DETERMINATION OF CHROMIUM IN WATER AND WASTEWATER

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DECLARATION

I hereby declare that all the materials in this dissertation are original except for certain quotations, excerpts and summaries which have been duly acknowledged.

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ABSTRACT

The colorimetric analysis of chromium (Cr) in aqueous solution according to DPC method was investigated. The absorbance measurement can be taken at λ = 540 nm using a UV – VIS spectrophotometer at least 5 minutes after addition of required reagents to the Cr solution. The absorbance – concentration relationship obeyed the Beer Lambert Law at Cr concentration range 0 – 5 μg/mL. Analysis of unknown, river water, acid mine drainage (AMD) and wastewater samples using the colorimetric method gave Cr concentrations 0.211 – 1.815 μg/mL, 0.001 – 0.006 μg/mL (average = 0.007 ± 0.002 μg/mL), 0.001 - 0.006 μg/mL (average = 0.004 ± 0.002 μg/mL) and 0.010 μg/mL,respectively. Comparatively, the Cr concentrations were 0.247 - 1.815 μg/mL, 0.082 - 0.021 μg/mL (average = 0.034 ± 0.007 μg/mL), 0 - 0.048 μg/mL (average = 0.008 ± 0.001 μg/mL) and 0.123 μg/mL, respectively, when the analysis was carried out by atomic absorption spectrophotometry (AAS). Depending on the type of sample, the concentrations obtained according to DPC method were comparable or lower than those obtained by AAS method.

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ABSTRAK

Analysis colorimetrik kromium (Cr) berdasarkan kaedah DPC telah dikaji. Nilai serapan boleh diukur pada λ = 540 nm dengan menggunakan spektrofotometer UV – VIS. Sekurang - kurangnya 5 minit selepas penambahan reagen kepada larutan chromium. Hubungan nilai serapan dan kepekatan yang diperolehi mematuhi Hukum Beer Lambert pada kepekatan Cr 0 – 5 μg/mL. Analisis sampel – sampel 'unknown', air sungai, AMD dan air buangan industri dengan menggunakan kaedah colorimetrik memberikan nilai kepekatan Cr masing - masing 0.211 – 1.815 μg/mL, 0.001 – 0.006 μg/mL (purata = 0.007 ± 0.002 μg/mL), 0.001 - 0.006 μg/mL (purata = 0.004 ± 0.002 μg/mL) dan 0.010 μg/mL. Kepekatan Cr berdasarkan kaedah spektrofotometry serapan atom (AAS) pula ialah masing - masing 0.247 - 1.815 μg/mL, 0.082 - 0.021 μg/mL (purata = 0.034 ± 0.007 μg/mL), 0 - 0.048 μg/mL (purata = 0.008 ± 0.001 μg/mL) dan 0.123 μg/mL bagi sampel yang sama. Kepekatan Cr yang diperolehi berdasarkan kaedah DPC adalah setara atau lebih rendah daripada kepekatan yang diperolehi berdasarkan kaedah AAS.

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LIST OF UNITS, SYMBOLS AND ABBREVIATIONS

Cr	Chromium
UV – VIS	Ultraviolet visible
AAS	Atomic Absorption Spectrometer
DPC	Diphenylcarbazide
H_2SO_4	Sulfuric acid
µg / mL	microgram per milliliter
gL^{-1}	gram per liter
g /mol	gram per mol
g	gram
cm	centimeter
M	Molarity
V	volume
t	time
λ	wavelength
L	litre
µm	micrometer
nm	nanometer
mL	millilitre

CHAPTER 1

INTRODUCTION

1.1 Context and Relevance of Study

Chromium (Cr) is one of the d-block elements of the periodic table. It's name comes from the Greek word, chroma, which means color (Sherwood, 1985). With six valence electrons, [Ar] $4s^1 3d^5$, Cr occurs in all possible positive oxidation states, that is 0, +1, +2, +3, +4, +5, +6, and +7. Like most elements in the group, Cr forms many highly colored compounds (Silberberg, 2006).

Chromium is found in nature mainly as the mineral chromite, which have an average composition of 68% Cr_2O_3 and 32% FeO (Figure 1.1). The metal can be obtained by reduction of the ore in an electric furnace, using either aluminium (Al) or silicon (Si), according to the following reactions (Sherwood, 1985):

$$Cr_2O_{3\,(S)} + 2Al_{(S)} \leftrightarrow 2Cr_{(S)} + Al_2O_{3\,(S)}$$

or

$$2Cr_2O_{3\,(S)} + 3Si_{(S)} \leftrightarrow 4Cr_{(S)} + 3SiO_{2\,(S)}$$

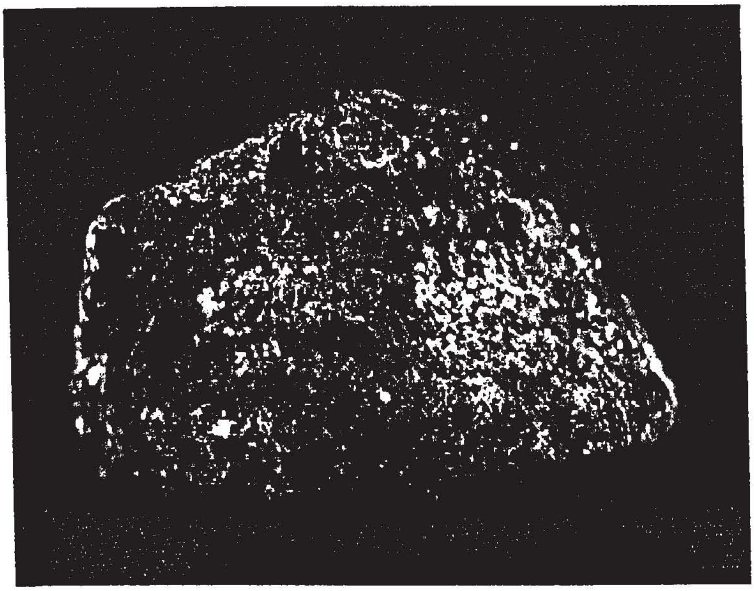


Figure 1.1 Mineral chromite

Chromium is released into the environment from various natural and industrial sources (Pressman & Aldstadt, 2003). Cr enters water supplies through the discharge of effluents from electroplating, tanning, dyeing, textile, cement, and chemical industries. Cr in the environment is found in two oxidation states, namely hexavalent chromium (Cr (VI)) and trivalent chromium (Cr (III)) (Balasubramaniam & Pugalenthi, 1999). Cr (III) plays an essential role in proper function of living organisms. On the other hand, Cr (VI) exerts serious toxic effects on biological systems (Themelis *et al.*, 2006). Comparatively, Cr (VI) is more commonly found in water and wastewater (Herrmann, 1994).

Analytical methods to determine total Cr (i.e Cr (III) and Cr (VI)) include differential-pulse polarography, X-ray spectrometry, neutron activation analysis, atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry (ICP), UV-visible spectrophotometry and amperometry (Balasubramaniam & Pugalenthi, 1999).

Colorimetrically, Cr in water and wastewater can be determined according to several methods, namely diphenylcarbazide (DPC) method, chromate method and EDTA method (Marzenko & Ramsay, 1976). The DPC method is specifically used to determine Cr (VI). For determination of Cr (III), it needs to be oxidized to Cr (VI) with potassium permanganate before determination (Marzenko & Ramsay, 1976). Subsequently, total chromium can be determined as the sum of Cr (III) and Cr (VI).

1.2 Objectives of Study

The objectives of this study are:

a) To evaluate the diphenylcarbazide (DPC) method for determination of chromium in water;

b) To determine chromium concentration in selected water and wastewater samples;

c) To compare the DPC method with AAS method for chromium determination in water and wastewater samples.

1.3 Scope of Study

This study focused on colorimetric analysis of chromium according to diphenylcarbazide method. It involved the reaction of chromium (VI) with 1,5-diphenylcarbazide (DPC) under acidic conditions and absorbance measurement at $\lambda = 540$ nm using a UV - Visible spectrophotometer. The effect of concentration and reaction time on the absorbance measurement was investigated. Subsequently, analysis of Cr was performed on water and wastewater samples. The results were compared with those obtained by AAS method.

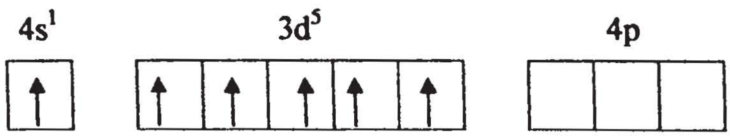
CHAPTER 2

LITERATURE REVIEW

2.1 Basic Chemistry, Properties and Uses of Chromium

2.1.1 Atomic number, atomic mass and electronic configuration

Chromium is a heavy metal which is known as d-block transition metal. The atomic number of Cr is 24 with atomic mass 51.996 (Sherwood, 1985). The full electron configuration of Cr is [$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$] $4s^1\ 3d^5$ while condensed electron configuration of Cr is [Ar] $4s^1\ 3d^5$. Cr has one electron in the 4s sublevel and five in the 3d sublevel. Thus, both the 4s and 3d sublevel are half filled. The partial orbital diagram for chromium is as follows (Silberberg, 2006):



2.1.2 Properties

Chromium is a naturally occurring element which is found in rocks, animals, plants, soil and in volcanic dust and gases. It is insoluble in water (Kirk & Othmer, 1993). Chromium is a very hard, shiny, silvery, lustrous and brittle metal which is found primarily in chromite (Silberberg, 2006). It is also odourless but malleable metal. Cr has body centered cubic structure. Its specific gravity is 6.8 with melting point about 1700°C and boiling point 2200°C. Chromium is stable in moist air at ordinary temperatures but burns with a bright flame when strongly heated (Cotton & Wilkinson, 1972).

Chromium has four naturally occurring nonradiogenic isotopes (Table 2.1). Chromium is resists corrosion and oxidation. When used in steel at greater than 10 wt %, it forms a stable oxide surface layer, which makes it particularly useful in making stainless steel to prevent corrosive effects of water. The ability of Cr to resist corrosion and accept a high polish has made it almost ubiquitous as a coating on household water faucets (Kirk & Othmer. 1993).

Table 2.1 Isotopes of chromium

Isotopes	**Abundance**	**Atomic Mass**
${}_{24}Cr^{50}$	4.35 %	49.946
${}_{24}Cr^{52}$	83.79 %	51.941
${}_{24}Cr^{53}$	9.50 %	52.941
${}_{24}Cr^{54}$	2.36 %	53.939

(Source: Kirk & Othmer. 1993)

Chromium also dissolves readily in non-oxidizing mineral acids such as hydrochloric acid and sulfuric acid. At high temperatures, chromium reacts with halogens, silicon, boron, nitrogen, carbon and oxygen to form chromium compounds (Cotton & Wilkinson, 1972).

2.1.3 Oxidation states and compounds of chromium

One of the most characteristic chemical properties of transition metals is the occurrence of multiple oxidation states. Chromium occurs in several positive oxidation states, namely 0, +1, +2, +3, +4, +5, +6 and +7, but the two most important are +3 and +6 (Cotton & Wilkinson, 1972). The properties of the various oxidation states of chromium are shown in the Table 2.2.

Table 2.2 Properties of the various oxidation states of chromium

Oxidation number	**Cr (II), d^4**	**Cr (III), d^3**	**Cr (IV), d^2**	**Cr (V), d^1**	**Cr (VI), d^0**
Coordination number	6	6	6	4	4
Geometry	Distorted octahedral	Octahedral	Octahedral	Tetrahedral	Tetrahedral
Stability	Borderline	Stable	Disproportionate	Disproportionate	Stable
Color	Blue	Green, violet	-	Green	Yellow,Orange
Acidity	Basic	Basic (kinetically amphoteric)	Strongly hydrolyzed amphotheric	Acidic	Acidic
Rate of ligand exchange	Very strong	Robust	Moderately fast	Moderately slow	Moderately slow
Strength as reducing agent	Very strong	Good	Strong	Strong	None
Strength as oxidizing agent	Weak	Weak	Strong	Strong	Strong

(Source : Howald & Manch, 1971)

2.1.4 Uses of chromium

The uses of chromium compounds are shown in Table 2.3.

Table 2.3 Uses of chromium compounds

Industries	Product	Uses
Building industry	Chromium (III) oxide	Pigments for coloring materials
Chemical industry	Dichromates, chromium (VI) oxide, Chromium (III) oxide	Oxidation of organic compounds, bleaching of montan waxes, manufacture of chromium complex dyes catalysts
Printing industry	Dichromates, chromium (VI) oxide	Photochemical reproduction processes, chromium plating of printing cylinders
Petroleum industry	Chromate (VI)	Corrosion protection
Paints and lacquers	Chromates, chromium (III) oxide	Pigments
Refractory industry	Chromium (III) oxide	Additive for increasing slag resistance
Electroplating	Chromium (VI) oxide	Bright and hard chromium plating
Wood industry	Chromate, chromium (VI) oxide	In mixture of salt for protecting wood against fungi and insects
Leather industry	Chromium (III) sulfates	Tanning of smoothed skins
Metal industry	Chromium boride, chromium carbide, chromium (III) oxide	Flame sprays, polishing agents
Metallurgy	Chromium (III) oxide	Aluminothermic extraction of pure chromium metal
Textile industry	Dichromates, chromium (III) acetates, chromium (III) fluorides	Dyeing with chrome dyes, mordanting of textiles
Recording industry	Chromium (VI) oxide	Magnetic information storage
Pyrotechnics industry	Dichromates	Additive to igniting mixtures

(Source : Gerhartz *et al.*, 1986)

The major ore of Cr is chromite ($FeCr_2O_4$). Chromite is reduced with carbon to produce ferrochromium which is primarily useful in metallurgical industry as an alloying element in steel. Stainless steel contains about 13% Cr to increase corrosion resistance (Housecroft & Sharpe, 2001). Stainless steels are important to industrialized societies because they are widely used in jet engines, nuclear power plants, chemical resistant valves and other applications in which a material that resist heat and chemical attack is required (Manahan, 2000).

Since Cr is a hard and bright metal, it can be plated onto other metals, generally by electrolysis, from a solution containing CrO_3 in H_2SO_4 solution. As this electrolysis involves reduction of Cr (VI) to Cr (0), it takes 6 moles of electron to produce 1 mole of Cr plate. Chromium plating consumes more electric energy and requires a higher current density (Hill & Petrucci, 2002). The silvery appearance of chromium has leaded it to be used in coating the bumpers and other bits of bicycles and cars (Acaster, 2001). Chromium plating for decorative purposes is generally applied in an extremely thin layer about 10 nm thick. This metal is first plated with a copper or nickel layer about 100 times thicker followed by the chromium layer. The function of chromium is to provide an unusually bright surface. Some of the common uses of chromium plating include metal working machinery, cutting tools, engine cylinders, hydraulic ramp coatings and hospital hygiene equipments (Hill & Petrucci, 2002).

The bright color of Cr (VI) compounds led to their wide use in pigments for artist's paints and ceramic glasses (Silberberg, 2006). Insoluble chromates, particularly

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