EVALUATION OF CHROMITE ORE AND THE OPTIMUM METHODS FOR INDUSTRIAL EXTRACTION OF CHROMIUM

A THESIS SUBMITTED BY

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IN CANDIDATURE FOR

THE DEGREE OF

MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

(P.O.BOX 321)

UNIVERSITY OF KHARTOUM

OCTOBER 1999

بسم الله الرحمن الرحيم

(ألم تر أن الله أنزل من السماء ماءاً
فأخرجنا به ثمرات مختلفاً ألوانها
ومن الجبال جدد بيض وحمر مختلف
ألوانها وغرابيب سود (٢٧))

سورة فاطر

TO
THE SOULS OF
MY
FATHER AND BROTHER

ABSTRACT

Samples of chromite ore, collected from Gam and Cheikay mining area (Ingessana Hills) in east Sudan, were analysed to assess the chromium content. Methods for extraction and analysis of chromium metal were developed and established. Analysis were carried out using atomic absorption spectroscopy (AAS) to estimate the contents of chromium, iron, calcium, and magnesium. X-ray fluorescence (XRF) was used to evaluate the levels of chromium, iron, and calcium in the ore. Volumetric analysis was performed to assess chromium and iron, whilst gravimetric analysis was employed to measure the amounts of calcium, magnesium, aluminum and silicon present in the ore.

The data was chemically and statistically analyzed to compare the results obtained by the given analytical methods. The results are in good agreement except iron oxide, which displayed a significantly different value when measured by x-ray fluorescence. The data obtained exhibited similarity in almost all cases, when compared with local and global researches, reports, and literature. The study has revealed the average contents of Cr_2O_3, FeO, CaO, MgO, Al_2O_3, and SiO_2 as 40.66, 11.96, 11.94, 0.36, 16.94, 11.45% respectively. MnO and NiO were detected in trace amounts, the corresponding levels in the ore being 72 and 27 ppm.

The average chromium content in extracted potassium dichromate measured by using AAS, XRF, and volumetric methods was found to be 31.7%. The highest grade reached by individual technique being 33.10%. The extraction with sodium peroxide is the optimum method for preparation of potassium dichromate. X-ray diffraction analysis, has showed that the d spaces and intensities of prepared potassium dichromate are isostructral with the corresponding ones of standard potassium dichromate. This suggests that the composition of the two samples is identical. Chromite samples were analyzed using gamma ray spectroscopy in order to estimate the levels of radioactive elements present. It was found that the concentrations of ^{232}Th and ^{40}K range from 7.62 to 10.98 Bq/kg and 47.38 to 56.28 Bq/kg respectively.

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ACKNOWLEDGEMENTS

Praise be to Allah. He by his Grace deeds of righteousness are completed. Iam deeply indebted to my honourable supervisor Dr. Mubarak Elsayed Osman. To whom one owes special gratefulness for his kind treatment, encouragement, continuous support, valuable counsel, patience, and understanding throughout the course of this work. His ever pleasant, realistic, elegant, and dedicated supervision of this thesis has always been appreciated by the author.

Iam greatly indebted to my honorable co-supervisor Dr. Mustafa Mohamed Osman Ahamed (Sudan Atomic Energy Commission) (SAEC) who paved the way for me with his assistance, continuous support, encouragement throughout the course of this work. Respectful style of far-sighted guidance has always been acknowledged by the author.

Lot of thanks to Dr. Elamin Elsayed who started the supervision of this work until he left for Saudi Arabia on secondment.

My thanks are also due to Chemistry and Physics Departments and Atomic Energy Commission (Sudan) for making their facilities available for me at all stages of this work.

I would like to express my thanks to my brother Dr. Eltigani Mustafa for his continuous financial support through out this work. At last and not least, I wish to express my deepest gratitude to my friends in Chemistry Department, University of Khartoum, and in (SAEC) especially in Chemistry section for their assistance, the fruit and pleasure time I spend with them.

CHAPTER ONE
INTRODUCTION

1. INTRODUCTION

1.1. Chromium:

1.1.1. History:

The history of chromium dates from 1762 when the mineral Crocosite was found in a Siberian gold mine.[1] It was first isolated in 1797 by the French chemist Vaguelin who named the new element chrome from the Greek word chroma, meaning colour.[1] In the following year the mineral chromite was discovered in the Ural mountains in Russia, and it has been the only commercial chromium mineral.[1] Since their discoveries, the metals and their compounds have become vitally important in many industries.[2] Chromite was produced near the end of the 18th century from deposits in the Ural mountains. These deposits were about the only source of chromite until Tyson's discoveries in Hartford country in 1827. Tyson[1] soon established a world monopoly that lasted to about 1860 when large Turkish deposits were developed sufficiently to supply the world market.[1] Chromium metal is very hard, but it is quite reactive in the powdered form and quite resistant to corrosion in massive form.[3]

1.1.2. Occurrence:

Chromite is the only ore of chromium metal. It consists mainly of oxides of chromium and iron (Cr_2O_3 68 %, FeO 32 %). It shows considerable variation in composition and rarely conforms to the theoretical formula. Iron may be replaced by magnesium or aluminum, and ferric oxide may substitute chromium.[4] The varieties containing chromium up to 14.6 % Cr_2O_3 are classified under picotite or chrome spinel (Mg, Fe) O. $(Al, Cr)_2O_3$.[4] It does not occur free in nature. It is most important ore is chromite $FeCr_2O_4$.[5] It may also occur as lead chromate ($PbCrO_4$). Traces of chromium may occur in minerals like emerald, Jdge, and serpentine.[5] It found in certain mafic igneous rocks specially large layered intrusions or accumulates as possibly oxide liquid segregation.[6] Chromite may occur as cores within magnetite grains iron rich rims of chromite, commonly observed in serpentine are known as ferric

chromite.[6] Chromium occurs principally in the silicates of very basic rocks where it substitutes easily for magnesium.[6] Rather high concentration of chromium is found in so called serpentine soils derived from the weathering of ultra basic rocks.[7] Chromium is usually found in ultra basic rocks such as peridotite and peroxenite as $FeCr_2O_4$ or as picotite.[7] The chrome spinel may also occur as the chrome ferrous varieties of many rocks commonly forming minerals.[7] Chromium is found for the most part with ferromagnesium mineral or separately as chromite.[8] Chrome occurs as frequently in serpentines as the results of decomposition of basic igneous rocks chiefly olivine rock.[8] These deposits are considered to be as a result of oxide liquid segregation, while the mass was plained due to after action which took place during the alteration of the fresh rock to be serpentine or even to vaporous actions of the time of the rocks consolidation.[9] From studies of chrome ores of North Carolina, scientests arrived to the same conclusion as others for other regions namely that the ores were actually magmatic segregation.[9] They favoured the same origin for other chromite deposits in the United States. Kemp after examining chromite deposits, he found that the most of these deposits have originated as magmatic segregation from the enclosing peridotitic rock.[9] The chrome content in $(Mg,Fe)Cr_2O_4$ varies from about 40% to 50% chrome oxide, depending on iron content. Chromite occurs in association with rocks like pyroxenite, serpentinite, dunite, and gabbro.[10] The occurrence of this metal in silicate rocks was also reported.[10] It appears to large extent in the earliest magmatic rocks to be crystallized in the olivine rock and to a lesser extent in the pyroxenites.[11] Most of the chromium present in chrome rich silicate rocks is to be magma deposited in early ferromagnesium minerals.[11] Among the sedimentary iron ores, carbonate rocks contain very little amount of chromium.[11] The levels in some basic igneous soils such as serpentine are relatively high.[12] No class of deposits shows more clearly than chromite, the need for a better understanding of the processes which the mineral was employed if prospecting and development are to be carried out with system instead of haphazard dependence on chance which is now common.[13] To be

sure, it has long been recognized that chromite invariable lies within rocks were rich in olivine, but no other generalization seems to have gained general acceptance.[13]

It widely distributed in soils although the concentrations are generally very low. In mining practice, the chrome ores that consist of chrome spinels are important commercially and serve as unique source of metallic chromium and the products of its chemical compounds.[14]

1.1.3. Terminology of chromite:

The most important chromium mineral found in nature exists in the form of ferrochromite ($FeO.Cr_2O_3$). The term chromite, however, is often used indiscriminately in the literature. In its strict sense, chromite refers only to one group of the spinel series of minerals composed of multiple solid oxides .The spinel series may be represented by the general formula ($A^{II}O.B_2^{III}O_3$), where A^{II} and B^{III} refer to divalent and trivalent cations respectively.[15]

In the trivalent group $B_2^{III}O_3$, metals such as chromium, iron, and aluminum, and sometimes manganese and titanium may exist. In the other divalent group $A^{II}O$, however, metals such as iron and magnesium, and some times zinc, manganese, and nickel may occur. Each specific chemical formula of the spinel series refers to specific term chromite, where the main trivalent metal in the $B_2^{III}O_3$ group is chromium. The chromite spinel ($A^{II}O.Cr_2O_3$) may be identified as, ferrochromite, ($FeO.Cr_2O_3$) or picochromite, ($MgO.Cr_2O_3$) when the metals in the divalent group $A^{II}O$ are iron or magnesium respectively . If the chromite is associated with gangue in the form of silicates or non-silicates it is called chromitite.[15]

1.2. The world production of chromite:

Since 1900, the world production of chromite has doubled on the average of about every 10 years, increasing from an estimated 5900 tons in 1900 to a peak of more than 5 million tons in 1957. Estimated output during 1950-1958 average 4 million tons annually of which less than 3 % was produced by the

domestic industry. In order of estimated production 1950-1958, the major producing countries were Turkey, South Africa, the U.S.S.R, the Republic of Philippine and Rhodesia. These countries produced 78% of the estimated world output.[1] However, world production of marketable chromite with chromium oxide content in the range of 40 to 50% have been grown to several million tons per year.[16] South Africa remained the largest world producer in 1980, but its out put at an estimated 3.13 million tons.[17]

The U.S.S.R which is the second largest world producer, account for the most of it's output, but Albania is an important producer.[17] The largest producer country of chromite in South African Republic is Transfail whose output has exceeded one million tons per year for many years. South Africa is also leading producer of ferrochrome.[17] The chief sources of supply of chromite, roughly in order of production are U.S.S.R, Turkey, Rhodesia, South Africa, Cuba, Yugoslavia, New Caledonia, India, Greece, Japan, and Philippine.[18] The principal chromite producing countries in normal times are New Caledonia and Rhodesia, and to some lesser extent Russia, Greece, India, Japan and other countries.[19] The Indian desposits in particular are large and high grade but has been handicapped by inadequate transportation.[19] The production of chrome in New Caledonia, Rhodesia, Russia and Turkey has usually amounted to more than 90% of the total world's production. During the second world war, The United States was temporarily an important producer, as were also Canada, Brazil, Cuba, and to a minor degree Guatemala.[19] The richest chrome ore mined at the present comes from Guatemala, but the mines are relatively inaccessible.[19] The New Caledonian, Rhodesian, Russian, Turkish and Indian ores are also of high grade. The ores mined in U.S.A, Canada, Brazil, Cuba, Greece and Japan are of lower grade.[19]

1.3. Chromium compounds:

A number of chromium compounds obtained by the chemical treatment of chromite have important uses in industry.[19] Such compounds include the chromate, dichromate of sodium and potassium, some chrome pigments, and

the compounds used in the chromium plating.[19] Chromium has oxidation states of (VI) (oxidizing), (III) (the most stable), and (II) (reducing).[20] These are readily demonstrated by shaking an acidified solution of potassium dichromate with zinc amalgam, the colour changes from orange to green and then to blue respectively.[20]

1.3.1. Chromium (VI) compounds:

1.3.1.1. Chromium (VI) oxide:

This is prepared by adding concentrated sulphuric acid to a cold concentrated solution of potassium dichromate, red crystals of chromium (VI) oxide separate from the solution.[20] The chromium (VI) oxide is very soluble in water, forming chromic (VI) acid, and is used for cleaning laboratory glassware.[20] Although chromic acid has never been isolated; it seems likely that a solution of chromium (VI) oxide in water contains $H_2Cr_2O_7$.[20] Chromium (VI) oxide is powerfully oxidizing,[20] thus it immediately inflames ethanol and on heating it forms chromium (III) oxide with liberation of oxygen:

$$4CrO_{3\,(s)} = 2Cr_2O_3 + 3O_2$$

It reacts violently with many reducable materials, such as sulphur dioxide, ferrous sulphate, hydrogen sulphide etc.[21] When CrO_3 is melted, it loses oxygen to give lower oxides.[22]

1.3.1.2. Chromate and dichromate:

Sodium chromate and sodium dichromate are prepared industrially from chromite.[20] The chromate ion can only exist in solution under alkaline conditions.[20] These solutions are yellow in colour; insoluble chromates are often yellow if the cation is colourless, although silver chromate is red.[32]

In laboratory, sodium chromate may be made by the oxidation of chromium (III) salt with sodium peroxide in aqueous solution.[20] The addition of acids to aqueous solution of chromate results in the elimination of water and formation of a condensed anion.[20] The colour of the solution changes from yellow to

orange, the reaction is easily reversed by addition of alkaline solutions.[20] Sodium and potassium dichromates are common laboratory reagents.[20] The former, which is more soluble in water than potassium dichromate is used in the presence of acid as an oxidizing reagent. Thus, its solution acidified with sulphuric acid is used for oxidizing alcohol to aldehyde or ketones and aldehyde to carboxylic acids.[20] Sodium dichromate can not be used as a primary standard in volumetric analysis, since the solid is too deliquescent.[20] However, potassium dichromate is an ideal primary standard since it does not hydrate, and as its solubility in water increases rapidly with increasing temperature, it is readily obtained pure by recrystallisation.[20]It is made by mixing hot concentrated solutions of sodium dichromate and potassium chloride, filtering off the precipitated sodium chloride and cooling the resultant solution, when the less soluble potassium dichromate crystallizes from solution.[20] The great advantage of potassium dichromate reagent is its availability as primary standard, and the solution needs not to be standardized in most cases.[23] In the titration of iron (II), standardization of potassium dichromate against iron is preferable because the green color of chromic ion introduces a small error in the end point.[23]

1.3.1.3. Chromyl chloride and potassium chlorochromate:

Chromyl chloride is the acid chloride of chromic acid, itself not isolated.[24] Potassium chlorochromate, is a salt of chlorochromic acid, also not isolated.[24] Chromyl chloride is prepared by addition of concentrated sulphuric acid to an intimate mixture of sodium chloride and potassium dichromate followed by gentle distillation.[24] It is a dark liquid, immediately hydrolyzed by water to give yellow solution containing hydrochloric and chromic acid.[25] Potassium chlorochromate may be prepared by repeated evaporation of finely divided potassium dichromate with concentrated hydrochloric acid on water bath at 60-70 ^{0}C. Then, red crystals of potassium chlorochromate were deposited from the resultant solution.Itis hydrolyzed by water, potassium salt is recrystallized from hydrochloric acid.[25] Alternatively, chromylchloride will react with

saturated potassium chloride solution to give potassium chlorochromate.[25] On gentle heating decomposition occurs and chloride is evolved with oxygen:

$$4(KO.CrO_2.Cl) + \Delta = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + O_2 + Cl_2$$

The chromyl bromide and iodide do not exist and the fluoride is made only by the action of fluoride on chromyl chloride, so the latter compound distinguishes chlorine from the rest of the halogens and is used in this way in quantitative analysis.[26] The chromyl halides are covalent compounds which hydrolyze in water to chromate, and there is no evidence for any CrO_2^{2+} cation.[26]

1.3.2. Chromium (III) compounds:

1.3.2.1. Chromium (III) oxide:

Chromic oxide is prepared by igniting either chromium hydroxide or ammonium dichromate:

$$(NH_4)_2Cr_2O_7 + \Delta = Cr_2O_3 + 4H_2O + N_2$$

It is a green powder insoluble in water or in dilute acid, but it may be converted to sodium chromate by fusion with sodium peroxide.[27] Chromic (III) oxide is a dark green solid having a similar ionic structure to that of aluminum oxide. It is amphoteric, dissolves in concentrated mineral acids to give chromium (III) ions and concentrated solution of alkali to give chromate.[20] Chromium (III) oxide is a refractory materials used in making chromium, as abrasive, a pigments and as a catalyst in organic reactions.[28]

1.3.2.2. Chromium (III) hydroxide:

This is formed as a green precipitate on adding hydroxide ions to a solution of chromium (III) salt.[28] The composition of the precipitate varies and it may be a hydrated oxide, Cr_2O_3 X H_2O.[28] Like the oxide, it is amphoteric and can be oxidized to chromate by heating with hydrogen peroxide in alkali solution.[28] It reacts with acids to give chromic salts and with alkalis to give chromate; it is therefore amphoteric. On heating, it gives chromic oxide and water.[29]

1.3.2.3. Chromium (III) salts:

These are made by reaction between chromium (III) oxides and acids[27] such as chromium (III) sulphate $Cr_2(SO_4)_3.8H_2O$ and chromium (III) chloride $CrCl_3.6H_2O$).[27]Chromium (III) salts are usually purple in colour.[27]

Solutions of chromium salts give green precipitate of the hydroxide on adding sodium hydroxide or ammonia solution.[27] The precipitate can be converted into chromate by heating with hydrogen peroxide in alkali solution.[27]Chromic carbonate does not exist and chromic sulphate immediately undergoes hydrolysis.[25] Addition of aqueous sodium carbonate or ammonium hydroxide to a solution of chromic salt precipitates the hydroxid. Anhydrous chromic chloride ($CrCl_3$) may be prepared by heating chromium in chlorine to a high temperature.[25] It sublimes in chlorine to a reddish-violet solid:

$$Cr_2O_3 + 3C + 3Cl_2 + \Delta = 3CO + 2CrCl_3$$

On heating in air, it forms chromic oxide and chlorine. In the absence of air, however, chromous chloride ($CrCl_2$) and chlorine are produced.[25]Chromium potassium sulphate or chrome alum is the most important salt and is readily obtained by reduction of potassium dichromate solution containing sulphuric acid.[25]

1.3.3. Chromium (II) compounds:

This is the least stable oxidation state of chromium being powerfully reducing.[20] Chromium (II) chloride can be made by passing dry hydrogen chloride over heated chromium. It is a white solid which dissolves in water to give the blue ions.[20] Solutions containing Cr^{2+} ion can be obtained by reduction of either an acidified solution of a dichromate or an acidified solution of a chromium (II) salt using zinc amalgam:

$$2Cr^{3+} + Zn = 2Cr^{2+} + Zn^{2+}$$

Solutions containing Cr^{2+} ions are readily oxidized by air to Cr^{3+} and can only be preserved in the presence of an inert atmosphere.[20] Chromous salts are

powerful reducing agents, being oxidized in air and by water in the presence of platinum or hydrochloric acid:

$$2H^{+} + 2Cr^{2+} = 2Cr^{3+} + H_2$$

Anhydrous chromous chloride may be prepared either by heating chromic chloride in dry hydrogen or by the action of hydrogen chloride on the metal.[25]

1.4. Properties of chromium:

1.4.1. Physical properties:

Chromium is silver-white metal, (m.p. 1920 ^{0}C, b.p. 2300 ^{0}C).[29] It is hard and malleable.[29] It is fairly good electrical and thermal conductor.[29] Its density is 7.1 g/cm^3.[29]

1.4.2. Chemical properties:

Chromium does not corrode in air at normal temperature, but form chromic oxide Cr_2O_3 when heated strongly:

$$4Cr_{(s)} + 3O_{2(g)} = 2Cr_2O_3$$

It is unattacked by water under normal conditions, but reacts slightly with steam when red hot to give chromic oxide and hydrogen:

$$2Cr + 3H_2O = Cr_2O_3 + 3H_{2(g)}$$

The metal dissolves in dilute mineral acids to give chromous salts and hydrogen:

$$Cr + 2H^{+} = Cr^{2+} + H_{2(g)}$$

However, dilute nitric acid has very little reaction with metallic chromium.[29] Concentrated hydrochloric and sulphuric acids react with the metal more vigorously than the diluted acids.[29] Hot concentrated sulphuric acid attacks the metal to give chromic sulphate.[29] Chromium combines with several other elements,[29] e.g. chlorine when hot:

$$2Cr + 3Cl_{2(g)} = 2CrCl_3$$

The chief oxidation states of chromium are (II), (III), and (VI). A few compounds of Cr^{4+} and Cr^{5+} are known, but they are unstable. Chromium (0) occurs in $Cr(CO)_6$ and $Cr(C_6H_6)$.[30]

1.5. Uses of chromium:

Most chromium consumption is closely related to the metallurgical industry, despite the fact that the ore is used by the refractory and chemical industry as well.[1] Distribution of chrome ore consumption in the United State, reveals that 56% was used in ferroalloys manufacture, 33% in making of refractors and 11% was used in chemical production.[1] Most of the chrome refractors are used by the metallurgical industry for lining and patching furnaces, and a fair percentage of the chemicals is used for metal treating and plating and the manufacture of chromium metal.[1] A large portion of chromium produced is used in production of steel alloys that are very hard and strong.[7] Stainless steel, which usually contains chromium and some nickel, is used in the manufacture of cutlery because of its corrosion resistance.[7] Non ferrous chromium alloys include nichrome and chromel (Ni and Cr) which are used in various heating devices because of their electrical resistance property.[7] Chromium is widely used as a protective and decorative coating for other metals such as plumbing fixtures.[7] Chromium is also used as paint pigments and mordent.[7]

potassium chromate and sodium dichromate are used as oxidizing agents.[31] Sulphuric acid solutions of chromium (VI) are powerfully oxidizing agents that are widely used in organic chemistry, and as cleaning solution for laboratory glassware.[32] The cleaning action is largely due to oxidation of grease and organic residues.[32] Potassium dichromate is largely used as an oxidizing agent in the manufacture of other chromium compounds such as chrome alum, lead chromate in dyeing industry, in the preparation of insoluble pigments, and in manufacture of inks.[21] Dichromate solutions in concentrated sulphuric acid are used in degreasing glassware.[21]

Potassium and ammonium chrome alums are a source of chromium sulphate, which can be converted into basic salts by the addition of alkali.[33] The chromium sulphates has penetrating power and poor tanning properties, but on

being made basic, it forms basic cationic chromium salts with good tanning properties.[33] The chrome alums are useful for making white[33] leather:

$$K_2SO_4Cr_2(SO_4)_3 + H_2O + Na_2CO_3 = Cr_2(SO_4)_2(OH)_2 + CO_2 + Na_2SO_4 + K_2SO_4$$

1.6. Detection and determination of chromium:

Chromium is precipitated by ammonium hydroxide as bluish-green chromium hydroxide along with the hydroxides of iron and aluminum.[34] The chromic compound is oxidized to chromate by action of chlorine, bromine, sodium peroxide, or hydrogen peroxide added to the substance containing an excess of alkali.[34] The chromate dissolves and is thereby separated from iron, which remains insoluble as $Fe(OH)_3$.[34] The alkali chromates colour the solution yellow. Barium acetate or chloride added to neutral or slightly acetic acid solution of chromate precipitates yellow barium chromate. Addition of ammonium acetate to neutralize any free inorganic acid aids the reaction.[34] Lead acetate produces yellow precipitate with chromates, in neutral or acetic acid solution. Mercurous and silver nitrates form red precipitates with chromates.[34]Hydrogen peroxide added to chromate and heated with mineral acids, yields a greenish-blue coloured solution. Chromates are reduced by hydrogen peroxide in acid solution.[34] Reducing agents like hydrogen sulfide, ferrous salts, and alcohol form green chromic salts when added to chromates in acid solution. Chromic salts are bluish-green; chromic acid is red, chromates are yellow, dichromate is orange, and chrome alum is violet. The powder mineral, containing chromium when fused with sodium peroxide, produce a yellow coloured mass of chromates.[34] In dilute sulphuric acid, the exhibition of an intense blue colour indicates the co-existences of chromate and dichromate.[21]

The highly refractory mineral chromate is brought into solution by fusion with sodium peroxide. Upon leaching the melt with water, the sodium chromate dissolves and the iron is precipitated as an iron (III) hydroxide.[35]

1.7. Extraction of chromium oxide:

The process of extracting pure chromium from the ore is rather more involved. Chromate is heated strongly with sodium carbonate in the presence of air; or sodium peroxide, sodium chromate is obtained which is dissolved in hot water.[20]The sodium chromate is then converted into sodium dichromate by acidifying the solution with sulphuric acid.[20] Sodium sulphate can be crystallized out first on concentration followed by sodium dichromate.[20] Finally, sodium dichromate mixed with ammonium chloride, and heated whereby chromic oxide is formed.[21]The residue is washed with water and dried:

$$K_2Cr_2O_7 + 2NH_4Cl + \Delta = (NH_4)_2Cr_2O_7 + 2KCl$$

$$(NH_4)_2Cr_2O_7 + \Delta = Cr_2O_3 + N_2 + 4H_2O$$

1.8. Analytical methods and instrumentation:

1.8.1. Volumetric analysis:

Volumetric analysis is one of the most useful analytical techniques. It is fairly rapid and produces results of very high accuracy.[35]The term volumetric analysis refers to quantitative chemical analysis carried out by determining the volume of the solution of accurately known concentration which required to react quantitatively with the solution of the substance to be determined.[35] The experimental conditions should be so selected that the difference between the visible end point and the equivalence point is as small as possible.[35] Sometimes a reaction is slow to go to completion and a sharp end point cannot be obtained. In these cases a back titration will often yield useful results.[23] In this technique, measured amount of the reagent, which would normally be the titrant, is added to the sample so that there is slight excess. After the reaction with the analyte is allowed to go to completion, the amount of the excess (unreacted) reagent is determined by titration with another standard solution. The analyte reaction also may speed up in the presence of excess reagent.[35] By subtracting the number of millimoles unreacted from the number of

millimoles of reagent taken, the number of millimoles of sample that have reacted [35] can be calculated as follows:

mmoles reagent reacted = mmoles taken - mmoles back titrated

1.8.2. Gravimetric analysis:

Gravimetric analysis or quantitative analysis by weight is the process of isolating and weighing an element or definite compound of the element in as pure form as possible.[35] In most cases the constituent being estimated is weighed in a form other than that in which it was precipitated.[23] Usually in the form of one of its compounds.[23,36] The term gravimetric factor is frequently employed. It is the number of grams of the desired constituent in one gram (or the equivalent of one gram) of the substance weighed.[37] Multiplication of the weight of the precipitate by the gravimetric factor gives the number of grams of the desired constituent in the sample.[37] Division by the weight of the sample and multiplication by 100 gives[37] percentage of the desired constituent:

$$\% \text{ of constituent} = \frac{\text{Weight of the precipitate} \times \text{gravimetric factor} \times 100}{\text{Weight of sample}}$$

1.8.3. Atomic absorption spectroscopy (AAS):

Atomic absorption spectrometry may be defined as a method for determining the concentration of an element in a sample by measuring the absorption of radiation in atomic vapour produced from the sample at wavelength that is specific and characteristic of the element under consideration.[38] This technique has enjoyed rapid growth and success. The sample solution aspirated into a flame and the flame then contains atoms of that element.[23] Some are thermally excited by the flame, but most remain in the ground state.[23] These ground state atoms can absorb radiation given off by special source made from that element.[23] The wavelength of radiation given off by the source are the same as those absorbed by atoms in the flame (O_2-C_2H_2).[23] Radiation in the visible and ultraviolet regions of the spectrum characteristic of particular element is passed through the flame and the decrease in the intensity is measured using a

detector after passing through a monochromotor.[39]The degree of the absorption is a quantitative measure of concentration of the ground state atoms in the vapor.[39] The reduction in the intensity of the incident radiation is related to the concentration of the absorbing medium, as indicated by Beer-Lambert's low, through the following mathematical formula:

$$Log\ I_0/I_t = \varepsilon CL \qquad (1.1)$$

where, I_0 = intensity of the incident radiation, I_t = intensity of transmitted radiation, ε = molar absorbtivity or molar absorbency, C = concentration of the analyte (g/ml), and L = path length of absorbing medium (cm), $\log I_0/I_t$ is known as the absorbance (A). Equation (1.1) can then be rewritten as:

$$A = \varepsilon CL \qquad (1.2)$$

In this method, measuring the absorbance of samples of known concentrations (standard solutions) makes a calibration curve. The unknown concentrations can be calculated after measuring its absorbance or the system is interfaced with a computer for the automatic calculation of the cncentration.[40]

1.8.4. X-ray fluorescence analysis (XRF):

X-rays are generated by electron bombardment of heavy metal targets.[41] Like ordinary light, they are forms of electromagnetic radiation of very short wavelength.[41] X-ray fluorescence is an analytical tool for elemental analysis.[42] It is widely used as qualitative elemental technique as well as quantitative one.[43]

X-ray fluorescence is based on the detection of x-ray fluorescence emitted when electron falls into inner vacancies in analyte atom. The vacancies are created by bombardment of the sample with high energy source, such as x-rays, gamma rays, protons and ions.[44] The spectra produced yield quantitative and qualitative information.[44] The emitted wavelengths may be used to identify elements and intensities to measure their amounts.[44] The x-ray spectra produced can be measured either by wavelength dispersive or energy dispersive such as (Si-Li) detector system.[44] The fluorescence intensities depend on two sets of parameters; those which are directly related to the

specimen such as the concentration of the element present and those which are related to the instrumentation such as spectral distribution.[45] X-ray fluorescence includes bombarding of the sample with "primary" x-ray from x-ray tube (usually with tungsten target)."Secondary" or fluorescent x-ray produced from the sample are then conducted to a single crystal which acts as an analyzer or dispersion grating and split the fluorescent spectrum into its components for identifying the elements in the sample emitting the x-rays.[46]

1.8.5. X-ray diffraction:

X-ray diffraction occurs when a monochromatic beam of x-ray radiation interacts, and scattered in different directions[47]. Every crystalline compound exhibits a characteristic x-ray diffraction spectral, and so the placement of lines or rings in the spectrum may be used as the basis of the qualitative determinations.[47] Further more, the diffraction spectrum of a mixture of substances is a simple combination of the various component spectra, and the relative intensities of the two or more component spectra are determined by the relative concentration of the substance in the mixture. Therefore, intensity measurement permits quantitative determinations.[47]

X-ray diffraction methods are very useful for many purposes, other than straight forward qualitative and quantitative analysis. Since the diffraction characteristics of a crystalline specimen are determined by the geometrical arrangements of the atoms or ions within the crystals, its possible to arrive at ultimate structural information on crystalline substance.[48] The Bragg condition is the basic equation of x-ray crystallography, the study of the internal structure of crystals.[48] Its primary use is the determination of the spacing between the layers in the lattice, because once the angle 0, which corresponds to a maximum intensity is measured, it can be determined readily be calculation using[49] Bragg equation:

$$n\lambda = 2d \sin\theta$$

1.8.6. Gamma ray analysis:

Gamma ray spectroscopy is based on the resonance absorption of gamma quanta by atomic nuclei.[50] As the nuclei undergo radioactive decay, isotopes in an excited state are formed.[50] their transition to ground state is accompanied with gamma radiation.[50] Unexcited atomic nuclei in turn can absorb gamma quanta, and so be excited but only in special conditions.[50] The gamma spectroscopy assess the character of the distribution of electron density in compounds and establishes their structures. The method is very useful for studying the concentration and state of radioactive elements in ores and minerals.[50]

1.8.6.1. Gamma ray instrumentation:

The main parts of gamma ray system are detector, electronic package system, and computer and software for analysis.[51] When a gamma ray falls on the pure germanium coaxial detector, generates a linear charge pulse, which is delivered to the preamplifier. The preamplifier converts the charge into voltage pulse and amplifies it. The linear beside amplification acts as a signal processor, it converts the signal received from the preamplifier into a form suitable for measurements. It cuts the signal tail to prevent pile up and restore the base line.[51]The amplification linearity must maintain proportionality of voltage pulsing time of r seconds. This pulsing time is a function of the detector size.[51] The detector shielded with lead which has much lower back scatter and walls of 5-10 cm thick lined inside with graded liner to degrade x-rays.[52]

1.9. Estimation of chromium ore in Sudan:

Interest in hard minerals continuous to rise in Sudan as local and foreign Companies compete for potential and based metal producing area.[53] Gradual improvements in infrastructures are found to have considerable influence on mining, due to expansion of asphalt roads south to Damazin by the end of 1983, chromite production expected to rise as road transport costs are expected

to compare favorably with rail. Prospecting for chromite was undertaken mainly in Blue Nile State. [53]

The chromites in the Ingessana Hill area have been exploited since the 1960s.[54] However, the ore reserves in the whole area have not been determined yet. Japanese survey team explored the deposits at Gam mining area twice in 1977 and estimated at 438600 tons.[54] In addition, Chinese survey team conducted large scale exploration over a period of three years from 1974 to 1977 and its report has been currently finalized.[54]According to their interim reports, the amount of the reserves in the whole Ingessana Hills area estimated to about 700000 tons. The deposits in this mine are scattered widely in small quantities under such circumstances, it is necessary to design an exploration plan which would exploit the pits economically.[54] Chromite exist in the south eastern part of the Blue Nile State, other occurrences had reported as Qala Elnahal regions, the Red Sea Hills regions, and Gadarif area of the Kassala State in eastern Sudan. The chemical analysis carried out in some samples indicated that the ore in this locality is containing high ratio of iron.[55] Recent discoveries proved the existence of chromite in Jabel Tawilla in Gadarif area.[55] Also in Halaib area chromite was reported.[55] No economic chromite deposits have yet been found in the Red Sea Hills area.[56] However, chromite occurrence have been reported and investigated and production continued in the hope of finding large deposits.[56] The results of the chromite ore reserves calculations were as follows: Grade one ore of chromium oxide 48% is 43500 tons, grade two ranges from 32 to 48% is 213341.47 tons, and grade three ranges from 25 to 32% is 8296.57 tons. Estimation of the total chromite ore reserves in Ingessana Hills region sums 695133.4 tons average 47% Cr_2O_3.[57] Small chromite pods is present in most of the other ultrabasic masses in Blue Nile State, although non have been exploited.[58] The western serpentinite in the Ingessana complex contains high chromium ores up to 60.1% chromium oxide whereas those in eastern part carry chromite with higher aluminum and iron.[58]

1.10. Economic minerals related to the chromium rocks:

During the course of chromite prospecting and exploration, a preliminary survey was made on minerals related to the ultrabasic rocks such as platinum and magnesite.[59] Assay samples for determining the platinum group elements were collected of which 89 were taken from chromite ore bodies and 15 from the ultrabasic rocks of various types in Gam mining area, and one from the Chickay mining area.[59] Analysis of the samples has indicated the presence of the platinum group elements mainly rhodium, iridium, and osmium, and secondly ruthenium, palladium, and platinum.[59] The content of platinum group elements increases with increasing chromium oxide content.[59]The results of neutron activation analysis for the 6-platinum group elements and gold showed that, the lower group chrormites are enriched relatively to silicates rich host rocks. The platinum group elements and gold contents increase up the sequence, and the middle group chromites are richer than lower group chromites, these elements of the 2-platinum group elements (Pt, Pd, Rh) and (Ru, Os, Ir), the former is more abundant in the middle group chromites whereas the second group is slightly enriched.[60] Two chromite specimens are selected as reference samples for determination of gold and platinum contents. One of these samples is enriched in the platinum elements, the other has much lower concentration.[61] Thus the platinum metals are usually associated with the mineral chromite. In the Ural mountains, ultrabasic igneous rocks such as dunite and serpentine which contains considerable amount of chromite also contain small grains of platinum sparsely disseminated in the rocks.[62] Platinum is also associated in the original basic igneous rocks with chromite.[62]So the bulk chemistry of Os, Ir, Ru of the spinels from dunite and chromite reflect the composition of the platinum group mineral trapped in the spinels.[63]The geochemical behavior of the platinum group elements during partial melting and crystallization is used to define the conditions of formation of chromite and platinum group elements concentrations.[63] Radiochemical modification of neutron activation analysis was used to study the Pt and Au distribution in

different rocks and minerals.[64] The concentrations of Pd and Pt in chromite are comparatively high.[64]

1.11. Objectives of this study:

1.To evaluate elemental composition in the chromite ore using different analytical techniques; Volumetric, gravimetric, AAS, XRF, XRD, and gamma ray spectroscopy.

2.To measure, and for the first time the natural radioactivity related to the chromite ore.

3.To extract and for the first time chromium compounds by better methods for different uses.

4.To add new information to the base line data system in Sudan.

CHAPTER TWO
EXPERIMENTAL

2. EXPERMINTAL

2.1. Sample collection:

Samples of chromite rocks were collected from different locations along Ingessana Hills in the eastern parts of the Blue Nile State, mainly Gam and Cheikay mining area, about eighty km southwest to Damazine. Samples have been collected from fifteen mining areas, the distance between each mine and the other is about 200-300 m. The area is bounded by the following coordinate latitudes $11^0.15$ - $11^0.30$ N, longitudes $33^0.55$ - $34^0.12$ E. The samples were collected in a fresh clean polyethylene bags and stored in small glass bottles with labels showing the locality of samples. A map showing the mining area from which chromite samples have been collected is presented in Figure 2.1.

2.2. Sampling:

The principal of the sampling of chromite ore is to select numbers of portions from different mines by using humor to break off the rock chips and then to combine them. The samples were crushed mechanically upon apex of the cone and walking around the cone, to ensure a comparatively even distribution. The top of the cone is flattened out and divided into quarters. Opposite quarters of the pile are then removed, mixed to form a smaller conical pile and again quartered. This process is repeated until samples of suitable weights are obtained. The samples are ground and quartered for many times until a sufficiently small final sample for laboratory work is obtained which is then kept in plastic containers for use.

2.3. Analysis of chrome ore contents:

2.3.1. Volumetric analysis of chromium:

0.5g of powdered sample were weighted accurately into a 30-35 cm^3 nickel crucible, 4g of sodium peroxide were added and mixed thoroughly by means of a thin glass rod. Powder adhering to the rod was removed by adding about 1g of sodium peroxide. The mixture in the crucible was covered with peroxide and gently heated (for about 10 minutes) in the fume cupboard over

small flame until the mass was quite liquid. The sample was kept fused for a further 10 minutes at a dull red heat and allowed to cool. When a solid crust formed, about 4 g of sodium peroxide were added, the mixture was fused again at a cherry-red heat for 10 minutes. The crucible was allowed to cool, and then placed in 600 cm^3 pyrex beaker containing little distilled water. The beaker was covered with a clock glass, little warm water was added, after the violent reaction has subsided, the crucible was removed and washed thoroughly, the washings being collected in the same beaker. The liquid was boiled for 30 minutes, to decompose hydrogen peroxide, 250 cm^3 of boiling water were added, and the precipitate allowed to settle. The resultant solution was filtered off through 15cm filter paper. The residue was washed thoroughly with boiling water until free from chromate. The residue should be completely soluble in concentrated hydrochloric acid; no black gritty particles should remain. If this is not the case, decomposition is not complete, and the determination must be started a fresh. The filtrate was evaporated to about 200 cm^3, cooled and acidified with 4.5M sulphuric acid. After cooling, it was transferred to a 250 cm^3 graduated flask, and the volume was made up to the mark by adding distilled water. Then, the resultant solution was shaken frequently to achieve uniformity. 50 cm^3 of the resultant solution were added into 50 cm^3 of 0.1M ammonium iron (II) sulphate, and 200 cm^3 of 4M sulphuric acid, and 0.5 cm^3 of N-phenyl antharanilic acid as indicator were then added. The excess of iron (II) sulphate salt was titrated with standard 0.0166M potassium dichromate until the colour changes from green to violet-red. The ammonium iron (II) sulphate solution was standardized against 0.0166M potassium dichromate, using N-phenyl antharanilic acid as indicator. The volume of the iron (II) sulphate solution which was oxidized by the dichromate originating from the chromium salt was calculated. The percentage of chromium in the sample of chromite, and the percentage of chromium oxide were determined from the results[35] obtained using the formula:

$$Cr\% = \frac{(\text{moles of } Fe^{2+} \text{taken} - \text{moles of } Fe^{2+} \text{reacted with } Cr^{6+}) \times 1/6 \times 52 \times 100}{0.5\ g}$$

2.3.2. Determination of FeO, Al_2O_3, MgO, CaO, and SiO_2:

The method is designed for standard chrome ores. After dissolution in a mixture of sulphuric and perchloric acid, chromium is removed by volatilization as CrO_2Cl_2. SiO_2 is separated and any insoluble oxides are removed from it. After double separation, iron is separated with cupferron and aluminum with NH_4OH. Calcium and magnesium are precipitated as phosphates, and then calcium as $CaSO_4$.

1.0g of the sample which has been dried for one hour at 105 to 110 ^{0}C were placed in a 250 cm^3 beaker, 50cm^3 of H_2SO_4 (1:4), 5.0g of $(NH_4)_2SO_4$, and 20 cm^3 of 60% $HClO_4$ were added. The beaker was covered with a small watch glass and heated gently until fumes of $HClO_4$ were freely evolved and the chromium is oxidized to chromic acid. The cover was removed, the heating continued while the chromium is volatilized as CrO_2Cl_2 by the introduction of a stream of dry HCl gas, or by addition of small portions of sodium chloride. In case were chromic acid was deposited on the sides or bottom of the beaker, the solution was cooled and 5 to 10 cm^3 of water was added. The solution was heated as described above. When fumes of $HClO_4$ began to be evolved, HCl gas was bubbled at a moderate rate until all the chromium has been volatilized. The sample solution was cooled, 75cm^3 of water were added, and the solution was boiled for several minutes. The solution was filtered off using 9 cm paper containing a little paper pulp, catching the filtrate in 400 cm^3 beaker. The precipitate was washed thoroughly with hot water. The paper and silica were ignited in weighed platinum crucible at a dull red heat until the carbon has burned off completely. The crucible was cooled and weighed, several cm^3 of hydrofluoric acid. 1-2 cm^3 of concentrated nitric acid and 0.5 cm^3 of sulphuric acid (1:1) were also added. The solution was evaporated to dryness to volatilize the silica, weighed, the loss in weight is equal to the amount of SiO_2 in chromite. from the silica.

$$SiO_2\ \% = \frac{\text{weight of } SiO_2 \times 100}{\text{weight of sample}}$$

2.3.3. Separation of Al_2O_3 and FeO, from MgO and CaO:

5.0g of NH_4Cl were added to the filtrate and the solution was heated just to boiling. Excess of dilute ammonia solution (1:2) were added, and then heated to boiling for 2 minutes. The precipitate was allowed to settle down, and then filtered off on 11cm paper containing a little paper pulp. The precipitate was washed several times with hot NH_4Cl solution. The paper containing the precipitate was returned to the original beaker and treated with $5cm^3$ of hydrochloric acid (1:4). The solution was heated to boiling, diluted to 100 cm^3 with hot water and precipitated with NH_4OH.The precipitate was filtered off, and washed as previously described. The two filtrates were combined and used for the determination of calcium and magnesium.[65]

2.3.4 Separation of Al_2O_3 and FeO:

The precipitate of ammonia and paper were returned to the original beaker and 10 cm^3 of 96% H_2SO_4, 20 cm^3 of 63% HNO_3 were added. The mixture was heated until the paper is destroyed. Finally, the solution was evaporated to dense fumes, cooled to < 20 °C, and allowed to precipitate iron by addition of a freshly prepared cold aqueous solution of cupferron in slight excess. Excess is present when a drop of the precipitant forms a transient white precipitate. Filtration was carried out on an 11cm filter paper containing a little paper pulp, catching the filtrate in a 600 cm^3 beaker. The precipitate was washed thoroughly with HCl (1:9) containing 10 cm^3 of cupferron reagent 1%. The precipitate was ignited at low temperature, in a porcelain (or silica crucible) until the carbon was oxidized. Cooled, 10 cm^3 of HCl and few drops of $SnCl_2$ (5% of HCl) (1:1) were added, heated until the iron oxide dissolved. The contents of the crucible were transformed to a 400 cm^3 beaker, heated to boiling, and then cooled to <20 °C. 10 cm^3 of saturated $HgCl_2$ solutions were added, stirred well, and then allowed to stand for 2 minutes. The resultant

solution was diluted to 200 cm^3 with cold water, 5cm^3 of H_3PO_4, 10cm^3 of H_2SO_4 (1:1). Few drops of sodium diphenylaminesulfonate were added as indicator. The solution was titrated with 0.1N $K_2Cr_2O_7$ to a purple end point. The FeO content is calculated as follows:

$$FeO\ \% = \frac{A \times 0.00\ 7185 \times 100}{B}$$

where A = ml. of 0.1N $K_2Cr_2O_7$, B = weight of sample in grams.

2.3.5. Determination of Al_2O_3 :

The precipitate from the cupferron filtrate was boiled down until the volume reduced to about 45 cm^3. 25 cm^3 of 63% HNO_3 were added and the evaporation continued again until the volume was reduced to about 50 cm^3.10 cm^3 of HNO_3 and 15 cm^3 of 60% $HClO_4$ were added, and the evaporation continued until dense fumes of $HClO_4$ evolved, and all organic matter has been oxidized completely. More nitric acid was added in case were the solution becomes dark upon fuming with $HClO_4$.The solution was cooled, diluted with 100 cm^3 of warm water. Approximately 5.g of HN_4Cl were added, aluminum was precipitated by addition of NH_4OH (1:2) in very faint excess .The precipitate was boiled for 1-2 minutes and allowed to settle. The precipitate was filtered and washed, about 10 times with 2% hot NH_4Cl solution. The precipitate and the paper returned to the original beaker, treated with 100 cm^3 of HCl (1:4) and heated to boiling. Precipitation was repeated, filtered off and washed as previously described. The paper and the precipitate were transferred to a preweighed platinum crucible and ignited first at a low heat and finally to constant weight at 1150-1200 °C, cooled and weighed as Al_2O_3. [65]

2 .3.6. Separation and determination of MgO and CaO:

The combined ammoniacal filtrates separated from Fe_2O_3 and Al_2O_3 solution was acidified with HCl, evaporated to 250cm^3 and then allowed to cool to about 15 °C. 50 cm^3 of diammonium phosphate solution 10% were added,

followed by NH_4OH until the solution was ammoniacal and crystallized precipitate appeared. An excess of 25cm^3 of NH_4OH was added, the solution stirred thoroughly, and finally cooled to about 15°C. It was allowed to stand for several hours, preferably overnight, with frequent stirring. The solution was filtered off using 9 cm paper containing a little paper pulp and filtered about 4 times by decantation and washed with cold NH_4OH (2:98). 25cm^3 of hot HCl (1:1) poured through the filter paper and collected in the original beaker containing the bulk of the precipitate. The filter paper was washed thoroughly with hot HCl (5:9), diluted with cold water to a volume of 150 cm^3 and cooled to room temperature. 3cm^3 of diammonium phosphate solution were added, and allowed to cool to a temperature of about 15 °C, filtered, washed, first about 15 times with cold NH_4OH (2:98), and then twice with NH_4NO_3 solution. Ignited in a weighed platinum crucible at a dull red heat until the carbon has been completely burned, and finally to a constant weight at 1000 to 1050 °C, and finally weighed as $Mg_2P_2O_7 + Ca_3 (PO_4)_2$.

2.3.6.1. Determination of CaO:

The pyrophosphate precipitate ($Mg_2P_2O_7 + Ca_3 (PO_4)_2$ was dissolved in 20 cm^3 of hot diluted hydrochloric acid (1:4). 10 cm^3 of sulphuric acid were added to the solution, and evaporated to fumes of sulfur dioxide.5cm^3 of H_2O and 100cm^3 of 95% ethyl alcohol were added, and the solution was stirred vigorously for several minutes. precipitate of calcium sulphate was allowed to settle for several hours. The precipitate was filtered using 9 cm paper containing little paper pulp, and washed at least 20 times with 80% alcohol containing 2cm^3 of 0.2% Sulphuric acid to ensure complete removal of all phosphoric acid. It was then transferred to a preweighed crucible, ignited to a dull redness to constant weight, cooled, and weighed as $CaSO_4$.[65] The percentage of CaO is calculated according to the following formula :

$$CaO\ \% = \frac{A \times 0.41196 \times 100}{B}$$

where; A = weight of $CaSO_4$ in grams, B = weight of sample.

The result was multiplied by the factor 1.8437 to convert to $Ca_3(PO_4)_2$ to deduce from the impure $Mg_2P_2O_7$.The percentage of MgO was determined using the formula:

$$MgO\% = \frac{(A - B) \times 0.3622 \times 100}{E}$$

where; A = weight of crude $Mg_2P_2O_7$, B = weight of $Ca_3(PO_4)_2$ and
E = weight of sample

2.4. Atomic absorption spectroscopy:

Atomic absorption measurements were achieved using Perkin Elmer 1130 spectrometer. It consists of a light source (Hollow cathode lamp), burner, a monochromator, and a photomultiplier tube as detector. The system was interfaced to a computer for calculation of concentration.

2.4.1. Sample preparation for atomic absorption spectroscopy:

Samples for atomic absorption spectroscopy were prepared in solution forms to attain the homogeneity of the sample. Therefore the solid chromite samples should be brought into solution by dry ashing at high temperature, then the ash is dissolved in acid as follows:

0.50g of very finally powdered chromite ore were weighed accurately into 30-35cm^3 nickel crucible. 5.0g of sodium peroxide were added, and mixed thoroughly by means of glass rod. The lid was placed, and the crucible was then gently heated in the fume cupboard over small flame for about 10 minutes until the sample liquefied. The sample was kept fused for further 10 minutes at red heat. The crucible was then allowed to cool, and placed in a 600 cm^3 pyrex beaker containing a little distilled water. The crucible was removed and washed thoroughly. The washings were collected in the same beaker. 25cm^3 of 60% perchloric acid were added, shaked well, and then kept over night. The sample was then transferred into 250cm^3 volumetric flask and diluted up to the mark with distilled water. The resultant solution is now

appropriate for determination of chromium, magnesium, calcium, and iron using AAS technique.

2.4.2. Preparation of standard solutions:

Standard (stock), solutions containing 1000 ppm of magnesium, calcium, chromium, and iron were prepared by weighing 4.952g of magnesium sulphate $MgSO_4$, 2.4980g of calcium carbonate $CaCO_3$, 2.8280g of potassium dichromate $K_2Cr_2O_7$, and 4.9710g of ferrous sulphate $FeSO_4.7H_2O$ respectively. The weight of each metal salt was dissolved in a minimum amount of nitric acid, this was transferred quantitatively to 1000 cm^3 volumetric flask and brought to volume with deionized water.

2.4.3. Preparation of standard working solutions of magnesium, calcium, chromium, and iron:

Standard working solutions containing 100ppm of magnesium, calcium, chromium and iron were prepared by dilution of the, respectively, stock solutions. 10 cm^3 of each standard solution were diluted with distilled deionized water in 100 cm^3 of volumetric flask up to the mark. Series of standard metal solutions were prepared by suitable dilutions of the working solution.

2.4.4. Measurements:

The spectrometer was set for each element. A series of dilutions of each element were prepared and the absorption for each was measured. Using computerized spectrometer the calibration curves were plotted automatically and the concentration was determined.

2.4.5. Analysis by atomic absorption spectroscopy:

The instrument was operated after preparation of all samples and standard solutions. Standards were analyzed at the beginning, and the absorbance of

each concentration was recorded and a calibration curve for standards against their absorbance was plotted automatically. The samples were analyzed and the concentration of each sample was directly recorded. Standards were analyzed periodically during fifteen sample runs and at the end of the run. Blank solution (distilled-deionized water) was run between samples and standards to check stability of calibration curve. The instrument was calibrated by standard. The elements such as magnesium, iron, and chromium exist in high concentration in chromite ore, the corresponding solutions, therefore were diluted by distilled deionized water, to get them within the range.

2.4.6. X-ray fluorescence spectroscopy:

An energy dispersive x-ray fluorescence (XRF) spectrometer with a Cd109 source with energy 22.1 kev was used (Si-Li) detector with resolution of 180 eV at K_{α} line of iron (Fe) with 6.4 kev. MCA Camberra 35 plus, a preamplifier and amplifier. A computer was used for collection and analysis of spectra.

2.4.6.1. Sample measurements:

For analysis with XRF, 1.0g of the chromite sample was weighed accurately and then pressed into a pellet at 20 tons using 25 mm diameter die. The time of the collection was 1000 seconds for each chromite sample. Spectrum of each sample was obtained using XRF spectrometer of Cd 109 source and (Si-Li) detector. The signals passed to the preamplifier and collected on a feed back capacitor giving, pulses which were read out through external computer programs. 1.0g of finely ground powder of soil 7and British geological standard of chromite G308 were weighed, pressed into pellets to 20 tons, reweighed again and stored in a wide closed petri dish individually.

The analysis of spectrum was done using AXIL-IPM-BVC 3.00 data analysis program (IAEA). Certain measured samples were selected and saved as a model similarity of the fitting condition during the analysis.

2.4.6.2. Calculations:

Results were printed out, and the concentrations of different elements were determined by calculating their net intensities in relation to the background and comparing this with parallel series in standard samples using the equation:

$C_x = C_s (I_x / I_s)$ {total absorptionλ_i by x/ total absorption $\lambda_i$by s } . {Total enhancement of λ_i by x/ total enhancement of λ_i by s}.

where C = concentration, i = element, I = intensity, λ = measured wavelengths, X= sample, and s = standard.

2.5. Measurement of x-ray diffraction:

Large single crystals of the sample are not always available. It is more convenient to grind the sample to fine powder (200 to 300 meshes). In such a sample, the large number of microcrystals will be randomly oriented so that there will be many particles oriented to satisfy the Bragg equation:

$n\lambda = 2d\sin\theta$. The sample need not be carefully oriented as is necessary with single crystals, nor it is necessary to reposition it to obtain the entire set of diffraction patterns. Diffraction patterns are usually recorded with powder camera. The powder sample is held in a thin glass tube or spread with a binder on a plastic film. X- rays from a tube are filtered to produce a nearly monochromatic beam. The undiffracted portion of the beam is trapped and absorbed, while the diffracted rays take a conical shape emanating from the sample. Portions of these beams are intercepted by a photographic film mounted in circular fashion on the side of the camera. Thus, the diffraction patterns appears as a series of concentric arcs whose radii are determined by the diffraction angles, θ, and the interplanar distances d. Since both λ and θ are known, then values of d are calculated from Bragg equation. For most routine work, the identification of crystals is based on the comparison of d spacing and relative intensities with files of known compounds.

Modern X-ray spectrometers are highly automated, incorporating electronic scanning detectors. Computer controls the entire operation including the

comparison to known compounds for which the relevant data are stored in its memory. In contrast to emission and absorption methods, diffraction leads to the identification of compounds.[66]

2.6. Samples for gamma ray analysis:

Rock samples were powdered using specific hammer and silicate mortar. 500g of sample were sealed in a 500 ml marineli beaker with plastic covers and set aside for three weeks so as to allow for ingrowth of gaseous ^{222}Ra (half-life, 3.8 days) and its short-lived decay products (^{214}pb&^{214}Bi) to reach equilibrium with the long-lived ^{226}Ra precursor in the sample.[67] The activity of ^{232}Th and ^{40}K in chromite ore was measured using a high-resolution γ-spectrometry equipped with high purity germanium detector (HPGe). The detector was calibrated with respect to energy, efficiency, and resolution using Amersham mixed radionuclide standard.[67] At the end of the ingrowth period the samples were counted for four hours. The spectra were analyzed using GANAAS software (providing by IAEA). ^{232}Th was determined by means of its progeny photopeaks: ^{208}Ti (583 Kev). The activity of ^{40}K was measured directly through its 1461KeV. Locally prepared Mari standard was used as a quality control sample throughout the measurement period to check the consistence of the system.

2.7.Extraction of potassium dichromate:

Rock chromite is the row material for extraction of chromium metal. Sodium dichromate is the starting material for the preparation of other derivatives of chromium. Methods for extraction of potassium dichromate are as follows:

2.7.1. Extraction with sodium carbonate:

1.0g of finely powdered chromite was weighed into a 30 –35 cm^3 nickel crucible. About 8.0g of sodium carbonate were added, mixed thoroughly by means of a glass rod, and heated strongly over flame for about 10 minutes, cooled, and finally transferred into a 600 cm^3 pyrex beaker. 100cm^3 of

distilled water were added, and the system was heated to extract sodium chromate. It is worth noting that some black gritty particles remained unreacted.

The same steps were followed once more, and (about 12-14g) excess sodium carbonate was added and the mixture was heated over flame for about 20 minutes. 100 cm^3 distilled of water were added, and filtered off to extract sodium chromate from the resultant solution, black gritty particles remained in the precipitate which are not dissolved in concentrated hydrochloric acid.

The same procedure was repeated using maffle furnace. The mixture was heated to a temperature of about 900 °C, for about 15 minutes. The system was cooled, then100 cm^3 of distilled water were added, and then filtered off, small particles remained unfused, and not dissolved in concentrated hydrochloric acid, which fused with about 1g of sodium peroxide, 15 cm^3 distilled water were added, and filtered off to extract chromate, then added to the previous filtrate. Slight excess of ammonia solution was added to the filtrate and filtered off. Sodium sulphate precipitated by acidifying the solution with 4.5M sulphuric acid, and was removed by filtration; followed by dropwise addition of the same solution of sulphuric acid until yellow colour of chromate disappeared. The persistence of orange colour indicates formation of dichromate. The solution was heated to evaporate water. About 2-3.0g of potassium chloride were added to the concentrated solution of dichromate. Sodium chloride was precipitated and filtered off. The resultant solution was cooled, to allow the less soluble potassium dichromate to deposits from the solution, which is filtered and dried to about, 105 to 110°C.

2.7.2: Extraction with sodium peroxide:

Potassium dichromate was prepared by heating powder chromite with sodium peroxide. About 1.0g of powdered chromite was weighed into a 30-35 cm^3 nickel crucible. About 5.0g of sodium peroxide were added, and mixed thoroughly. The mixture was heated gently over small flame for about 10 minutes. The crucible was cooled, and the contents were placed in a 600 cm^3

pyrex beaker, containing little warm water. About 100 cm^3 of distilled water were added for extraction of sodium chromate, and filtered off, there is some gritty solids remained unfused, and not dissolved in concentrated hydrochloric acid. The same steps were repeated by adding 7.0 to 8.0g of sodium peroxide, and heated over flame for 10 minutes, cooled, and then filtered the resultant solution, the precipitate dissolved in concentrated hydrochloric acid. Slight excess of ammonia solution was added to the filtrate. After filtration of the resultant solution, 4.5M sulphuric acid was added dropwise until complete precipitation of sodium sulphate, which was removed by filtration; followed by dropwise addition of the same solution of sulphuric acid until yellow colour of chromate disappeared. The persistence of orange colour indicates formation of dichromate. The solution was heated to evaporate water. About 2-3.0g of potassium chloride were added to the concentrated solution of dichromate. Sodium chloride precipitated and filtered off. The resultant solution was cooled, to allow the less soluble potassium dichromate to deposits from the solution, which is filtered and dried to about 105 to 110 °C .

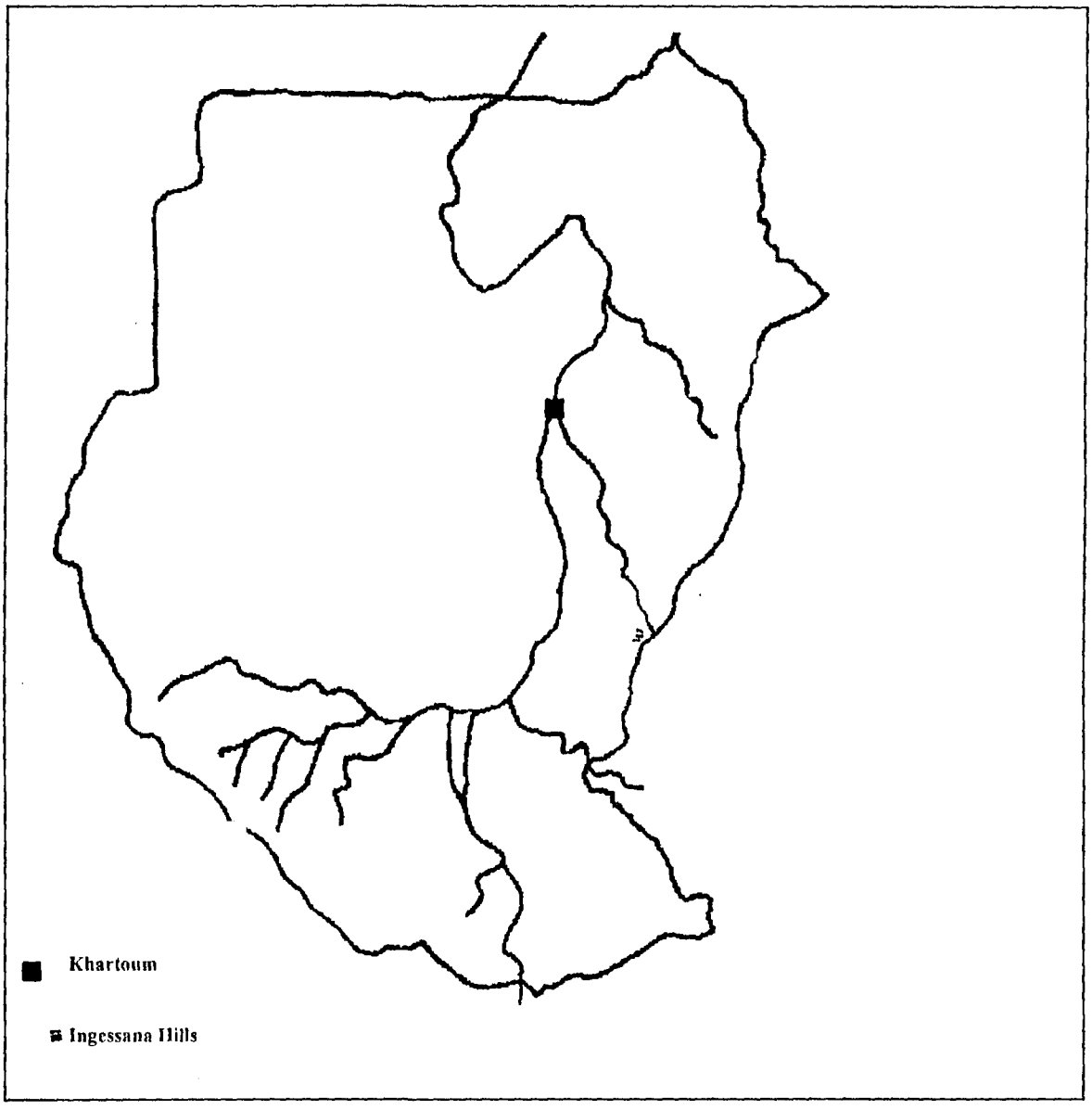


Figure 2.1.Amap showing sites of sample collection.

CHAPTER THREE
RESULTS AND DISCUSSION

3. RESULTS AND DISSCUSSION

In this work, chemical analysis was performed for all samples of chromite that collected from Gam and Cheikay mining area along Ingessana Hills, where chromite is found to occur in commercial quantities.

Samples were dried in an oven at 105°C and ground to a fine powder. Dry ashing and wet digestion are combination methods used to digest the powdered samples. Dry ashing was carried out using sodium peroxide at high temperature in flame burner. The heat from the flame was gradually raised to full temperature to prevent rapid combustion and foaming. The wet digestion was carried out using different combination of acids. In this case, sample preparation carried out by adding a mixture of perchloric and sulphuric acids. The optimum amount of the acid needed to complete the digestion was obtained by increasing the amount of acid mixture until a clear solution of the digested material was formed.

The digested samples were analyzed using volumetric, gravimetric, and AAS. Pellets were prepared from the powder for XRF analysis. The same fine powder of the sample was used for gamma ray analysis, for safety instructions, while x-ray diffraction analysis applied in the prepared powder of potassium dichromate.

The amount of chromium in potassium dichromate, extracted from the chromite ore was measured by volumetric, AAS, and XRF techniques.

3.1. Assessment using volumetric and gravimetric measurements:

Volumetric analysis was used to measure the amount of chromium in chromite rock after preliminary treatments to convert chromium into dichromate. Iron content is also measured by volumetric analysis after reduction to Fe(II) oxidation state. The amounts of silicon, aluminum magnesium, and calcium were measured gravimetrically.

The standard of chromite ore was fused by sodium peroxide and digested to gain a clear solution for analysis to check the accuracy of the method. The results are contained in Table 3.1.

3.2. Assessment employing AAS technique:

The elements, chromium, iron, calcium, and magnesium were measured using AAS technique. All chromite samples were wet digested. The standard of the chromite was digested for AAS and analyzed to check the accuracy of the method. Results given in Table 3.1. The accuracy was less than 10% for all elements indicating that both digestion and measurement were acceptable.

3.3. Assessment using XRF:

This technique was used to measure all of the elements under study except aluminum, magnesium, and silicon. These elements can not be measured using Cd109 as a radioactive source because they are of low atomic number. The accuracy of the method was determined by analyzing British chemical standard of chromite rock G308. The results were contained in Table 3.2. It exhibits an accuracy of about 3.9, 6.5, and 4.1% for chromium, iron, and calcium respectively. Some elements when determined by this technique had some fitting problems due to statistical reasons (software). The parameter that determined the extent of the agreement between the expected and the experimental value is the chi square (χ^2) which is defined as :

$$\chi^2 = \frac{\Sigma(O--E)^2}{E}$$

where O is the observed frequency and E is the expected frequency. Value of X^2 = O-1 signifies an exact agreement between the experimental and certified value, but a large chi square indicates a poor agreement.[40] For some samples, the chi square value of the chromium and iron are greater than 4.5 indicating some fitting problems.

To check the accuracy of the technique for the second time, a standard material lake sediment STM5 was analyzed which supplied by the IAEA were analyzed. The comparison of the certified and experimental values, (see Table 3.2) exhibit an accuracy of about 7.24 % for chromium, 12.5 % for calcium, and 13.4% for iron.

3.4. Comparison between volumetric, AAS, and XRF analyses:

The AAS and XRF as analytical techniques are complementary. However, each one has its own merits. The AAS is mostly single elemental analytical method and enjoyed rapid growth and success. The XRF is multi- elemental, non destructive, and a very fast technique. The sample needs minimum preparation steps but this technique needs to give an attention to the error arising from matrix effect.

Table 3.3 compares the AAS/XRF ratio. It also shows the correction coefficient between these two variables. The closer the observed values, which are very close to unity, indicate a good agreement between the two techniques involved. It should be mentioned that it is possible to have a high degree of correlation between two methods, but to have statistically significant difference between the results of each, according to the T test.

Table 3.4 compares AAS and volumetric determination results for chromium oxide and their ratios. It also shows the correlation coefficient between these two analytical methods. It compares between all elements, except aluminum and silicon; measured only by gravimetric method. When volumetric, AAS, and XRF results were compared for elemental oxides determined, T test was performed for elements determined by all techniques, it shows that, the comparison between AAS and XRF results for chromium oxide are significantly similar, although there is a little variation. The T test was also carried out to compare the chromium oxide content measured by AAS and volumetric analyses. It revealed that the results are in good agreement.

All elements except chromium were removed from the given solution. Chromium contents were then measured using AAS and volumetric techniques. The results were similar. This refers to the presence of iron in the stock chromite solution, which cause serious chemical interference, depressing the absorption of chromium in using AAS technique. (see Table 3.4). For this reason, iron must be separated from chromium by alkaline fusion. In case of extracting the melt with water, only traces of iron will pass into the filtrate that can be neglected. The presence of other chemical compounds in the flame

affects absorption by changing the flame temperature. It is obvious that any change in temperature will affect absorption because most compounds are incompletely dissociated.As Table 3.5. reveals, the concentration of chromium oxide in chromite rock was found in most samples to be similar. Concentration of chromium oxide in some samples measured using XRF showed little deviations. These differences refer to the fitting problems due to statistical reasons (software), in addition to AAS and volumetric measurements are obtained in solution. They are more homogeneous than in the powder form as in the case of XRF analysis. AAS2 results of chromium oxide are free from interference and so volumetric analysis. They were complementary analytical techniques for estimation of chromium, but they consume a lot of time to reach the final result. (see Table 3.5). All these methods are suitable for evaluation of chromium in chromite rocks while the AAS2 and volumetric analysis given the preference. Figure 3.1. shows the chromium oxide content obtained by AAS1, AAS2, XRF, and volumetric techniques. The results obtained for chromium oxide in this study compares well with those reported by control union Khartoum[68] for samples brought from Blue Nile mines. Similarty is observed with this, since samples in both studies belongs to the same location, Ingessana Hills area. Considerable difference however exists when compared with BGR[69] specimens collected from different parts of Nuba Mountains as Table 3.6. displays.Table 3.7 also indicates that the contents of chromium oxide in Gam mining area, which is far away for about one km west to Cheikay higher than Cheikay, which has poor quality in the lower parts for about 23.4%. A good agreement was noticed between this evaluation and that reported by the Chinese company worked in the same area as Table 3.7. displays.[59] The Cr_2O_3/FeO ratio ranges from 2.80 to 4.30 in Gam and from 1.8 to 3.1 in Cheikay. While in Chinese report,[59] ranges from 2.0 to 4.3. The difference indicates that the distribution of iron oxide in chromite rocks increases with increasing chromium oxide content. It also depends on geological setting of particular rock types. Figures

3.2(A) and 3.2(B) display the relative concentrations of elements in Gam and Cheikay.

The results of this study compare well with those reported by the Japanese technical team[54] worked in the whole Ingessana Hills. The similarity observed between these two studies is mainly due to the fact that the chromite rock samples investigated belong to the same area.

When comparing results obtained in this study with data from global literature, it is clear that there is a significant difference in some locations which may be attributed to the different geological formation of volcanic igneous rocks to which chromite belongs. However, there is a close result reported by Russians.[18]

The average content of chromium oxide in the studied area using AAS, XRF, and volumetric analysis is 40.2%, while volumetric analysis of fifteen samples collected from different mines in the studied area showed the content of chromium oxide as high as 55.1%, The highest percentage reported in South[15] Africa is 58.1%. Sudanese chromite ore must therefore be rated as of a very high grade. The results are given in (Table 3.8). When AAS, XRF, and volumetric results for iron oxide compared and T test performed, a significant difference occurs in case of XRF analysis. This deviation refers to multiple excitation, which occurs when fluorescent radiation from one element in the sample excites fluorescent radiation from another element in the same sample.[58] The fluorescent radiation from iron was of shorter wavelength than the absorption edge of chromium, so the effect was to increase the intensity of the radiation emitted by chromium and its intensity being greater than would be expected. The results are contained in Table 3.9.

No significant difference exists between the results employed the two analytical techniques AAS and volumetric analyses. The results are displayed in Figure 3.3.

The results of calcium oxide measured by AAS, XRF, and gravimetric analyses are compared employing T test methods. No significant difference exists. The slight difference observed in case of AAS, however, was due to the

depression of calcium responses, which occurs in presence of aluminum. The results are given in (Table 3.10). Sometimes ionization interference may also reduce calcium oxide content. Figure 3.4. Shows a result of calcium oxide measured by XRF, AAS, and gravimetric methods. The measured magnesium oxide contents using AAS and gravimetric techniques were also compared employing T test. It was clear that there is similarity between the results of the two techniques. The results of gravimetric analysis is slightly higher than those obtained using AAS technique because the presence of aluminum in the same solution seriously depresses the absorption of magnesium as a result of formation of heat stable aluminum-magnesium compound. Table 3.11 compares results of magnesium oxide measured by AAS and gravimetric methods. Figures 3.5. compares between the concentration of magnesium oxide measured by the given techniques. The contents of aluminum and silicon oxides in chromite rock determined gravimetrically, however, provides no basis for comparison with other technique.

As Table 3.12 indicates the positive correlation coefficient suggests irreversible existence between chromium, ferrous, and calcium oxides. The amounts of ferrous and calcium oxides in chromite rock are directly proportional to the content of chromium oxide. They increase with increasing chromium oxide in the sample. Magnesium, aluminum, and silicon oxides are reversibly proportional to chromium oxide contents. They increase with decreasing chromium oxide. Tables 3.13 and 3.14 compare elemental concentrations in Gam and Chikay determined by volumetric and gravimetric methods to illustrate the proportionality of the two processes.

3.5. Measurement of chromium content in prepared $K_2Cr_2O_7$ from rock chromite:

The content of chromium in potassium dichromate prepared from rock chromite was measured, using volumetric, AAS, and XRF techniques. The comparison of results obtained by standard potassium dichromate with that prepared from rock chromite, shows some deviation which refers to the

presence of sulphate and chloride in the prepared compound. Results are shown in Table 3.15.

When compared the results of prepared potassium dichromate using the above mentioned analytical techniques, it was found that the results are similar. Therefore, all these techniques are suitable for evaluation of extracted chromium compound. Figure 3.6. Compares chromium content in prepared potassium dichromate. The average chromium content in prepared potassium dichromate was found to be 31.7%, and the highest grade reached by these analyses individually is 33.10%. Table 3.16 compares chromium content in prepared $K_2Cr_2O_7$.

Sodium carbonate is not strong enough to decompose all chromite powder, so that, for complete fusion of chromite as chromate, prefer using sodium peroxide because it supplies enough hydroxyl ions in aqueous solution, so it is not important to add more alkali, and it melts the chromite powder within few minutes in small flame, while sodium carbonate needs strong temperature and consume a lot of time, even though decomposition does not take place completely. For these reasons, the fusion with sodium peroxide is more convenient for extraction of potassium dichromate. On the other hand, sodium carbonate can be used with 80% efficiency and cheaper than peroxide, the rest of 20% chromite can be extracted by a little amount of sodium peroxide.

For instance, 1kg of potassium dichromate prices about 70000 dinars, so it is better to develop the extraction with sodium carbonate to prepare this compound for industrial and economic purpose to increase the national income instead of being exported by hard currency.

3.6. X-ray diffraction analysis:

X-ray diffraction gives available information about the structure of crystalline materials. The identification of crystal based on comparison of d spacing and relative intensities with compounds for which the relevant data are stored in the memory of computer or compares with files of known compounds. When

compared the chart of standard potassium dichromate with that of potassium dichromate extracted from rock chromite, it was found that they are isostructural except that some additional minor peaks were observed associated with the prepared sample indicating the presence of some impurities. Figures 3.7(A) and 3.7(B) illustrate the d spacing and the intensities of standard potassium dichromate with prepared one using XRD analysis.

3.7. Levels of radioactive elements:

The levels of radioactive elements ^{40}K and ^{232}Th were measured in chromite rock samples collected from Ingessana Hills mainly Gam mining area, are given in Table 3.17. ^{232}Th concentration ranges from 7.62 to 10.98 Bq/kg with an average value of 9.49 Bq/kg. The level of ^{40}K ranges from 47.38 to 56.28 Bq/kg with an average value of 52.45Bqkg. No previous reports about radionuclide concentration in Ingessana Hills is available. In Figure 3.8 the concentrations of ^{232}Th and ^{40}K nuclides were plotted against the number of samples. The occupational exposure of any worker shall be so controlled that an effective dose limits not exceeded 20 mSv per year averaged over five consecutive years.[70] Therefore, the radioactivity found in the studied samples has very low values when compared with the dose limits of the world recommended values.

3.8. Conculation:

X-ray fluoresces (XRF), atomic absorption spectroscopy (AAS) and volumetric analysis as cross checking techniques, were used for evaluation of chromite ore. A comparison between these analytical methods showed that a good agreement exists mainly between AAS and, volumetric analysis. The correlation coefficient between results of chromium oxide obtained by the three techniques showed that AAS2 and volumetric analysis gave identical results. Implying that they were the best optimum methods for evaluation of chromium in chromite ore.

Analysis of rock chromite revealed that the amounts of iron and calcium oxides in the ore are irreversibly proportional with chromium oxide. They increase with increasing content of chromium oxide. Magnesium, aluminum and silicon oxides are the other hand, are reversibly proportional with chromium oxide in rock chromite. The average values of chromite rock analysis in this study compares well with data reported by other researchers locally, it revealed a good agreement, However, slight differences exists when compared with global data.[18]

The results indicated that, the concentration of chromium oxide in Gam mining area is higher than at Chikay area.

X-ray diffraction spectrum of prepared potassium dichromate revealed very close chart with standard potassium dichromate suggests that they were identical in composition. The average chromium content in extracted potassium dichromate measured using AAS, XRF, and volumetric methods was found to be 31.7%. The highest grade reached by individual technique being 33.10%. The extraction of chromium with sodium peroxide is the optimum method for preparation of potassium dichromate, but it is cost more that prefer using sodium carbonate which about 15 to 20 % of chromite remained unaffected that fused with 1g of sodium peroxide. Gamma ray spectroscopic analysis of rock chromite showed that the concentrations of ^{40}K and ^{232}Th ranges from 47.38 to 56.28 and 7.6 to10.98 Bq/Kg respectively.

Table 3.1. Certified values as compare to AAS, volumetric and ravimetric measured values for concentration of China national analysis center of chromite standard No NC5DC72303.

Element oxide%	Certified value%	Experimental value ⬡%	Accuracy ⬡%	Experimental value □%	Accuracy □%
Cr_2O_3	49.44	48.86±0.12	01.17	47.23±0.19	04.47
FeO	13.06	12.74±0.18	02.45	12.16±0.12	03.09
MgO	16.66	15.65±0.13	06.06	15.43±0.27	07.20
Al_2O_3	12.10	11.28±0.36	06.77	NM	NM
SiO_2	4.08	03.72±0.20	08.60	NM	NM
CaO	0.36	0.33±0.08	08.30	00.34	05.50

⬡ = Values measured using volumetric and gravimetric methods .

□ = Values measured using AAS techniques.

NM = not measured

Table 3.2. Certified values compared to measured concentration in British standard of chromite rock and lake sediment STM5 using XRF.

Element	Certified value ⬡	Exp. Value ⬡%	Accuracy ⬡%	Certified value □%	Exp. Value □%	Accuracy □%
Ca	00.24	00.23	04.16	04.47	5.03±1.20	12.50
Cr	28.40%	29.5+0.60	03.90	6.9ppm	06.4±.26	07.20
Fe	11.90	11.12+0.4	06.60	09.29	8.04±.30	13.40

⬡ Standard of chromite

□ Standard of STM5

Table 3.3. The content of chromium oxide in chromite rock measured by AAS compared with XRF and their correlation coefficient.

Sample No	AAS1	XRF	XRF/AAS1	R1	AAS2	XRF/AAS2	R2
1	53.80	49.60	00.92	0.79	54.96	0.90	0.87
2	29.00	38.80	01.33	0.79	35.2	1.10	0.87
3	35.10	46.80	01.33	0.79	40.35	1.16	0.87
4	41.70	46.20	01.10	0.79	44.1	1.05	0.87
5	45.30	54.50	01.20	0.79	46.11	1.18	0.87
6	42.80	58.50	01.40	0.79	49.65	1.18	0.87
7	39. 00	51	00.76	0.79	43.24	1.18	0.87
8	50.20	45.20	00.90	0.79	51.38	0.88	0.87
9	27.30	29.10	1.070	0.79	28.86	1.01	0.87
10	20.60	20.60	01.00	0.79	23.42	0.88	0.87
11	35.70	37.90	01.06	0.79	37.90	1.0	0.87
12	30. 00	29.70	00.99	0.79	31.41	0.94	0.87
13	39.5	43.9	01.10	0.79	39.82	1.1	0.87
14	36.90	34.50	00.93	0.79	39.6	1.0	0.87
15	33.90	35.30	01.04	0.79	34.02	1.01	0.87

Where, AAS1 is stock solution of chromite used for estimation of chromium oxide by AAS .

AAS2 is pure solution of potassium dichromate prepared from rock chromite for estimation of chromium oxide by AAS.

R1, R2 correlation coefficient between AAS1, XRF and AAS2, XRF.

Table 3.4. The mean of chromium oxide content in chromite measured by AAS compared with volumetric analysis and their correlation coefficient.

Sample No	AAS1	Volumetric	AAS1/V	R1	AAS2	AAS2/V	R2
1	53.78	55.10	0.97	0.97	54.96	0.997	0.99
2	29.09	35.26	0.83	0.97	35.2	0.998	0.99
3	35.07	40.80	0.86	0.97	40.35	0.988	0.99
4	41.71	44.90	0.92	0.97	44.10	0.98	0.99
5	45.30	46.25	0.98	0.97	46.11	0.996	0.99
6	42.82	49.72	0.86	0.97	49.65	0.998	0.99
7	39.02	43.42	0.9	0.97	43.24	0.996	0.99
8	50.18	51.22	0.98	0.97	51.38	1.00	0.99
9	27.33	28.92	0.95	0.97	28.86	0.998	0.99
10	20.61	23.39	0.88	0.97	23.42	1.00	0.99
11	35.66	37.98	0.94	0.97	37.90	0.998	0.99
12	29.96	31.36	0.96	0.97	31.41	1.00	0.99
13	39.46	39.88	0.99	0.97	39.82	0.998	0.99
14	36.98	39.74	0.93	0.97	39.60	0.996	0.99
15	33.91	34.48	0.98	0.97	34.02	0.98	0.99

V = volumetric analysis

Table 3.5. Comparison between AAS1, AAS2, XRF and volumetric analysis of chromium oxide.

Sample No	AAS1	AAS2	XRF	Volumetric
1	53.72	54.96	49.60	55.10
2	29.02	35.20	38.79	35.26
3	35.07	40.35	46.88	40.80
4	41.70	44.10	46.19	44.90
5	45.30	46.11	54.50	46.25
6	42.80	49.65	58.50	49.72
7	39.00	43.24	51.03	43.42
8	50.10	51.38	45.21	51.22
9	27.33	28.86	29.05	28.92
10	20.61	23.42	20.62	23.39
11	35.66	37.90	37.98	37.98
12	29.96	31.41	29.70	31.36
13	39.46	39.82	43.94	39.88
14	36.98	39.60	34.45	39.74
15	33.91	34.33	35.29	34.48

Table 3.6. Average mean and range of element oxide concentrations in this work compared with other local studies.

Element oxide	This Work		Blue Nile		Nuba Mounts	
	Mean	Range	Mean	Range	Mean	Range
Cr_2O_3%	40.66	22.5-53	41.18	36.9-48	45.50	42.0-48.3
FeO%	13.27	8.20-19.90	19.58	17-24.5	18.05	09.6 -22.5
CaO%	00.36	0.18-0.67	-	-	-	-
Al_2O_3%	14.50	5.3-24.6	08.95	7.90-10.1	09.00	5.00-12.6
SiO_2%	11.45	6.1-19.8	10.85	5.70-13.2	04.80	3.10-7.90
MgO%	16.94	9.9-25.3	21.50	14.9-25	12.30	10.7-13.0

Table 3.7. The mean and range of element oxide concentration in Gam and Chikay compared with Chinese and Japanese reports.

Element oxide	Gam mining		Chikay mining		Chinese report		Japanese report	
	Mean	Range	Mean	range	mean	range	Mean	Range
Cr_2O_3%	45.60	35-54.9	33.62	23-39.8	40.34	20-60.4	44.60	41.3-48
FeO%	14.40	10.7-20	11.64	8- 13.3	13.4	7.8-24	-	-
CaO%	00.41	.21- .66	.28	.15- .42	.69	.11-1.3	-	-
MgO%	13.59	9.3-21	19.92	15.5-26	21.45	15.3-27	-	-

Table 3.8. The mean of elemental oxide concentration of chromite rock measured by AAS, XRF and volumetric analysis compared with data from global literatures .

Element oxide	This work	Transval	Russia	Turkey
$Cr_2O_{3\%}$	40.20	54.20	40.50	51.70
$FeO_{\%}$	12.08	18.60	19.02	14.34
CaO%	00.36	-	01.40	00.50
$Al_2O_3\%$	14.50	14.70	17.70	13.80
$SiO_2\%$	11.45	1.00	03.50	02.50
MgO%	16.14	11.70	14.70	15.80

Table 3.9. Iron oxide content in chromite rock.

Sample No	AAS%	XRF%	Volumetric%
1	11.99	09.00	11.50
2	10.71	09.41	10.67
3	14.85	11.36	14.23
4	13.70	10.31	12.92
5	12.42	09.71	12.02
6	13.71	10.42	13.85
7	17.40	13.63	16.67
8	20.42	09.90	19.42
9	10.71	09.91	09.47
10	08.28	09.06	08.14
11	12.71	09.88	12.60
12	12.82	10.68	12.46
13	12.28	09.01	11.57
14	13.42	09.98	12.93
15	11.28	10.34	10.64

Table 3.10. Calcium oxide content in chromite rock.

Sample No	AAS%	XRF%	Gravimetric%
1	0.38	0.38	0.41
2	0.27	0.33	0.32
3	0.31	0.34	0.36
4	0.41	0.42	0.42
5	0.66	0.64	0.71
6	0.58	0.58	0.6
7	0.44	0.44	0.45
8	0.21	0.27	0.24
9	0.15	0.18	0.20
10	0.22	0.16	0.22
11	0.29	0.31	0.33
12	0.24	0.21	0.23
13	0.42	0.41	0.42
14	0.34	0.20	0.32
15	0.32	0.34	0.34

Table 3.11. Magnesium oxide content in chromite rock.

Sample No	AAS%	Gravimetric%
1	15.17	16.01
2	21.18	22.97
3	15.33	17.50
4	13.16	14.30
5	13.34	13.36
6	11.00	13.13
7	10.33	13.56
8	09.28	08.61
9	23.72	23.77
10	26.00	24.65
11	15.52	15.40
12	22.89	20.90
13	17.15	17.06
14	16.50	16.27
15	17.67	20.46

Table 3.12. Correlation coefficient between elemental oxides in rock chromite.

	Cr_2O_3	FeO	CaO	MgO	Al_2O_3	SiO_2
Cr_2O_3	1.00					
FeO	0.57	1.00				
CaO	0.71	0.16	1.00			
MgO	-0.88	-0.78	-0.61	1.00		
Al_2O_3	-0.87	-0.52	-0.41	0.70	1.00	
SiO_2	-0.92	-0.68	-0.61	0.89	0.76	1.00

Table 3.13. Results of metal oxide contents in Gam mining area measured by volumetric and gravimetric analysis consecutively.

Sample No	Cr_2O_3%	FeO%	CaO%	MgO%	SiO_2%	Al_2O_3%
1	55.10	11.50	0.41	16.01	09.80	05.28
2	35.26	10.70	0.32	22.97	12.20	14.24
3	40.8	14.20	0.36	17.50	10.30	12.90
4	44.90	12.90	0.42	14.30	08.50	13.80
5	46.30	12.00	0.71	13.40	08.12	14.70
6	49.70	13.90	0.60	13.13	06.90	12.80
7	43.40	16.70	0.45	13.60	09.92	11.62
8	51.20	19.40	0.24	08.61	06.12	09.65

Table 3.14. Results of metal oxides content in Chikay mining area measured by volumetric and gravimetric analysis consecutively

Sample No	Cr_2O_3%	FeO%	CaO%	MgO%	SiO_2%	Al_2O_3%
1	29.92	09.47	0.2	23.77	15.59	18.56
2	23.39	08.14	0.22	24.65	19.85	24.69
3	37.98	12.60	0.33	15.40	13.90	16.76
4	31.36	12.46	0.23	20.90	14.72	19.66
5	39.88	11.57	0.42	17.06	11.28	13.84
6	39.74	12.93	0.32	16.27	09.66	15.91
7	34.48	10.64	0.34	20.46	14.89	13.73

Table 3.15. Standard $K_2Cr_2O_7$ values compared with volumetric, AAS, and XRF for chromium content in prepared $K_2Cr_2O_7$.

Chromium	Standard $K_2Cr_2O_7$	Prepared $K_2Cr_2O_7$
Volumetric analysis%	35.50	31.70
AAS%	35.20	31.50
XRF%	35.90	31.80

Table 3.16 Compares chromium content in prepared $K_2Cr_2O_7$ using volumetric, AAS, and XRF.

Compound No	XRF%	AAS%	Volumetric %
1	33.10	32.60	32.80
2	32.50	31.80	32.10
3	30.72	30.10	30.40

Table 3.17. Levels of radioactivity of ^{232}Th and ^{40}K in chromite rock.

Sample No	^{232}Th Bq/Kg	^{40}K Bq/Kg
1	8.56	56.28
2	10.98	52.00
3	10.80	54.14
4	07.62	47.38

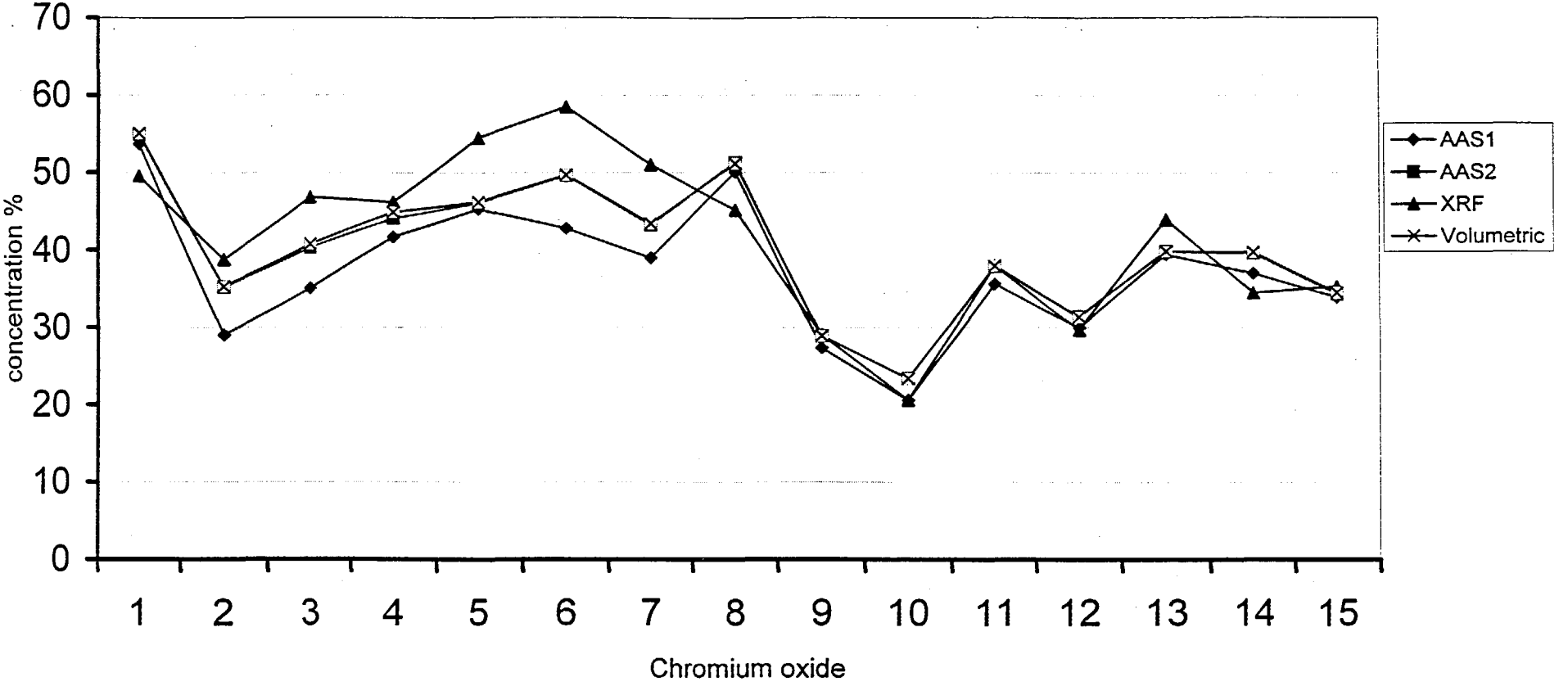


Figure. 3.1. Chromium oxide content in rock chromite.

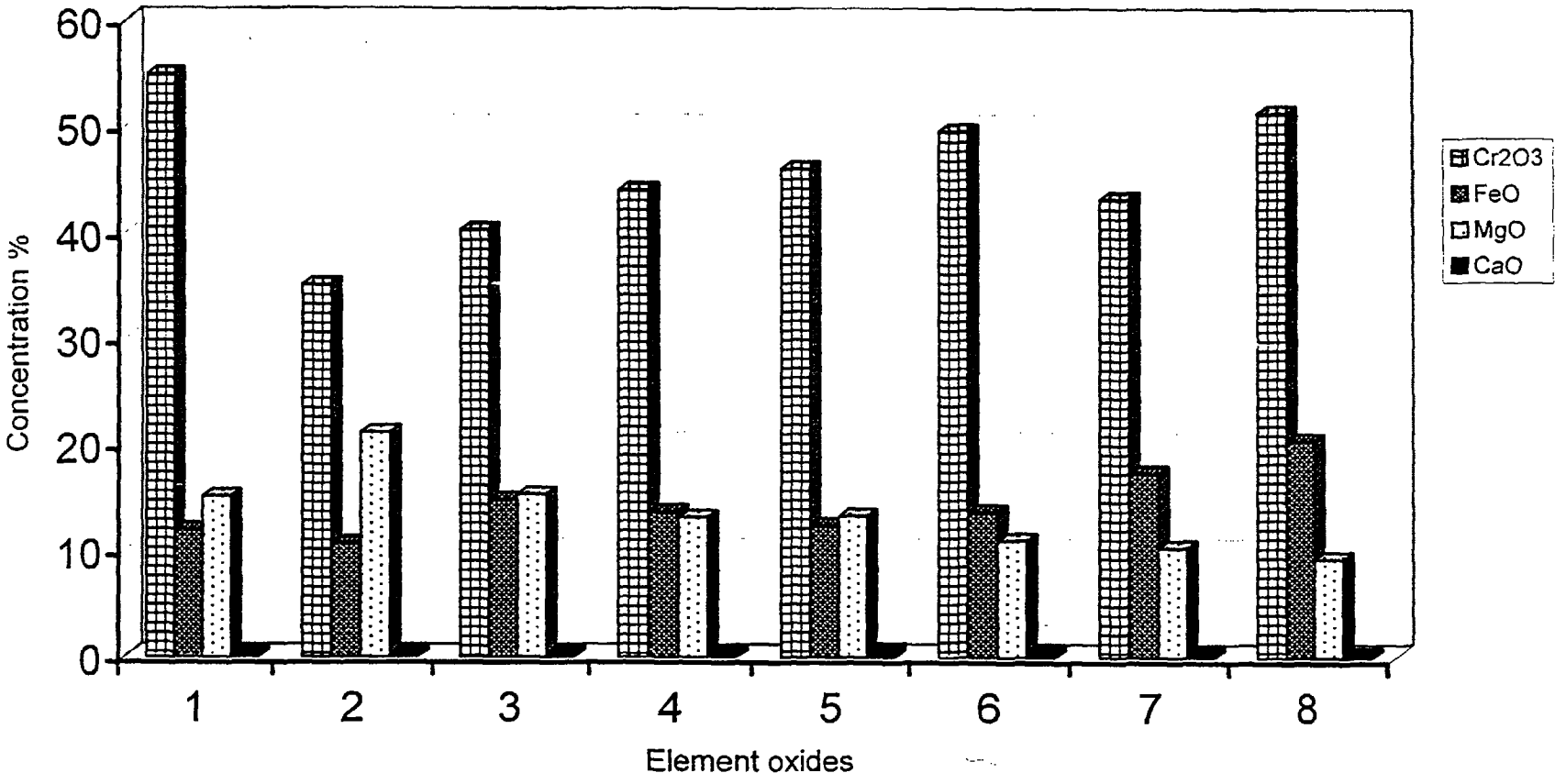


Figure. 3.2(A). Elemental oxide concentrations in Gam mining area.

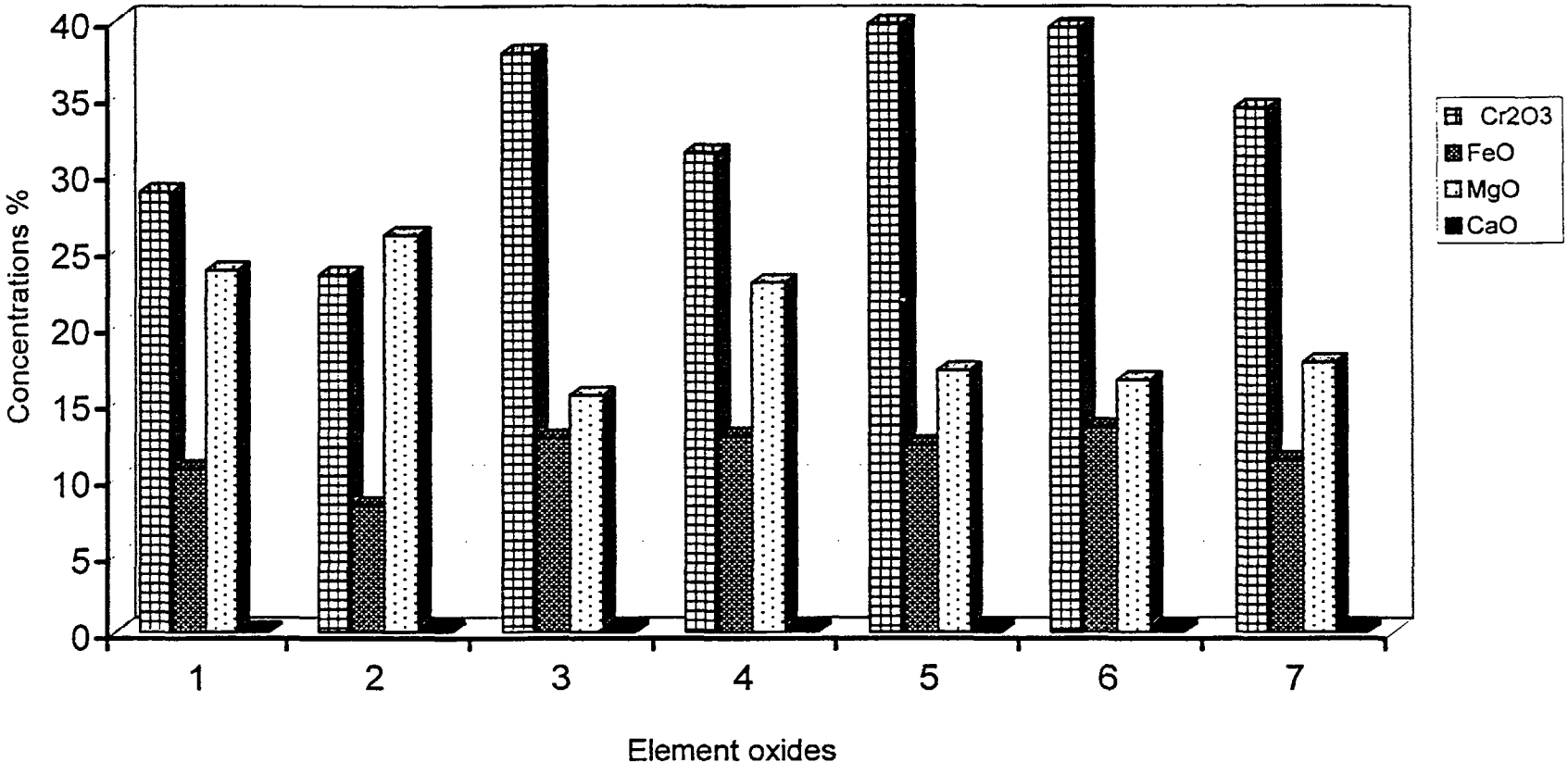


Figure. 3.2(B). Chart of elemental oxide concentrations in Chikay mining area.

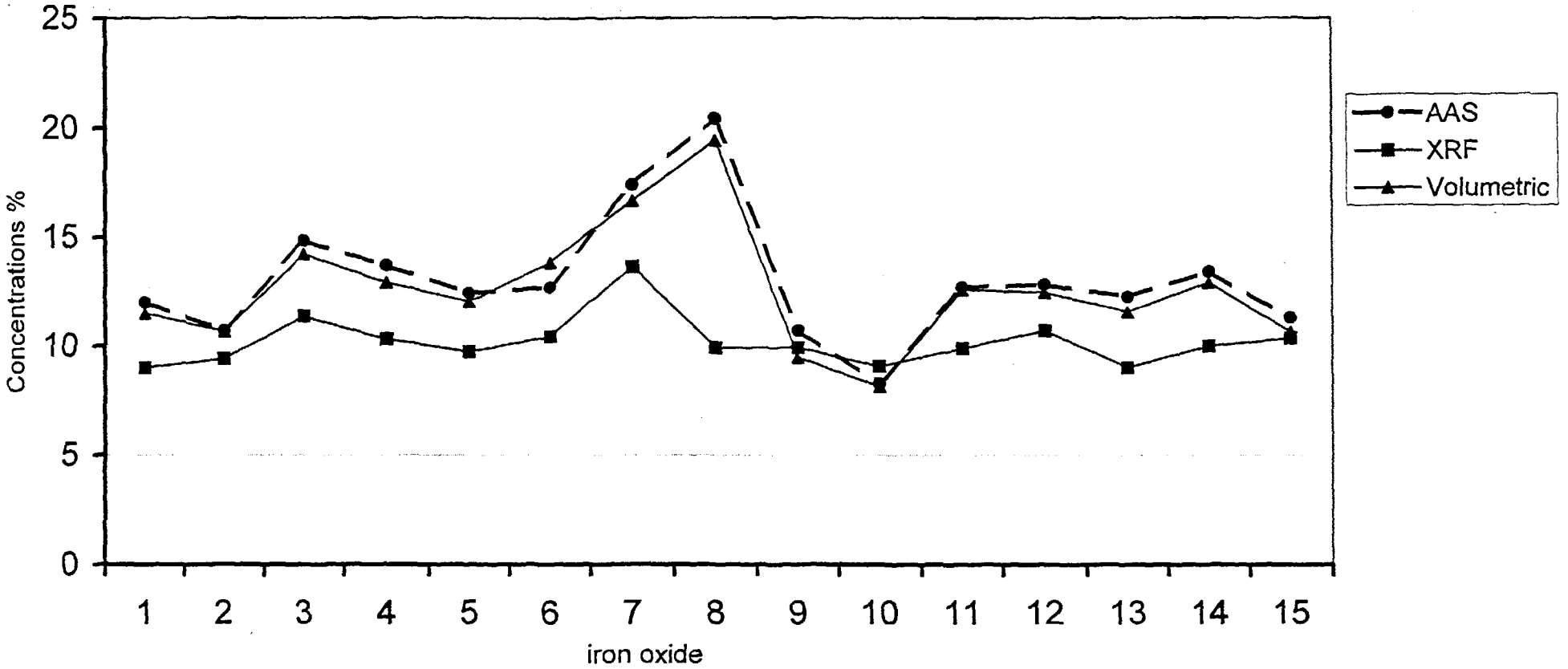


Figure. 3.3. Iron oxide concentration in rock chromite.

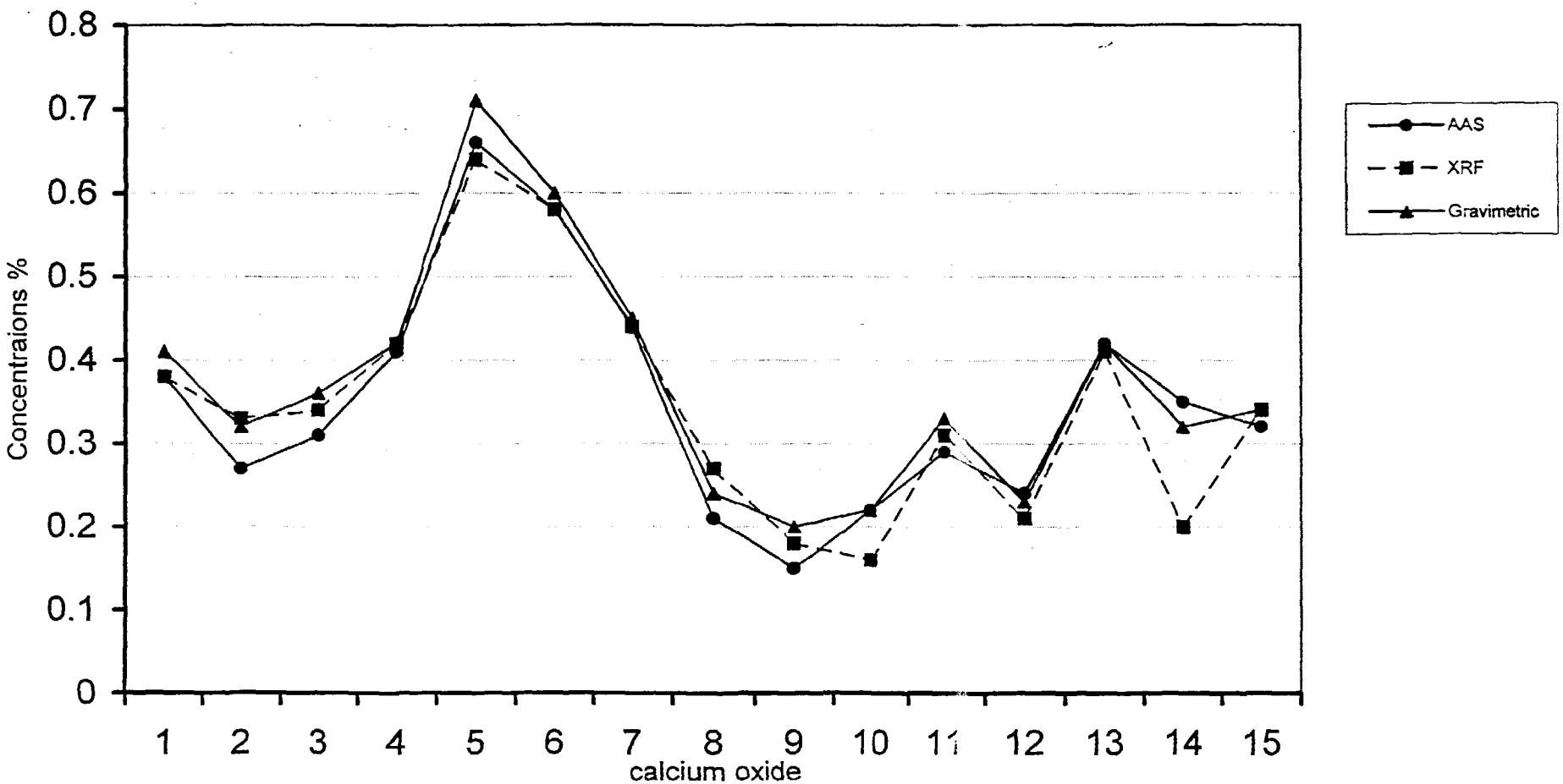


Figure. 3.4.chart of calcium oxide conen in rock chromite.

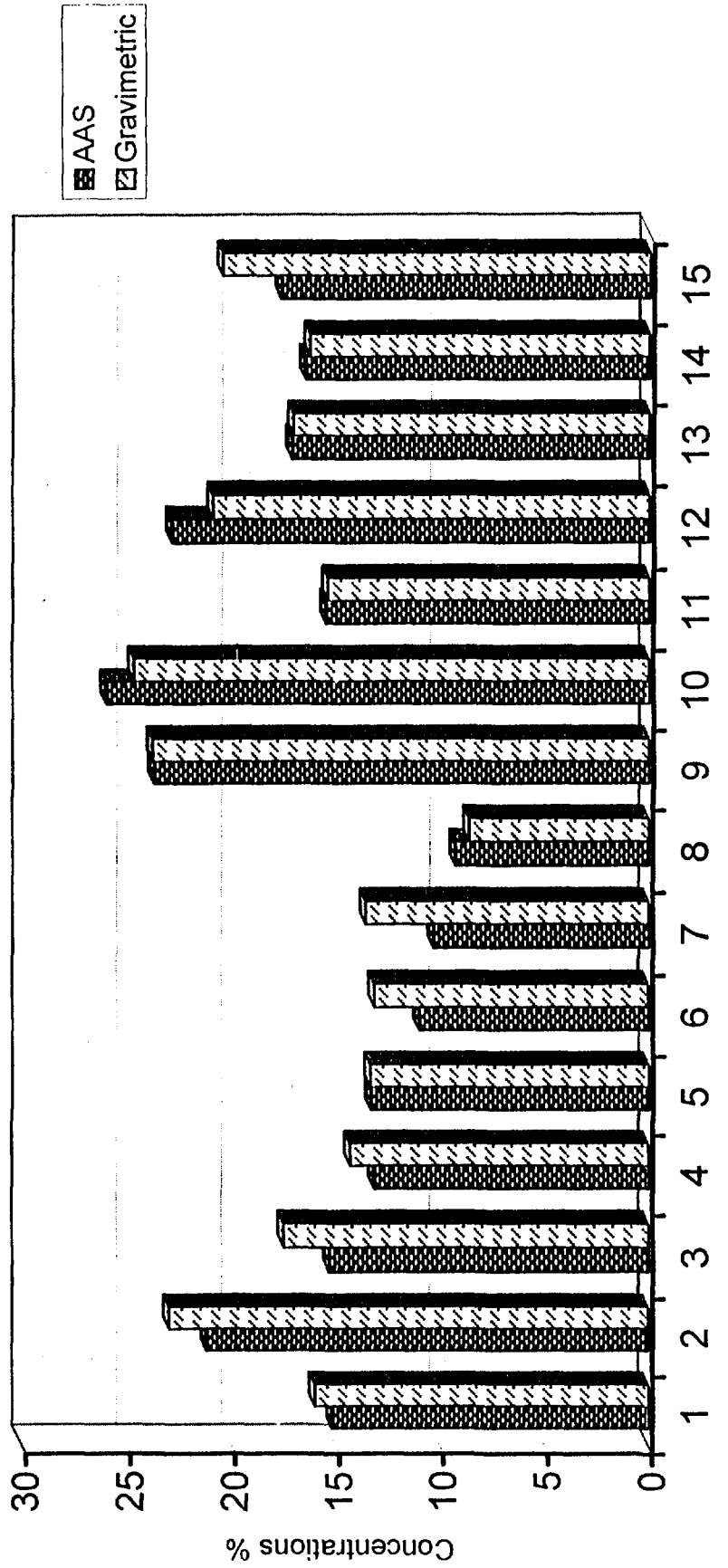


Figure. 3.5. magnesium oxide content in rock chromite.

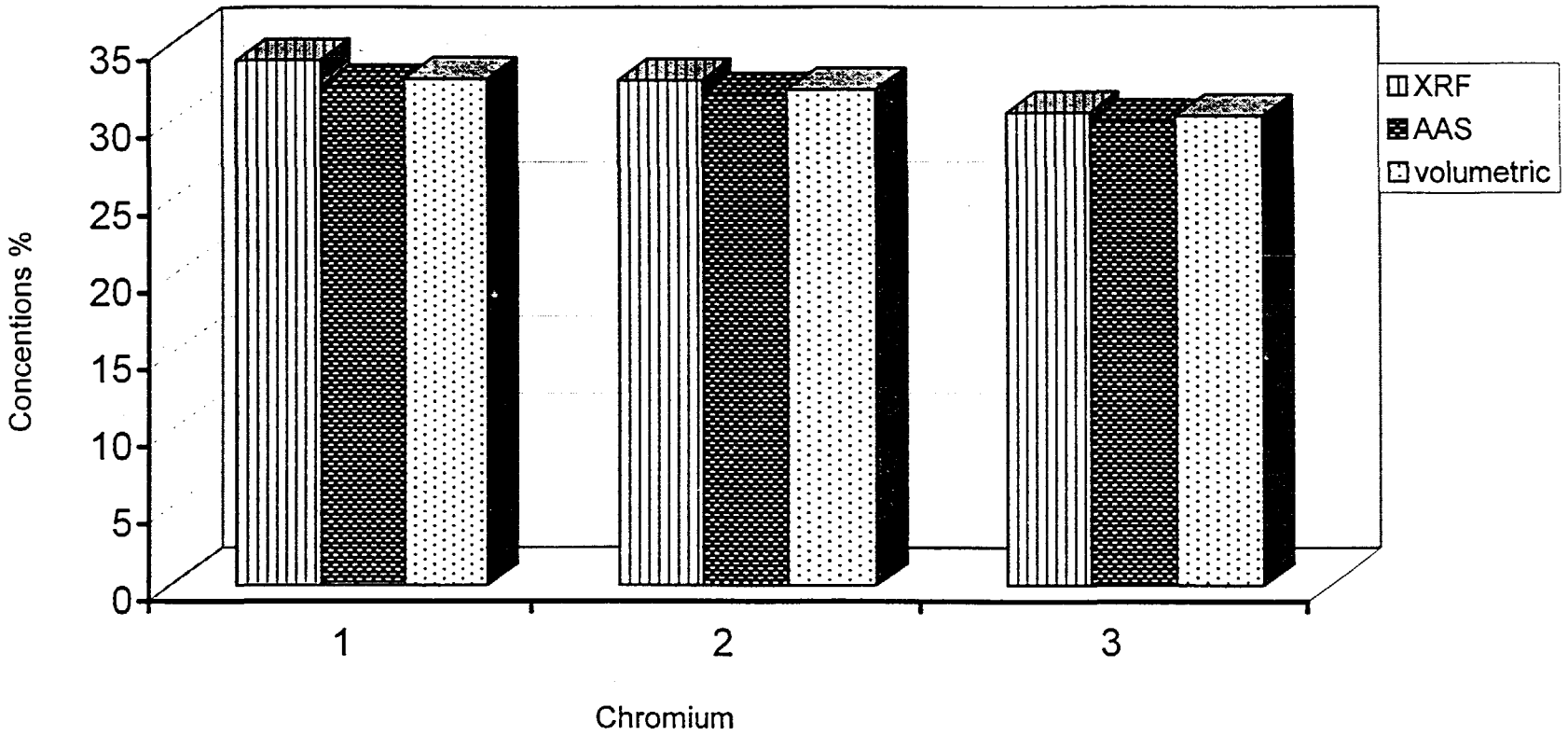


Figure. 3.6. Compares chromium content in prepared potassium dichromate.

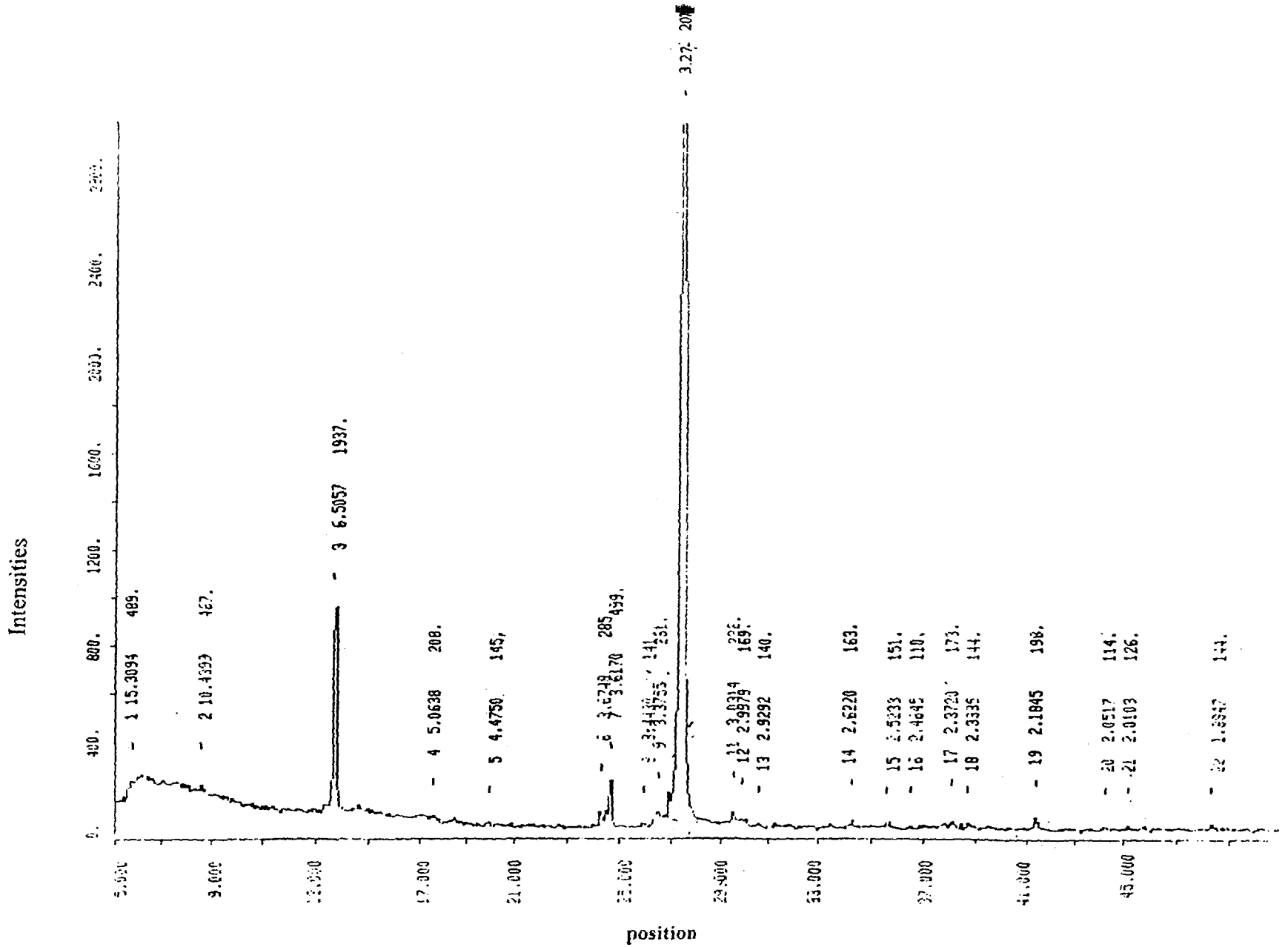


Figure 3.7 (A) Chart of prepared potassium dichromate by using XRD analysis

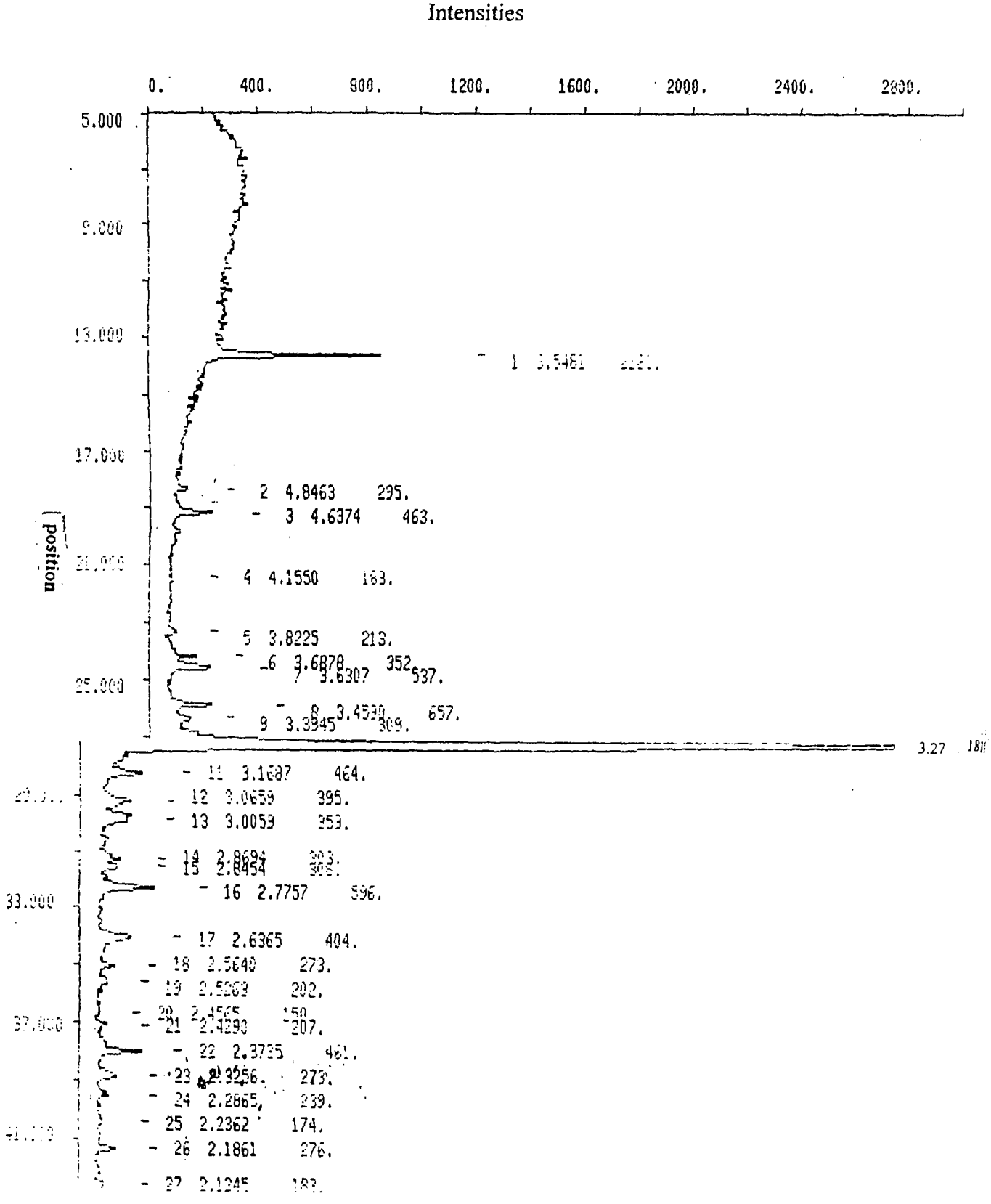
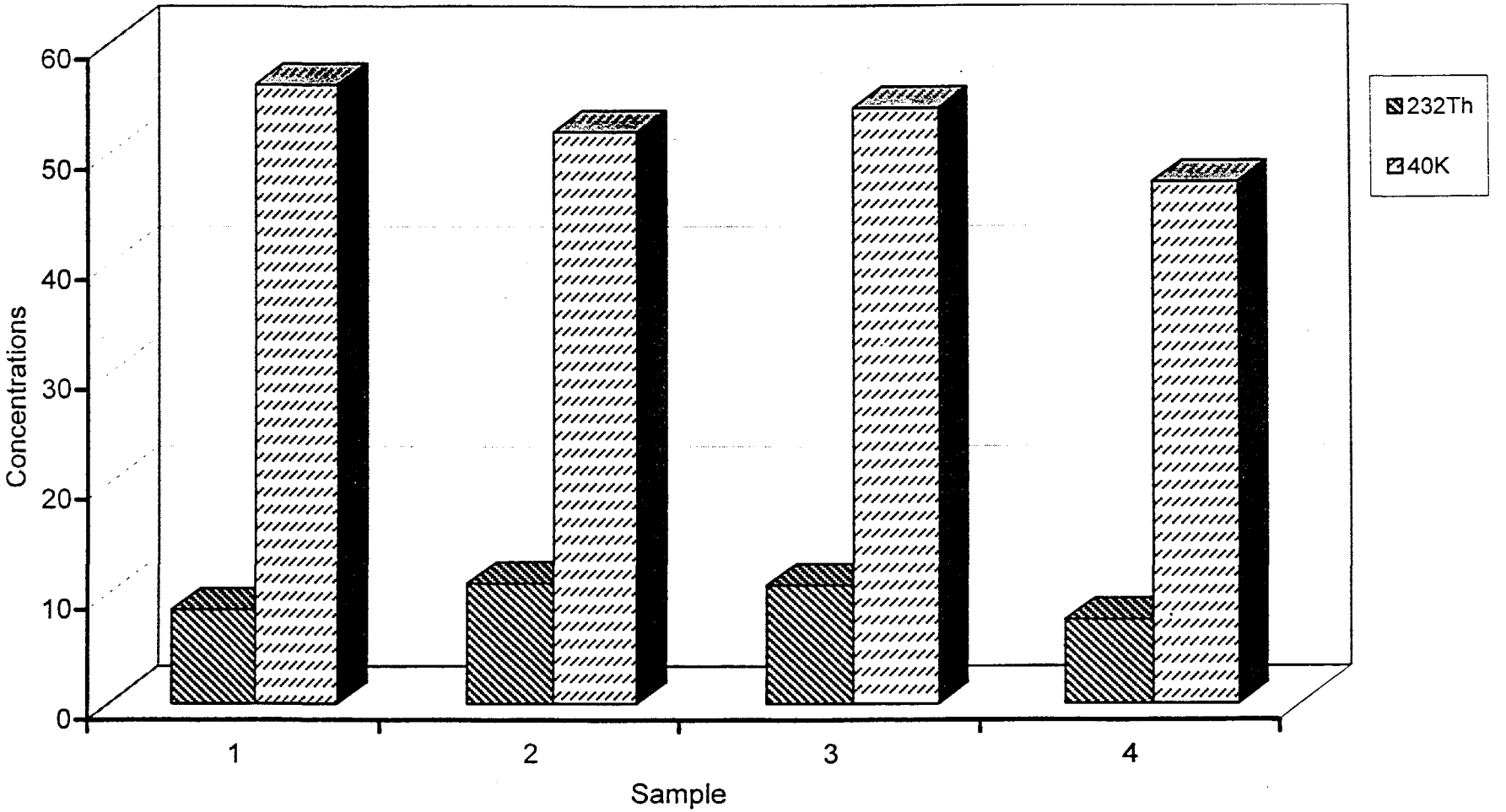


Figure 3.7 (B) Chart of prepared potassium dichromate by using XRD analysis



Figuer. 3.8. Levels of radioactivity of 232Th and 40K in the study area.

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3.9. REFERENCES

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