. Compounds of hexavalent chromium penetrate biological membranes easily and can thus interact with essential constituents of the cells, including genetic material which they can damage through oxidation and complication with resulting trivalent species. On the other hand, oxidation of trivalent chromium has not been demonstrated in the living organism, and for practical purposes, the reduction of hexavalent chromium to trivalent chromium in lungs and other animal tissues is irreversible.

1.8.1 Carcinogenicity

Carcinomas of the lung have been reported in animals as a result of the administration of chromium chemicals. Calcium and zinc potassium chromate produced a number of bronchogenic carcinomas, but soluble chromates and trivalent chromium chemicals failed to produce cancer.

Barium and lead chromate evoked only a very weak carcinogenic response compared with strontium and calcium chromate. It is also observed that chromium trioxide produced hepatocellular carcinomas. The inhalation studies on animals revealed that sodium dichromate was not carcinogenic after exposure on 5 days/week. With calcium chromate, the carcinogenic effect was more pronounced after treatment once per week, than after treatment 5 times per week.

There is sufficient evidence for the Carcinogenicity of calcium chromate and some relatively insoluble chromium (VI) compounds (sintered calcium chromate, lead chromate, strontium chromate, sintered chromium trioxide and zinc chromate) in rats. There is limited evidence for the Carcinogenicity of lead chromate (VI) oxide and cobalt-chromium alloy in rats. The data were inadequate for the evaluation of the Carcinogenicity of other chromium (VI) compounds and of chromium (III) compounds. A number of effects can result from occupational exposure to airborne chromium including irritative lesions of the skin and upper respiratory tract, allergic reactions, and cancers of the respiratory tract. The data on other effects, e.g., in the gastrointestinal, cardiovascular, and urogenitally systems are insufficient for evaluation. Epidemiological studies have shown that workers engaged in the production of chromate salts and chromate pigments experience an increased risk of developing bronchial carcinomas.

No detailed data on dose-response relationships are available from epidemiological studies. Although a suspicion of increased lung cancer risks in chromium plating workers has been raised, the available data are inconclusive as are data for other industrial processes where exposure to chromium occurs. There is insufficient evidence on the role of chromium as a cause of cancer in any organ other than the lung. Evidence from studies on laboratory animals shows that hexavalent thorium compounds, especially those of low solubility, can induce lung cancer. In the lymphocytes of workers in chromium-plating factories, the frequency of sister chromatid exchanges was higher in exposed than in control groups. Mutagenicity and related studies have convincingly shown that hexavalent chromium is genetically active. Hexavalent chromium can cross cellular membranes and is then reduced to trivalent chromium, which can cause DNA cross-links and increase the infertility of DNA implication. Trivalent chromium compounds have been shown to be genetically inactive in most test systems, except in systems where they can directly interact with DNA

1.8.2 Respiratory Tract

It has been reported that the threshold for acute irritative effects in the upper respiratory tract is 25 $\mu g/m^3$ for the most sensitive individuals. Long-term exposure to doses over 1$\mu g/m^3$ chromic acid can cause nasal irritation, atrophy of the nasal mucosa, and ulceration of perforation of the nasal septum. Bronchial asthma was previously attributed to exposure to chromium compounds, but scientific data are too scarce to draw conclusions.

1.8.3. Skin

Skin rashes, ulcers, sores, and eczema have been reported among occupationally - exposed workers. Both trivalent and hexavalent chromium compounds can give rise to sensitization of skin, especially under certain environmental conditions, such as those encountered in the cement industry, where the high incidence of chromium-induced skin lesions can be attributed to the alkaline exposure conditions. Eczematous dermatitis, which manifests first as a diffuse erythematous type, progresses in severe cases to an oxidative stage and is associated in 8 – 15% of patients with sensitivity to chromium, as revealed by skin-patch tests. Although opinion is divided on the oxidation state of chromium responsible for inducing sensitization, there is evidence of hexavalent chromium penetrating the skin as a hapten to be reduced to the trivalent state and conjugated with proteins and transformed into the full antigen that initiates the sensitization reaction, involving presumably only a cell-mediated immune response. It should be noted that patients suffering from chromium-induced skin allergy tend to become hypersensitive to cobalt and nickel. Furthermore, 48% of cases of skin allergy induced by chromium, with or without clinically observed light sensitivity, showed a significantly more intense reaction by a standardized photo patch test procedure, when they were exposed to a 4/5 minimal erythema dose of irradiation.

1.8.4. Kidney

After high-dose, short-term oral ingestion of chromium, acute nephritis and tubular necrosis were observed. A few epidemiological studies on workers in chrome-plating industries include data on diseases of the kidney, most of them without giving exact exposure levels. A recent study related increased urinar-β_2 micro globulin levels to exposure ranges between 2 and 20 μg/m3. The dose-response relationship observed in this study needs confirmation on a larger number of exposed workers. There are no conclusive data to evaluate the effects of chromium compounds on the liver or gastrointestinal and circulatory systems.

1.8.5 Teratogenicity

Both oxidation states, when injected at high levels parenterally into animals, are teratogenic, with the hexavalent form accumulating in the embryos to much higher concentrations than the trivalent.

1.8.6 General Population

Persons living in the vicinity of ferro-alloy plants, exposed to an ambient air concentration of up to 1 μg/m3, did not show increased lung cancer mortality. The results of many studies suggest that exposure to chromium through inhalation and skin contact can pose health problems for the general population. Very little information is available on the health effects of chromium ingested through untreated drinking-water, though, in a single study, a correlation was observed between frequency of malformation in the central nervous system and the chromium content of water samples. In order to assess the nature of the magnitude of these problems, there appears to be a need for more general population studies on the effects of inhaled, absorbed, or ingested chromium on respiratory, cardiovascular, and renal functions, and on the skin. Studies on animals and man have established trivalent chromium as an essential micronutrient that interacts with insulin and enhances the physiological effects of the hormone. And also improve their glucose metabolism and, in some instances, fat metabolism, by ingesting trivalent chromium compounds. These observations suggest that some populations are at risk of chromium deficiency. Children suffering from protein-energy malnutrition may be at special risk. As chromium concentrations in the body fluids of unexposed persons are generally less than 1 μg/litre, analysis for chromium requires the strictest quality control, including measures to exclude sample contamination. Even with adequate analytical methods, it is not possible, as yet, to diagnose chromium deficiency in individuals by chemical or biochemical methods alone. Therefore, a quantitative assessment of the prevalence of chromium deficiency in human populations is not yet possible.

1.9 OBJECTIVES OF THE PRESENT WORK

The present was undertaken with the following broad objectives:

1. To analyze various soil samples with the view to determine their Cr. (III) and Cr. (VI) contents especially for those soils in areas suspected for chromium contamination at the work place.
2. To investigate interrelationship between the Cr. (III) and Cr(VI) species both for background as well as for chromium contaminated soils.

3. To identify correlation between water related pH(pH_w) and moisture content of soil as related to chromium contents.

4. To check the levels of distribution of chromium in soil samples in terms of permissible safe limit.

5. To employ statistical methods for ascertaining origin of various chromium sources in various soil samples.

6. To compare the present data with the international data on chromium distribution, to evolve the current status of chromium contamination and to be able to use this for future control.

CHAPTER 2

HISTORICAL PERSPECTIVE

2.1 ANALYTICAL TECHNIQUES USED

The metal analysis in various media, in soil & sediment, has been a subject of great environmental consequence during the present decades. Several attempts have been made to bring out analytical methods for the precise analysis of metal contaminants in various media. A research paper outlined field portable X-ray florescence unit by the USEPA (United States Environment Protection Agency) team for analyzing metals in soils & sediments at hazardous waste side nation wide. This method took a proper account of calibration methods, precision & detection limits. Additionally the quality assurance program furnished data on the control procedures and quality assurance for the sample (14).

Another method using the synchrotron X-ray microprobe was used for the determination of chromate content in oxides, silicate glasses & cement wastes. The estimated accuracy is worked out in terms of Cr(VI) & total chromium, with a detection limit of 10ppm. The result of the study demonstrate the use of synchrotron based non-destructive quantification of the transition metal species in general (31). In addition, laser ionization technique has also been employed for trace metal analysis (28)

The sample atomization is carried out through a YAG laser operated at a wavelength of 1064nm. The detection limit determined was at ppb level for Boron Aluminum iron & chromium. The layer by layer analysis of the dopped samples were examined for the process. A high performance flame atomic absorption spectrometric method with preconcentration of Cr(VI) was developed for automated analysis (29).This method was basically a combination of an HPLC integrator at the output of the flame spectrometer. Case studies were done on drinking water, waste water & extracts of soils, with detection limits at 0.03 mg/ml for Cr(III) & 0.02 mg/ml for Cr(VI).

A new continuum source atomic Absorption spectrometric method was developed for metallic toxics. This method was based on a furnace system & a continuum UV light with oscillating entrance slit. With this kind of special lamp several metals were estimated, including chromium (21). Trace analysis of micro electronically heavy metals in purity problems was described in a recent publication (27). Since in micro electronically devices several metals are present at traces, the measurement of each could be based on ion exchange chromatography simple extraction, electrolytic deposition, and coprecipitation. The purity limits achieved by the isotope dilution mass spectroscopy method for chromium ranged between 0.01 – 30 mg/gm. Some work has also appeared on the detection of trace amounts of chromium by laser based spectroscopic method, already cited (32). The transpassive dissolution of chromium & chromium oxide by x-ray spectroscopy in-situ samples has been reported by a relevant publication that appeared in 1996 in the Journal of electrochemical society (46). This publication is based on a work describing chromium oxide films & passivated chromium determined by x-ray spectroscopy. The pH dependence was also investigated in the sputter deposited chromium oxide films.

In all the above cited methods a new technology based on either the use of laser or a doping procedure has been introduced for multilayer analysis of various metals. A similar study based on iron doped mullite by the positron annihilation technique is described. The study was taken up for Fe, Mn, Cr & Ti (49). Similarly for samples from organic soil pollutants the soil analysis study has been reported by a recently introduced electron paramagnetic resonance spectroscopic method (52).

The modern electrothermal AAS method with heated graphite tube remain the most proper method for the direct determination of Ca, Co, Cr, Cu, Fe and other metals. In this technique the high background is eliminated using hydrogen purge gas. There is complete freedom of blanks with high sample inputs, of the order of 5-100 mg (83). The more common UV/visible spectroscopic method has also been used in viable applications for bichromate determinations. The study (85) clearly showed the dissociation constant decreasing with temperature followed by a lowering of the density (85).

The nature of chromium species present in different media has always been a subject of great interest. Towards this end an EPR method has been used in conjunction with X-ray photoelectron method to determine chromium through coprecipitation from aqueous solutions. The catalyst materials were used to disperse chromium (III) and the X-ray flux was found to be consistent with the material calcined at high temperature. The spectra indicated the presence of chromium species, which were later quantified (89). The metal speciation in the precipitate has also been conducted by HPLC and diode laser atomic absorption spectrometry(90). This being a new technique has been applied to the measurement of very low concentration of Cr(VI) in tap water. The technique functions on the principal of a double beam absorption (90).

The classical electrothermal atomic absorption method has also been introduced using a semiconductor diode laser. This new type of method yielded chromium detection limit of 0.03ng/mL (92). In the case of other media such as chromium polluted soil, a magnetic separation method with an electron probe microanalysis was used for chromium estimation in effluents from leather industry. The method was extended to Cr Polluted soils. (94). The contribution of Raman spectroscopy for anion exchange membrane used for electrolysis of Cr(VI) solutions has also been used to show the presence of polychromate ions (102).In addition to the above cited methods the cathodoluminiscence spectroscopy (104), the photochemical method based on photophysics of Cr.(III) (108), and the total reflection X-ray fluorescence methods (111) have also been incorporated for the determination of chromium alongwith other heavy metals. The later method (111) has been a WHO method for water quality control in terms of trace elements.

2.2 PHYSICAL ASPECTS OF SPECIATION

Several physical aspects of the speciation process need mention here. Firstly the kinetic aspect will be mentioned. Chromium is a potential soil and water pollutant, in this respect a kinetic study was made on the feasibility of using an iron rich material (IRM) containing Mn and Cr in agriculture and non agriculture environments. The kinetic study revealed that Mn and Cr were stabilized while being processed at the industrial plants and also they got reabsorbed by the IRM after the initial solubilization(8).Similarly, a kinetics based chromate reduction by ferrous ion studied through the stopped-flow kinetic technique, monitored by UV-visible spectroscopy and initial rate method, was used to determine the rate constant and the rate dependence of each reactant (15).Kinetics of the cross linking of polyacrylamide with Cr(III) was described in a recent publication. The cross linking was believed to proceed through a rate determining introduction of the first hydrolyzed polyacrylamide(HPAM) to Cr(III) (18) and the investigation of possible mechanism of reaction between Cr(III) and HPAM has been studied by UV-visible Spectroscopy (18). A comparative study of kinetics of bacterial reduction of chromium has been described in another recent publication (99).

As for the remediation, a research paper outlined the remediation of chromium contaminated soil by heap leaching. The paper intended to address Cr(VI) removal from contaminated soils typical of low organic alkaline solids from an arid environment (4).In an another process bioremediation of chromate- contaminated ground water by reduction and precipitation in surface soils, was reported. Accordingly, it was found that removal percentages of Cr(VI) from enriched water varied from 51 to 98 percent and increased with increasing organic matter loading (9).Similarly a new bioremediation process for cleaning ground water and soil contaminated with transition metals and radionuclides was developed(10).Another publication described the challenge of remediating Cr-contaminated soil(39).

Chromium speciation in soil is important in assessing risk related to ingestion of Cr-contaminted soils.Cr (VI) was found to be mobile and toxic while Cr(III) was retained in the soil column, indicating that reduction of Cr(VI) to Cr(III),and the proportion of Cr(III) in the soil, will constrain remedial efficiency(45).Electrodialytic remediation experiments on contaminated soil samples were performed and also the primary soil parameters for remediation was identified to be soil pH, lime contents and the speciation of other heavy metals(65).

Surfactant enhanced remediation of subsurface chromium contamination revealed that surfactants when used alone, enhanced the extraction of chromate 2.0-2.5 times more than did water, but when surfactants were used along with a well known complexing agent (e.g; diphenyl carbazide) it was possible to remove 213 percent of Cr(VI) relative to deionized water in less than 20 pore volumes (34).In an another relevant publication laboratory tests on remediation of Cr-contaminated soils were conducted in order to check the ability of certain extractants to remove Cr from soil(117).Another study on electrokinetic remediation of heavy metals-contaminated soil under reducing environment, demonstrated that the reducing agent like humic acid, ferrous ion and particularly sulfides, in soil may effect redox chemistry and soil pH, ultimately affecting the electrokinetic remediation process(118).This advancement in the quantification of chromium in the soil, together with the expected establishment of Cr(VI) standards and development of remediation techniques, offers promise that humans can be protected from adverse effects of Cr(VI) (39).

The reduction aspect of Cr(VI) is quite important. The Cr(VI) solubility and reduction in soil enriched with Chromites Ore Processing Residue(COPR) has been studied in literature. Addition of Mn^{2+},Fe^{2+},steel wool, leaf litter and lactic acid reduced the amount of soluble and insoluble Cr(VI) in various quantities depending upon the reducing agent, pH and soil type(12).Other reported information highlighted the microbial reduction of Cr(VI) during anaerobic degradation of benzoate. Bacterial degradation of benzoate with the transport of electrons to Cr (VI) was achieved using nitrate or molecular oxygen as an initial stimulator. The addition of nitrate up to 5.0mM did not inhibit Cr(VI) reduction but enhanced benzoate degradation in the enrichments(40).

Reduction of Cr(VI) by amorphous iron sulfide has also been reported(75).The iron(III) catalyzed photochemical reduction of Cr(VI) by oxalate and citrate in aqueous solutions has been investigated in a parallel study(72).A recent method of reduction of Cr(VI) by wetland plant has the potential to be used for the in-situ detoxification of Cr(VI)-contaminated waste streams(82).Also, the influence of organic ligands on Cr(VI) reduction by Iron(II) (84) by using UV-visible spectroscopy and kinetic fitting and the influence of mineral surface on Cr(VI) reduction by Iron(II) has been reported and studied. A similar line of action was employed by other workers to study the reduction in residential chromium following site remediation. The house dust samples were collected from different sites, extracted with HNO_3 and analyzed for Cr thereby showing that site remediation could have beneficial effect on household loadings of Cr(122). The redox processes of Cr in soils (124), the redox interaction of Cr(VI) and substituted phenols(17) and the redox behavior and dispersion of supported chromium catalysts(19) were also discussed in relevant publications.

The more advantageous aspect of in-situ measurements have also been reported. In-situ diffused reflectance spectra of supported chromium oxide catalysts were investigated at high temperature and kinetics of reduction process with carbon monoxide was studied. The study revealed that activation of CO by adsorption took place followed by the reduction of Cr(VI) with the formation of surface carboxylates(77).Equivalently, in-situ raman microscopy of chromate effects on corrosion pits in aluminum alloy were examined. The interactions of dilute Cr(VI) with corroding alloy probably caused the self healing property of components of chromate conversion coatings(CCCs)-(105).

Cr(VI)-contaminated sediment samples from a plating-waste disposal site were collected and analyzed for Cr(VI),total chromium and related constituents and then treated with H_2S gas to evaluate this procedure as a possible in-situ remediation technique(106). Identically, the in-situ reduction of Cr(VI) in alkaline soils enriched with chromite ore processing residue, was described in yet another publication(95).A similar approach was then employed by other workers using Fe(II) solution for in-situ Cr(VI) reduction within coarse textured, oxide-coated soil and aquifer systems(116).In-situ reduction was confirmed by loss of Cr(VI) and Fe(II) from solutions and drop in pH compared to control systems used(116).

2.3 COMPARATIVE & CORRELATION STUDIES

In recent year there has been a considerable concern over environmental pollution, especially with respect to metal-contaminated soils. A variety of research papers have appeared in various journals highlighting different chemical methods for the remediation of metal contaminated soils. This has been taken up in a recent publication comparison of solvents for ex-situ removal of Cr and Pb from contaminated soil have been made. For this very reason, the ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and sodium dodecyl sulfate(SDS), were compared for their ability to solubilize Cr and Pb from contaminated soil. The EDTA was found to be the best solvent among the three (58). Similarly, comparison of XANES analysis and extraction to determine chromium speciation in contaminated soil was made (73). XANES provides a physical method for determining the ratio of both the chromium species in contaminated soil. In most soil samples less than 10% of the total Cr was presented as Cr (VI)-(73).

Leachability of heavy metals from growth media containing source separated municipal solid waste (MSW) has been studied. The levels of heavy metals including Cr present in leachates were measured by atomic spectroscopy & were found to remain below the current drinking water standards (22).In a parallel study, the chemistry and phototoxicity of soil trace elements from repeated sewage sludge application has been examined. The results of the study suggested that soil loading of Cr were of great environmental concern (36). In an another relevant study the essential oil quality and heavy metal concentrations of peppermint grown on a municipal sludge amended soil, was investigated (81)

The study on bioaccessibility of metals in soils for different liquid to solid ratios in synthetic gastric juice revealed that bioaccessibility is not the same for each metal within a given soil, nor between the soils and that it will only be affected by slightly variation in gastric fluid liquid to solid ratios, in – vitro synthetic gastric juice for the range 100:1 to 500:1 (mg/L) (100). In another research paper, the results were reported of a study on the concentrations of heavy metals including chromium and macronutrients in soils and in three species of evergreen plants. Analysis of both plant and soil samples evidenced the pollution of the garden under investigation by heavy metals via atmospheres and soil (117). A study of the concentration and distribution of eleven heavy metals including chromes was reported in another research paper. The results showed that background values of most metals in a given soil were different than those for other soils (67). In a case study of anthropogenic impact on distribution of heavy metals in urban soils revealed that industrial soils have extremely high level of chromium (123).An X-ray Absorption Near Edge Structure Spectroscopy (XANES) study of concentration and mobility of chromate in conversion coatings was presented in another publication (101).

A research paper outlined the speciation of selected heavy metals in soil; plant availability was also presented. A chemical review of the fundamental advances into the surface chemistry and spectroscopy of chromium in inorganic oxides also appeared in literature. The fate and transport of Cr (VI) in undistributed heterogeneous soil was investigated and the results indicated the effectiveness of natural organic matter (NOM) to reduce the Cr (VI) to Cr (III) under acidic conditions (112). The background air concentrations of Cr (VI) in New Jersey (United States) was also reported in another research paper (69). Another comparative study outlined the trace methods geochemistry in spodosols of the north Eastern United States (70). The study on metal accumulation by aquacultured seedlings of Indian mustard clearly showed that the use of the seedlings provided a novel approach to the treatment of various metals contaminated waste streams, industrial runoffs, and leachates (76). The metal retention via thin karstic soil in Missouri was investigated with the result that chromium was near or below detection limit and appeared to offer no threat of groundwater contamination (119). Hexavalent chromium reduction by Bacillus Coagulants isolated from contaminated soils was also reported (120). The heavy metals in urban soils of East St Louis were analyzed demonstrating the high concentration heavy metal heterogeneously distributed in the soil

(121). Study of sulfate adsorption on type 316 stainless steel indicated that adsorption of sulfate facilitated oxidation of Cr (III) to higher oxidation states (91). An NMR, XRD and EDS study of solidification/stabilization of chromium with portland cement and tricalcium silicate (C_3S) confirmed that the chromium ion got easily incorporated into C_3S paste and hydrated portland cement and it also affected the hydration process and along with hydration products (78). The trace amounts of chemical warfare agents and related Cr compounds in rubber, paint and soil samples were detected by NMR spectroscopy (37), thus offering an alternative approach to the determination of the metal.

2.4 VARIABLES OF THE PROBLEM

More recently, the effect of different parameters on the remediation of chromium polluted soils have been studied by several workers. In one such study, the effect of temperature, ionic strength, background electrolytes and Fe(III), on the reduction of Cr. (VI),by soil humic substances (SHSs) was investigated. Rates of reduction were not significantly altered due to the changes in either background electrolyte or ionic strength (38). Also electrokinetics experiments were conducted on soil samples in order to investigate the effect of soils composition on the removal of chromium from these soil samples (64). Similarly the effect of acidification on metal mobility in paper mill ash amended soil were examined using column leaching studies (114) and the effects of soil on trace metal leachability from paper mill ashes and sludges were investigated. The leachates were analyzed for pH, electrical conductivity, dissolved organic carbon, and concentrations of heavy metals, including chromium. It was found out that the presence of organic matter improves the metal sorption and enhances metal leachability (120).

In an another research paper, the Cr leaching versus oxidation state for contaminated solidified/stabilized soil has been reported. Solidification/solubilization (S/S) is a potential method for preventing Cr leaching from contaminated soil . The Cr leaching was expected to be dependent upon the chromium oxidation state (68). Additional studies aspects of trace metals by tension lysimeters fabricated with polyacrylic and fitted with either a porous nylon membrane or porous ceramic cup, were examined (80). Later in the year 1998, a research paper outlined the methods of recovery of biosolids applied heavy metals sixteen years after application. The result indicated that complete recovery of biosolids- applied heavy metals was possible only when cross mixing of treated soils got prevented and sediments losses became minimal(97). This was followed by another research paper highlighting the effect of biosolids application rate on the soil properties (98). Determination of total chromium in whole blood, blood components, bone and urine by fast furnace program electrothermal atomization atomic absorption spectrometry was carried out in a comparative study (20).

Auxiliary studies showed that the sorption and speciation of heavy metals from incinerator fly ash in a marine clay, was dependent on soil pH, time and the metal elements (61). Density functional studies of chromium oxide clusters including structures, bonding, vibrations and stability were reported in a recent publication. A good agreement has been found between the available experimental data and the data on geometrical parameters (87). Ionic size and metal uptake of Cr(VI), Mo(VI) and W(VI) species on ZrO_2-based catalyst precursors, were also touched upon with the reported results claiming that the W-containing samples based on ZrO_2 differed from Cr-and Mo-samples in the uptake dependence on pH (103). Work was also undertaken to study the behavior of heavy metals, nutrients, and major components during roof run off infiltration (113).

2.5 METHODOLOGY

The remediation of metal contaminated soil has always been a rewarding exercise for analytical chemists. Only recently, several experimental methods have been employed to this effect. In one of several such studies, called the hot water washing method, Cr(VI) was removed from chromium contaminated soil. The observed facile removal with such a mild solution indicated that Cr (VI) may be able to migrate through soils relatively easily (5). Similarly, another method of reduction of Cr(VI) in presence of excess soil fulvic acid has been studied by other researchers (6). A study based on a laboratory method was undertaken by a group of workers to evaluate the accuracy of a proposed alkaline digestion method in quantifying Cr(VI) in soils (7). In a recent publication, the mechanism of Cr(III) sorption on silica and the effect of reaction conditions was reported. In these studies multitude of molecular level experimental techniques, including Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy and High Resolution Transmission Electron Microscopy (HRTEM), were employed to ascertain the Cr(III) surface structure on silica and the reaction conditions that affect the sorption mechanism (25). In a parallel study, the Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy was used to discern the local structure environment of Cr(III) sorbed on silica (26).

Another case study has been carried out regarding the determination and correction of analytical biases related to chemical mechanisms in the analysis of Cr(VI) in soil samples using EPA-protocol (35). Another research paper outlined the thermospray sample introduction method for direct speciation of selenite and selenate (48). In this study, the high temperature and high pressure characteristics of thermospray were exploited for selenium speciation with Inductively Coupled Plasma Atomic Emission Spectrometric (ICP-AES) method. The thermospray methods for rapid, sensitive and non-chromatographic speciation of chromium oxidation states have also been employed by a group of researchers in the recent past. The results revealed that accuracy of measurements for Cr(VI) was within 1% of certified value for NIST(USA) standard reference material (107) The assessment of technique and the role of organic Cr(III) complex in chromium speciation in tannery effluent has been reported in a recent publication that appeared in 1996. It was shown that chromium speciation in presence of organic complexes can lead to erroneous results. The techniques of DPC (1,5-diphenyl carbazide) spectrophotometry, organic extraction with methyl isobutyl ketone and coprecipitation with iron and bismuth salts were considered (33) The analysis of priority pollutant (bis(2-ethylhexyl)pthalate) (2-EHP) in soil by rapid spectroscopy methods employing methanol extraction and UV-visible spectroscopy has been reported in a relevant publication (13).

The improved data processing method for Atomic Absorption Spectroscopy with Electrothermal Atomization was described in another research paper. The principal advantage expected and observed for the new approach is its ability to reduce the critical effect of variables such as atomization temperature (30). Chemical interaction between Cr(VI) and hydrous concrete particles in synthetic ground water solutions were also reported together with detailed results that indicated that redox, adsorption, and precipitation were the three major reactions occurring at the concrete water interface (42). In another attempt blast furnace slag-modified grouts were used for in-situ stabilization of soils contaminated with Cr(III) and Cr(VI) (43). A comparative evaluation work on the five methods reported for the speciation of chromium were compared in extraction of Cr(III) from soils. Out of these, the heated carbonate hydroxide solution method was found to be the most effective in that the remediation of Cr-contaminated soil was most effective(44). Several other researchers took the challenge of remediating chromium contaminated soil by developing new analytical methods that offered promise of application towards protection of human health from adverse effect of Cr(VI)-(56). Removal of Pb(II), Cd(II) and Cr(III) from sand by electromigration has been carried out in a recent study. The experimental results showed that metal removal efficiencies are higher than 90% (63).

A group of researchers at Massachusetts, has developed an in-situ geochemical fixation technology for remediating chromium and other metals in soil and ground water, the proposed method is cheaper than the traditional method (79). The evaluation of methods and Eh-pH effects for extraction of sparingly soluble chromate from soils was investigated (71). The selective removal of chromate anion by a new carbon adsorbent has also been brought out in another publication. The results suggest that removal of metal cation by arc-assisted carbon (ACs) was more effective at high pH(86). The identification has been achieved for an accurate soil suspensions/dispersion modeling method for use in estimating health based soil clean up levels of Cr(VI), in Chromite Ore Processing Residue (CORP)-(66). In addition, the chelant extraction of heavy metals from contaminated soil (115), and use of acids and chelating agents for removing heavy metals from contaminated soil (59) ranked the most effective soil remediation methods, as they are less harmful to soil environment in terms of degradation and reclamation.

CHAPTER 3

ANALYTICAL METHODOLOGY

3.1 PREPARATION FOR ANALYSIS

3.1.1 The Ashing Procedure

In general, chromium is encountered as an oxygen compound when in association with organic matter. As the chromium oxygen bond is exceptionally stable, and Cr_2O_3 is one of the most refractory of chromium compounds, no difficulty is usually to be anticipated in applying the usual ashing procedures to organic materials containing chromium. A few unusual exceptions may be noted. Chromyl compounds are volatile and will be lost from their solutions in halogenated solvents. A few chromium chelates, such as the acetylacetonate, volatilize unchanged at moderately high temperatures. These compounds rarely are encountered in the usual analytical procedure, and hence ashing is frequently a favored method of attacking organic materials for the determination of chromium. After ashing, the chromium is normally in the form of oxide.

3.1.2 The Wet Oxidation Procedures

If the amount of chromium is small, the use of wet oxidation procedures frequently is more desirable. Again, standard procedures are available. The use of sulfuric acid alone should be avoided since, on heating to fumes with this acid, insoluble sulfates of chromium form and these are redissolved only with extreme difficulty. Prechloric acid is the oxidant of choice, but care must be exercised. In general, if the sample is first digested with hot concentrated nitric acid, the perchloric acid oxidation can be completed with safety. The difficulty with chromium sulfates can be avoided as long as perchloric acid is present to retain most of chromium in the sexivalent state. Sodium molybdate is reported to catalyze this oxidation .

For biological materials, Grogan and his co workers have recommended wet ashing with nitric acid and hydrogen peroxide. In this case the hydrogen peroxide is used to reduce the chromium to the tervalent state and prevent loss as chromyl chloride if chlorides are present. The procedure also has been studied for use in the analysis of water containing organic matter. Here difficulties were encountered with high chloride samples The Grogan procedure has given good results in our hands on samples with high organic content. A typical example of this procedure, as applied to a liquid sample, is as follows.

Pipet 10 ml. of sample into a 25 x 150 mm. heat resistant glass tube. (If a blank has not been run on reagents, use 10 ml of water and carry through the analysis.) Add 0.5 ml. of HNO_3 and 4 drops of 30% H_2O_2. Mix by swirling and let stand 20 to 30 minutes. Holding the tube in a suitable holder in a nearly horizontal position, heat it to gentle boiling over a flame. Evaporate the acid slowly, allowing it to reflux. The addition of HNO_3 and fuming may have to be repeated if large amounts of organic matter are present. When oxidation is complete, the residue on completing evaporation will be white or yellowish. Do not allow baking, but remove substantially all HNO_3.

Dissolve the ash by washing down the tube with 4 to 5 ml. of water. Add 2 ml. of sodium hypobromite solution (6 ml. saturated bromine in water added to 100 ml. of NaOH (40 g./l.), kept in the dark in a refrigerator), mix well, and heat in a boiling water bath for 10 to 20 minutes.

From a microburete add 0.92 ml. of 1:7 H2SO4. The pH should be 1.3 to 1.7 and a brown color due to free bromine should appear. (If no color appears, organic matter was incompletely destroyed or the NaOBr is not fresh. Reject the sample.)

Transfer the sample to a volumetric flask of proper size, rinsing with 2 to 3 ml. of water. Add 0.5 ml. of phenol solution (12 g. of C6H5OH/liter). The sample is now ready for color development, dilution to the mark, and analysis. If much phosphate, alkaline earth metals, or iron are present, the procedure of Saltzman may be preferred. In this case, the usual nitric sulfuric acid mixture is used of wet ashing. The solution is cooled and diluted, and the impurities are precipitated with NH_4OH. The filtrate is reoxidized with 0.6 ml. of $KMnO_4$ (3.2g./1) and heated on the steam bath for 20 minutes. If the pink color does not persist, a second portion of $KMnO_4$ is added. Cool, and add NaN_3 (50g./1) dropwise with swirling until the permanganate color or any brown tint is discharged.

The ammonium persulfate oxidation, similar to that used in steel analysis, also has been suggested by Serfass. Since this proeedure, like the perchloric acid digestion, results in oxidation of the chromium, the possibility of loss of chromyl chloride from high-chloride materials must be considered. Because of the wide variety of materials tested and the range of chromium contents encountered, it is difficult to give a typical procedure. Particular care must be taken when microgram quantities of Cr are to be determined; not only is chromium readily lost as chromyl compounds, but complete oxidation to the sexivalent condition in which it is determined is difficult, and the possibility of traces of chromium in reagents is very real. Nitric acid should be redistilled before use; the reagent grade frequently contains appreciable Cr.

3.1.3. Volatilization

There are no procedures known in which chromium remains as a residue with other elements volatilizing. The opposite process (in which chromium is converted into a volatile compound) is well known. The procedure is normally used when it is desired to eliminate chromium, although chromium obviously can be recovered by the use of a suitable condenser

Chromium is normally volatilized as chromyl chloride. The usual procedure is to oxidize the chromium by heating to fumes of perchloric acid and then to introduce concentrated hydrochloric acid, dropwise, or to drop crystals of sodium chloride carefully into the boiling solution. An apparatus for this operation has been described. The bulk of the chromium will be volatilized as chromyl chloride, but some will be reduced to Cr^{+3}, in which form it is not volatile. Consequently, it is necessary to allow the mixture to reoxidize by bringing it to fumes of perchloric acid after each addition of chloride. Since the oxidation of the last traces of chromium by perchloric acid is difficult, it is hard to remove the final traces of chromium.

Chromium could be volatilized as chromyl fluoride, since fluoride does not reduce Cr^{+6}, this procedure should eliminate the repeated reoxidations required in the chloride separation. A disadvantage is the need for platinum apparatus, which, incidentally, should not be used in the chloride procedure because of the possible evolution of chlorine.

3.1.4 Extraction

Chromium forms a variety of extractable compounds, but care is required in their use. Whereas chromium forms extractable complexes such as the acetylacetonate and 8-quinolinolate, the slow rates of formation of these chelates make it necessary for excess reagent and sufficient time to be used to insure complete conversion to the complex.The chromium halides in aqueous solution resemble aluminum rather than iron. The chromium ion remains strongly coordinated with water and hence chromium halides are not extractable by ether.

The colored perchromic acid formed in solutions containing peroxide and chromium in weakly to strongly acidic solutions can be quantitatively extracted by ethyl acetate if chromium is present in amounts of from 0.5 to 5 mg. Optimum conditions for extraction are pH 1.7 to 0.2, hydrogen peroxide concentration of 0.02 molar, and temperatures below 10°C. The chromium can be returned to the water phase as chromate by shaking with sodium hydroxide solution Free peroxide must be present to ensure oxidation to chromate. Diethyldithiocarbamate has been employed for the complexing of trace quantities of chromium at pH 3 for spectrographic analysis. A large excess of the reagent is required and the chromium complex is extracted with chloroform. A carrier technique in which chromium is coprecipitated with indium, using 8-quinolinol, tannic acid, and thionalid (thioglycollic β-aminonaphthalide), and then is extracted if desired, also has been described .

Iron, which in large amounts interferes with the colorimetrie determination of chromium as diphenylearbazide, is removed by complexing with cupferron and extraction. The method is especially applicable to industrial wastes. Vanadium can be similarly separated.Vanadium, in amounts exceeding 4 ppm., also interferes with the diphenyl carbazide color reaction for chromium. It may be separated by adding 8-hydroxyquinoline to the solution at pH 4 and extracting the compound $V_20_3(C_9H_60N)_4$ with chloroform. Chromium(VI) in hydrochloric acid solution is extracted by 4-methyl2-pentanone. Iron also is extracted. Advantage is taken of the slow rate of formation of the acetylacetone complex of chromium by treating a solution containing chromium(lII) with acetylacetone at pH 3 to 4 and extracting with chloroform to remove other metals that form acetylacetonates. The aqueous phase is adjusted to pH 6 and refluxed for 1 hour with 10 ml. of additional acetylacetone The chromium complex then may be extracted at an acidity of 1 to 3N with chloroform. Perfluorobutyric acid in ethyl ether at pH 4 is reported to separate chromium(III) from uni-and divalent ions.

In 7N hydrochloric acid, chromium(III) is extracted by tri-n-octy1 phosphine oxide. However, antimony(III), gallium, gold(I), hafnium, iron(III), molybdenum(VI), tin(IV), titanium(IV), uranium(VI), vanadium(IV), and zirconium also are extracted. The colored complex that chromium forms with s-diphenyl carbazide also can be extracted into isoamyl alcohol , chloroform , hexanol, or cyclohexanol.

3.2 DETERMINATION OF CHROMIUM

Many analytical methods are available for the determination of chromium at trace levels, often in the 0.001-mg/kg range. Among these are flameless atomic absorption spectrometry, atomic emission spectrometry with various excitation sources (the inductively coupled plasma torch is particularly advantageous), gas chromatography destructive or non-destructive neutron activation analysis, and mass spectrometry using double-isotope dilution. Depending on the particular sample under examination as well as the analytical technique selected for the determination, wet or dry ashing procedures may be necessary to destroy the organic/inorganic matrix and minimize interelemental effects.

Determination of very low chromium concentrations in “unexposed” biological material (animal and human tissues, blood, urine, food, as well as water and air) is extremely difficult and many problems still have to be solved. An accurate assessment of human exposure and nutritional chromium requirements depends on reliable analytical results. Chromium concentrations in blood, urine, and some low-chromium foods are close to or less than 1 μg/kg, which is near the detection limit of even the most sensitive analytical methods. Thus, agreement as to “normal” levels of chromium among analytical investigators has been poor and results of interlaboratory comparisons have differed widely, usually by one order of magnitude. Only in recent years has agreement been reached that “ normal” chromium concentrations in unexposed blood and urine are in the range of 0.1 – 0.5 μg/litre. In this concentration range, it is not only the sensitivity of the final determination step that is limiting. The preceding steps of sample collection, preparation, and digestion are equally important. Contamination, easily introduced through cutting instruments and dust during collection, must be carefully controlled. Digestion procedures are of the greatest importance. Too rigorous treatment by heat or certain acids can cause a loss of chromium. Few biological standard reference materials, certified for chromium, are available and almost all of the older and most of the recent, published data were not checked using certified standards. For this reason, quantitative data concerning chromium concentrations in the range of <1-100 μg/kg in biological materials must be considered uncertain, and caution must be used in interpreting their health-related significance.

Differential analysis for chromium species is of great scientific and public health concern in view of the substantial differences in the biological availability and in the toxicity of hexavalent chromium (Cr VI) compared with trivalent (Cr III). Though methods based on solvent extraction, with or without prior oxidation, differentiate between these two oxidation states, few analytical data contain this important information. The understanding of the chemical and physical principles of chromium determination is increasing, and existing methods are being improved and new methods developed. However, at present, analysis for chromium is a sophisticated procedure requiring the full attention of a highly trained analytical chemist.

3.2.1 Gravimetric Methods Of Determination

1. As Barium Chromate:

Because of the greater ease and applicability of volumetric methods for chromium, gravimetric methods are not often used. The precipitation of barium chromate more often is used as a separation. However, in solutions free of sulfate, fluoride, and oxalate, chromium(VI) may be precipitated as barium chromate in weakly acid solution. Acetic acid is the usual acid. The chromium is precipitated by the addition, for each 0.1 g. of chromium, of 10 ml. of 0.5N barium chloride or barium acetate dropwise or in a fine stream to the boiling solution. The precipitated barium chromate is allowed to settle on a steam bath, then is filtered through a tared Gooch crucible and is washed with 10% ethanol solution. The filtrate should be free of any yellow chromate color. After drying for 1 hour at 105 to 110°C., the Gooch is gently ignited at about 600°C. and weighed. Other authors recommend weighing after drying at 180°C. and still others favor igniting at high temperature.

Thermogravimetric studies of barium chromate indicate a gradual loss of weight amounting to slightly over 1% between room temperature and 1015°C, so that it may be difficult to establish exact, optimum conditions for the ignition.

2. As Lead Chromate

The low solubility of lead chromate and the favorable gravimetric factor, plus the reported stability of the salt to drying and ignition , would appear to recommend this compound for the gravimetric determination of chromium. However, lead chromate is trimorphic, forming a stable monoclinic modification and unstable rhombic and tetragonal forms. The rhombic form tends to be stabilized by and to occlude excess lead, so that, in the precipitation of CrO_4^{-2} by excess lead, the precipitate frequently has a composition deviating appreciably from $PbCrO_4$. Furthermore, the insolubility of many other lead salts renders the method far from specific, and hence the procedure is better adapted as a separation or qualitative test than for quantitative determination. The homogeneous precipitation by oxidation of Cr^{+3} by bromate gives satisfactory results; use of urea gives a precipitate contaminated with carbonate.

3. As Mercurous Chromate

The relatively low chromium content of the precipitate and the uniform composition of the precipitate led many early workers to use this method. Recent thermogravimetric studies have shown that the precipitate is stable below 256°C.; hence it may be dried and weighed accurately. The gravimetrie factor Cr/Hg_2CrO_4 is 0.10055. The solution to be precipitated must be free of most foreign ions because of the insolubility of most other mercurous salts.

3.2.2 Titrimetric Methods Of Determination

3.2.2.1 Precipitation Reactions

These reactions find little general use in view of the greater specificity and convenience of the redox methods. Barium and lead salts may be used as titrants; tetrahydroxyquinone serves as the indicator for barium and dithizone for lead. Both methods are subject to interference by sulfates and both are subject to the inaccuracies.

Phthalate has been used as the precipitant in ethanol solution for mixtures of iron(III), aluminum, and chromium(III) solutions.

A precipitation reaction that is commonly used is the determination of basicity of chromium(III) solutions, which are commonly encountered in the leather and textile industries. The method involves titration of the chromium salt with standard sodium hydroxide in boiling solution, using a phenolphthalein indicator. The end point is difficult to detect, but is taken as the first appearance of pink in the supernatant solution, as seen against the light or against a porcelain dish.

3.2.2.2 Titration of Chromium(VI) with Iron(II)

The direct titration of chromium (VI) with iron (II) is the simplest procedure and, in general, the most accurate available for macrodetermination of chromium. There is no longer any real necessity for back-titration with permanganate or dichromate, although this is still extensively practiced. The iron salt titrant is made by dissolving either ferrous sulfate or ferrous ammonium sulfate in water acidified with sulfuric acid to produce the approximate titer desired. The solution has the disadvantage of oxidizing slowly in air, our experience being that the rate, with solutions stored in 19-liter carboys, is about 0.l to 0.2% per day. Hence, regardless of whether the solution is used in excess and back-titrated or is titrated directly, it must be standardized, at least daily, either against the standard back-titrant or against a primary chromium standard. Since potassium dichromate is such an excellent primary standard, this standardization is little trouble. Some improvement in stability of titer can be attained by keeping a little mossy tin in the reagent. The tin has sufficient over voltage to keep from reacting with the hydrogen ion present, but it reacts with any Fe^{+3} formed by oxidation:

$$Sn + 4Fe^{+3} \rightarrow Sn^{+4} + 4Fe^{+2}$$

maintaining the titer at approximately its original value for some time.

Ferrous ammonium sulfate solutions are reported to be more stable than ferrous sulfate, but we have been unable to confirm this. The salt is normally available in higher purity than the simple sulfate, but its use as a directly weighed standard in the analysis is not wise, even if back-titration is used.

The titration proceeds rapidly and quantitatively, provided the acidity is sufficiently high. About 20 to 25 ml. of 1:1 sulfuric acid is desirable in a titration volume of 250 to 350 ml. The end point can be determined potentiometrically, using a smooth platinum electrode, or by using ferroin (o-phenanthroline ferrous complex) as indicator. Diphenylamine sulfate or barium diphenylamine sulfonate also can be used, but the end point is better adapted to the back-titration with dichromate. The potentiometric end point is sharp and no difficulties are experienced, except when chlorides and acidity are both high in the solution being titrated, when the platinum electrode may become unresponsive. In this case, the electrode should be rinsed and reactivated by holding in an oxidizing flame for a few moments. Some colloidal materials may behave similarly. Dilute solutions of chromium(VI) also may be conveniently titrated amperometrically, with a rotating platinum electrode. The end point with o-phenanthroline is quite sharp if acidity is high, and results are obtained that are comparable to those with the potentiometric titration. It is advisable not to add indicator until the end point is approaching, as evidenced by the disappearance of a yellowish-green color (in pure chromium solutions) and the gradual change to blue-green. The indicator color change is from colorless to a deep red, which is readily seen in the colored solution. Diphenylamine and its derivatives give a deep blue color with chromium(VI), but the color is not too easily discharged by ferrous ion. It is thus best used as an external indicator, the end point being reached when the deep blue color of the complex is no longer noted.

As noted above, vanadium(V) or manganese(IV) or (VII) may interfere with the titration. Vanadium(V) is reduced quantitatively to vanadium(IV). It may be compensated for by a correction based on a separate determination of vanadium, or very conveniently by boiling the titrated solution with nitric acid, at about 3N, for 1 hour to reoxidize the vanadium. The beakers are left open to prevent refluxing of concentrated acid, which will oxidize some chromium(III) to chromium(VI) and yield too high a correction. Any losses due to evaporation are restored. The solution is cooled to 20°C. and retitrated with ferrous sulfate, diluted 1:10 if desired. The oxidation is not quite quantitative, but the correction is very satisfactory if the amount of vanadium is small relative to chromium, as it is in many ores and metals. Manganese also should be corrected for; this is best done in preparing the solution for titration.

3.2.2.3 Iodometric Titration

This method has been widely used in the assay of chromium chemicals. It is not as generally applicable as the ferrous salt titration, because many more ions liberate iodine from iodide than oxidize ferrous salt. In addition to the interferences listed for the ferrous salt titration, such common ions as iron(III), copper(II), arsenate, and molybdate interfere. Since the ferrous salt titration usually is carried out in sulfate solution and the iodide titration in the presence of chloride or acetate, the iodide titration may be favored in the analysis of lead chromate or barium chromate. However, the potentiometric titration appears to be less subject to manipulative error. Nitric acid free of the oxides of nitrogen, or dilute perchloric acid, may be used to prepare the sample for titration in this case.

In the iodometric method, iodine is liberated in acid solution from an excess of iodide and is titrated with standard thiosulfate.Hydrochloric acid, 2 to 5 ml. per l00 ml. of titration volume, should be present, acetic acid tends to give a fugitive starch end point. The starch should be added just before the end point and the titration run moderately slowly with good mixing. Otherwise, the usual precautions of iodometric titration should be observed: the iodine preferably is liberated in a closed flask, which is allowed to stand for 5 minutes before titration. The standing time should be increased to 15 minutes if dilute solutions (0.0001N) are being titrated. The color change at the end point is from a deep blue to a light green or blue-green. A typical procedure is: To a 100-ml. sample containing about 0.06 g. of chromium(VI) and 20 meq. of free hydrochloric acid in a glass-stoppered Erlenmeyer flask, add 2 g. of potassium iodide. Stopper the flask, mix thoroughly, and allow to stand in the dark for 10 minutes. Titrate with 0.1N sodium thiosulfate solution, adding starch as indicator near the end point. The color change described above is sharp.

Another iodometric method depends on the titration of iodine liberated from an iodate-iodite mixture by hydrolysis of a chromic salt. The method seems impractical, as free acid, basic salts, and other hydrolyzable cations must be absent for accurate results.

3.2.2.4 Permanganate Methods

Although permanganate oxidizes chromium(III) to the sexivalent state, the reaction is slow in acid solution and is better carried out in neutral or alkaline solution at the boiling point. A sample containing 10 to 15 mg. of chromium(III) in a volume of 300 to 400 ml. is treated with 2 g. of sodium acetate, heated to boiling, and titrated with 0.lN permanganate. Shaking assists the settling of the MnO_2 formed. The color change at the end point is from yellow to orange-yellow. The addition of barium sat facilitates detecting the end point.

3.2.2.5 Other Redox Methods

The volumetric oxidation of chromium(III) to chromium(VI) in strongly alkaline solution by standard potassium ferricyanide, using potentiometry to determine the end point, has been described. A small amount of thallium salt is used as catalyst, and a voltage change at the end point of about 400 mv. per 0.1 ml. of 0.1N ferrocyanide is reported. The method is not satisfactory in the presence of iron because of occlusion of the chromium(III) oxide, and hence has been little used. The use of uranium(IV) as a reductant in potentiometric titrations in the presence of iron(III) as catalyst is reported to give successive inflections representing reduction of $Cr_2O_7^{-2}$, MnO_4^{-1}, and VO_3^{-1} Stannous chloride solution has been suggested as a reductant suitable for titrating chromium(VI). Vanadium(V), iron(III), bromate, iodate, iodine, ferricyanide, and other oxidants also can be similarly titrated. Titanous salts have been used similarly. Arsenite may be used to reduce chromate in the presence of vanadate. In acid solution, the chromate is reduced and the excess arsenite can then be titrated with permanganate.

The Jones reductor may be used to reduce chromium quantitatively to chromium(II). The reduced chromium is extremely susceptible to air oxidation and cannot be titrated directly unless collected under an inert gas; it may, however, be caught in a ferric sulfate solution and the ferrous ion produced can then be titrated. Titanium, vanadium, and molybdenum interfere. Chromate may be titrated against the leuco form of methylene blue,which is then back-titrated with titanous chloride.

Chromium (III) is not reduced in a silver reductor.

3.2.2.6 Complexometric Methods

The development of ethylenediaminetetraacetic acid (EDTA) and other powerful chelating agents, plus the strong tendency of chromium(III) to form octahedral complexes of high stability, has inevitably led to complexometric methods for chromium. Many of these are colorimetric. Brief descriptions of some of these methods follow. In many cases interferences have not been established completely. The governing principle in most cases appears to be that the chromium(III) complex is stable, but because of the "inner orbital" structure of all chromium(III) ions, the EDTA complex forms slowly. Direct titration is hence not practical; the chromium complex is formed by heating with excess EDTA, which is then back-titrated with a rapidly chelating ion, using a dye sensitive to the ion as the indicator.Manganous solutions have been recommended as the back-titrant, using Solochrome Black T as the indicator. The need for boiling with excess EDTA for 15 minutes to quantilatively complex chromium(III) is stressed. Zinc ion also is used, with zincon as the indicator. In a further variant, chromium(III) sulfate solutions are boiled at pH 3 with excess EDTA, which is then titrated with 0.1N ferric chloride, using the brown decomposition product of Bindschedler's Green as the indicator. A similar method carries out the complexing in boiling acetate-buffered solution at pH 4.7 for 5 minutes and titrates the excess EDTA with ferric chloride potentiometrically, or with zinc ion using Eriochrome Black T, after compensating for the color of the chromium(III) complex with Eriogreen B and Congo red. The method is reported applicable to the determination of chromium(III) in the presence of chromium(VI). These workers used nickel salts as back-titrants with murexide as the indicator. Alkali earths, iron, aluminum, copper, zinc, and nickel interfere.

Sulfosalicylic acid is reported as a reagent liberating hydrogen ion equivalent to the chromium(III) content of the solution as a result of complex formation. Oxalate forms stable complexes with chromium(III) and use is made of the preferential complexing of oxalate to hydroxyl in determining the basicity of basic chromium salts. By treating basic salts with excess oxalate, titratable hydroxyl is released; this is determined by back titration, the oxalate complexing being carried out in acid solution. For a typical sample containing 0.04 to 0.10 g. of Cr_2O_3 equivalent, 15 ml. of 0.5N sulfuric acid is added, and the solution is refluxed in a total volume of 100 ml. for I hour after the addition of 25 ml. of 1M potassium oxalate solution. The sample is cooled and back-titrated with 0.25N sodium hydroxide to a pH of 7.5, using a meter standardized against pH 7 buffer. The method is also applicable to chrome-tanned leather.

3.2.2.7 Polarographic (Amperometric) Methods:

The reduction of chromium(VI) to chromium(III) in acid solution, which forms the basis of conventional redox methods, is not usable since the resulting wave is mixed with the wave derived from the mercury anode. In alkaline solution, however, a well-defined wave results, and this has been the basis of many of the proposed methods, since none of the elements commonly associated with chromium (in ferrous alloys, for instance) interfere. The method has been further examined with respect to interferences, and only large amounts of phosphate (100 mg.), perchloric acid, lead, zinc, and cadmium interfere in the determination of 50γ quantities of chromium. In this method it is not necessary to remove precipitated oxides unless the quantity is large and occlusion is a serious factor. Two well-defined waves result from the reduction of chromium(III). In general, however, the height of the second wave is more than twice that of the first, indicating that the chromium(II) → chromium(0) portion of the wave is contributed to by the co reduction of hydrogen ion. The potential of the first wave may show change on standing, possibly reflecting the slow equilibration of the numerous coordinate ions that chromium (III) may form through hydrolysis and coordination. The change is particularly noticeable in unbuffered solutions. Since the first chromium(III) wave is 0.4 v. in advance of the iron(II) wave, small amounts of chromium can be determined in the presence of large amounts of iron as long as the iron is completely in the ferrous state.

The high negative potentials of the reversible chromium salicylate complex and the chromicyanide ion (—1.23 v. and—1.38 v., respectively) are of particular interest in denoting the strong reducing character of divalent chromium in these complexes. The cyanide electrolyte should be of considerable practical use. Application of the procedure has been made to the analysis of industrial waste waters, using the waves at 0.60 and 1.10 v. vs. S.C.E. The amperometric titration of dilute chromate solutions with ferrous sulfate, using a rotating platinum microelectrode. A typical procedure is as follows.

The sample is made 0.1 M in acid (perchloric, hydrochloric, nitric, or sulfuric) and is transferred to a suitable beaker equipped with a rotating platinum microelectrode and low resistance salt bridge. A saturated calomel electrode is used as outside reference electrode. A 1-v potential difference is applied across the platinum anode and saturated calomel electrode. 0.01 N Standard ferrous ammonium sulfate, 0.05 N in sulfuric acid, is added from a microburet until a current is observed on the microammeter. The sides of beaker are rinsed with distilled water and the diffusion current of Fe^{+2} is measured, and then measured again after successive 0.2-ml. increments of ferrous solution. The volume of ferrous sulfate gives a linear plot against microamperes, and extrapolation of this line to zero current gives the volume of standard ferrous sulfate equivalent to the Cr^{+6} in the sample. The method is accurate to 0.5% even with chromate as dilute as 10^{-4}M.

This method applied to chromium vanadium mixtures. Both chromium and vanadium are oxidized by perchloric acid, supplemented by permanganate. Chromium and vanadium then are titrated together with ferrous sulfate; the vanadium then is reoxidized with permanganate, titrated separately, and the chromium determined by difference. The method has been applied to alloys, crude oil, asphalt and petroleum residuals. Others have applied similar procedures to alloy analysis.

3.2.2.8 Photonometric Methods

An ingenious photonometric titration method for chromium (VI) has been devised. Advantage is taken of the fact that the reaction

$$2Fe^{+3} + C_2O_4^{-2} \rightarrow 2Fe^{+2} + 2\,CO_2$$

is photosensitive and that the number of moles of Fe^{+3} reduced is proportional to the time of exposure to a constant ultraviolet source. If chromium (VI) is present, the Fe^{+2} is immediately reoxidized, maintaining a constant concentration of Fe^{+3}. The chromium (III) formed by reduction of the chromium(VI) thus is proportional to the time of exposure, and its increase may be measured photometrically. When the chromium(VI) is completely reacted, there is an abrupt change in the increase in absorbance.

3.2.2.9 Photometric Methods

Colorimetric Determination as the Diphenyl Carbazide Complex:

The outstanding colorimetric determination of chromium is that depending on the intense red-violet color developed on the addition of a solution of s-diphenyl carbazide (1,5-diphenyl carbohydrazide) to an acidified solution of a chromate or dichromate.

The diphenyl carbazide reagent was originally prepared in alcohol-water solutions, but it oxidizes and darkens very quickly when stored. It was soon found that acetic acid improved the stability somewhat; ethyl acetate also was suggested as solvent. It was proposed that phthalic anhydride-alcohol solution was stable for a month or more. A systematic investigation of the stability indicated oxidizing agents and bases (including alcohols and water) as the principal agents causing instability. The reagent acetone from which all traces of basicity have been freed gives solutions stable for several months. Thioglycollic (mercaptoacetic) acid has been recommended as a preservative.

The work cited above on the nature of the complex also indicates that the usual commercial diphenyl carbazide is an equimolar compound of carbazide and carbazone. Consequently, much of the early work on reagent stability, the effects of concentration, the chemistry of the complex, and so on, is open to question.

The colored species is extractable if desired. It is cation. The acetate, perchlorate, or chloride are extractable by isoamyl alcohol or chloroform. Extraction by chloroform in the presence of alkyl sulfate surfactants is also studied.Hexanol and cyclohexanol.

Acetone-isoamyl alcohol also has been suggested & used. The chromium(VI) is also extracted with trioctyl phosphine oxide in benzene, then measure the color by addition of alcoholic diphenyl carbazide directly to the extract.

Diphenylcarbazone has been suggested as a reagent for chromium(II). The color developed evidently is the same as the chromium(VI)-diphenyl carbazide color. There are not too many interferences with the diphenyl carbazide method. With chromium in the range of 0.4 p.p.m, no interference from 200 p.p.m. of molybdenum or mercury is indicated. Iron at 200 p.p.m. and vanadium at 4 p.p.m. are slightly interfering, giving a brown color, and had best be removed in accurate work. However, the vanadium color is more fugitive than the chromium color and if the vanadium does not exceed 10 times the chromium, good results can be obtained by waiting 10 to 15 minutes before reading the sample. If copper is present in amounts 500 times the chromium concentration, chromium readings will be about 10% low .

The molar extinction coefficient is given as 31,400 at 540 mμ, on the basis of the dichromate content of the solution .The extinction curve of the colored complex, showing a maximum at 540 mμ, with I/I values falling to one-half of this at 500 and 580 mμ have also been plotted. The Beer's law line for a 1-cm. cell with a Cenco No. 2 green filter, where log $I_o/I = 0.55\ C$, where C is the chromium(VI) concentration in parts per million also has plotted. The practical limit of sensitivity of the method in ordinary use is 0.01 ppm. of chromium. The color is best developed in acid solution. Sulfuric acid is preferred because the interference from iron is lessened. Hydrochloric acid also is widely used, and phosphoric acid has been suggested.

A suitable normality of acid is 0.2N; at low acidities the color does not develop properly, whereas at higher acidity it is not stable. Also, under these recommended conditions, any color developed by vanadium fades quickly. Other workers prefer adjustment of pH to 1.3 to 1.7 instead of acid normality.

In carrying out the analysis, it is unwise to use glass that has been cleaned in CrO_3 "cleaning solution." A "wash acid" consisting of 50 ml. of nitric acid (sp. gr. 1.42) and 150 ml. of hydrochloric acid (sp. gr. 1.19) in 200 ml. of water is recommended. Conversely, processing of very small amounts of chromium (~1 ppm.) in glassware under acid conditions for long periods of time may result in a loss of chromium through adsorption. The losses may be lessened by alkaline oxidation and the use of new glassware.

A general procedure for carrying out the analysis is given below.

Reagents

s-Diphenyl carbazide, 0.25% in A.C.S. acetone, weakly acidic. The solution should keep some months without appreciable discoloration; discard it when it becomes brownish. Sulfuric acid, 6N, free of reducing substances. Add dilute permanganate to the hot acid until a faint pink color appears Standard chromium solution, 10 γ chromium(VI) per ml. Dilute a 0.01 or 0.1% solution with distilled water free of reducing substances as required just before use. Either reagent potassium dichromate (2.83 g. = 1 g. Cr) or potassium chromate (3.73 g. = 1 g. Cr) make acceptable standards.

Procedure

To a 10- to 20-ml. sample containing 0.2 to 10 γ of chromium add sufficient sulfuric acid to make the acidity 0.2N at a volume of 25 ml., mix, add 1 ml. of diphenyl carbazide solution, and make up to 25 ml. with reductant-free distilled water. Read at 540 mμ immediately, unless vanadium is present, in which case wait 10 to 15 minutes. In accurate work, the transmittance of a blank also should be determined to compensate for color of the reagent.

3.2.2.10 Flame photometry

Since chromium gives lines rather than bands or a continuous spectrum in the flame, it is possible to use flame photometric techniques for the quantitative determination of chromium. The location of the principal lines of chromium; at 357.9 360.5 425.4 and 429.0 nm has been given. It is pointed out that only in the cyanogen-oxygen flame or the hydrogen-fluorine flame sufficient sensitivity can be obtained.

The sensitivity of standard methods can be improved by volatilizing chromium from a 4-methyl-2-pentanone solution. This solvent extracts chromium(VI) from HCl solution. It is claimed that emission intensity is increased 50-fold, compared to aqueous solutions. Iron is the only element that accompanies chromium in the extraction. Spectral interference is observed at iron concentrations of 500 γ/ml. and greater. The 359.4-mμ chromium line is not interfered with, and background can be measured at 360.0 mμ.Of the lines listed above, using a Beckman DU spectrophotometer with photomultiplier and oxyacetylene burner, the following scale divisions are recorded per microgram of chromium per ml.:

Wavelength,mμ	Intensity,division/γ/mL
357.9	5
359.4	4
360.5	3
425.4	10
427.5	8
429.0	6
520.6	2

Down to 0.1 ppm., chromium can be measured less can be detected. Quantitative measurements using the procedure on a variety of standard samples, ranging from 0.029 to 1.15% of chromium, show good accuracy and precision varying from 1 to 10%, depending on the sample.

3.2.2.11 X-Ray Diffraction and Fluorescence

X-ray diffraction has proved useful in the semiquantitative analysis of mixtures containing chromium compounds. Because chromite and chromic oxide form crystals of a relatively high degree of symmetry and the energy of the diffracted radiation is concentrated in a few lines, these compounds are relatively well suited to estimation as crystalline phases in a mixture. However, both of these compounds are end members of a solid solution series, and therefore both the lattice constants and the estimation of the chromium content will be subject to variation that can be determined only by knowledge of thc exact nature of the crystalline phases. The percentage of chromium in a spinel sometimes can be estimated from its x-ray diffraction pattern.

X-ray fluorescence analysis has been used successfully for the analysis of chromium ores and stainless steels. The analysis of stainless steel is carried out effectively by use of a solution of the steel in perchloric acid. Use of dilute solutions eliminates the interelement effect, which may cause up to 25% error in unknown samples, and also eliminates error due to local variations in the solid sample. A solution containing about 5 mg. of metal per ml. is suitable for the analysis, and results accurate to 1.5% arc obtainable with a scintillation-type counter. The lower limit of detection is 5 to 10 p.p.m. of each element in the test solution. This sensitivity is attained by use of a helium or vacuum atmosphere in the spectrograph. In the analysis of chromium ores, results within 0.2% of the values obtained by careful chemical analysis have been obtained by x-ray fluorescence based on standard samples of ore.

3.2.2.12 Radiochemical Methods

The chemistry of chromium as it applies to radiochemical work has been reviewed. The separation of chromium isotopes that may be formed in radiochemical transformations is given special consideration.Cr^{51} frequently is used as a radioactive tracer, often in conjunction with Fe^{59}. Various procedures have been described for the radiochemical measurement of Cr^{5I}. The decay of this isotopic occurs through orbital electron capture, with emission of K-capture x-rays and also of soft gamma rays of 0.323 M.e.v. in about 8 to 10% of the disintegrations. Either a well-type scintillation counter to measure the gamma rays (efficiency about 4%) or a Geiger proportional counter filled with heavy gas for the K-capture x-radiation (efficiency 1%) may be used. In general, 5-ml samples containing less than $2x10^{-3}$ μc. is best studied with the Geiger counter, while the scintillation detector serves if the activity is greater .A simple lead absorber may be used to obtain the Fe^{59} and Cr^{51} activities in mixtures. Chromium forms radioactive species, in common with many other elements, under neutron irradiation in an atomic pile. The resulting induced radiation characteristic of chromium can be detected and measured if as little as 10^{-7} g. of chromium is present in the original sample. However, chromium is less responsive to this technique than many other elements. As little as 10^{-11} g. of europium, for instance, can be detected.

3.3 DETERMINATION OF CHROMIUM IN SPECIFIC MATERIALS

Analysis for chromium in certain materials is very frequently required and a brief summary of appropriate procedures for these determinations would appear to be in order at this point. A general bibliography of recommended methods for methods of analysis of a wide variety of materials has been studied.

3.3.1 Ores

Different methods describe the sampling, fusion procedures, and volumetric analysis usually employed in the analysis of chrome ores for chromium. The methods used at various commercial laboratories and the precision and accuracy of results to be expected have been discussed, and a rapid method for the complete analysis of ores have been described. Various analytical methods as applied to a Turkish ore also have also been reviewed .

The universal method employed is based on opening the ore with a sodium peroxide fusion. Various workers favor iron, porcelain, zirconium, and sodium carbonate-lined platinum for the crucible. The cooled fusion is leached with water, boiled to destroy excess peroxide, and acidified. In routine determination, the acidified extract may be titrated directly. In accurate work, any chromium(III) in the solution is oxidized with permanganate and the manganese is reduced to manganese(II) before titration. A correction also is made for the vanadium content of the ore

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3.3.2 Wood And Leather

Chromium compounds are used in the preservative treatment of wood and the tanning of leather. These organic materials respond to the general dry and wet ashing procedures. If a dry ashing procedure is used, the chromium is normally recovered as free or combined Cr_2O_3 and is best determined by fusing the ash, and by then proceeding as for chromium ores. Wet ashing procedures commonly use perchloric acid after destruction of most of the oxidizable organic matter with nitric and sulfuric acid. Rigid adherence to published procedures must be observed to prevent serious accidents. Procedures have been described by the American Leather Chemists' Association and the American Wood Preservers' Association. After destruction of the organic matter, the bulk of the chromium is in the hexavalent condition and usually may be titrated directly for routine analysis. For accurate results, the small amount of unoxidized chromium should be oxidized to chromium (VI) before titrating.

Man receives high dose, of Cr, not only from contaminated air/water, but also from soil. Soil contamination with respect to chromium has been profoundly investigated throughout the world in areas in close vicinity to tanneries.

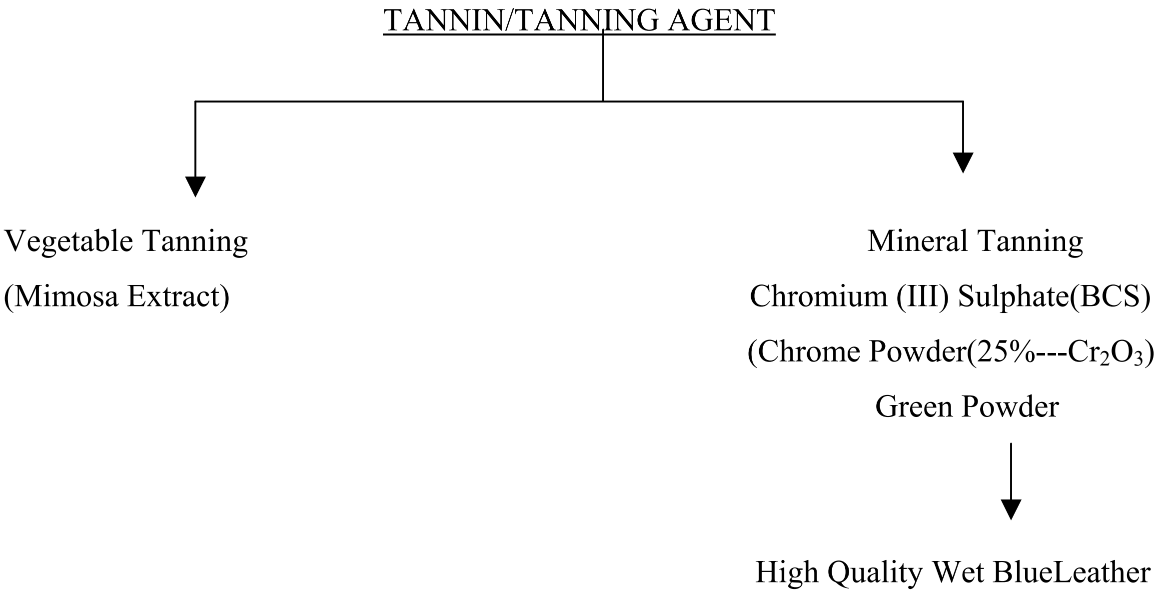
STAGES INVOLVED IN TANNING PROCESS
PROCESS STAGES

1. HIDES AND SKINS STORAGE
2. SOAKING
3. LIMING AND FLESHING
4. DELIMING

5. BATING
6. PICKLING
7. TRANNING
8. DRAINING AND SETTING
9. PADDING AND DRYING
10. FINISHED GOODS STORAGE

TANNING

The process of Conversion of Hides/Skin (Collagen Fibres) into non-putrescible (Non-Decomposable) leather by addition of Tannin.



The basis of tanning reaction is the formation of non-labile covalent complex of Cr(III) in which protein ligand is bound via it’s free carboxyl groups.

3.3.3 Industrial Water And Waste Water

These samples include recirculating waters and brines in which chromate is used to inhibit corrosion, wastes from tanning, metal finishing, and chemical manufacturing, both before and after treatment to remove chromium, and samples from rivers and other industrial supplies.

Samples of the first group usually contain between 50 and 3000 ppm. of chromium(VI), calculated as Na_2CrO_4. If no other colored materials are present, and this is usually the case, a simple direct colorimetric measurement of chromate ion is sufficient. Samples down to 20 p.p.m. of sodium chromate can be titrated readily with 0.1N ferrous sulfate if color is present, not due to organic matter which will reduce chromate on acidification. This procedure also is useful in measuring the chromium(VI) content of untreated wastes.

Chromate is sometimes employed as an inhibitor in automotive anti freezes containing methanol or polyhydroxy alcohols. If there is color not due to chromate in these samples, separation of the chromate as barium chromate is helpful. The most serious problems in determining chromium in water samples arise when chromium is below 5 ppm. and organic matter is present. The chromium eventually will be determined colorimetrically as the diphenyl carbazide complex. It will be necessary to oxidize the organic matter and the chromium to obtain total chromium. Frequently an accurate value for chromium(VI) cannot be obtained by direct measurement, because organic matter present will reduce chromium(VI) to chromium(III) at the pH level at which the colored complex is formed. A recent A.S.T.M. standard gives detailed procedures for testing such samples. Polarographic methods have been employed for chromium in industrial wastes.

3.3.4 Recommended Procedures

The element chromium is usually determined titrimetrically if it is present in the sample to the extent of 1% or over. The method believed to be most reliable is the direct titration with ferrous sulfate, freshly standardized against reagent potassium dichromate. Only manganese and vanadium, of common elements, interfere, and these are readily corrected for. The end point is determined potentiometrically or with o-phenanthroline or one of its derivatives as indicator. Amounts of chromium less than 1% are determined by colorimetric methods. The highly sensitive s-diphenyl carbazide color reaction also is highly specific and is recommended. It may be used to determine down to 0.01 ppm. of chromium.

Preparation for both these methods is predicated on converting the chromium quantitatively to chromium(VI). Many samples have the chromium in this valence and can be titrated directly. Oxidation is achieved reliably by sodium peroxide fusion, followed by boiling, acidification, reoxidation with permanganate, and reduction of the manganese with dilute hydrochloric acid. It is particularly applicable to refractory inorganic materials, such as ores containing more than 1% chromium.

Alloys and acid-soluble samples are dissolved in nitric-sulfuric acid mixtures, with or without perchloric acid. The oxidation of the chromium is accomplished by persulfate in the presence of silver. Whereas ashing may be used for organic materials containing less than 1% chromium, wet oxidation procedures are generally preferred. Hypobromite oxidation is used alternatively with persulfate-silver to oxidize chromium prior to development of the diphenyl carbazide color. These methods are relatively simple and give excellent results on the vast majority of samples. Special instrumental methods using the emission spectrograph, polarography, and x-ray spectrograph have been described and are especially useful for rapid analysis and to eliminate the need for separations.

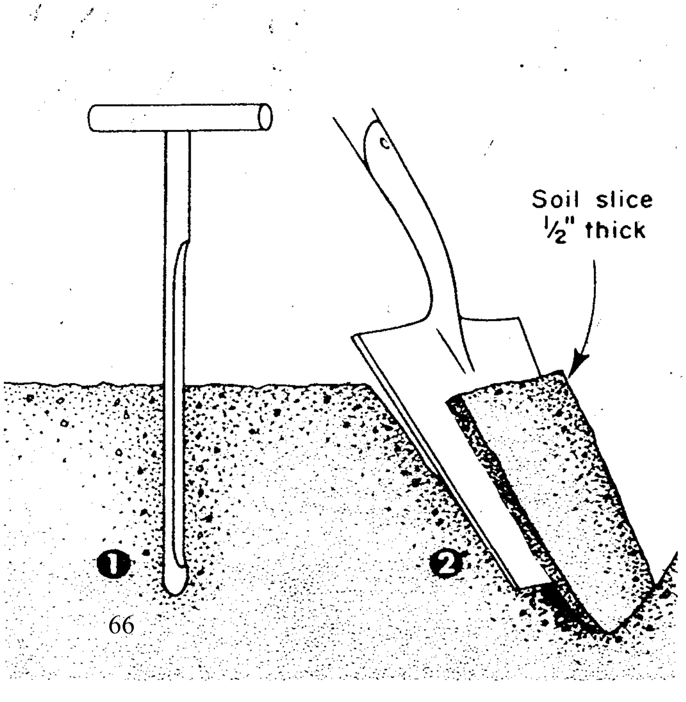
CHAPTER 4

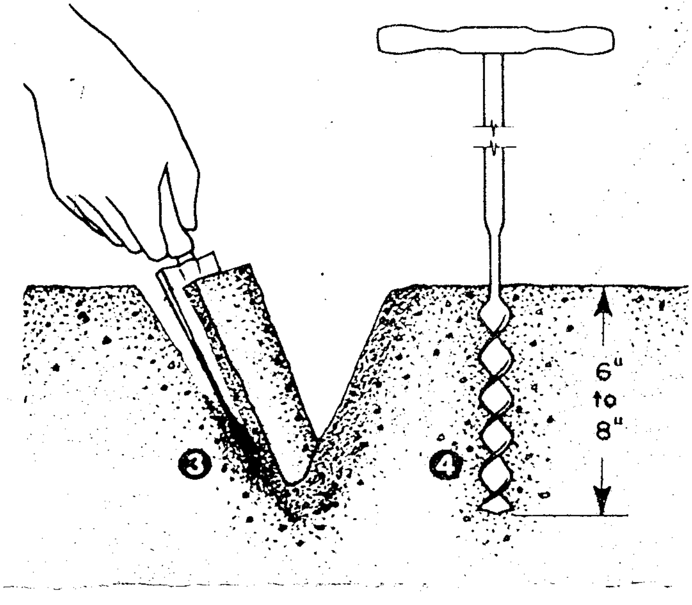
EXPERIMENTAL

4.1 SAMPLING

The sampling of a chromium containing material such as soil can be carried out quite easily and as such presents no major sampling problems. The sampling procedure for the present work was divided into two major categories; one comprising fifteen soil samples taken from the suburbs of Islamabad referred to as background soil samples, and the other comprising seventeen soil samples procured from close vicinity to tanneries, hereafter called contaminated soil samples.

The later class of samples is expectedly enriched in chromium, as chromium compounds are used in the processing of the tanning of leather. Normally top soil, 0-2.5cm, was scooped for sampling. The soil samples were stored in zip-mouthed polythene bags prior to analysis. Approximately 100g of soil samples was taken in each case. The samples were then analyzed for Cr(III) and Cr(VI) by the spectrometric method and the total chromium concentration was determined by the AAS method.





4.2 MOISTURE DETERMINATION

An exactly weighed portion of 5.000 g of a given soil sample was put in a china dish, placed it in an oven maintained at 100ºC (±1ºC) for 6-8 hours. After complete dehydration of the sample, it was cooled down and then weighed onto an analytical balance. The weight loss was a direct measure of the amount of moisture in the sample.

4.3 DRYING

The sample was placed in the open for drying purpose for about twenty four hours. The drying of samples is important, otherwise it becomes difficult to pass the samples through the 10 mesh sieve. After proper drying, the lumps of soil samples were ground in a mortar thoroughly and uniformly. The soil sample was then passed through a 10 mesh sieve which was shaken well during the process. The soil sample so obtained, was then used for further treatment and tests, as outlined in the forthcoming section.

4.4 pH$_w$ DETERMINATION

An exactly weighed 5.00g of the thoroughly ground soil was dissolved in 10.00ml of distilled water in a conical flask which was than clamped to a shaker run for three to five minutes at 2000 rpm. After shaking the matter in the flask was allowed to settle down. With the help of a precalibrated pH meter, the pH of the soil sample solution was measured.

4.4.1 Calibration Of The pH Meter

Most successful analytical application of direct pH measurements rely upon a empirical calibration technique which minimize the effect of variation or error in the measurement of hydrogen ion activity of a given solution. For this purpose buffer solution was made by dissolving the 9.19 pH buffer powder packets in 200ml of distilled water. Infact, if the range of measurement was in the acidic medium then the buffer solution of 4.01pH was prepared. Depending upon the requirement of the buffer solutions at known pH could be prepared using standard BDH buffer packets.

In each case, the powder from the packet was dissolved in 200ml of water, now ready for calibration of the pH meter. Each time a fresh buffer solution was prepared prior to pH determination. The corresponding pH value as provided on the label of packets has adjusted with the help of adjusting knob on pH meter. This calibrated pH meter was then used for further measurement of hydrogen ion concentration in the unknown soil solutions prepared by the above cited procedure.

4.5 DIGESTION FOR AAS

Weighed exactly 5.0g of 10 mesh soil sample into a small beaker and added 15ml of 0.10M (37%) hydrochloric acid, guaranteed 99.9% pure and intended for use with AAS analysis.

4.5.1 Standardization Of HCl

An exactly weighed portion, 2.65gm of sodium carbonate (anhydrous) was dissolved in 50.0mL of distilled water, in order to get 0.5M Na_2CO_3 solution . Since each millimole of sodium carbonate reacts with two millimoles of acid, so 0.5M Na_2CO_3 would be used to standardize 0.1M HCl.

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2CO_3$$

The 0.1M HCl solution was prepared by pipetting out 8.29ml of 37% HCl and make up the volume upto 1000ml with pure distilled water. The indicator solution was prepared in advance of standardization, by dissolving 0.1g of methyl orange indicator solution. The sodium carbonate solution (titrand) was titrated against the hydrochloric acid solution contained in a 50ml burette. The titration was continued until the colour of methyl orange turned from pure canary yellow towards orange-yellow. From the titration data the concentration of hydrochloric acid solution was calculated to ensure its use as 37% HCl as a digestion medium. After standardization of HCl, 5.0g of soil samples was added to 15.0mL of 0.1M HCl solution. The solution was well shaken for about 10minutes, either manually or on a shaker. The solution was then filtered and the filtrate so obtained was diluted upto 50.0mL. The clear digested sample was run directly on to AAS system. The details of standard preparation, aspiration and quantification are given in sections to follow.

4.5.2 Preparation Of AAS Standards

The AAS standards of desired concentration were prepared using either the ready stock solutions (BDH or E. Merck) or pure soluble salts of the relevant metals with guaranteed purity of 99.9%. Subsequent dilutions from the stock solutions, usually 100 ppm, were made using double distilled water. The final finished volume of each standard was 50.0mL in a flat-bottomed measuring flask. In cases where soluble salts were taken for the preparation of standards, nitrates were preferably selected. For the stabilization of standards about 5mL of dilute nitric acid (5% v/v) was added to each sample solution. The standards thus prepared were intended for use within a week after which time fresh standards were prepared following the procedure outlined above.

4.5.3 Aspiration

The clear digested sample solutions were aspirated onto the Atomic Absorption Spectrophotometer(AA-670 Shimadzu) under defined optimized analytical conditions for determination of total Cr content. The selected analytical line for Cr was 357.9nm with an automatic slit width adjustment of 0.50nm. The air-acetylene flame was used at temperature of 2250ºC at a burner height of 10cm and with fuel rate of 2.6 L/min.. Normally the instrument automatically selects the flame conditions. The hydrochloric acid and distilled water were used as blanks. The working standards in the range of 2,4, and 6 ppm were prepared and the standard calibration method was used for the determination of unknown chromium concentrations in samples. The finished data were displayed automatically by the readout of the instrument. Three sub-samples of a given sample were run simultaneously to measure levels of chromium as 8±SD.

4.5.4 Quantification

The results were quantified by using the following formula for the total chromium contents in the given soil sample by AAS.

Concentration(mg/kg)=(displayed sample concentration – blank) x 10.

The above formula is valid only if the 5.0 gm of soil sample is dissolved and diluted up to 50.0mL To convert the measured absorption values into concentration of the metal being determined it is necessary either to make use of a calibration curve or to carry out the standard addition procedure. The calibration curve procedure is described since it was used for the quantification.

4.5.5 Calibration Curve Procedure

A calibration curve for use in atomic absorption was plotted by aspirating into the flame samples of solutions containing known concentration of the element to be determined measuring the absorption of each solution, and then constructing a graph in which the measured absorption was plotted against the concentration of solution. At least four standard solutions were used covering the optimum absorbance range of 0.1 to 0.4 A, and if the calibration curve was found to be non-linear the measurements with additional standard solutions were carried out. In common with all absorbance measurements, the readings were taken after the instrument 'zero' was adjusted against a blank which may be either distilled water, or a solution of similar composition to the test solution but without the component to be determined. It was usual to examine the standard solutions in order of increasing concentration, and after making the measurements with one solution, distilled water was aspirated into the flame to remove all traces of solution before proceeding to the next solution. At least two, and preferably three, separate absorption readings were made with each solution, and an average value was taken.

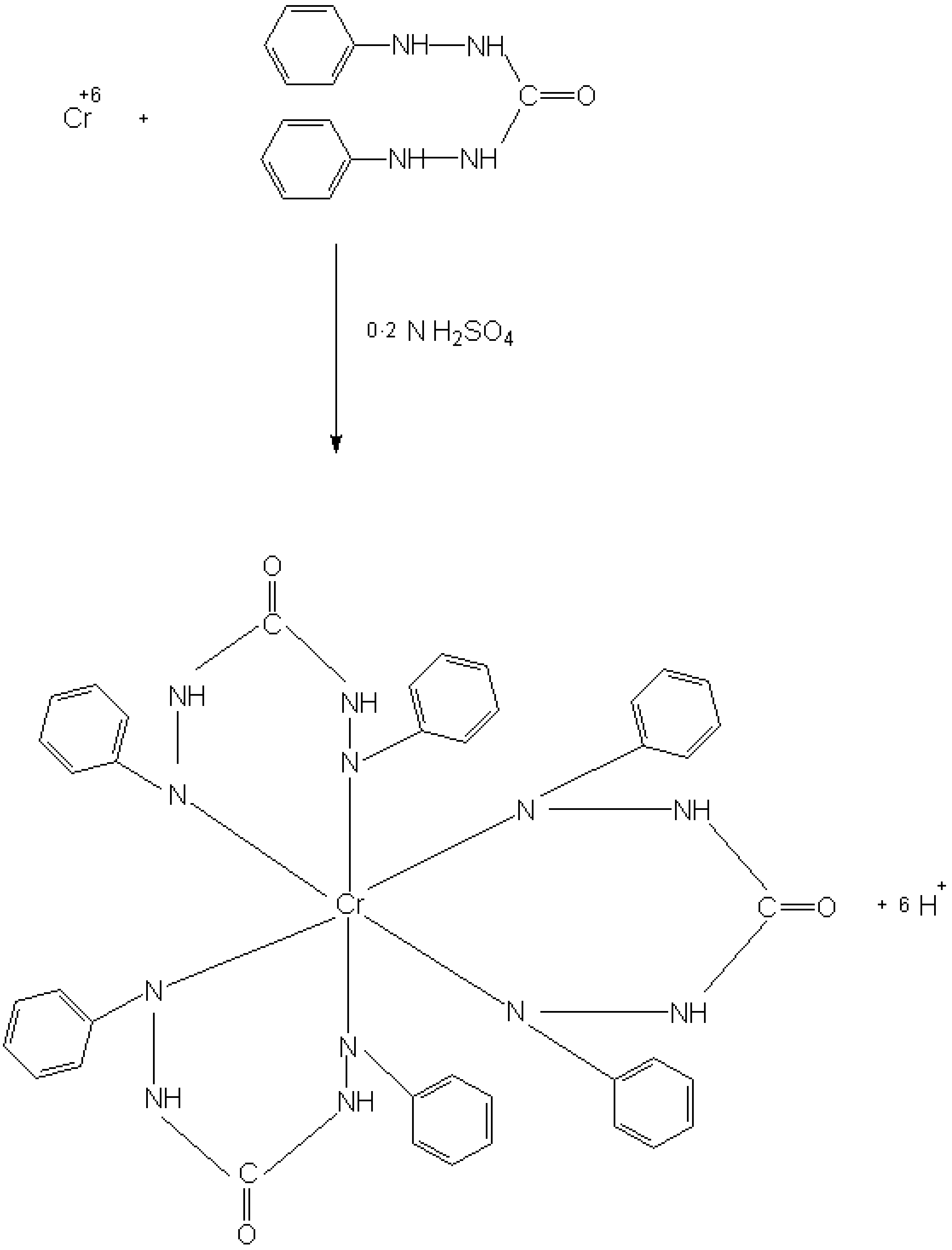
Using calibration curve it is a simpler matter to interpolate from the measured absorbance of the test solution the concentration by the relevant element in the solution. The working graph was checked occasionally by making measurements with the standard solution and if necessary a new calibration curve was drawn to ensure previously maintained accuracy, which for the most cases varied between ±1.0-1.5% of the finished result.

4.6 OXIDATION TO Cr (VI)

This process was carried out in acid solution. Oxidation in acid solution could be carried out with permanganate, with persulfate in the presence of silver ion, or with silver peroxide, concentrated nitric acid and perchloric acid mixture, chlorate, lead dioxide, sodium bismuthate, ceric ion, and other strong oxidizing agents. The most preferable method also used in this work involves oxidation with nitric acid and perchloric acid mixture. The following procedure was adopted for the oxidation of Cr III to Cr (VI).

A 5.0 g portion of the soil sample was dissolved in 15.0 mL of 0.1M standardized HCl solution, and after thorough shaking, the solution was filtered, and the filtrate so obtained was taken in a 50 mL volumetric flask. Added to this filtrate was 5.0mL of 0.1M nitric acid, heated on a hot plate allowed to cool and then added 5ml of 0.1M $HClO_4$ (perchloric acid) was added and after proper heating and cooling again the sample was diluted upto 50mL. All the chromium was quantitatively oxidized to chromium (VI) marked by no evolution of white fumes from the solution. There is a possibility of loss of chromium as chromyl chloride, if chlorides are present. The method has the advantage that the acid solution frequently can be diluted and titrated directly.

After the completion of oxidation, the determination of Cr(VI) in the given soil samples was carried out colorimetrically. The colorimetric determination of chromium was based on development of intense red violet color obtained by the addition of a solution of S-diphenyl carbazide (1,5 diphenyl carbohydrazide) to the acidified solution of chromium containing Cr(VI) soil sample solution. The following complexation reaction is involved.



The method for the preparation of reagent solution for carrying out analysis is as follows: Accurately weighed 0.25g of s-diphenyl carbazide ($CO(NHNHC_6H_5)_2$), and it was added to 100ml of pure acetone, in order to get 0.25% s-diphenyl carbazide solution. Pipetted out 20ml of test solution Cr(VI) under consideration and added to it 10.0ml of 0.2N H_2SO_4, mixed the contents well and then added 1.0ml of 0.25% diphenyl carbazide fresh solution and the volume of solution made up to 50.0ml with distilled water. Took absorption readings at 540nm immediately using a UV/VIS spectrometer(Model UV-1601CE).

The λ_{max} values recorded were:

λ_{max} = Cr-DPC complex = 540nm; λ_{max} = Cr(VI) aqueous = 360-370nm;

λ_{max} Cr(III) aqueous = 427nm .

CHAPTER 5

RESULTS AND DISCUSSION

5.1 LAYOUT OF DATA

The data pertaining to the present work, along with the relevant information, are cast in various tables and figures. Table 1 describes basic information on the soil samples collected for the speciation of chromium, their codes, dates of sampling and relevant information as to the type of soil, depth from which sampling was done, soil colour and location of the sampling sites. The table lists 32 soil samples obtained from within Islamabad and from other cities of the country for which details are given in table 1. The outstation sampling was done to comparatively evaluate the levels of the chromium in real environment against the background, if possible. The sampling period spanned over three months, and only top soils samples were collected with conventional depth (0-2.5cm). It is noteworthy to mention that soil samples from close vicinity of tanneries in Kasur were obtained with the view to look into the hazardous level of chromium present in their effluents.

Table-2 provides information on two important physical characteristics of soils, namely moisture and pH_W. The moisture content was considered an important parameters as it not only prepares a given soil system for the supply of macro- nutrients to vegetation, but also attempts to establish a natural equilibrium between various oxidation states of elements present, specially at defined pH values. The reported pH values in this table relate to the “water-extract” as it is conventionally referred to in literature. Other media, $Ca(OH)_2$, HCl and KCl have not been used here since evaluation of soil alkalinity and / or acidity were not the prime objectives of the present work.

Tables-3&4 give separately the standard optimum analytical conditions for AAS estimations, and for spectroscopic estimations respectively. For the AAS case, the optimizing parameters selected were wavelength, lamp current, slit width, flame type, fuel flow rate and detection limit. The values reported for these parameters in the table reflect optimized values giving rise to maximized absorption signals. Like wise, all relevant analytical parameters adjusted on to UV/visible spectrometer stand for the optimized values, some of these being selectable, e.g., scan speed or sampling interval.

Table-5 summarizes the total chromium content of the soils determined by the atomic absorption method. The data are reported as 8±SD, where SD represents the standard deviation for triplicate sub-samples of a given soil sample. The units of concentration are reported as mg/kg soil on dry weight basis. The corresponding data on determination of chromium(VI) by the spectrometric method based on complexation are cast in Table 6. Here, again, the results are expressed on 8±SD basis as mg/kg dry weight basis. The successive samples were run in parallel for this estimation, as in the case of atomic absorption method.

Table-7 brings out the comparative data on the chromium(III) and chromium(VI) estimated by the two procedures. The level of the metal in each oxidation states are expressed in mg/kg soil ,on dry basis. Here, the listed Cr(III)levels were determined as the difference between total chromium and chromium(VI).

Table 8 lists selected statistical parameters related to the total chromium distribution in soil samples. As may as 10 basic parameters have been listed in this table to provide better perception of data in term of distribution of total chromium. The counterpart data on Cr(VI) and Cr(III) are reported in Tables 9 & 10, all for 32 soil samples.

Table-11 affords a comparison of the averages of Cr (III) and Cr(VI) in various samples of soil. The listed data are based on t-test pertaining to a degree of freedom of 62 for a one-tail evaluation of t-value at p=0.05. The mean and variance values are listed separately for the two sets [Cr(III) and Cr(VI)], and the overall standard deviation, SD overall, was computed using $(\Sigma SD_i)^{1/2}$.

Augmented to the comparison of averages study, is the correlation study between Cr(III), Cr(VI) and total Cr, given in a matrix form of linear correlation coefficient, r, values in tables 12. This table affords a two dimensional correlation for each pair of variables, Cr(VI) vs Cr(III), and these two against total chromium.

The spectrometric absorption data are illustrated in various figures, depicting absorption curves for Cr(III) (figure 1), Cr(VI) (figure 2) Cr (III), Cr(VI) and Cr-DPC complex (figure 5), Cr(III) and Cr (VI) (figure 3). Typically expected absorption curves for Cr(VI) are reflected in Figure 6 and for Cr-DPC complexes in Figure 4. The standard calibration curve for the Cr-DPC complex is shown in figure 9, for Cr(VI) in figure 8 and for Cr(III) in figure 7.

The data are portrayed as histograms for a relative comparison of Cr(III) vs. Cr(VI) in various soil samples (figure 10), in local samples (Figure 11) and in outstation samples (figure 12). Some specific data on outstation samples from individual cities are reported in form of histogram bars in figure 13 for Lahore, figure 14 for Kasur, figure 15 for Gugranwala and figure 16 for Sialkot. Typical pie-chat diagrams show relative orders of magnitude expressed as percent, of Cr(VI) at the maximum and minimum level (figure 17 & 18, respectively). Corresponding data for Cr(III) are cast in figure 19 and 20.

5.2 STRATEGY OF PRESENT WORK

During the present work an attempt was made to characterize various soil samples with the view to determine their Cr(III) & Cr(VI) contents. As has been seen in the theoretical sections of the chapter 1 & 2, such study on the speciation of chromium is important. Specifically this is true for those soils in adjacent areas of a work place dealing with the use of chemical compounds rich in chromium. As these compounds are drained out of the work place into the open land or directly discharged as effluents, thus causing the soil to be enriched with chromium, which by further action of water through rain or run off are carried ultimately to plants & vegetation in the vicinity.

According to one of the strategies of the present work, a two fold chromium characterization effort was made: one involving the estimation of total chromium in a given soil sample & the other involving estimation of Cr(VI) by the spectroscopic method. The former technique was based on the use of atomic absorption method and the later on complexation based spectroscopic method. Ample literature survey that has been cited in the previous sections provides evidence that these two analytical procedures are by far accepted as standard methods for the quantification of chromium, as total chromium and hexavalent chromium, complexed with DPC(s-diphenyl carbazide).

The selection of the soil samples was done from such areas of Rawalpindi and Islamabad, which represent background areas not under the influence of any work place dealing with the use of chromium based chemical compounds. For this purpose as many as thirteen sectors form Islamabad were scanned, while one location from Rawalpindi was selected for the sampling purpose. Typical soil samples representing soils rich in chromium, were taken from Haripur, Lahore, Kasur, Gujranwala and Sialkot. Some of these cities, such as Gujranwala, Kasur and Lahore represented some typical small and big industrial estates, dealing with the tanning of leather both for local and foreign markets.

The description of the soil samples on a chronological basis is given in table-1, highlighting the type, depth, colour and location of each of the thirty two soil samples procured as per detail given in the foregoing paragraph. Normally the top soil, from about an average depth of ½ inch to 2inches was sampled with a plastic scoop. The depth information given in the table as 0-2.5cm represents only by definition the top soil, which in the present case has been listed for convenience only. The colour of each soil samples was recorded at the time of sampling. The colours normally ranged from light brown to dark tan through dark brown greyish and finally to be darkish tan. All these samples were properly coated as soil samples with serial number attached to them.

5.3 OPTIMUM ANALYTICAL CONDITIONS

Tables 3 & 4 bring out the standard optimum analytical conditions for total chromium estimation by the AAS method and by the spectroscopic method respectively. The variables optimized for the AAS method were wavelength, hollow cathode current, slit width, air fuel system and fuel rate. All chromium estimations were made at 357.9nm at hollow cathode current of 5mA operatable at a slit width of 0.5nm for air-acetylene flame ignited at fuel rate of 2.6 L/min. Under the optimized conditions a detection limit at 1% absorption was achieved to be 0.09mg/L. All soil samples were analyzed under these conditions and their existence was ensured through automated selection by the C.P.U of the Shimadzu Atomic Absorption System (Model-AA-670).

The standard absorption conditions optimized for the Shimadzu UV/VIS Spectrometer (Model UV-1601 CE) were also made in terms of selectable wavelength, recording mode, absorption interval, optical slit width and scan speed. Its noteworthy that in case of AAS system, the reproducibility falls between 1.0 to 1.5% for replicate sub-samples and for UV/VIS spectroscopic methods the photometric accuracy varies between 0 to 0.5 absorption which could be translated as a comparative value against 1% absorption of AAS system. In this case the operating mode was selectable between absorption or % transmittance. In the present study the absorption mode was selected between the scanning wavelength of 190-900nm, a range that almost coincides with that of atomic absorption system. The measurement of total concentration of chromium and those of Cr(VI)by these two methods were conducted as per optimum conditions given in these two tables.

5.4 ESTIMATION OF MOISTURE & pH_w

Some physical parameters of soils are important from the view point of their chemical characteristics .Of these the moisture & water related pH(pH_w) are considered to be the basic ones. While the moisture content of soil determines the availability of both macro and micronutrients present in the soil, the pH_w factor ensures this availability at a specific pH value. Many other media in addition of water have been used to find out the pH of given samples of soils, more commonly $Ca(OH)_2$ aqueous, KCl aqueous, HCl aqueous, have been used extensively in irrigation applications. In the present work water has been used to define the pH of soil, since this solvent is important in respect of it's environmental significance attached to the precipitation & subsequent leaching process of most chemical substances from the soil. The moisture content in the soil samples varied considerably from as low as 0.81% w/w to as high as 13.50% w/w. This situation indicates an almost dry condition of sample, for example, SS-31,sampled from Samrial, Sialkot. On the other extreme, the maximum moisture of 13.50% was encountered in a sample SS-09, taken from G-6/1-4 Islamabad. Some comparative minimum moisture contents at 0.87% and 1.17% were found in SS-29 and SS-30,from Gujranwala and Sialkot respectively. The high moisture content necessarily indicated that the soils in question were in one way or other, either in contact with the water body or they were in close proximity of a water source, as a work place or a household system.

The pH_w values listed in table 2, also showed quite divergent levels of hydrogen ion concentration in the various soils. The minimum value was found to be 7.28 in the soil of sample SS-30,while the maximum at 11.24, was found for SS-20,from Sialkot & Lahore respectively. Incidentally for these two soil samples the moisture contents are quite varied, and are therefore inconsistently related with the moisture, as is the case with other soil samples. The data in table 2, therefore suggests no correlation between the pH_w and moisture content. The listed values of pH_w ,however, do indicate that all the soil samples were basic in nature and not a single sample was encountered to posses less than 7.This defines the general alkalinity associated with these soils, rendering them suitable or unsuitable towards plant growth. It can be examined from the information given in table 1& table 2,that higher pH of soils was basically related to those sampling areas which represent typical work place. For other places the pH_w parameter has shown consistent values falling in very narrow range of about 8.11 to 8.95 for those areas of Islamabad and Rawalpindi wherefrom samples SS-01 through SS-15 were taken.

5.5 LEVELS OF TOTAL CHROMIUM IN SOILS

The estimated concentrations of total chromium in various soil samples appear in table 5. The levels range from average of 32.18 to 310.12 mg/kg, thus showing a tenfold increase in in the enhanced level of 310.12 mg/kg. An examination of table shows that the local soil samples from SS-01 to SS-15 were all consistent in terms of total chromium content from a minimum of 42.25 mg/kg chromium to 66.0 mg/kg. This range was found to be independent of moisture content & pH_w as can be seen with reference to table 2.However in the case of soil sample from tanneries sites the total chromium was again found to be onto a higher side with an enhancement ratio of two to three fold. This is specially true of samples from SS-16 to SS-21.

It's noteworthy to mention here that even in the case of soil samples taken from Niaz Nagar, Kasur, the total chromium content very closely matches to the background chromium in that part of the sampling location. The reason for this observation stems from the fact that under strict municipal order the tanneries in the area have been directed to dispose off their effluents in drains made from brick work and not opening into nearby field or agricultural land. The effluents from these industries are carried away from the source and discharged farther away from any nearby water body . The estimated concentrations appear in table 5 as averaged over three parallel runs & the associated standard deviation with each measurement is also reported. It may be seen that variation in triplicate sub-samples lie between ±1.0- 1.5% .

Some useful basic statistical parameters for the distribution of total chromium in the soil samples appear in table 8. This table reveals that the average total chromium stands at 91.31 mg/kg with an overall standard deviation of 60.86 for all the soil samples included. This indicates a large dispersion of the measured concentration around the mean value. Therefore the listed standard error is substantially high ,as is coefficient of variation(66.66).The variance being a direct measure of standard deviation is expectedly quite high too.

As far as the situation on the distribution of the levels of total chromium in all the samples ,the data on curtosis and skewness listed in table 8 reflect that the distribution is not normal with a fairly high skewness value of 1.803.Likewise the curtosis value representing the total chromium distribution also does not favour a sharply defined distribution as a function of frequency for the given count (n=32).

5.6 LEVELS OF Cr (VI) IN SOIL SAMPLES

The estimated levels of Cr(VI) as part of total chromium in various soil samples determined by the spectrometric method are reported in table 6. As in the case of total chromium the estimated levels of Cr(VI) were found to be divergently distributed in soil of various origins. An inspection of table 6 indicates that the local soil samples from Rawalpindi & Islamabad contained the barest minimum Cr(VI) running from 27.24 to 46.00 mg/kg. However in the case of soils from the workplace the Cr(VI) levels are substantially high, reaching to peak values of about 230 mg/kg. As in the case of total chromium the Cr(VI) content remained almost threefold to sevenfold in case of soil having origin closed to work places involved in chemical processing of the leather. The table again represents the listed values pertaining to triplicate sub-samples & the observed dispersion around the mean value may again be found to lie between 1.0 to 1.5%.

Some basic statistics for the distributions of Cr(VI) in various soil samples is presented in table 9 with usual parameters on minimum, maximum, average, standard deviation, coefficient of variation, standard error, variance and symmetry/asymmetry parameters like curtosis and skewness. The average Cr(VI) level was 63.08 mg/kg with the corresponding standard deviation of 46.80 mg/kg. This indicated a large spread around the mean, almost of the same size as was observed for total chromium. The corresponding coefficient of variation and the standard error parameters are also comparable in both the cases, with a little decrease in the variance compared with the total chromium case. The curtosis and skewness factors are again reflective of the fact that the distribution of the Cr(VI) follows a distribution that is not normal but it could follow any other distribution pattern, may be a log normal distribution pattern.

5.7 COMPARATIVE LEVELS OF Cr(III) and Cr(VI)

Table 7 finalizes the chromium contents of various soil samples by bringing out the Cr(III) levels deduced from total chromium and Cr(VI). A review of the table indicates clearly that Cr(VI) is a dominant species in the soil samples investigated in that the normal pattern of Cr(VI) to Cr(III) ratio is far greater than 1. As a consequence this poses an alarming situation with respect to soil taken for analysis form closed vicinity of tanneries for which case the Cr(VI) to Cr(III) ratio goes as high as about 4, while in contrast this ratio lies between 1-2 for soil samples belonging to Rawalpindi and Islamabad background. For this background it’s anticipated that the Cr(VI) to Cr(III) ratio stands close to 2 , while any ratio greater than that certainly reflect contamination of the soil with Cr(VI).

For Cr(III) distribution table10 lists the useful statistical parameters outlined in the previous sections. Although the degree of spread of the individual Cr(III) measurements around the average value was naturally high enough in view of a similar observation made in the previous case of total chromium and Cr(VI). Likewise the standard error and variance are high to the tune that both curtosis and skewness show an enhanced degree of asymmetry and flatness of the distribution curve. The curtosis and skewness parameters show in this case that the distribution is not normal and Cr(III) distribution is perhaps more randomized as compared with the previous cases of Cr(VI) and total chromium distributions.

On the whole , the Cr(VI) levels in local soils is higher than Cr(III), indicating thereby a dominatingly prevailing oxidation state of chromium in local soils. Although the take up of Cr(VI) by plants and vegetation is restricted by natural processes to about 1mg/kg of plant weight the Cr(VI) enlarged abundance of concentration as the one indicated by values in table 7 does pose a serious health threat to the humans and animals lives. This threat comes in force by the fact that chromium in this oxidation state might be involved as a solubilized species in drinking water. Certain oxidizing agents in natural soil system could be responsible for conversion of Cr(III) to Cr(VI) as a favourable process and therefore in order to limit this process its reversal could be achieved through some reducing agents added to the soil in those locations where Cr(VI) levels are surplusly very high.

5.8 STATISTICAL EVALUATION OF THE DATA

The comparison of Cr(III) and Cr(VI) as to their origin in various samples was conducted using the t-test. Table 11 lists some of the typical parameters used in the t-test. The test was conducted by selecting an 8 equal to 28.23 for Cr(III) and a Ỹ equal to 63.08 for Cr(VI), the variance based on individual standard deviation are also recorded in the table with an overall pooled variance of 1251.13. The t-test, summarized in table 11 then formulated an overall standard deviation through the use of($\sum SD_i)^{1/2}$ for the two pooled averages, the hypothesis was based on a mean difference of zero for the two sets with degree of freedom=62. The calculated statistical t-value turned out to be 3.94 as against the one-tail critical t equal to 1.67 reported in statistical books, in agreement with the "SPSS 8.0 for Windows" used in the present computation. The test therefore clearly evidenced a common origin between Cr(III) and Cr(VI) which is in conformity with the actual situation. It may therefore be concluded that both the levels of chromium belong to the same origin of soil from which the are derived.

A further important aspect for Cr(III) and Cr(VI) in relation to total chromium was to examine statistically the correlation between the two oxidation states in the first place and then between these oxidation states and total chromium, taken in pair. The paired variables appear in table 12 with respective correlation coefficient values spread as a matrix between these variables. It may be seen from the table that the correlation between Cr(III) and Cr(VI) is a very strong positive correlation at r=0.728.Also, two other important correlation coefficient individually between Cr(III) and Cr(IV) on one hand and total chromium on the other hand are also reported in sub-part of table 12. The reported r values respectively stand at 0.980 between Cr(VI) and total chromium and 0.849 between Cr(III) and total chromium. Considering that r=0.500 at p=0.005 is defined to be a very strong correlation, these two r values evidence a super strong positive correlation between the two oxidation states of chromium and individually between any chromium oxidation state and total chromium. This study therefore, indicates that based on the statistical analysis both Cr(III) and Cr(VI) are derived from common origin and they are correlated to each other as well, further supporting their inter-relationship to each other.

5.9 ABSORPTIOMETRIC ASPECTS OF THE STUDY

The results obtained on the basis of spectrometric method have already been cast in tables discussed in the earlier sections. However equally important are certain absorptiometric considerations that need mention in terms of absorption of Cr(III); Cr(VI); Cr(III) and Cr(VI); Cr(III), Cr(VI) and the DPC complex, etc. as a function of their characteristic wavelengths.

. Figure 1 is a typical curve obtained for Cr(III) aqueous solutions, indicating a height characteristics of the concentration content, and a λ_{max} of 410nm with an absorption of 0.234 for a given Cr(III) solution scanned at medium with a slit width of 2.0nm. This figure marks only one λ_{max} as indicated above.

However it does point out another wavelength which could correspond to an acceptable absorption prior to 410nm. Throughout the present work this wavelength was found to be consistently a maximum wavelength of absorption for Cr(III) absorptions in an isolated matrices. This means that the case of Cr(III) absorption would differ in terms of λ_{max} when the same aqueous solution would contain Cr(VI) or the DPC-complex. This fact is brought to focus in figures 2 & 3 where typical absorption curves for Cr(VI) and for Cr(III) and Cr(VI) are presented. Accordingly it is evident that Cr(III) in an isolated system (fig.1) absorbs at 410.00nm, while in presence of Cr(VI) (fig.3), this absorption switches over to 427.20nm. This shift is based on the mutual interaction of the two kinds of species interacting with radiation thereby causing an energy of transition balance which is compatible with the excitation energies of the two species taken together. Fig.4 brings out an absorption vs. wavelength relationship for Cr-DPC complex. In this typical absorption curve the wavelength corresponds to 586.2nm for the complex, a value which was considered for the present work in terms of quantification.

Likewise, figure 5 demonstrates a further event in which Cr-DPC complex enters the matrix with a further shift in the corresponding λ_{max} values. Here in this case Cr(VI) absorbs at 302.02nm, Cr(III) at 410nm and the Cr-DPC complex at 576nm. This observation is again in line with the one stated above. In the same figure 5 a sharp shoulder indicates the presence of a well defined species with a comparable concentration with that of the complex that is being generated either as a fresh species or as a dissociation product of the complex. Being outside the periphery of the present work, the presence of this shoulder absorption was not touched upon for any further investigation. The combined effect of the absorption of Cr(III) and Cr(IV) may now be viewed form the view point of Cr(III) and Cr(IV) species present together & Cr(VI) being present in isolation. For this a reference may be made to figure 3 and figure 6, wherein, Cr(VI) is shown to absorb at λ_{max}=360.00, while Cr(III) has λ_{max} =427.2. In fig.6 a drastic decrease in Cr(VI) wavelength is observed at 350.8nm. This situation indicates that the shift in the wavelength is not only species specific but also depends on the relative interacting concentrations of the two ionic entities.

The spectrometric calibration for standards of known concentrations for various analyte systems are given in figures 7,8 and 9. In figure 7, a typical standard calibration curve for Cr(III) aqueous up to a concentration range of 3.00 ppm starting from 0.50 ppm is shown. The line exhibits an acceptable linearity with almost all the four points of measurements falling on the line, with a maximum absorption of about 0.68 absorbance corresponding to the maximum concentration. In Fig.8 the corresponding system shows up a concentration range of 1 to 3 ppm of Cr(VI) aqueous in which case the absorption corresponding to maximum concentration stands at 3.00 corresponds to an absorbance value of 0.920 compared with the case of Cr(III) the sensitivity of absorption in this case is greater. Finally, the standard calibration curve for Cr-DPC complex, shown in figure 9, reflects the corresponding absorption curve for Cr-DPC complex concentrations from 1ppm to 3ppm. Here an absorption of 0.211 is met with corresponding to 3ppm concentration which clearly reflects that based on the stoichiometry of the reaction, the absorption of the complex is followed by attenuated values compared with the original Cr(III) and Cr(VI) species. It may be concluded that by far Cr(VI) exhibits maximum absorption followed by the complex & then by Cr(III).

5.10 COMPARATIVE ASPECTS OF Cr(III) AND Cr(VI) DISTRIBUTION

Although the Cr(III) and Cr(VI) contents of various soils have been earlier on reported in relevant tables, a comparative look on the basis of those tables cannot emerge unless the data are given a graphic manipulation. Figure 10 through 16 present a comparative outlook on the data. To begin with figure10 depicts Cr(III) and Cr(VI) levels in various soil samples .An examination of the plotted information shows that these levels are marginal upto sample no.15, but these increase drastically afterwards upto sample no.21,followed by regular decrease upto sample no.25, & finally the maximum elevated level of hexavalent chromium in sample no.30. This situation is in agreement with the previously noted situation .However this figure clearly demonstrate that there are only a few cases where the Cr(III) and Cr(VI) levels are almost comparable, such as in sample no.02,sample no.10 and sample no.32.In all other cases the dominant species is Cr(VI).

Figure11 demonstrate the comparative levels of Cr(III) in various local soil samples. The following information can be readily seen as depicted in the figure: samples no.03 and no.12 marked the highest Cr(VI) level only to be followed by sample no.11, no.09 and no.13. A common feature between figure 10 and figure 11 is enhanced levels of Cr(VI) except for a couple of instances where the two levels are just comparative in sample no.02 and sample no.10. The situation in figure 12 reflects the outstation soil samples. Here, same elevated levels of Cr(VI) were also observed alongwith a falling trend of Cr(VI) and Cr(III) both of which again rises to a maximum in sample no.30. As has been pointed out earlier samples no.22, 23, 24 and 25 belong to locations farther removed from the influence of any chemical activity that could render these soil polluted with chromium. Infact these samples were taken to effect a background estimate of the actual situation.

Figure 13 present a comparison between the two chromium levels in soil samples from Lahore alone, figure 14 for Kasur alone, figure 15 for Gujranwala alone and figure 16 for Sialkot alone. An examination of these figures show that the tannery effected area reach a maximum Cr(VI) level of 140 mg/kg for Lahore which drops to about 90 mg/kg for Kasur site, followed by about 130 mg/kg for Gujranwala site and about 240 mg/kg for the Sialkot site. The study therefore shows maximum effect of Cr(VI) in the Sialkot area where very large number of tanneries are housed. Figures 17 to 20 reflect the maximum levels of Cr(VI) in the form of pie diagram for SS-30 indicating 26% Cr(III) and 74% Cr(VI), thus with a three fold high concentration in favour of Cr(VI). The pie-diagram for SS-22 shows 40% contribution of Cr(III) and 60% Cr(VI), with a 1.5 fold enhancement in favour of Cr(VI). For figure 19, the two levels for SS-32 are comparable at 50% distribution. In the extreme case for SS-12 the Cr(VI) to Cr(III) ratio is more than seven fold. These figures taken together clearly explain a widely divergent distribution of Cr(III) and Cr(VI) both in local soil samples and outstation soil samples.

5.11 SOME SALIENT FINDINGS OF THE STUDY

Keeping in view the data and the discussion based on the data, it may be stipulated that the present study puts forward some salient findings as follows.

1. The average estimated total chromium concentration ranged from 32.18 to 310.12 mg/kg. In case of local soil samples, the total chromium contents were all consistent ranged from an average of 42.25 to 66.00 mg/kg being with in the permissible safe limit, but in case of soil sample in close vicinity to tanneries, the total chromium was again found to be onto a higher side with an enhancement ratio of two to three-fold, reaching to a peak value of 310.12 mg/kg.

2. The Cr(VI) levels as part of total chromium in contaminated soil samples remained almost three-fold to seven-fold reaching to a peak value of 230 mg/kg and the local soil samples contained the barest minimum Cr (VI) running from 27.24 to 46.00 mg/kg.

3. The comparison of Cr(III) to Cr(VI) reveals that Cr(VI) is a dominant species in the soil samples investigated, in that the normal pattern of Cr(VI) to Cr(III) ratio lies between 1-2 for local background soil samples, while in contrast, this ratio goes as high as about 4 in case of chromium contaminated soils.

4. The statistical t-evaluation of the data revealed that both Cr(III) and Cr(VI) are derived from common origin and they are correlated to each other.

5. No viable correlation was observed between the pH_w and moisture content of the sample, together with Cr-content.

5.12 CONCLUSION

The present investigation on the speciation of Cr(VI) & Cr(III) in local soil samples belonging to some background levels in the soils belonging to such area as Islamabad & Rawalpindi and those belonging to such areas as Lahore, Kasur, Gujaranwala, and Sialkot, where tanning activity is at the bloom, was quite revealing. It is observed that Cr(VI) is in larger proportion in these soil samples, irrespective of their origin. It is well known that Cr(VI) is profoundly very toxic as compared with Cr(III). However, it is also known that Cr(VI) is not retained in human body so that it's toxic effects can be alleviated by a simple control over its concentration, emanating from various sources. As has been observed, the tanneries in Pakistan are contributing a lot of chromium to the soil thereby contaminating it to a dangerous level that may add up to the naturally high level of Cr(VI) in the local soils. It is reported that natural background levels of Cr(VI) in soils from various parts of the world ranged between 21mg/kg to 85mg/kg (ref.WHO & ILO report). Seen from this perspective the Cr(VI) level in local soils of Pakistan are comparable at the background level but these are elevated by 3 to 4 fold in areas where the tanning process is being carried out on a mass scale. Although the municipal authorities in these areas are striving hard to implement legislative measures towards the control and abatement strategy of the effluent shooting out of the tanneries, still further efforts are needed to protect the environment from the ill effect of hazardous chemicals used in these industries. In Kasur and Sialkot reinforced drains have been implemented as a legal requirement to be structured for a safe disposal of the effluent to distant locations with no nearby water bodies and agricultural land. Another feasible option needs to be exercised in terms of recycling of the effluents from these tanneries where by precious chemicals can be regenerated from the waste matter and could thus be recycled for use. It is high time that relevant health authorities must look into the matter to take necessary steps to ward off people against the adverse effect of chromium.

Table-I Description and relevant information* for various soil samples

Sample Code	Date, (2002)	Sample Description/Location
SS-01	27 June	Top soil; 0-2.5cm; brown; G-6,Islamabad
SS-02	27 June	Top soil; 0-2.5cm; dark tan; G-7, Islamabad
SS-03	27 June	Top soil; 1-2.5cm ; dark tan; F-6, Islamabad
SS-04	28 June	Top soil; 1-3.0cm ; dark tan; F-7, Islamabad
SS-05	28 June	Top soil; 1-3.0cm ; light brown; F-8, Islamabad
SS-06	28 June	Top soil; 0-2.5cm ; light brown; F-8/3, Islamabad
SS-07	27 June	Top soil; 0-2.5cm ; light brown; Lalazar,Rawalpindi.
SS-08	27 June	Top soil; 0-2.5cm ; brown; G-6/1-3, Islamabad
SS-09	27 June	Top soil; 1-2.5cm ; brown; G-6/1-4, Islamabad
SS-10	27 June	Top soil; 0-2.5cm ; brown; H-8/4, Islamabad
SS-11	27 June	Top soil; 1-2.5cm ; brown; QAU Campus, Islamabad
SS-12	28 June	Top soil; 0-2.5cm ; brown; I-10, Markaz, Islamabad
SS-13	28 June	Top soil; 0-2.5cm ; brown; I-10/4, Islamabad
SS-14	29 June	Top soil; 1-3.0cm ; dark tan; I-9 Islamabad
SS-15	29 June	Top soil; 1-3.0cm ; brown; H-9, Islamabad
SS-16	25 June	Top soil; 0-2.5cm ; dark brown; Awami Shoes,Hattar,Haripur
SS-17	25 June	Top soil; 1-2.5cm ; brown; Kungston Shoes, Mansehra
SS-18	20 June	Top soil; 1-2.5cm ; light brown; Sheikhupura Road,Lahore
SS-19	20 June	Top soil; 0-2.5cm ; brownish; Sheikhupura Road,Lahore
SS-20	20 June	Top soil; 1-3.0cm ; dark tan; Mureedke Road,Lahore
SS-21	20 June	Top soil; 1-2.5cm ; greyish;. Mureedke Road,Lahore
SS-22	30 June	Top soil; 0-2.5cm ; dark tan;Niaz Nagar, Kasur.
SS-23	30 June	Top soil; 1-2.5cm ; brown;Niaz Nagar, Kasur.
SS-24	30 June	Top soil; 0-2.5cm ; grey;Niaz Nagar, Kasur.
SS-25	30 June	Top soil; 1-2.5cm ; light brown;Deen Garh, Kasur.
SS-26	30 June	Top soil; 0-2.5cm ; light brown;Deen Garh, Kasur.
SS-27	19 May	Top soil; 1-3.0cm ; brown;Small Ind. Estate, Gujranwala.
SS-28	19 May	Top soil; 0-2.5cm ; brown;Small Ind. Estate, Gujranwala.
SS-29	19 May	Top soil; 1-2.5cm ; brown;Small Ind. Estate, Gujranwala.
SS-30	20 April	Top soil; 1-3.0cm ; dark brown;Samrial, Sialkot.
SS-31	20 April	Top soil; 1-2.5cm ; brown;Samrial, Sialkot.
SS-32	20 April	Top soil; 0-2.5cm ; dark brown;Samrial, Sialkot.

*** Type; depth; colour; location**

Table-2 Moisture and pH_w values for various soil samples

Sample Code	Parameter	
	Moisture (%,w/w)	**pH_W**
SS-01	3.34	8.86
SS-02	11.80	8.37
SS-03	12.50	8.41
SS-04	6.60	8.30
SS-05	7.00	8.89
SS-06	12.78	8.82
SS-07	1.40	8.95
SS-08	2.00	8.60
SS-09	13.50	8.22
SS-10	3.60	8.24
SS-11	2.97	9.19
SS-12	5.87	8.56
SS-13	5.04	8.11
SS-14	12.00	7.89
SS-15	2.57	9.43
SS-16	6.18	8.59
SS-17	7.11	8.69
SS-18	0.98	8.28
SS-19	6.69	10.77
SS-20	5.89	11.24
SS-21	3.52	8.88
SS-22	2.52	8.91
SS-23	8.00	8.81
SS-24	1.36	9.19
SS-25	7.21	9.76
SS-26	9.46	8.68
SS-27	1.39	8.30
SS-28	1.74	8.03
SS-29	0.87	8.43
SS-30	1.17	7.28
SS-31	0.81	8.49
SS-32	1.18	8.12

Table-3 Standard optimum analytical conditions* for AAS based Cr estimation

ELEMENT	WAVE LENGTH (nm)	HC CURRENT (mA)	SLIT WIDTH (nm)	FLAME TYPE	FUEL RATE (L/min)	DETECTION LIMIT (ppm)
Cr	357.9	5.0	0.5	Air acetylene	2.6	0.09

*** At 1% absorption**

Table-4 Standard optimum absorption conditions for spectroscopic Cr estimation

Characteristic	**Parametric values**
Measuring mode	a/ ABS b/ %T
Wavelength	190-900nm
Recording mode	Overlay, Seq. And Off
Photometric range (in Abs mode)	-9.99~9.99 Abs at interval of 0.01 A, (for records) – 3~3 Abs (for display)
Sampling interval	2.0
Wavelength Accuracy	± 0.3 nm (at slit of 0.2.nm)
Wavelength repeatability	± 0.1 nm
Slit width (nm)	2.0
Photometric accuracy	± 0.002 Abs (for 0~0.5 Abs) ± 0.004 Abs (for 0.5~01 Abs)
Photometric repeatability	± 0.001 Abs (for 0~0.5 Abs) ± 0.002 Abs (for 0.5~1 Abs)
Baseline flatness	Within ± 0.001 Abs
Scan speed	a) Fast b) Medium c) Slow

Table-5 Estimated concentrations* (mg/kg, dry weight) of total chromium in various soil samples by AAS method

Sample Code	Total Chromium (8 ± SD)
SS-01	65.00 ± 0.68
SS-02	61.50 ± 0.65
SS-03	54.75 ± 0.51
SS-04	66.00 ± 0.76
SS-05	42.25 ± 0.32
SS-06	56.75 ± 0.60
SS-07	54.50 ± 0.49
SS-08	50.75 ± 0.57
SS-09	63.65 ± 0.60
SS-10	56.00 ± 0.51
SS-11	62.50 ± 0.52
SS-12	52.25 ± 0.42
SS-13	57.75 ± 0.70
SS-14	50.50 ± 0.30
SS-15	43.75 ± 0.53
SS-16	148.00 ± 1.51
SS-17	112.25 ± 1.19
SS-18	144.00 ± 1.24
SS-19	99.00 ± 1.09
SS-20	177.77 ± 1.80
SS-21	157.15 ± 1.60
SS-22	33.64 ± 0.40
SS-23	37.60 ± 0.50
SS-24	32.18 ± 0.30
SS-25	61.33 ± 0.71
SS-26	126.35 ± 1.30
SS-27	172.8 ± 1.18
SS-28	124.1 ± 1.12
SS-29	101.30 ± 1.03
SS-30	310.12 ± 3.02
SS-31	62.50 ± 0.72
SS-32	183.99 ± 1.20

*** For triplicate sub-samples.**

Table-6 Estimated levels*(mg/kg, dry weight) of Cr(VI) in various soil samples by spectrometric method

Sample Code	Cr (VI) Concentration (8 ± SD)
SS-01	37.67 ± 0.47
SS-02	30.66 ± 0.39
SS-03	46.00 ± 0.41
SS-04	36.21 ± 0.38
SS-05	27.24 ± 0.30
SS-06	29.98 ± 0.38
SS-07	35.21 ± 0.45
SS-08	33.08 ± 0.30
SS-09	39.96 ± 0.40
SS-10	27.78 ± 0.37
SS-11	41.18 ± 0.39
SS-12	45.91 ± 0.41
SS-13	38.61 ± 0.40
SS-14	33.00 ± 0.43
SS-15	29.33 ± 0.30
SS-16	118.88 ± 1.10
SS-17	88.48 ± 0.90
SS-18	111.48 ± 1.10
SS-19	69.30 ± 0.70
SS-20	140.21 ±1.30
SS-21	114.61 ± 1.40
SS-22	20.16 ± 0.20
SS-23	21.81 ± 0.19
SS-24	21.08 ± 0.25
SS-25	40.39 ± 0.43
SS-26	91.62 ± 0.89
SS-27	130.66 ± 1.30
SS-28	88.35 ± 0.98
SS-29	66.78 ± 0.76
SS-30	229.96 ± 1.90
SS-31	39.33 ± 0.43
SS-32	93.69 ± 1.00

*** For triplicate sub-samples**

Table-7 Comparative Cr (III) and Cr (VI) levels (mg/kg, dry weight) in various soil samples

Sample Code	Total Cr	Cr (VI)	Cr (III)
SS-01	65.00	37.67	27.33
SS-02	61.50	30.66	30.84
SS-03	54.75	46.00	08.75
SS-04	66.00	36.21	29.79
SS-05	42.25	27.24	15.01
SS-06	56.75	29.98	26.77
SS-07	54.50	35.21	19.29
SS-08	50.75	33.08	17.67
SS-09	63.65	39.96	23.69
SS-10	56.00	27.78	28.22
SS-11	62.50	41.18	21.32
SS-12	52.25	45.91	06.34
SS-13	57.75	38.61	19.14
SS-14	50.50	33.00	17.50
SS-15	43.75	29.33	14.42
SS-16	148.00	118.88	29.12
SS-17	112.25	88.48	23.77
SS-18	144.00	111.48	32.52
SS-19	99.00	69.30	29.70
SS-20	177.77	140.21	37.56
SS-21	157.15	114.61	42.54
SS-22	33.64	20.16	13.48
SS-23	37.60	21.81	15.79
SS-24	32.18	21.08	11.10
SS-25	61.33	40.39	20.94
SS-26	126.35	91.62	34.73
SS-27	172.80	130.66	42.14
SS-28	124.10	88.35	35.75
SS-29	101.30	66.78	34.52
SS-30	310.12	229.96	80.16
SS-31	62.50	39.33	23.17
SS-32	183.99	93.69	90.30

Table-8 Basic statistics for total chromium distribution in various soil samples (n=32)

Parameter	Value
Count(N)	32
Minimum	32.18
Maximum	310.12
Average	91.31
Standard deviation	60.86
Coefficient of variation	66.66
Standard Error	10.75
Variance	3704.03
Kurtosis	4.016
Skewness	1.803

Table-9 Basic statistics for chromium (VI) distribution in various soil samples (n=32)

Parameter	Value
Count(N)	32
Minimum	20.16
Maximum	229.96
Average	63.08
Standard deviation	46.80
Coefficient of variation	74.20
Standard Error	8.27
Variance	2190.88
Kurtosis	3.84
Skewness	1.78

Table-10 Basic statistics for chromium (III) distribution in various soil samples (n=32)

Parameter	Value
Count(N)	32
Minimum	6.34
Maximum	90.30
Average	28.23
Standard deviation	17.64
Coefficient of variation	62.50
Standard Error	3.11
Variance	311.37
Kurtosis	5.91
Skewness	2.18

Table-11 t-test comparison for Cr (III) and Cr (VI) for various soil samples

Parameter	Cr (III)	Cr (VI)
Mean	28.23	63.08
Variance	311.38	2190.88
Observations	32.00	32.00
Pooled variance	1251.13	
Hypothesized mean difference	0.00	
Degree of freedom	62.00	
t (statistical)	3.94	
P(T<=t) one-tail	0.00	
t Critical (one-tail)	1.67	

Table-12 **Correlation coefficient* matrix for Cr(III) vs Cr(VI) and for total Cr in various soil samples**

	Cr (VI)	**Cr (III)**
Cr (VI)	1.000	
Cr (III)	0.728	1.000

	Cr (VI)	**Cr (III)**	**Total Cr**
Cr (VI)	1.000		
Cr (III)	0.728	1.000	
Total Cr	0.980	0.849	1.000

* at p=0.005

Created: 12:51 05.06.02
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 2.0
Sampling Interval: 2,0

No.	Wavelength(nm)	Abs.
1	410,00	0,234

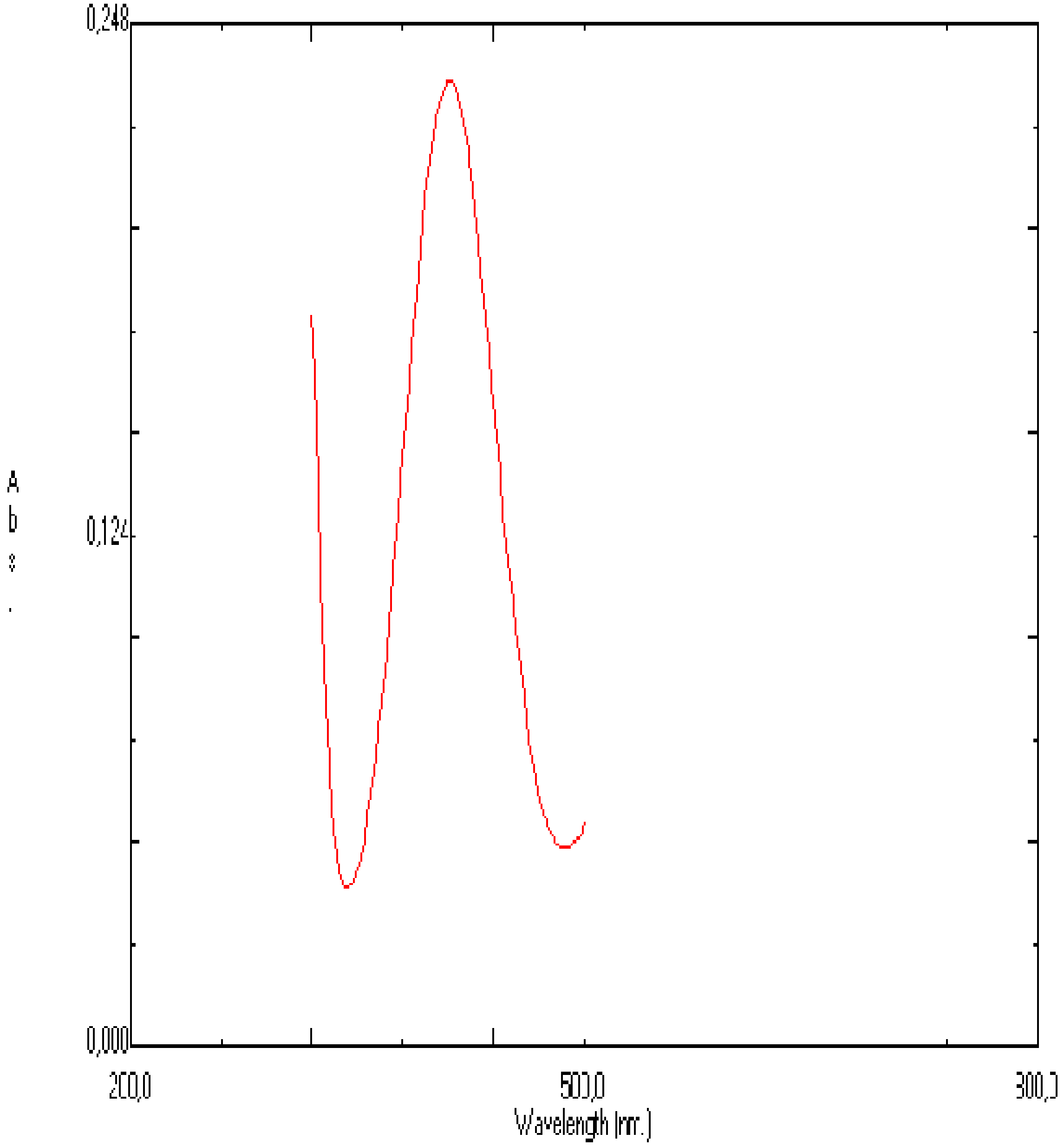


Fig. 1: Typical absorption curve for Cr(III) as a function of wavelength

Data:	Original
Measuring Mode:	Abs.
Scan Speed:	Fast
Slit Width:	2,0
Sampling Interval:	0,1

No.	Wavelength (nm.)	Abs.
1	360,40	1,925

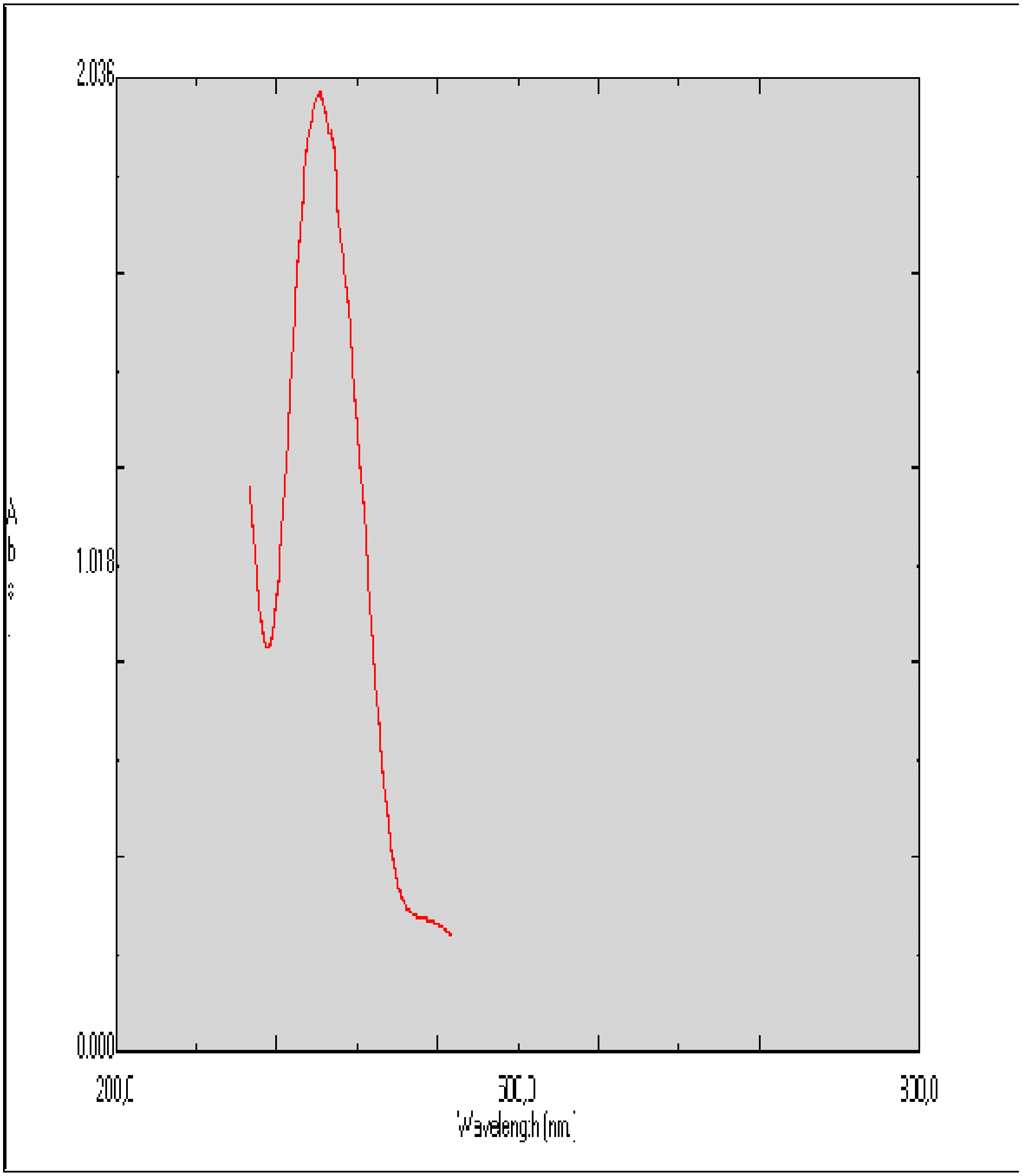


Fig. 2: Typical absorption curve for Cr (VI) as a function of wavelength.

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Created:  13:22      30.05.02
Data:                Original

 Measuring Mode:         Abs.
 Scan Speed:             Fast
 Slit Width:             2,0
 Sampling Interval:      0,2

 No.       Wavelength(nm)        Abs.
 1            360,00             0,109
 2              427,20           0,138
```

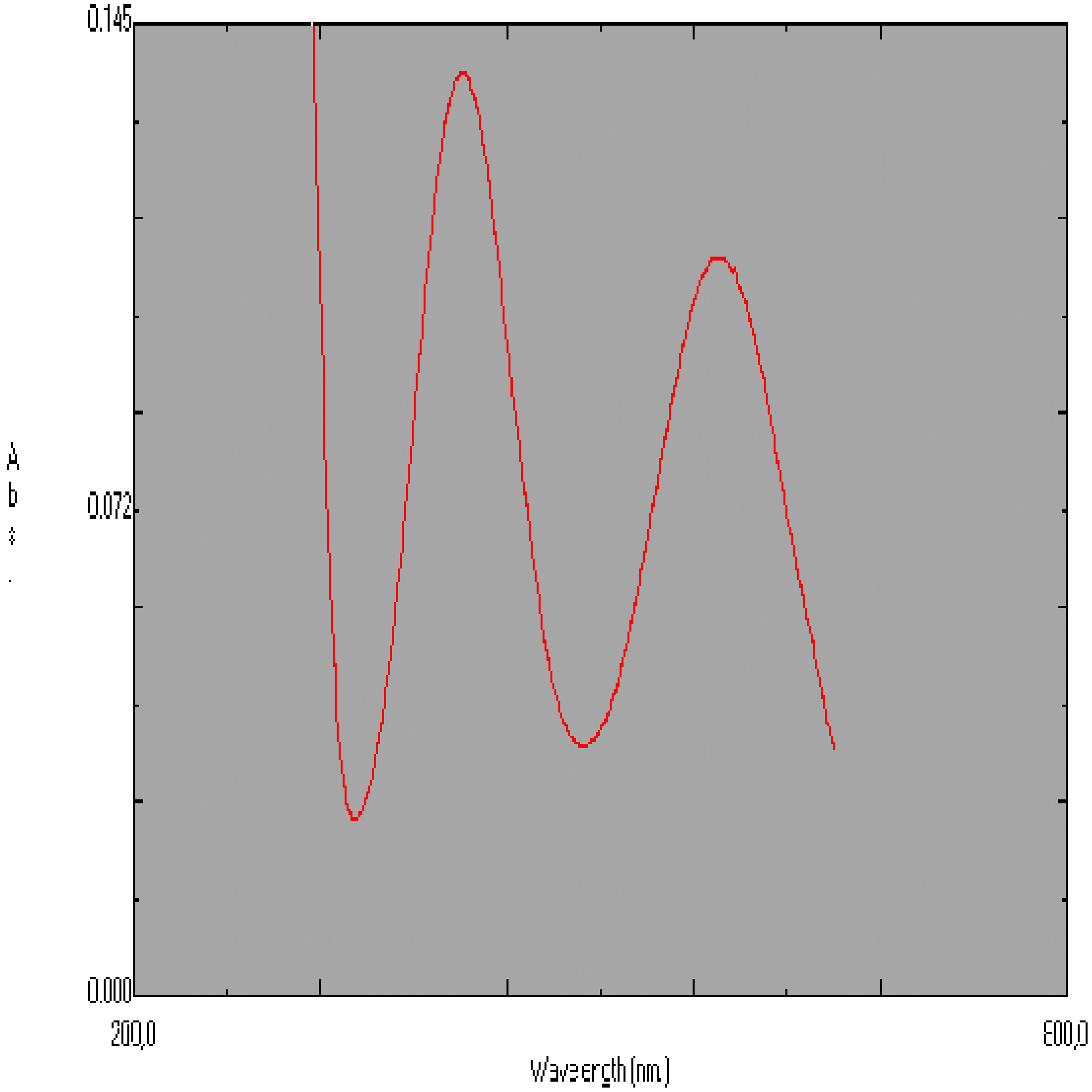

Fig. 3: Absorption vs. wavelength relationship for Cr(III), and Cr(VI)

Created: 13:22 30.05.02
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2,0
Sampling Interval: 0,2

No.	**Wavelength(nm.)**	**Abs.**
1	586,20	0,109

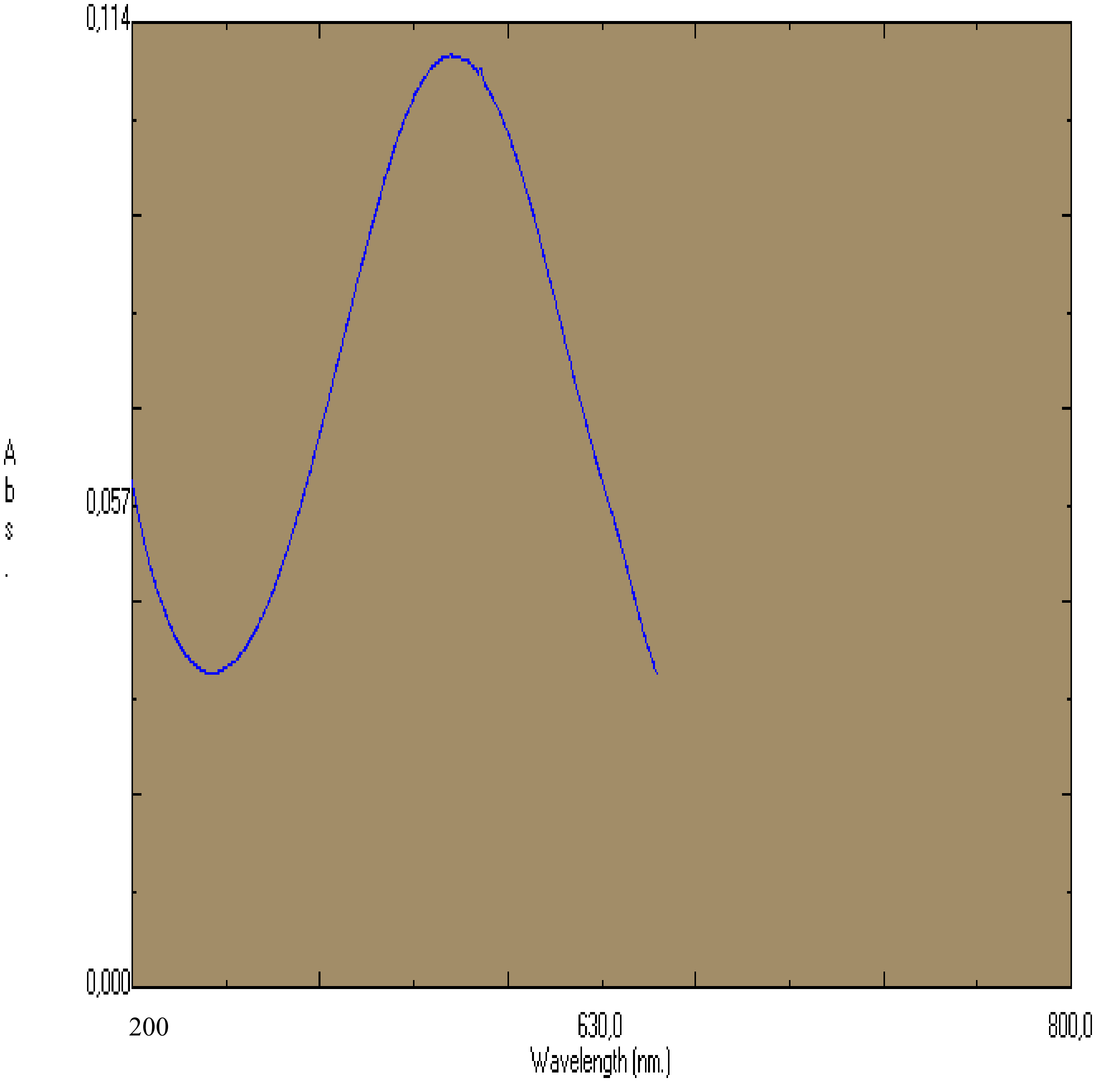

Fig-4: Absorption vs. wavelength relationship for Cr-DPC complex

Created: 12:46 05.06.02
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 2,0
Sampling Interval: 2,0

No.	Wavelength (nm)	Abs.
1	410,00	0,170
2	302,00	0,270
3	576,00	0,131

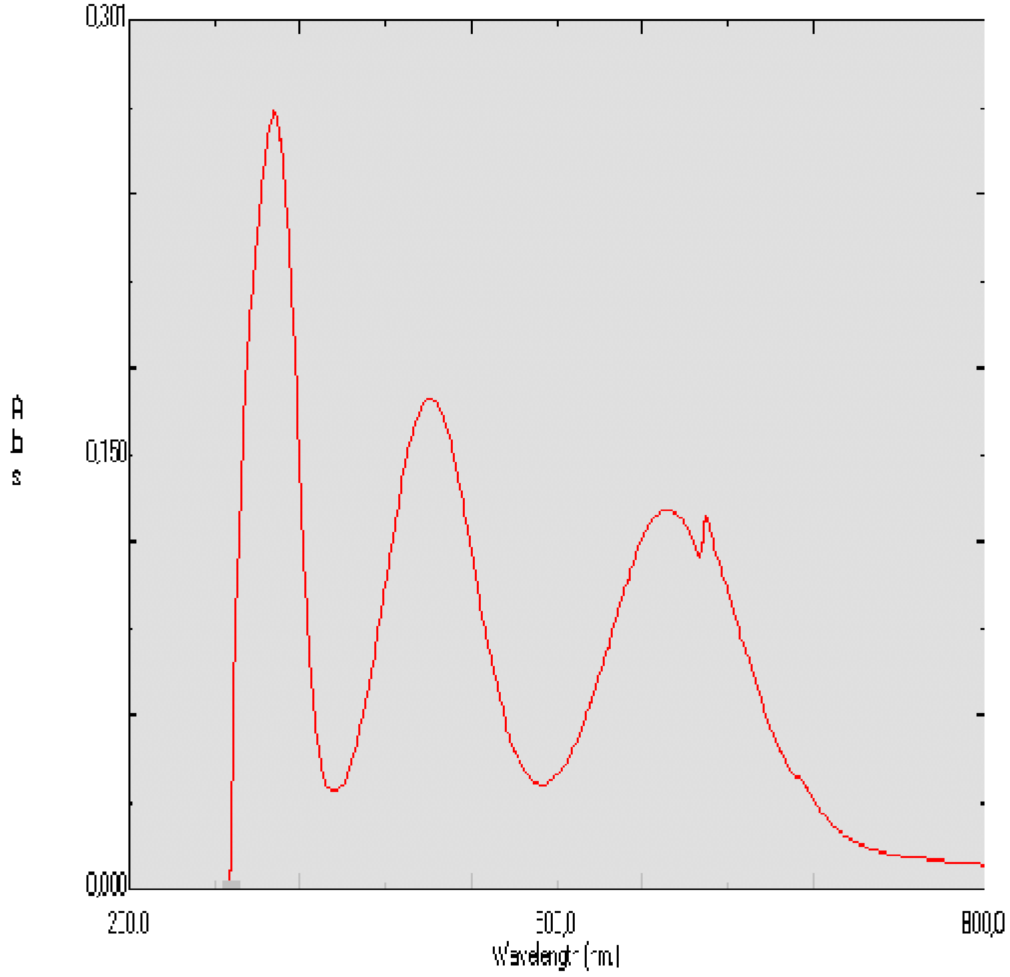

Fig.5: Absorption vs. wavelength relationship for Cr(III), Cr(VI), and Cr-DPC complex

Created: 16:14 28.05.02
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2,0
Sampling Interval: 0,2

No.	Wavelength(nm)	Abs.
1	350,80	1,147

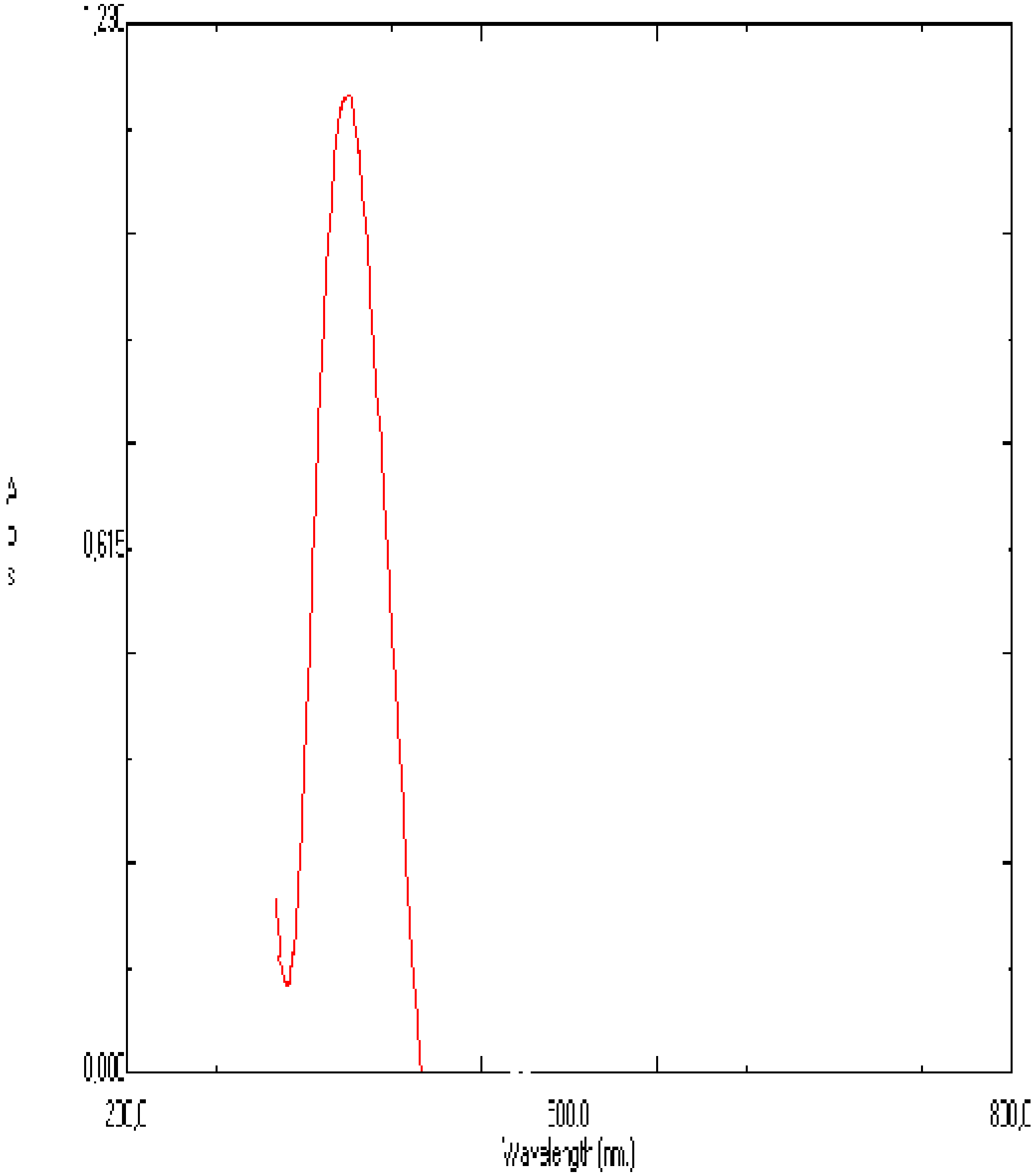

Fig.6: Typical absorption curve for Cr(VI) as a function of wavelength in sample SS-01

Std.No.	Concentration (ppm)	Absorbance
1.	0.500	0.111
2.	1.000	0.219
3.	2.000	0.490
4.	3.000	0.618

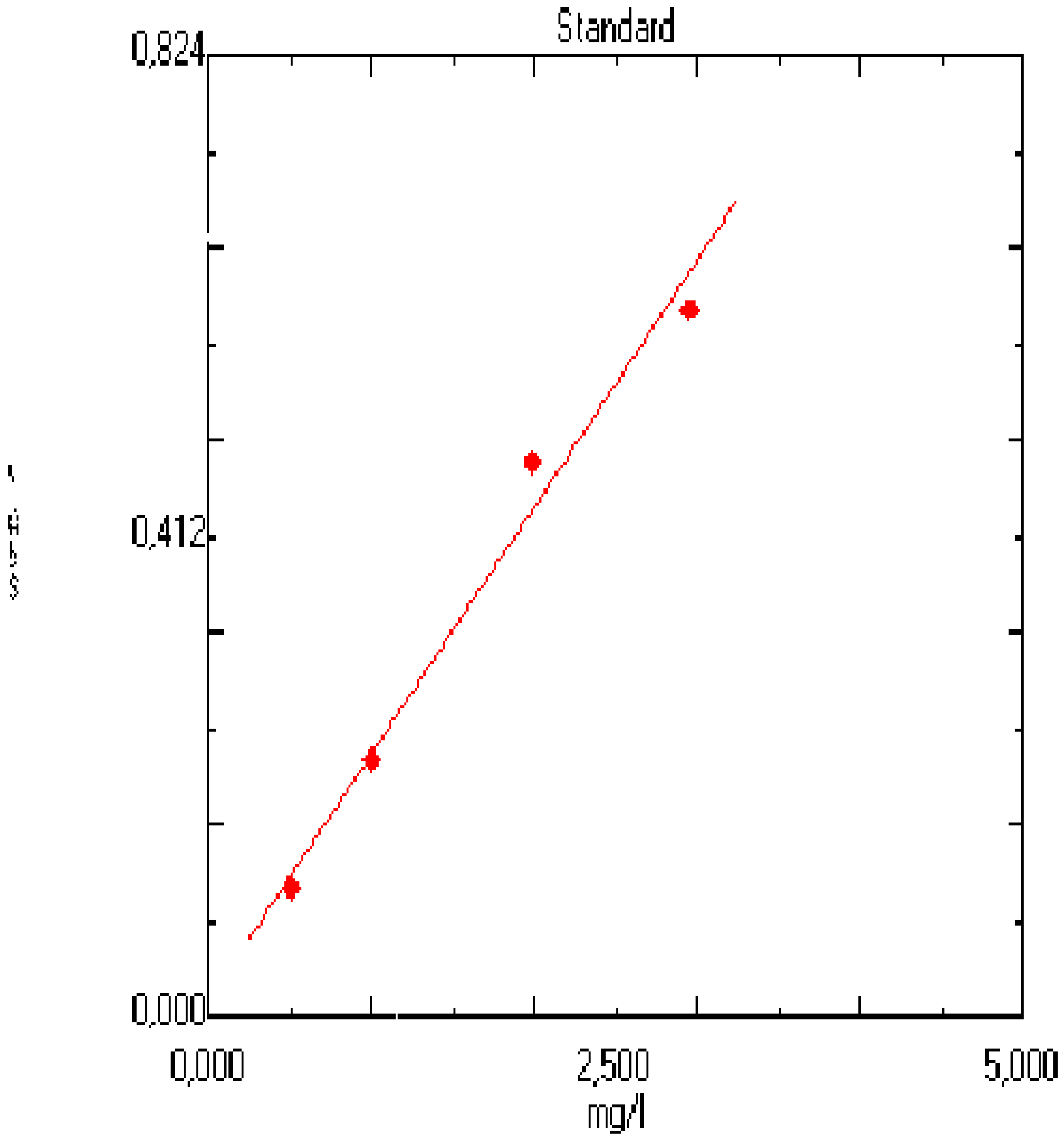

Fig. 7:Standard calibration curve for Cr(III)

Std.No.	Concentration (ppm)	Absorbance
1.	1.000	0.460
2.	2.000	0.690
3.	3.000	0.920

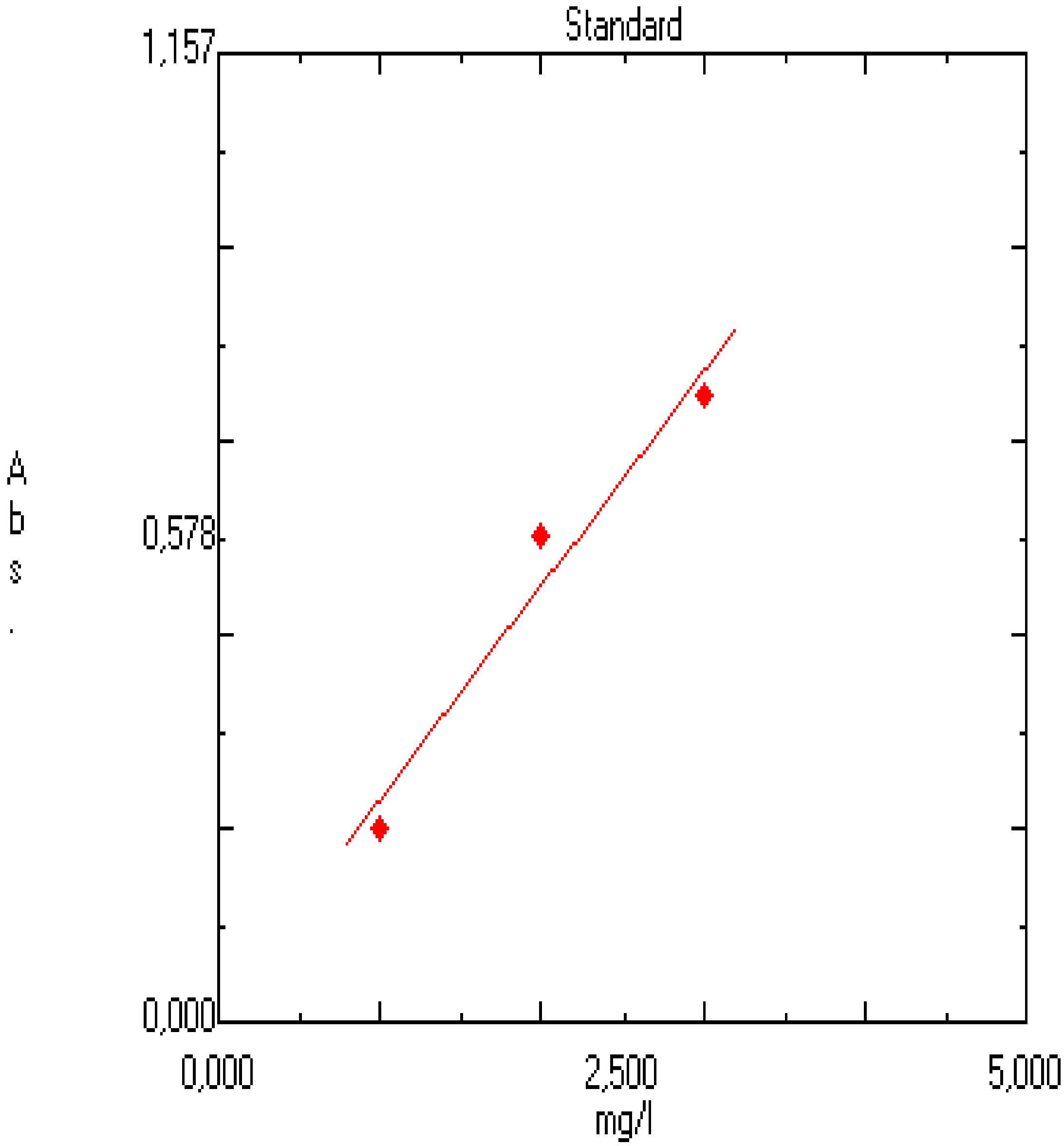

Fig-8: Standard calibration curve for Cr(VI)

Std.No.	Concentration (ppm)	Absorbance
1.	1.000	0.066
2.	2.000	0.129
3.	3.000	0.211

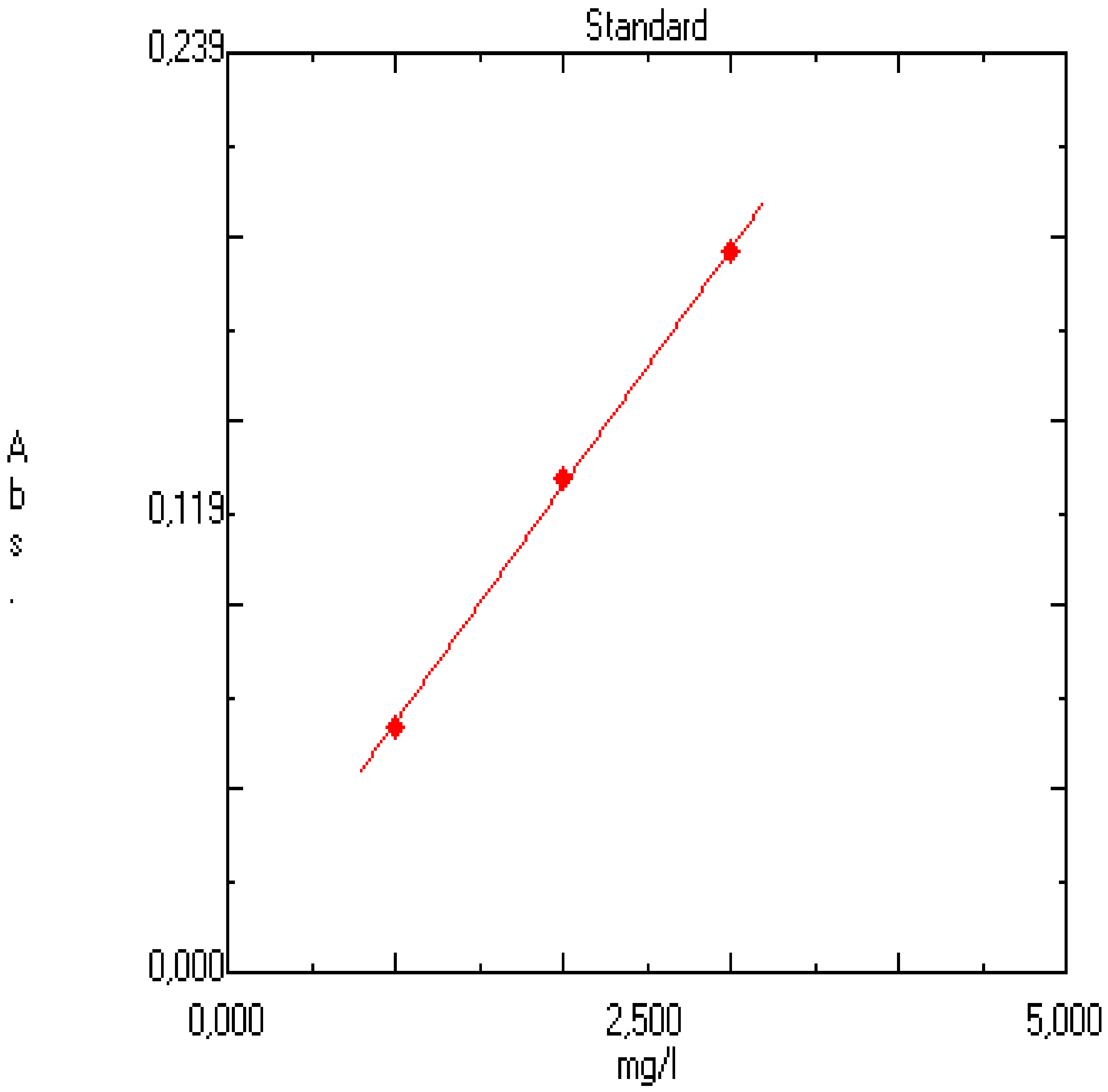

Fig-9: Standard calibration curve for Cr-DPC complex

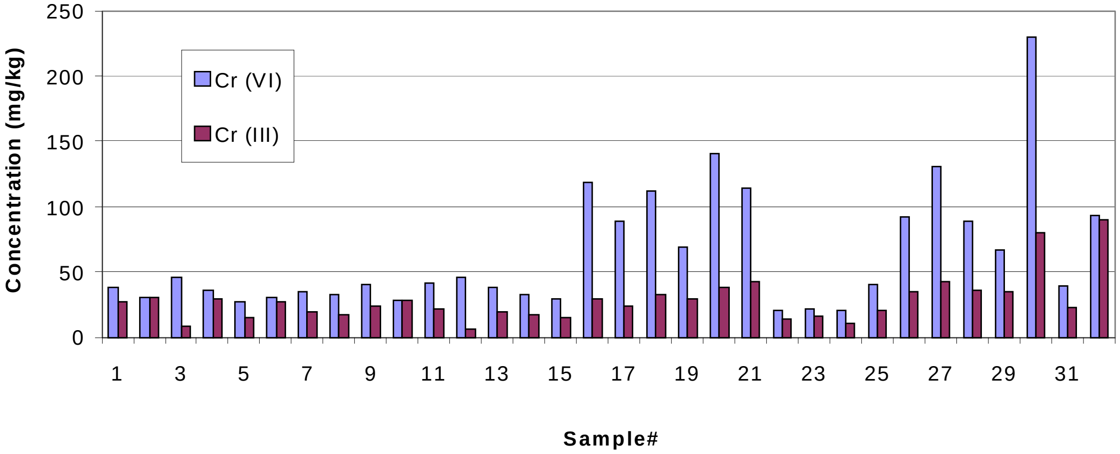

Fig.10: Comparison of Cr(III),Cr(VI) levels in various soil samples

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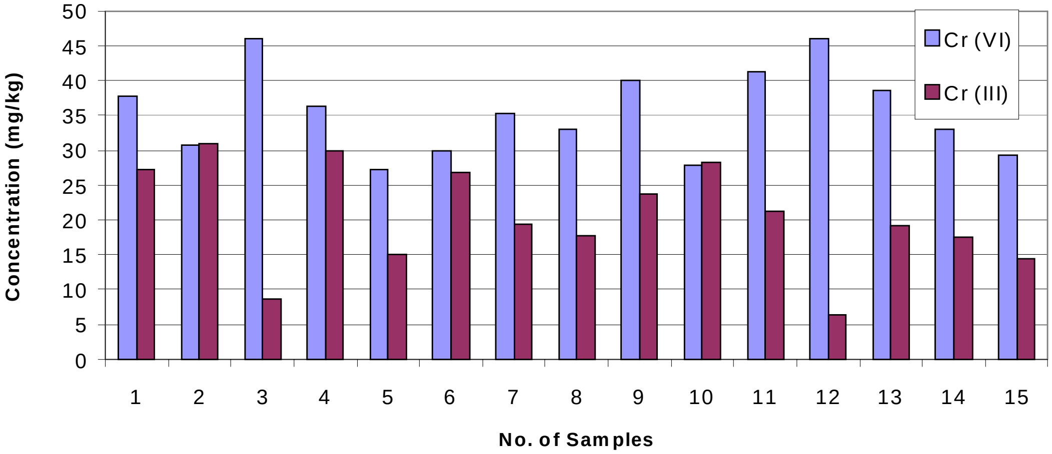

Fig.11: Comparison of Cr(III),Cr(VI) levels in various local soil samples

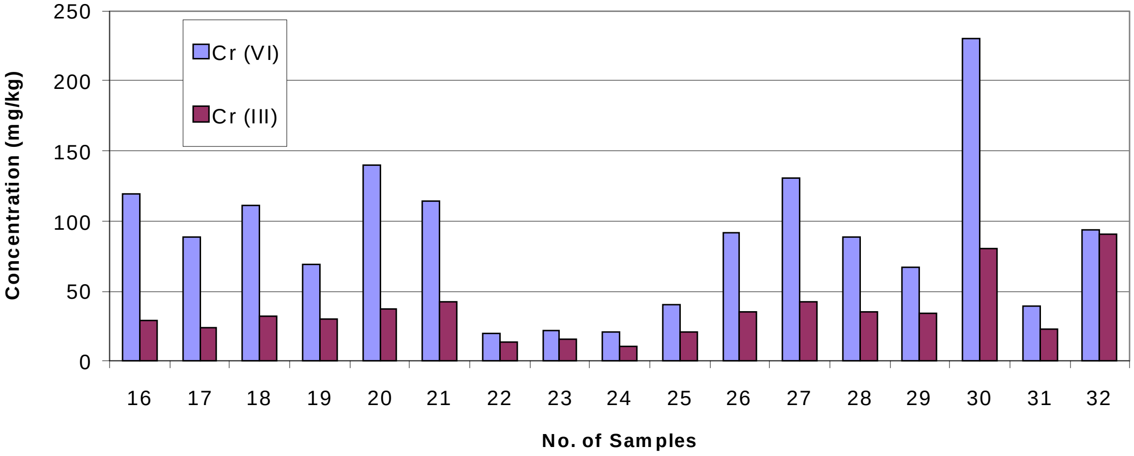

Fig.12: Comparison of Cr(III),Cr(VI) levels in various soil samples from outstations

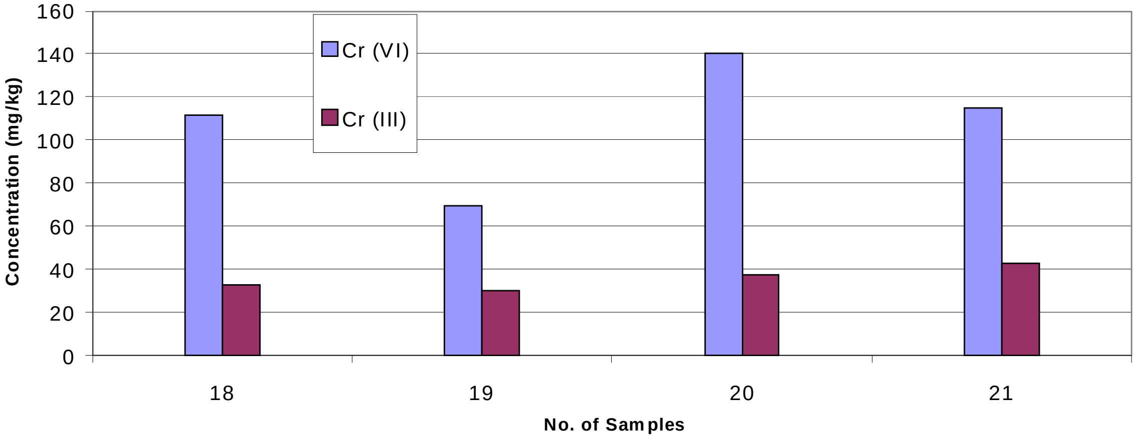

Fig.13: Comparison of Cr(III),Cr(VI) levels in various soil samples from Lahore

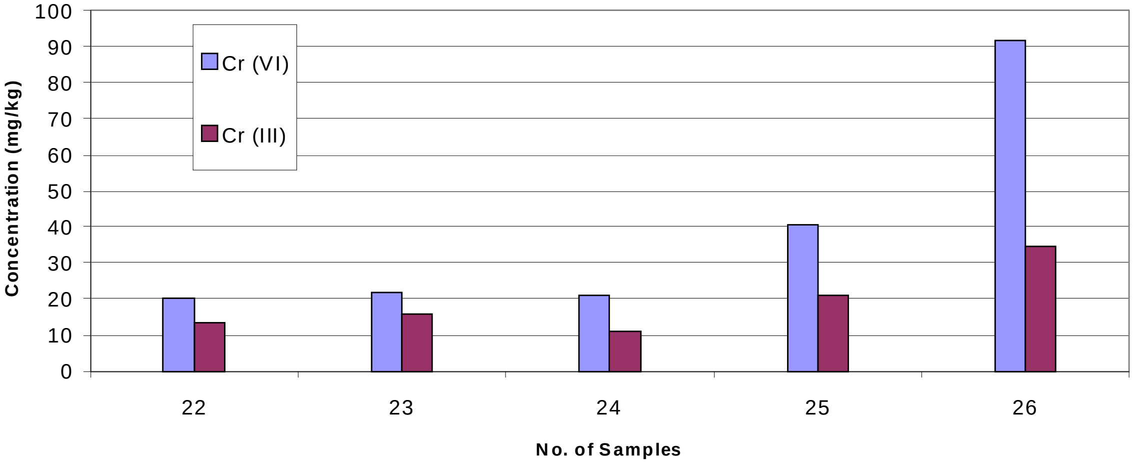

Fig.14: Comparison of Cr(III),Cr(VI) levels in various soil samples from Kasur

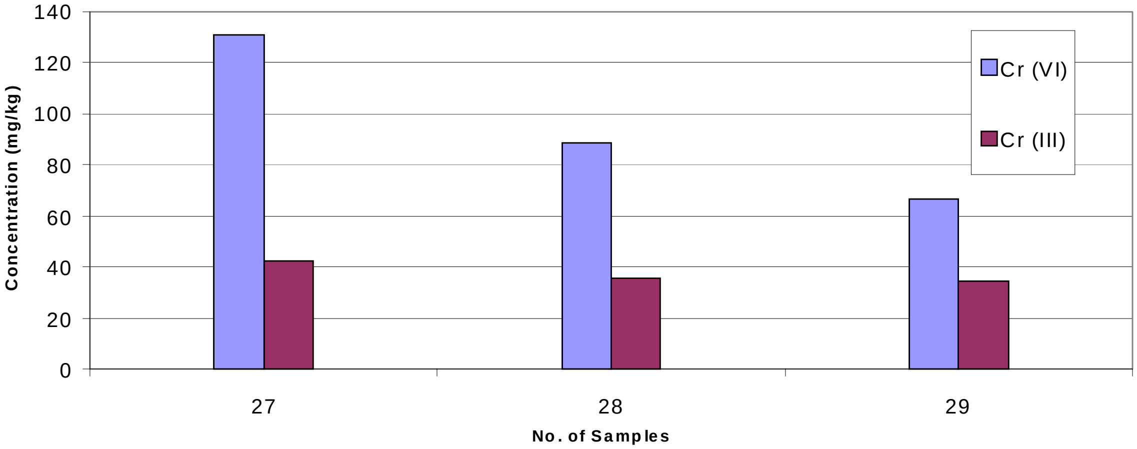

Fig.15: Comparison of Cr(III),Cr(VI) levels in various soil samples from Gujranwala

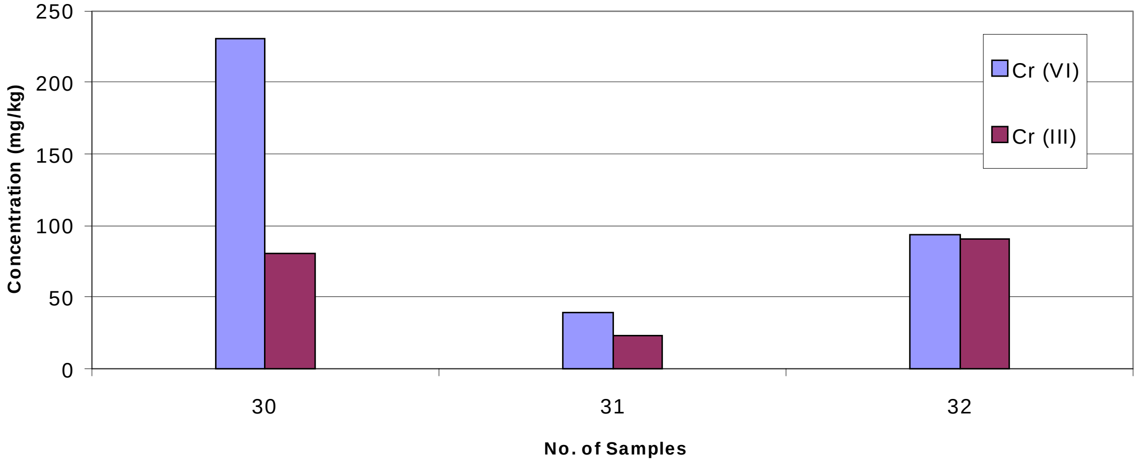

Fig.16: Comparison of Cr(III),Cr(VI) levels in various soil samples form Sialkot

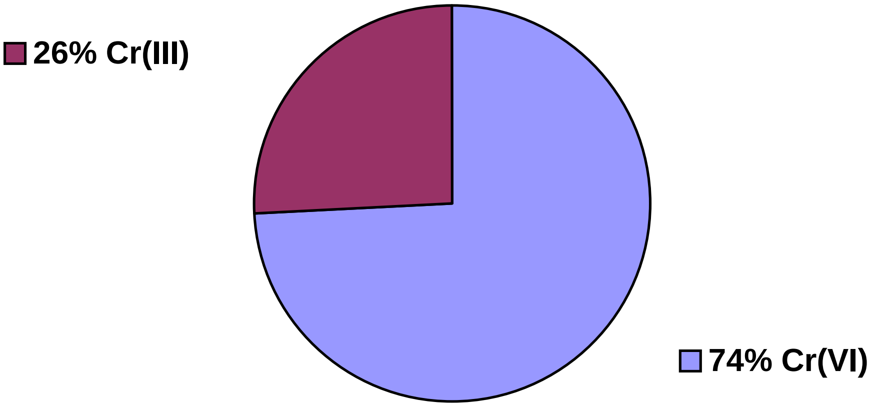

Fig.17: Typical Pie-diagram for the distribution of Cr (VI) at maximum level for SS-30

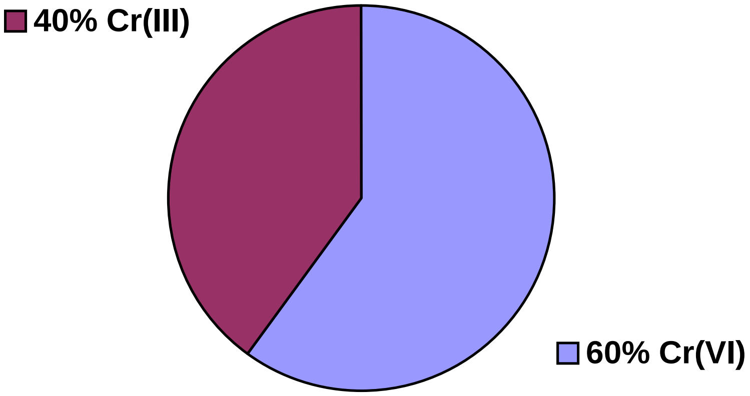

Fig.18: Typical Pie-diagram for the distribution of Cr(VI) at minimum level for SS-22

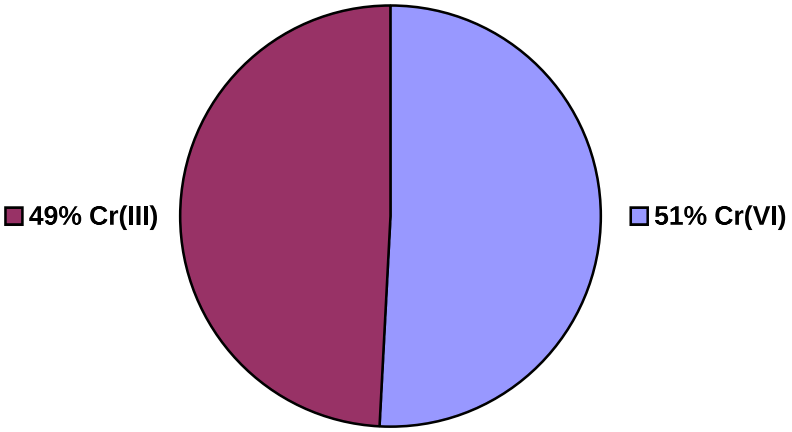

Fig.19: Typical Pie-diagram for the distribution of Cr(III) at maximum level for SS-32

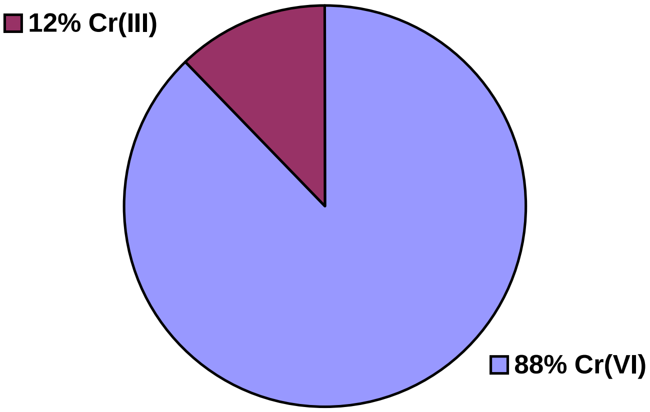

Fig.20: Typical Pie-diagram for the distribution of Cr(III) at minimum level for SS-12

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