Separation of Bi, Ca, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn, Ti, V and Zn in soil samples using thenoyltrifluoroacetone as the most selective single ligand by the appropriate use of solvent extraction under the optimum pH conditions

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BY

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A thesis submitted to satisfy

the requirements for the Degree of

Master of Science

in the Faculty of Science and Technology

at the University of Fort Hare

Supervisor : Professor D.K. Sanyal

Date : January 2003

DECLARATION

I hereby declare that this thesis is my own work and has not been submitted previously for any degree at any university

M.D.M

M.D. Manamela

Acknowledgements

I would like to convey my sincere gratitude and appreciation to my supervisor, Prof Dilip Kumar Sanyal, for his advice, guidance and patience during the preparation of the manuscript.

I also wish to thank the following people:

My parents, Ananias and Sarah Manamela, for help, support and the sacrifice they have made for my education

My family (Sis Zodwa, Mavis, Lebohang, Bobo and Nelly) for their love, care, support and encouragement throughout the years of my studies.

My friends and colleagues, particularly Mr David Meredith Katwire, for their encouragement and assistance in various ways.

Personnel of the soil science Department of the UFH for the collection of soil Samples.

Prof M. Magwa and Mr Errol Kelly for their assistance with the electron microscopy

Dedication

I dedicate this piec[illegible]n memory

Of MY BELOVED LATE uncle Samuel James Manamela

Abstract

In this investigation, three soil samples collected from non-arid land were qualitatively analysed using both the electron microscopy and AAS methods and elements such as Bi, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn Ti, V and Zn were positively identified in each of them. However, the electron microscopy method also revealed the presence of Na, K and Mg in these samples. Due to the logistical problems our scope of analysis was restricted to the first sixteen elements only.

Through the application of trial and error method TTA was found to be the most selective single ligand as it forms complexes with each of these elements. By varying the pH conditions in the presen[illegible], these elements were first separated into four smaller groups.

In group 1, Se, Mo, Ti and Sn, formed solid complexes with TTA in strong acidic media and were quantitatively extracted in the pH range 0.5 – 2.5. The components of this group were separated by carefully varying the pH and Mo, Ti and Se were 98%, 96% and 99% extracted respectively by the use of solvents such as benzene and MIBK.

In the second group, Fe, Bi, Cu, V and Cd were precipitated in the pH range 3.00–4.90 and the complexes were separated by taking advantage of their solubility in different solvents such as CCl_4, $CHCl_3$, benzene and n-butanol. Mannitol was used as a masking agent to eliminate any interferences.

Extraction of the elements, Bi, Fe, Cd, Cu and V was found to be 99%, 95%, 99%, 96% and 97% respectively in different solvents.

In case of the group 3, Cr, Mn, Pb, Zn and Ni, were extracted in the pH range 5.50 – 6.90 and then separated by solvent extraction under the optimum conditions. At pH 6.10, Pb and Mn were simultaneously extracted and separated by stripping off lead with nitric acid and manganese remained in the organic solution. Potassium cyanide was used as a masking agent for Ni, Cr and Zn. Extraction of the elements, Zn, Pb, Mn, Cr and Ni was found to be 96%, 98%, 96%, 95.6% and 96% respectively in benzene.

In group 4, Co and Ca, same method was applied and the separation was achieved at higher pH's (8.0 and 9.2). These elements, Co and Ca, were found to be 92% and 89% extracted respectively in different solvents such as benzene and isobutyl alcohol.

Concentration of the elements before and after separation was found to be almost quantitative under acidic media. It was however, found to be rather low for Ca and Co as these were determined under basic conditions. This is because of the fact that the ionic dissociation of the keto–form of the ligand in the acidic media was much higher than that of the enol form under the basic conditions.

So, it has been concluded that TTA is the most selective single ligand for the separation of large number of elements in a mixture as is the case in the current investigation.

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List of abbreviations

1. General

A.R.	analytical grade reagent
g/mol	gram per mole
ppm	parts per million
ml	millilitre
(s)	solid
U.F.H.	University of Fort Hare

2. Instruments

AAS	Atomic absorption spectroscopy
EM	Electron microscopy
UV–VIS	ultraviolet -visible
HCL	Hollow cathode lamps
DIBK	Diethyl-isobutyl-ketone

3. Solvents

$CHCl_3$	chloroform
CCl_4	carbon tetrachloride
MIBK	methyl isobutyl ketone

4. Ligands

PC-88A	2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester
Cyanex 272	bis(2,4,4 trimethyl pentyl) phosphoric acid
DADDTC	diethylammonium diethyldithiocarbamate
TEHP	tris(2-ethylhexyl) phosphate
Cyanex 302	[bis(2,4,4-trimethylpentyl monothiophosphinic acid)]
TTA	thenoyltriflouroacetone
APDC	Ammonium-1-pyrrolidine carbodithionate
DMG	dimethylglyoxime
PAR	4-(2-pyridylazo) resorcinol
Aliquat 336	Tricaprylmethylammonium chloride

Chapter 1

1.1 Introduction

Of the great many different kinds of soils on earth, each has its own special collective characteristics upon which its behaviour will depend; consequently, any definition of the term soil must be comprehensive in context. It is necessary to distinguish between soil as a substance and soil as a natural body. In the laboratory there is an unfortunate, yet persistent, tendency to regard soil as a material in a bottle, but in the field due notice must be taken of the fact that soils have shape, volume, boundaries and so on. A general definition of soil is given in the Soil Survey Manual of the United States Department of Agriculture (1951)[1]:

> *' Soil is the collection of natural bodies occupying portions of the earth's surface that support plants and its growth and that have properties due to the integrated effects of climate and living matter acting upon parent material, as conditioned by relief, over periods of time'*

The origin of soil is the earth's crust, the primary rocks of which have weathered to produce what is known as soil parent material. The rocks from which parent material is formed are known as parent rocks and these may in some cases be the primary rocks themselves, or secondary rocks by weathering.

The eventual soil is a chemically, physically and biologically complex, dynamic system, the constituents of which are constantly undergoing change. Hall[2] likens soil to a 'three-phase system of solid, liquid and gaseous components with constantly shifting equilibria'

Since the beginning of the past century a vast amount of research work has been done in the field of agronomy, in particular regarding the role of trace elements in soil fertility. Absorption of these elements in too low or too high quantities can bring about deficiency or toxicity related diseases in the plants and ultimately to animals which feed upon them.

The importance of trace elements and [illegible] have stimulated research with a view to understanding and appreciating the role they play in crop growth. In general, the presence–absence patterns in a variety of biological materials are frequently of importance to bio-scientists [3-5]. In recent times technology has made tremendous headway in the analysis of trace element content in material and some of the techniques are directly applicable to the analysis of soil and plant samples. The various instrumental techniques available today are used not only for the purpose of diagnosis of nutrients but also for the determination of the concentration of pollutants in soil/plant samples.

Chemical separation of components in a mixture, both inorganic and organic is the most important aspect in the analytical chemistry. To date several analytical methods[6-9] have been successfully tested for this purpose, accuracy of determination by some of these methods vary between gram to nanogram levels. To name a few analytical techniques that are most commonly used are, inductively coupled plasma mass spectrometry[10], ion-exchange chromatography[11-12] followed by flame atomic absorption spectrophotometry (AAS)[13], ion chromatography[14]. In order to avoid interference and also to improve sensitivity of the technique used, separation of a desired component(s) in a mixture is an important step prior to their analysis. As a result, a number of separation techniques, namely co-precipitation[15-17], ion exchange column method[18] and solvent extraction[19-22] have been developed and an analytical chemist is called upon nowadays to deal with this daunting task of analysis/separation of the ever increasingly complex nature of the samples. Of these methods, solvent extraction is the most preferred one because of its ease of operation, inexpensive, rapid, wide scope of application and excellent reproducibility. Many methods for the separation and preconcentration by solvent extraction of complexes have been developed, however some of these methods suffer from unacceptable limitations such as longer extraction time[23-24], critical pH[25], incomplete extraction[23-24], use of stripping agents[26] and co-extraction of commonly associated ions[27-30].

The main objective of the current study is two-fold, firstly to establish a single ligand that can form water insoluble complexes with all the sixteen elements namely Bi, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn, Ti, V and Zn that have been positively identified in all three soils samples that are under study here.

Through the application of the trial and error method most extensively, it has been found that thenoyltrifluoroacetone (TTA) is the desired ligand which upon variation of the pH forms solid complexes with each of these elements. Secondly to separate the components in this mixture by the selective application of the solvent extraction techniques under the most optimum conditions. The conditions that are found to be most critical are the variation of pH's, masking and demasking agents, solvents and stripping agent. Finally to determine the concentrations of the elements by atomic absorption spectrophotometer (AAS).

The use of solvent extraction as a technique with a single ligand to effect the separation of a mixture containing a large number of elements as in the present investigation has so far not been reported.

1.2 Literature Survey

Liquid–liquid extraction is a process based on the principle that a solute can distribute itself between two solvents, immiscible with each other, in a certain ratio. One phase is usually water and the other a suitable water immiscible organic solvent. This is a separation technique that enjoys popularity amongst analytical chemists because it is rapid, elegant and requires simple equipment. Separation of traces and large amounts of substances can be quickly and simply effected with high efficiency using separatory funnel. Equilibrium of the solute is achieved by vigorously shaking the two solvents for a reasonable period of time.

In the present study the factors that [illegible] the most positive influence on the successful separation of the components are the shaking and waiting times[31] and the concentration of the complexing reagent. It is necessary that the solutions be shaken long enough so as to reach equilibrium of the distribution of the metal complexes between the aqueous and organic phases.

Recent work[32-33] clearly indicates that another factor that enhances separation in a mixture is the use of a stripping reagent, where complete extraction is achieved by stripping off the desired metal ion from an organic solvent into an aqueous media under acidic conditions using aqueous solution of mineral acids. For example, separation of iron(III), titanium(IV), cobalt(II), copper(II) and chromium(VI) by liquid liquid extraction using 2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester (PC-88A) in toluene has been studied[34-35]. The mixture of iron(III), titanium(IV), cobalt(II) and chromium(VI) was resolved by first extracting iron(III) and titanium(IV) at pH 1.0 with 0.05 M PC-88A in toluene, under this condition cobalt(II) and chromium(VI) remain in the aqueous phase. From the organic phase iron(III) and titanium(IV) were separated by taking advantage of their difference of solubility in stripping agents. Iron(III) was first stripped off with 1M HNO_3, then titanium(IV) is quantitatively separated with a mixture of 2M H_2SO_4 and 3% H_2O_2. Cobalt(II) and chromium(VI) which remained unextracted in the aqueous phase were separated by first extracting cobalt(II) in acetate media with 0.005 M PC-88A in toluene. In acetate medium, chromium(VI) remained unextractable[36].

In the second set of multi-component [illegible] copper(II), zinc(II), iron(III) and chromium(VI), it was reported[34,35] that both copper and zinc get extracted with 0.02 M PC-88A in toluene at pH 6.0 and 4.5 respectively and then adjusting the pH to 2.0 iron(III) was extractable leaving chromium in the aqueous phase. Details for the separation of four sets of multi-component mixtures with variable concentrations are summarized in table 1.1

Table 1.1: Separation of iron(III) from multi-component mixtures[34-35]

Mixtures	Amount taken (µg)	PH	Extractant PC-88A	Stripping agent	% Recovery
1.Fe(III)	50	1.0	0.05 M	1M HNO_3	98.6
Ti(IV)	100	1.0	0.05 M	2MH_2SO_4 +3% H_2O_2	98.9
Co(II)	25	0.3	0.005M CH_3COONa	1 M HCl	99.1
Cr(VI)	25	5.0	Unextracted	Aqueous phase	99.6
2.Fe(III)	50	2.0	0.005 M	1M HNO_3	99.1
Zn(II)	25	5.0	0.02M	1M HCl	98.9
Cr(VI)	25	1.0	Unextracted	Aqueous phase	99.8
3.Fe(III)	50	1.0	0.05 M	1 MHNO_3	99.6
Ti(IV)	100	1.0	0.05 M	2M HNO_3 + 3%H_2O_2	98.2
Cu(II)	25	1.0	Unextracted	Aqueous phase	99.3
4.Fe(III)	50	1.0	Unextracted	Aqueous phase	99.6

Zn(II)	25	5.0	0.02 M	1M HCl	98.6
Co(VI)	25	5.0	Unextracted	Aquoeus phase	99.3
5.Fe(III)	100	1.0	0.05 M	1M HNO_3	99.2
Ti(IV)	100	1.0	0.05 M	2M H_2SO_4 + 3%H_2O_2	98.8
Cr(VI)	25	1.0	Unextracted	Aquoeus phase	99.8

M.N. Gandhi et al[37] did a sequential separation of iron(III), cobalt(II) and nickel(II). This separation is interesting because these metals belong to the same group of the periodic table. According to the authors, it was possible to separate the components of such mixtures by taking advantage of the differences in the extractability at a particular pH. In this case iron was selectively extracted at pH 3.0 with 0.005 M bis(2,4,4 trimethyl pentyl) phosphoric acid (Cyanex 272) after that cobalt was extracted at pH 8.0 with 0.005 M Cyanex 272. Nickel was not extracted under these conditions. This method is simple, rapid and selective. It permits separation of cobalt from commonly associated elements like manganese, zinc, molybdenum, chromium, nickel and vanadium.

Nikolova and Jordanov[38] investigated the use of diethylammonium diethyldithiocarbamate (DADDTC) and butyl acetate from 1 molar solutions of orthophosphoric acid, containing up to 55% pyrophosphonic acid and 20% tripolyphosphoric acid to determine copper, cadmium, lead and bismuth. The extraction of each element was made possible by varying the concentrations of mixed phosphoric acid solution. It was further claimed that in the presence of a mixture of 4 M H_3PO_4 and polyphosphoric acid, Cu, Cd, Pb and Bi were extracted simultaneously with 1% DADDTC in butyl acetate.

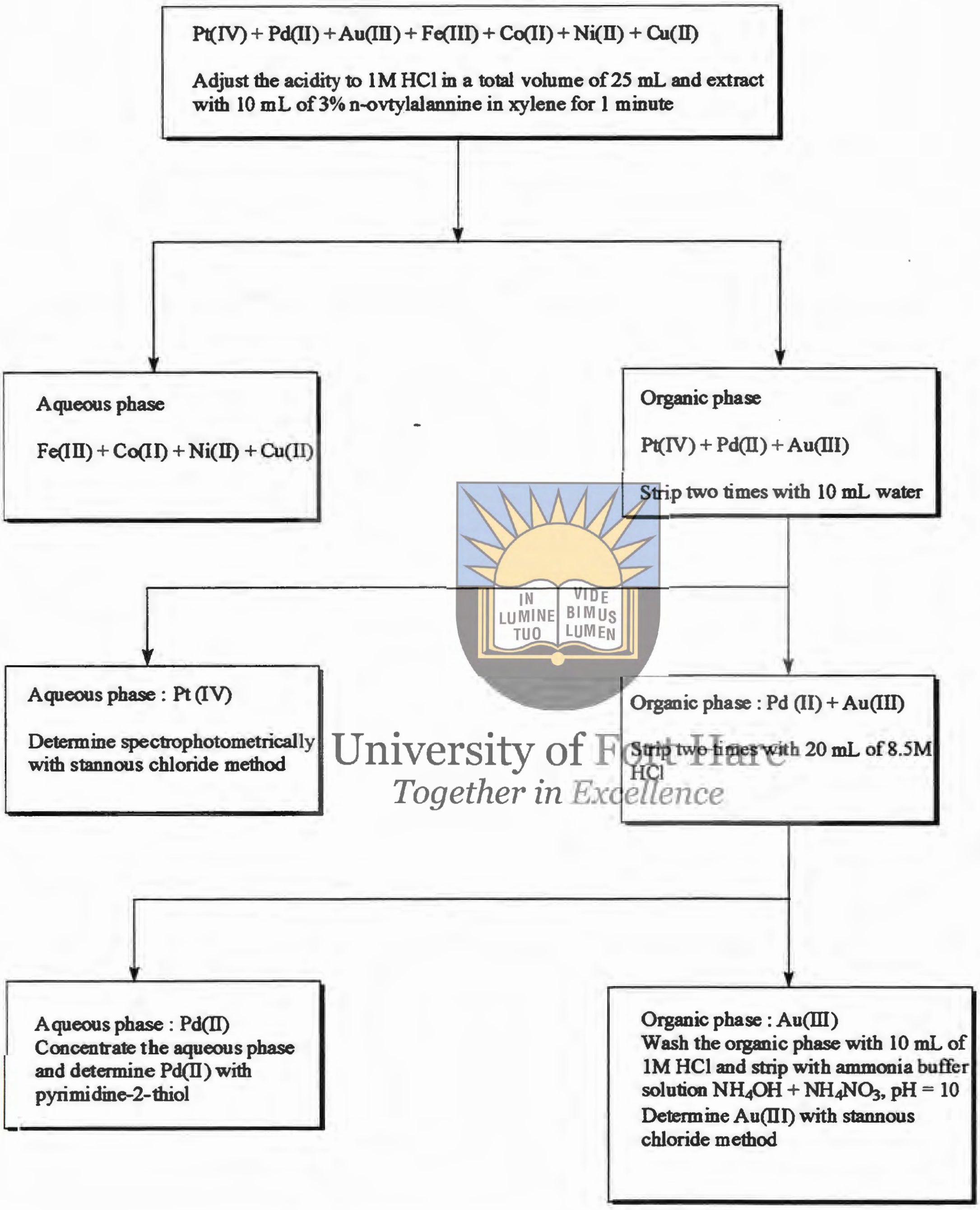
There has been increasing evidence in recent years about extraction and analysis of most of the complexes prior to their separation from the matrix. Preconcentration followed by analysis of these complexes from their natural sources after processing has been the common practise. Kinradie and Van Loon[31] used concentration of metal ions in natural waters prior to analysis by flame atomic absorption spectroscopy. These researchers used ammonium pyrrolidinedithiocarbamate (APDC) and DDDC as the complexing reagents and a number of organic solvents, most commonly ethyl acetate and methyl isobutyl ketone (MIBK). At pH 5, a total number of eight elements, such as cadmium, cobalt, copper, iron, lead, nickel, silver and zinc were simultaneously extracted into MIBK prior to analysis by the AAS.

Selective separation of a desired metal complex from the matrix prior to analysis is useful because of the reduced susceptibility of interference and improved sensitivity to the AAS.

Mali B.M[39] investigated the possibility of finding a systematic separation route for all the d-block elements using solvent extraction as a technique. These elements were firstly divided into a number of groups by the effective use of different ligands. Elements in each group were then separated by varying the pH and also by the use of appropriate masking and de-masking agents.

Looking at the work of the previous researchers[31,37-39], separation of groups of elements contained much fewer number of elements than that is intended in the current work. In cases where many elements were separated, a synergistic extraction approach[40-42] was applied not only to get a better recovery rate but also to enhance the selective separation. A synergistic extraction of palladium(II) with thenoyltrifluoroacetone and tri-n-octylphosphine oxide was studied for the separation of palladium(II) from platinum(IV)[43]. In the case of the separation of d-block elements[39], more than ten different ligands were used.

The following method[44] permits separation and determination of platinum (IV) from binary mixtures containing either iron(III), cobalt(II), nickel(II) or copper. Platinum is separated from these set of metal ions as a binary mixture by its extraction with 3 % N-n-octylalanine in xylene from 1 M HCl (Figure1.1). Under this condition all the other metal ions remain quantitatively in the aqueous phase where they are determined spectrophotometrically with thiocyanate, 1-nitroso-2-naphthol and pyrimidine-2-thiol. Palladium is also separated from iron(II), cobalt(II), nickel(II) and copper(II) by extracting it with 2% N-n-octylalanine in xylene from 1 M hydrochloric acid. Separation scheme is given in figure 1.1:



Pt(IV) + Pd(II) + Au(III) + Fe(III) + Co(II) + Ni(II) + Cu(II)

Adjust the acidity to 1M HCl in a total volume of 25 mL and extract with 10 mL of 3% n-ovtylalannine in xylene for 1 minute

Aqueous phase

Fe(III) + Co(II) + Ni(II) + Cu(II)

Organic phase

Pt(IV) + Pd(II) + Au(III)

Strip two times with 10 mL water

Aqueous phase : Pt (IV)

Determine spectrophotometrically with stannous chloride method

Organic phase : Pd (II) + Au(III)

Strip two times with 20 mL of 8.5M HCl

Aqueous phase : Pd(II)

Concentrate the aqueous phase and determine Pd(II) with pyrimidine-2-thiol

Organic phase : Au(III)

Wash the organic phase with 10 mL of 1M HCl and strip with ammonia buffer solution $NH_4OH + NH_4NO_3$, pH = 10

Determine Au(III) with stannous chloride method

Fig 1.1 : Separation scheme (flow chart) for the mixture

Scandium(III) and yttrium(III) were separated[45] from multicomponent and binary mixtures of iron(III), vanadium(V), chromium(VI), neodymium(III), lanthanum(III), samarium(III) and cerium(III) by tris(2-ethylhexyl)phosphate (TEHP) in toluene from salicylate media. Details as reported are, at pH 2.9-4.4, yttrium(III) (80%) co-extracted with scandium(III) using TEHP in toluene. After phase separation, yttrium was re-extracted from the organic phase with 2 × 5 ml of water and this facilitated the separation of yttrium(III) and scandium(III) since water does not strip scandium from the TEHP phase at all.. Then yttrium was determined spectrophotometrically with thoron-I[46] by adding 2mL of 0.1% of this solution and adjusting the pH to 4.0 with 0.1N hydrochloric acid and 0.1N sodium hydroxide solutions, diluting to 25mL with distilled water and measured the absorbance at 530nm against the reagent blank.

Finally scandium (III) was selectively re-extracted from the organic phase using 2 × 5 ml of 0.025 M hydrochloric acid and estimated spectrophotometrically with 4-(2-pyridylazo)resorcinol (PAR)[47]. It was determined by adjusting the pH 6.0-7.0 with 2.5 mL of 20% ammonium acetate buffer, adding 2 mL of 0.05% PAR and diluting to 25 mL with distilled water. The electronic absorbance of the orange-red complex of scandium was measured after 5 minutes at 515 nm against the reagent blank. Metal ions such as iron(III), vanadium (V), chromium and neodymium were not extracted at all in TEHP under these conditions and were determined by other known methods[48-51] directly from the aqueous phase. But ions such as thorium(IV), uranium (VI) and zirconium (IV) show co-extraction with yttrium(III) at pH 2.0-9.0

into TEHP. These co-extracted ions (that is, thorium(IV), uranium (VI) and zirconium (IV)), were selectively separated by stripping off with 2.0, 0.8 and 0.5 M hydrochloric acid, respectively.

There is claim that a new method[52] has been developed for the separation and extraction of lead from a binary mixture of Sn(IV), Bi(s), Sb(s), V(V), Ti(IV), Cr(VI), Cu(II), Zn(II) or Fe(III) in aqueous solution at pH 2.1 to 8.3 using [bis(2,4,4-trimethylpentyl monothiophosphinic acid)][53-54] (cyanex 302) in toluene as the organic solvent and the extractions were quantified spectrophotometrically with PAR. The separation of lead from the mixture was achieved quantitatively at pH 5.0. According to the following details[52], the total volume of the solution containing the elements was made to 25mL and [illegible] 5ml of 0.005 mol cyanex for a minute. After separation of the two phases, lead was quantitatively extracted into an organic solvent. Fe(II), Zn(II) and Cu(II) were then co-extracted with cyanex 302 into toluene at pH 5.0. Separation of these ions was also achieved by using different stripping agents. Fe(s), Zn (II) and Cu(II) were not stripped with 0.1 mol HNO_3 whereas Pb(II) was stripped off quantitatively. Thus separation of lead(II) from these metals was achieved. Fe(II) and Zn(II) were recovered by stripping these ions into 2 and 4 M HCl respectively whereas Cu(II) remained in the organic phase which after decomposition was estimated. The separation by solvent extraction of lead(II) was done as a function of pH, the concentration of the ligand, (cyanex 302) and various stripping agents.

Separation of tin(IV) by solvent extraction from hydrochloric acid media with 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC-88A) in toluene has been reported[55].The literature details are as follows: Separation of Sn(IV) from commonly associated metal ions such as antimony(III), bismuth(III), copper(II), lead(II), thallium (I) and nickel (II) was done taking into consideration of the difference in the extraction conditions. Tin(IV) and antimony(III) were quantitatively extracted with 0.15 M PC 88A in toluene from 0.1 M HCl. These two metal ions were quantitatively separated by differential stripping. Tin(IV) was first stripped off with 4 M HCl followed by antimony(III) with 8.5 M H_2SO_4. Tin(IV) was separated from bismuth(III), lead(II), thallium(I) and nickel(II) by taking advantage of the fact that these metal ions were not extractable under the conditions used for the extraction of tin (IV) with [illegible]C-88A in toluene from 0.1 M HCl (pH 1). Tin(IV) was separated from copper(II) in the presence of thiourea (masking agent for copper) with 0.025 M PC-88A in toluene when the acidity was maintained at 0.1 M HCl.

Tin(IV) was also separated from ternary mixtures[55]. An aliquot containing tin(IV), antimony(III) and bismuth(III) was equilibrated with 0.15 M PC-88A in toluene in the presence of 0.1 M HCl. Tin(IV) and antimony(III) were extracted in the organic phase, while bismuth(III) remained in the aqueous phase. Tin(IV) from the organic phase was first stripped off with 4 M HCl followed by antimony(III) with 8.5 M H_2SO_4. Similarly, tin(IV) was separated from the mixtures of tin(IV), antimony(III) and lead(II), as well as tin(IV), antimony(III) and thallium(I), where lead(II) and thallium(I) were unextracted. Separation details of Sn(IV) from various mixtures are summarized in table 1.2

Table 1.2: Separation of tin(IV) from multi-component mixtures[55]

Metal ions	Amount (μg)	pH / acidity	Reagent conc (M)	Stripping agent	% Recovery
1. Sn(IV)	50	0.1 M HCl	1.5×10^{-1}	4 M HCl	99.2
Sb(III)	50				99.14
2. Sn(IV)	50	0.1 M HCl + thiourea	2.5×10^{-2}	4 M HCl	99.2
Cu(II)	200		Unextracted	Aqueous	98.6
3. Sn(IV)	50	0.1 M HCl	1.5×10^{-1}	4 M HCl	99.2
Sb(III)	50			8.5M H_2SO_4	99.14
Bi(III)	200		Unextracted	Aqueous	100.0
4. Sn(IV)	50	0.1 M HCl	1.5×10^{-1}	4 M HCl	99.2
Sb(III)	50			8.5M H_2SO_4	99.14
Pb(II)	100		Unextracted	Aqueous phase	98.75
5. Sn(IV)	50	0.1M HCl	2.5×10^{-2}	4 M HCl	99.2
Bi(III)	150	0.1M AN	6×10^{-3}	2 M HNO_3	99.4
Ti(I)	100	At pH =1.5	Unextracted*		99.1

* Unextracted means direct determination in the remaining solution

Naidu et al[56] described a rapid atomic absorption spectrometric method for the determination of tin, antimony, bismuth, indium, gallium and arsenic in geological materials, steel and other alloys. Viets et al[57] recommended the use of Aliquat 336 solution in methyl isobutyl ketone (MIBK) for the extraction from 2 M hydrochloric acid and direct application of AAS. However, indium, tin and gallium were not included among the analytes they investigated. Donaldson and Wang[58] made a study of these elements and recommended that extraction should be done with MIBK in sulfuric acid media with the sequential stripping using appropriate reagents as per the following details.

A mixture of 20 % HNO_3 + H_2O_2 was used for stripping Sn, In and Bi; 40 % HNO_3 alone for Sb and water for As. Three [illegible] stripping steps were involved in each case to ensure maximum extraction. Before aspirating these solutions into the AAS, different matrix modifiers such as 4% HNO_3 + 2000 µg/ml of K for In, 10% HCl + 0.5% tartaric acid + 250 µg/ml of K for Sn, 10% HCl + 0.25% tartaric acid + 2000 µg/ml of K for Sb and 5% HNO_3 for Bi were added.

A method[59] was also developed for direct determination of trace amounts of Cr, Mn, Cu, Ni, Co, Li, Pb, Cd, Bi, Sb, Be and Ag in silicate rocks, lake and stream sediments using a microwave oven dissolution method and a multi-element graphite furnace atomic absorption spectrometer equipped with a Zeeman-effect background correction services. Extraction of suitable complexes of the analytes into organic solvents was necessary so as to improve the detection limits and eliminate interferences from major elements. A widely used method of the chelation of Pb, Cd, Bi and Zn with ammonium pyrrolidine dithiocarbamate and extraction with MIBK, followed by back extraction with an acid into aqueous phase before determination was also applied[60]. According to this report, major interferences of iron were avoided by using isopropyl ether to separate it from a silicate-rock-digest in HF-HNO_3-$HClO_4$ and from the solution, Pb and Cd were extracted along with some other trace elements such as Mn, Ni, Co, Bi and Zn with APDC-oxine-MIBK system.

Extraction systems used in trace element analysis in various investigations[41-50] are classifed in terms of the chemical compounds involved. In this particular work, uncharged covalent species such as chelates[61] are used. Chelate complexes were formed from the coordination of meta[illegible] appropriate polydentate ligand. If the metal ion coordination sites are all satisfied or occupied, then it implies that the compound is neutral or co-ordinatively saturated[62-63]. Such a chelate compound tends to be more soluble in non polar solvents than in aqueous solvents.

If some of all the coordination sites of a metal ion are not satisfied by anionic ligand but by water molecules (hydrophilic groups), then the complex is said to be coordinatively unsaturated. Hydrated chelates are only poorly extractable, so for a good extraction, the solvating water molecules must be removed.

1.2.1 Completeness of Extraction

In view of the fact that there are no side reactions either in the aqueous or in the organic phase, the extraction reaction may be described by the following general equation[64]

$$M^{n+} + nHA_{(o)} \rightarrow MA_{n(o)} + nH^{+}$$

where M^{n+} is the metal ion, HA is the organic chelate-forming reagent and MA_n is the chelate complex. It is to be noted that each chelate forming reagent is a weak acid HA, where the conjugate bases A^-, react with M^{n+}. The subscript (o) denotes the organic phase and for the aqueous [illegible] subscript are used. The equilibrium constant, K_{ex}, of this extraction reaction is given by:

$$K_{ex} = \frac{[MA_n]_o[H^+]^n}{[M^{n+}][HA]_o^n}$$

If there is no intermediate equilibrium, the ratio [MAo]/[M] would be equal to the distribution coefficient D. Then

$$K_{ex} = D\frac{[H^+]^n}{[HA]_o^n}$$

Hence,

$$D = K_{ex}\frac{[HA]_o^n}{[H^+]^n}$$

And taking the logarithms it gives

$$\text{Log } D = \log K_{ex} + n \log [HA] - n \log [H+]$$

$$\text{or, Log } D = \log K_{ex} + n \log [HA] + n \text{ pH}$$

On rearrangement we get,

$$\text{Log } D = n \text{ pH} + (\log K_{ex} + n \log [HA])$$

Thus a plot of log D vs pH should be a straight line with a slope of n and an intercept on the log D axis of (log K_{ex} + n log [HA]) (See Fig 1.2).

For a given system, the extractability of the metal complexes increases with both the concentration of ligand and the increasing pH of the aqueous phase.

1.2.2 Extraction Kinetics

In recent years increasing attention has been focused on the kinetic aspects of extraction processes. To elucidate the mechanisms of such processes require chemical reactions and distribution rate as the likely conditions for the successful extraction, otherwise the overall rates for such determination

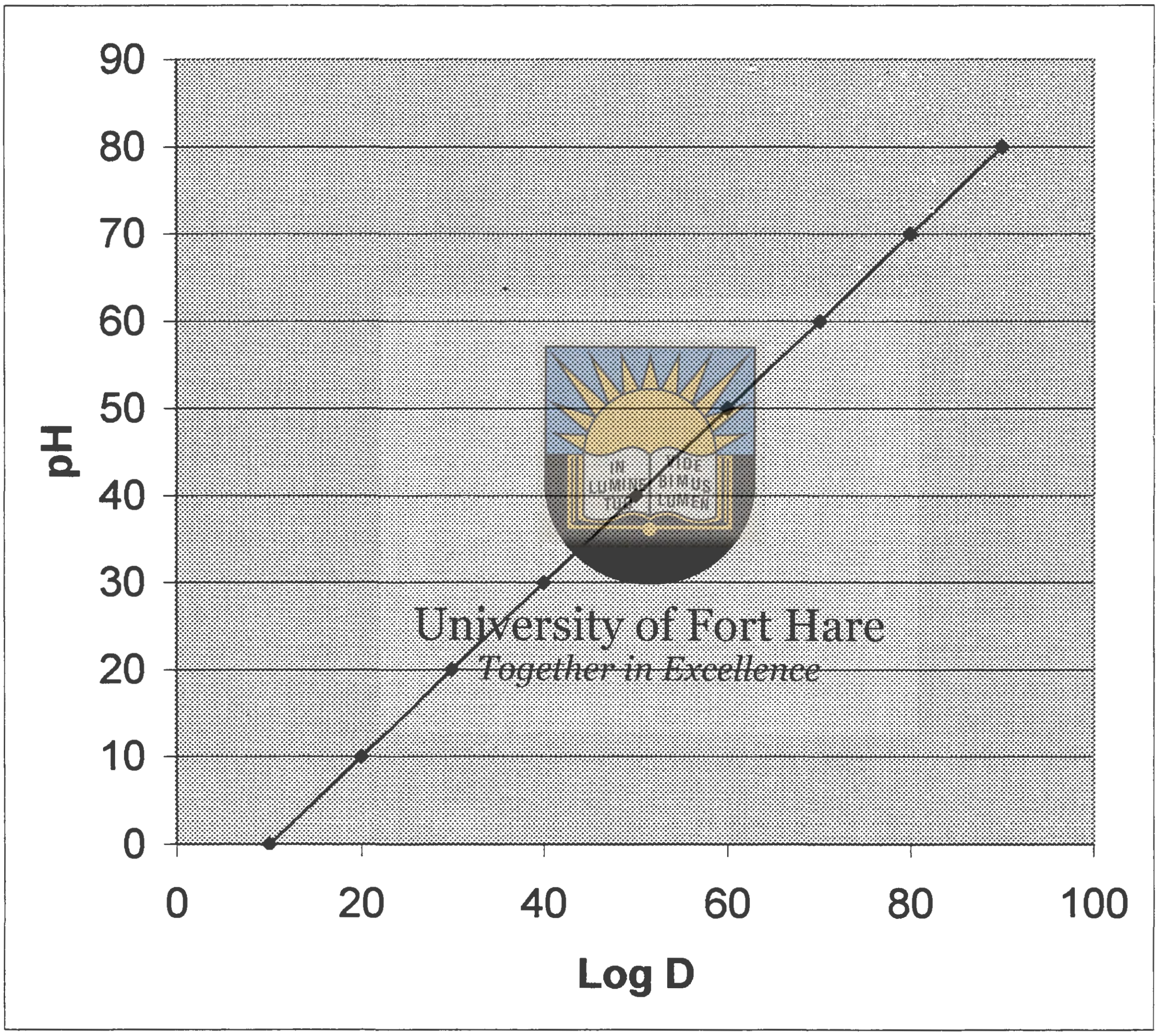
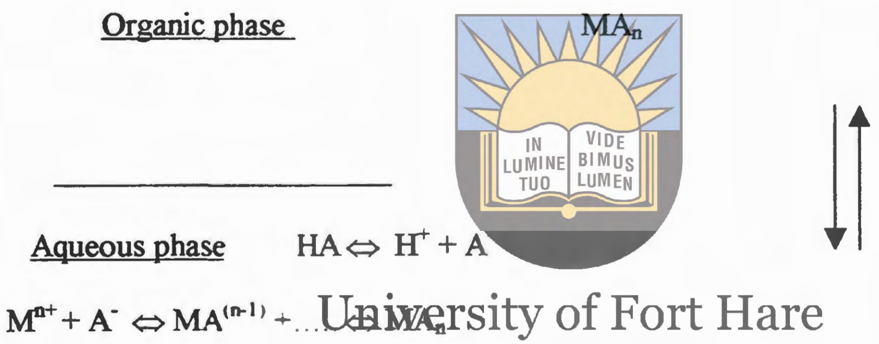


Fig 1.2 : Log D vs pH curve

by extraction would be a very slow process[65-66]. Three types of extraction can be distinguished here which are, (a) the kinetic type where the extraction rate is controlled by the rate of a chemical reaction, (b) the diffusion type where the rate depends primarily on the rate of mass transfer, and (c) the combined type where the rate of extraction depends on both the processes (a) and (b). The extraction process can thus be summarized as follows:



According to Fomin[67], the reaction rate, represented as K, may be expressed by the following formula

$$\text{Reaction rate } (r) = k[M][A]^n = k\frac{K^n_{HA}}{P^n_r}\frac{[M][HA]^n_o}{[H^+]^n}$$

where r is the rate of extraction, P_r is the reaction coefficient, k is the rate constant, [M] is the concentration of the component in the aqueous phase.

From the above equations, it follows that the reaction coefficient is inversely proportional to the rate of the reaction .If a compound is to be extracted from an aqueous phase, then the reaction rate will not depend on the concentration of this component in the aqueous phase but on the magnitude of the distribution coefficient, that is, lower the distribution coefficient, faster is the reaction process

Freiser[68] more recently studied the effect of some other complexing agents on the extraction kinetics of metal dithizonates. According to him a complexing agent, X, is present in the aqueous solution, intermediate complexes, MX_n, is likely to form, and these will then react with dithizone. The presence of ions of X^{n-} may cause the rate of extraction of the dithizonate to increase if formation of MX_n is faster than that of $[M(H_2O)_n]^{x-}$ when this complex reacts with dithizone faster than that do for the hydrated metal ions.

As mentioned earlier that in order to avoid interferences it is often necessary to separate the element of interest from the sample matrix to enhance the sensitivity. One of the most powerful approaches to separation involves a pair of phases in which a component of interest is transferred from one phase into the other more readily than do interfering substances. Separation, selectivity and isolation of individual elements from a mixture can be influenced by a number of factors such as pH, masking agent, extracting agent, stripping reagents etc.

Stability of a metal complex as well as the reaction media also influences the quality of exaction. At lower pH, the stability of the metal complex becomes higher leading to the ease of extraction. The important factors that affect the stability of complexes are:

a. Nature of the metal ion

b. pH

c. Nature of the ligand

d. Steric effect

e. Resonance effect

f. Size of the chelate ring

g. Basicity of the ligand

From the list above, only three will [illegible]ed here, namely the nature of the metal ion, the ligand and the pH effect

1.2.3 Nature of the metal ion

Electronic structure of the metal ion determines the electrostatic nature of the bond or the M-L bond strength. The stability of the complex is also determined by the electrostatic nature of the bond. The stronger the bond between the metal ion and the ligand, the more stable is the complex. The charge density on the metal ion also influences the bond strength. As the metal ion charge density increases, the bond coordination would be stronger-if the donor atoms of the ligands are O, N, or S.

1.2.4 Nature of the ligand

As mention above the donor atoms, through which the ligand bond to the metal ion plays an important role in the stability of the complex. Donor atoms such as N, O and S will form stronger electrostatic bonds with the metal ion than those with the weaker donor ability. According to the Hard and Soft Acids and Bases (HSAB) theory[69-71] the ligand donor atom and the metal ion combination should be a matching one, for a stable complex. A mismatch combination will result in the formation of an unstable complex.

1.2.5 pH effect

The acidity or basicity of the medium under which the complexes are formed also determines the complex stability. In general, the stability constant (K_{st}) for the reaction of the type

$$M^{n+} + nHA_{(o)} \rightarrow MA_{n(o)} + nH^{+}$$

is given by

$$K_{st} = \frac{[MA_{n(o)}][H^{+}]^{n}}{[M^{n+}][HA_{(o)}]^{n}}$$

where square brackets represent mo[illegible]ntration of the reactants and the products. From the equation above, increasing concentration of the hydrogen ion, will increase the value of K_{st}, which in turn signifies an increase in the complex stability. Therefore, at lower pH, that is, in stronger acid medium, the complex is more stable.

1.3 Reported extraction conditions for metal ions

1.3.1. Vanadium

N-Benzoyl-N-phenylhydroxylamine has been found[72] to be a highly specific reagent for vanadium, forming a water insoluble, deep violet complex in strongly acidic solution. Formation of this complex in fairly strong acidic solutions of 2 – 10 M HCl constitutes an advantage because the complexes of many of the diverse ions normally decompose under these conditions and thus making the extraction relatively free of interferences. Chloroform is the most suitable extractant because the chelating reagent is more readily so[illegible] than in other solvents.

The volume of the solution was adjusted to about 25mL with 6M HCl with a pH between 2.8–4.3 M before extracting it completely in 10 mL of 0.1% chloroform. The conc was finally determined spectrophotometrically.

1.3.2. Manganese

Extraction of manganese using APDC poses problems as its extraction efficiency is dependent on the concentration of the chelating agent. When 1ml of 1% APDC solution is added[73] to 80ml of 0.5 ppm Mn solution, no extraction is possible over a pH range of 1 to 10, but when 2.25ml of 5% APDC is added, maximum extraction of 30μg of Mn solution in 45ml of solution at pH 3 using 10ml of MIBK for the organic layer is achieved. Again, since the Mn-APDC complexes are not stable, analysis should be done within 30 minutes of extraction.

Theonyltrifluoroacetone in xylene may also be used as a suitable complexing agent for the separation and estimation of manganese[74]. At pH 6.5, maximum 97% extraction was possible in the presence of sulfuric acid and sodium borate both as oxidants.

1.3.3. Cadmium

Choi and Kim et al[75] developed a [illegible] method for the determination of cadmium based on the solid-liquid extraction principle. According to these authors trace levels of cadmium in 100ml water sample was chelated with 2.5ml of 0.001M oxine at pH 8 followed by addition of 0.07g benzophenone and the solution was heated to 70 degree celsius and stirring vigorously for a minute to dissolve the complex into molten benzophenone. Several experimental conditions such as the pH of the solution, the amount of 8-hydroxyquinoline and benzophenone, stirring and standing time were optimized. It is claimed that trace levels of cadmium can be recovered from any samples using this method.

1.3.4. Chromium

Chromium(III) is extractable at pH 6.0 with TTA in benzene solution. The interferences due to iron (III) and molybdenum (VI) can be removed by preliminary extraction-the former at pH 1 using acetylacetone-chloroform and the latter by TTA-butyl alcohol-acetophenone from 0.5M HCl[76].

Until recently[77-78], separation of chromium using APDC and MIBK was reported to be impossible unless the Cr-containig solution is concentrated by boiling and then allowed to cool thereafter.

The use of APDC and MIBK for [illegible]ation of chromium was virtually impossible until recently discovered that, upon heating of the complex –containing aqueous solution to boiling, and allowed to cool thereafter, it can be successfully extracted[77-78].

1.3.5 Calcium

A selective method[79] for the isolation and determination of calcium is based on its extraction with a 2 % solution of oxine in chloroform in the presence of n-butylamine. Interfering ions are removed by a preliminary extraction with oxine at a lower pH. Calcium can also be separated from strontium and other metals by its synergic method of extraction with TTA-TBP at pH 6.6. Using this method, about

99% of Ca is extracted with traces of strontium which is removed by washing the organic layer three times with water.

1.3.6 Bismuth

A solution of bismuth in dilute ammonia containing potassium cyanide is extractable using dithizone in chloroform. By preliminary extraction at pH 2.5, Pb, Sn and thallium interferences- can be avoided[80] by the addition of a relevant masking agent. Bismuth can also be extracted by using 0.2% sodium diethyldithiocarbamic acid into 10mL of carbon tetrachloride[81] from an aqueous solution at pH 11-12. Addition of EDTA and KCN in the aqueous solution can eliminate interference of any other ele

1.3.7 Cobalt

Cobalt(II) is extracted as the thiocyanate complex at pH 4, in the presence of citric acid, with acetylacetone[82]. If manganese and chromium are present, they should be removed first by ion-exchange, and thus the method can be made specific for cobalt. All the elements which form coloured thiocyanates are removed by preliminary extraction with acetyl-acetone except nickel and platinum.

1.3.8 Copper

Several organic solvents have been reported[83-84] as used in the determination of copper after extraction from aqueous solution with 8-hydroxyquinoline. 25 mL aliquot of copper was introduced into a 125 mL separatory funnel and a 25 mL aliquot of 0.02M 8-hydroxyquinoline in the appropriate organic solvent was added. 5.00 mL of the appropriate buffer solution and an amount of 0.5 M sodium chloride solution sufficient to give an ionic strength of 0.05 when diluted to 50 mL was added. This procedure was repeated with a variety of solvents such as ethyl acetate, MIBK, cyclohexene, 3-heptanone, n-butyl ether, diisobutyl ketone etc and ethyl acetate gave > 95% extraction. Therefore a 8-hydroxyquinoline-copper complex is almost 3 times more sensitive in ethyl [illegible] in any other organic solvent[85].

1.3.9 Nickel

Dimethylglyoxime method[86] is the most selective for the determination of traces of nickel. The determination was as follows: 2mL of 1% dimethylglyoxime in ethanol was added in the aqueous solution and the pH adjusted to 7.5. The solution is shaken with three 2-3 mL portions of chloroform for 30 seconds. The combined organic phase were scrubbed with 5ml of 0.5 M ammonia to remove copper. The ammonia washes are shaken with 1-2 mL of chloroform and then added back to the main chloroform extracts. The nickel complex was then stripped off from the organic phase by equilibrating with two 5 mL portions of 0.5 M hydrochloric acid.

1.3.10 Molybdenum

The simultaneous use of three organic solvents, MIBK, DIBK and isoamyl alcohol and two chelating reagents, oxine and toulene-3,4-dithiol[87] was done. 5ml of 1% oxine dissolved in MIBK/DIBK, and 5ml of aqueous dithiol were added and the mixtures shaken mechanically with one of the organic solvents (20ml) for 15 minutes. Optimum pH values for high percentage extraction of the Mo-complex are from strongly acidic (1.5 – 4) to moderately basic solutions (8 – 10). Thiocyanate, α-benzoinoximate and diethyldithiocarbamate as chelating reagents into MIBK are also suitable for the determination of Mo.

1.3.11 Titanium

The determination of titanium with mixed ligands flourine-alizarin, including optimum conditions of formation and extraction into MIBK is a method of high selectivity and sensitivity[88]. At pH 9.5-10.3 a red-violet Ti (IV)-flouride-alizarin complex is completely extractable into MIBK. Stary[88] proposed EDTA and KCN as suitable masking agents when Ti is isolated as the oxinate.

A simple method for extraction and spectrophotometric determination of titanium(IV) with an α-hydroxy acid has also been widely used in the past. Sato and Uchikawa[90] reacted p-Chloromandelic acid with titanium in weakly acidic aqueous solution at room temperature to a complex anion extractable into chlorobenzene with Malachite Green as counter ion.

1.3.12 Zinc

The extraction of zinc with oxine and its derivatives has been extensively studied. Izquierdo et al[91] extracted zinc with 5,7-dichloro-2-methyl-8-hydroxyquinoline into chloroform. The pH of the aqueous solution is adjusted from 4.5 to 9.5 with sodium acetate or borate. The tertiary amines, methyl-di-noctylamine and tribenzylamine are efficient extractants for zinc from dilute HCl. In the range 2-3 M HCl, Zn can be separated from Mn, Co and Ni.

1.3.13 Selenium

A complex of selenium-diethyldithiocarbamate is readily extractable into a 3 × 4 mL portion of carbon tetrachloride at pH between 5 and 6. Here EDTA was used as a suitable masking reagent for a number of interfering ions[92].

1.3.14 Lead

Lead can be readily extracted by 0.005% dithizone solution in carbon tetrachloride at pH 9-10 in the presence of 0,1M cyanide and 0,8 M citrate. Bismuth, thallium, indium(III) and tin (II) are also co-extracted in the absence of suitable masking agents. Lead can be separated from these interferences by shaking the organic extract with dilute nitric acid, and only lead will be stripped off[93].

1.3.15 Silver

This is a highly selective method[94] for extraction and determination of trace amounts of silver, based on the form[illegible] a ternary complex between silver, 1,10-phenathroline and bromopyrogallol red in nitrobenzene from near neutral aqueous solutions. In the presence of EDTA, mercury(II) and bromide ions as masking agents, the %extraction is almost interference free and > 96%.

1.3.16 Iron

Iron (III) can be extracted quantitatively from the aqueous phase with 15 mL of 0.5 M TTA in xylene. The pH of the solution must be adjusted to between 1 and 5 with 10 M nitric acid. The solution mixture must be shaken for 15 minutes and the first extraction yields more 90% of iron. Under these conditions only zirconium, hafnium and slightly niobium are extracted and iron can be separated from these ions by stripping with 0.25 M hydrofluoric-0.25 M hydrochloric acid[95-96].

Chapter 2

2. EXPERIMENTAL

2.1 INSTRUMENTATION, REAGENTS AND APPARATUS

2.1.1 Instrumentation

A Pye Unicam 939 (Solar system) Atomic Absorption Spectrophotometer (AAS) was used with an air-acetylene flame except Sn and Se for which required nitrous oxide-acetylene flame. A deuterium lamp was used for the background correction and separate single and multi-element hollow cathode lamps were used for the different elements.

Beckmann DU 7500 UV spectrophotometer were used throughout this study. Hitachi 450 electron microscope was also used for qualitative determination of elements in soils

2.1.2 Reagents

The following analytical grade mineral acids were used for processing the soil samples:

HCl (32-33%, A.R 1,16)-BDH

HNO_3 (68 – 71%, A.R 1.42) – N.T. Laboratories

$HClO_4$ (70 % A.R. 1.67) – BDH

HF (40 % A.R. 1.13) - MERCK

A freshly prepared 0.25 M TTA solution (molecular mass 222.2 g/mol by dissolving 55.6 g of TTA in benzene to a total volume of a litre) was used for every repetition. Other reagents used in the investigation are summarized in table 2.1

Table 2.1 List of reagents (salts and solvents) with suppliers / grades

Reagents	Grade/suppliers
Chloroform	AR/Holpro
Xylene	AR/Merck
Methyl isobutyl ketone	AR/Merck
Ethanol	AR/BDH
Sodium tatrate	AR/BDH
Sodium citrate	AR/BDH
Citric acid	AR/BDH
Oxalate	AR/Merck
Benzene	AR/Merck
Ascorbic acid	AR/BDH
Isobutyl alcohol	AR/Merck
n-Butanol	AR/Merck

2.1.3 Apparatus

Pyrex glassware, washed in a mixture of perchloric acid, nitric acid and hydrochloric acid in the ratio 1:1:1 and rinsed several times with distilled water, was used. Experiments in hydrofluoric acid media were carried out in Teflon wares. All fusion experiments were done in platinum crucibles. Unless stated otherwise, all standard solution of 1000 ppm are the spectrograde commercially available from Merck and BDH standard solutions.

2.2 PREPARATION OF STANDARD SOLUTIONS

All standard solutions were prepared by dilution with 1 M HCl of 1000 ppm spectrograde commercial stock solution (Merck or BDH). Since some of the stock solutions were not available commercially, so they were prepared as per the details below. All the standard solutions were stored in polythene bottles inside a cupboard to prevent photo-decomposition. It is to be noted that concentration of all stock solutions is 1000 mg/L.

Bismuth

0.5 g of cleaned bismuth metal was dissolved in 10 ml nitric acid, the solution was heated with sulfuric acid until white fumes were evolved. The solution was then cooled and diluted accurately to 500 mL with 2 M hydrochloric acid.

Cadmium

2.1032 g of cadmium nitrate, $Cd(NO_3)_2$, was dissolved in a litre of distilled water.

Calcium

2.77475 g of anhydrous calcium chloride, $CaCl_2$, was dissolved in a minimum volume of distilled water. The solution was then diluted to a litre in a volumetric flask with 1M HCl.

Chromium

3.7350 g of potassium chromate, K_2Cr[illegible]ken in a 1 Litre volumetric flask and then made up the volume with distilled water.

Lead

1.6 g of lead nitrate, $Pb(NO_3)_2$, was dissolved in a minimum volume of distilled water. The solution was diluted to a litre in a volumetric flask with 1 M HCl.

Tin

Granulated Sn was first washed with dilute HCl to remove any oxide coating and then oven dried. Thereafter 1 g of dried tin granules, Sn, were dissolved in a minimum volume of 1 M HCl. The solution was diluted to a litre in a volumetric flask with distilled water.

Titanium

26.72mL of 15% commercial solution was diluted to one litre followed by standardization using AAS.

Vanadium

0.2960 g of ammonium metavanadate, NH_4VO_3, was carefully dissolved in 20 mL of (30%) hydrogen peroxide. The solution was diluted to 100mL in a volumetric flask with distilled water.

Zinc

2.08458 g of zinc chloride, $ZnCl_2$, was [illegible] in a minimum volume of distilled water. 1 M HCl was used to make up the volume to a litre in a volumetric flask.

2.3 Sample collection

Sampling generally means collection of composite materials from the areas of interest. In this case the area of interest was the UFH farm and samples were collected from non-arid land at a depth of approximately 20cm from the surface. Personnel in the soil sciences department of UFH assisted in the sample collection.

2.4 Procedure of soil processing for analysis

To avoid contamination of samples by trace impurities all glassware was thoroughly washed with a detergent and hot water, rinsed several times with hot concentrated nitric acid and finally with doubly-distilled and deionized water.

Firstly the soil samples were separated from unwanted matters by screening through a 0.2-mm (10 mesh) sieve to give what is commonly referred to as the 0.2 mm fine earth. These samples were dried in an oven at 150°C for 12-14 hours. 1 gram of the dried sample was transferred into a platinum crucible and moistened with a few drops of water to avoid spluttering and then treated with 10 mL of conc HNO_3 and kept on a hotplate at 120°C until the evolution of the nitrous acid fumes had ceased and the organic matter had been completely destroyed. This reaction was carried out inside the fume hood and the heating was continued carefully until the volume of the sample was reduced to near dryness.

It was then cooled for 15 minutes and at this stage it looked dark brown. After cooling, a mixture of concentrated acids containing 5 mL HNO_3, 10 mL HCl and 5 mL HF was added with swirling and digestion was continued once again. The temperature of the hot plate was raised slowly to temperatures > 200°C over a period of two hours until the colour changed from brown to colourless. The colour change indicated the complete removal of perchloric acid fumes from the solution. A further 10 mL HCl acid was added to the mixture and boiled for another 10-15 minutes. During digestion, the volume was not allowed to fall below approximately 0.5 mL to prevent charring of the sample material and to decrease the likelihood of perchloric acid explosion.

Thereafter the crucible was removed fr[illegible] plate and cooled to room temperature. The solution was then diluted to 50 mL with triply distilled water. This is the test solution.

2.5 Qualitative analysis of elements

This was done by the following instrumental methods:

2.5.1 Electron microscopy using Hitachi 450 Electron Microscope

Procedure for electron microscopy detection

Accurately weighed 1 gram of the 10-mesh soil sample was mounted on nylon stubs coated with carbon. The targets were then scanned using 400 A° scanner fitted with a Hitachi high vacuum evaporator. Stubs were viewed at 20 KV in a Hitachi S-450 screen fitted with a PGT EDX-ray probe. Viewing involved a secondary dextrin imaging. The PGT 300 was calibrated [illegible] samples of aluminium and copper as standards. The detector efficiency programmes were run prior to the sample EDX analysis. The elements identified positively in the soil sample using this technique were Co, Cu, Ca. Ti. Mn, Fe, Bi, Se, Ni, Zn, Pb, Cr, Cd, Sn, V, Mo, Na, K and Mg.

2.5.2 Atomic Absorption Spectrometry

The qualitative identification were also performed by AAS using the appropriate energy of absorption of an element. Due to the logistical problem only sixteen elements, namely. Co. Cu. Ca, Ti, Mn, Fe, Bi, Se, Ni, Zn, Pb, Cr, Cd, Sn, V and Mo were used in this study for separation as well as their quantitative determination.

2.6. Quantitative analysis of elements before separation by AAS

Absorbances of the standard solution of each element were determined by AAS using appropriate energy sources and the results are given in tables 2.2 to 2.17. These results were also used to prepare calibration curves for each elements which are also shown in Fig 2.1 to 2.16. These curves provided the concentration of elements in the soil sample and these are summarized as mg/L in table 2.18

Table 2.2: Concentration vs Absorbance for copper

Concentration (ppm)	**Absorbance**
0	0
10	0.195
20	0.392
30	0.587
40	0.785
50	0.979
60	1.177
70	1.372
80	1.570
90	1.701
100	1.962

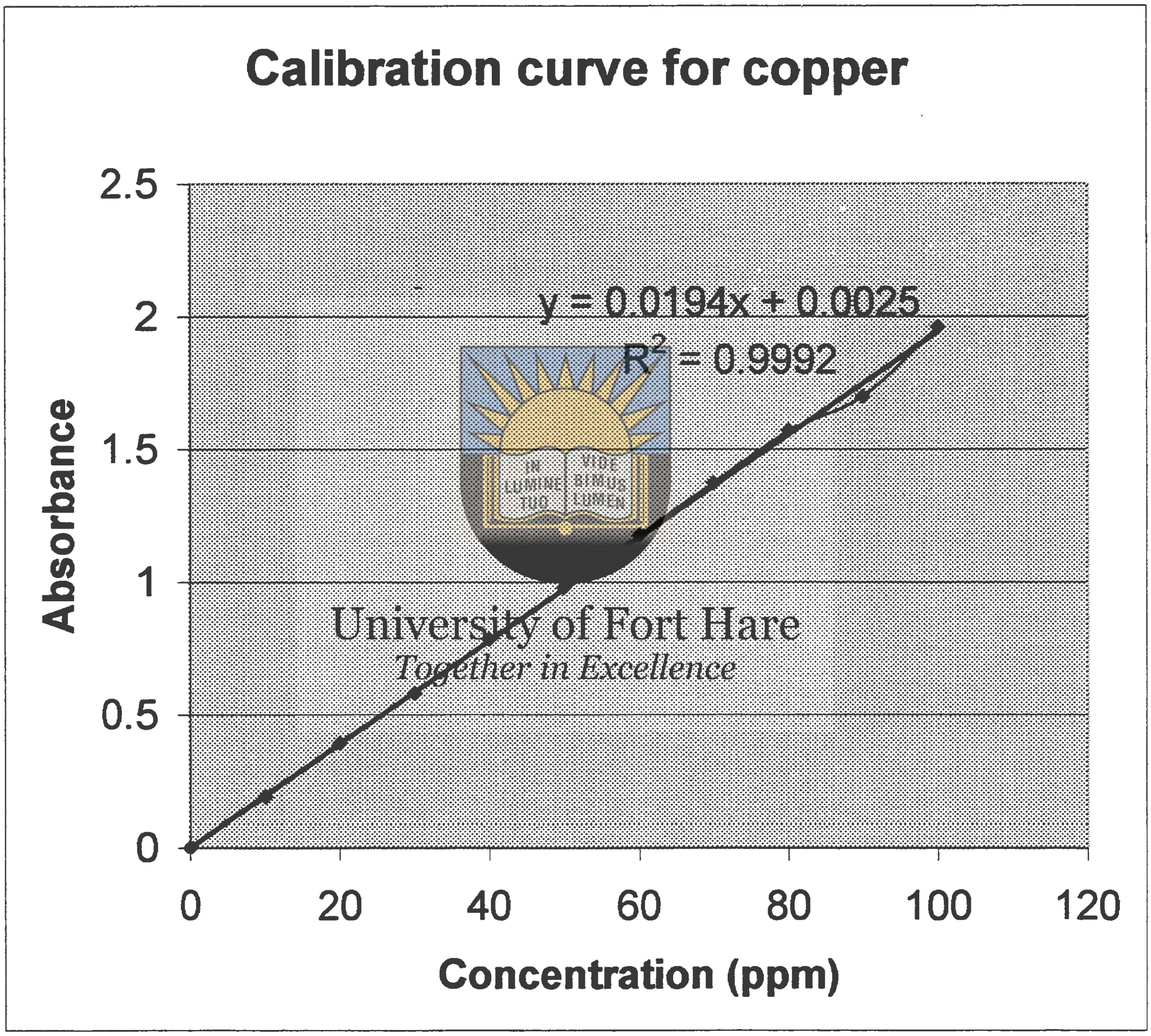


Figure 2.1: Plot of concentration vs absorbance for copper

Table 2.3 : Concentration vs Absorbance for cobalt

Concentration (ppm)	**Absorbance**
0	0
10	0.0917
20	0.1745
30	0.2650
40	0.3323
50	0.4583
60	0.5050
70	0.6717
80	0.7368
90	0.8260
100	0.9257

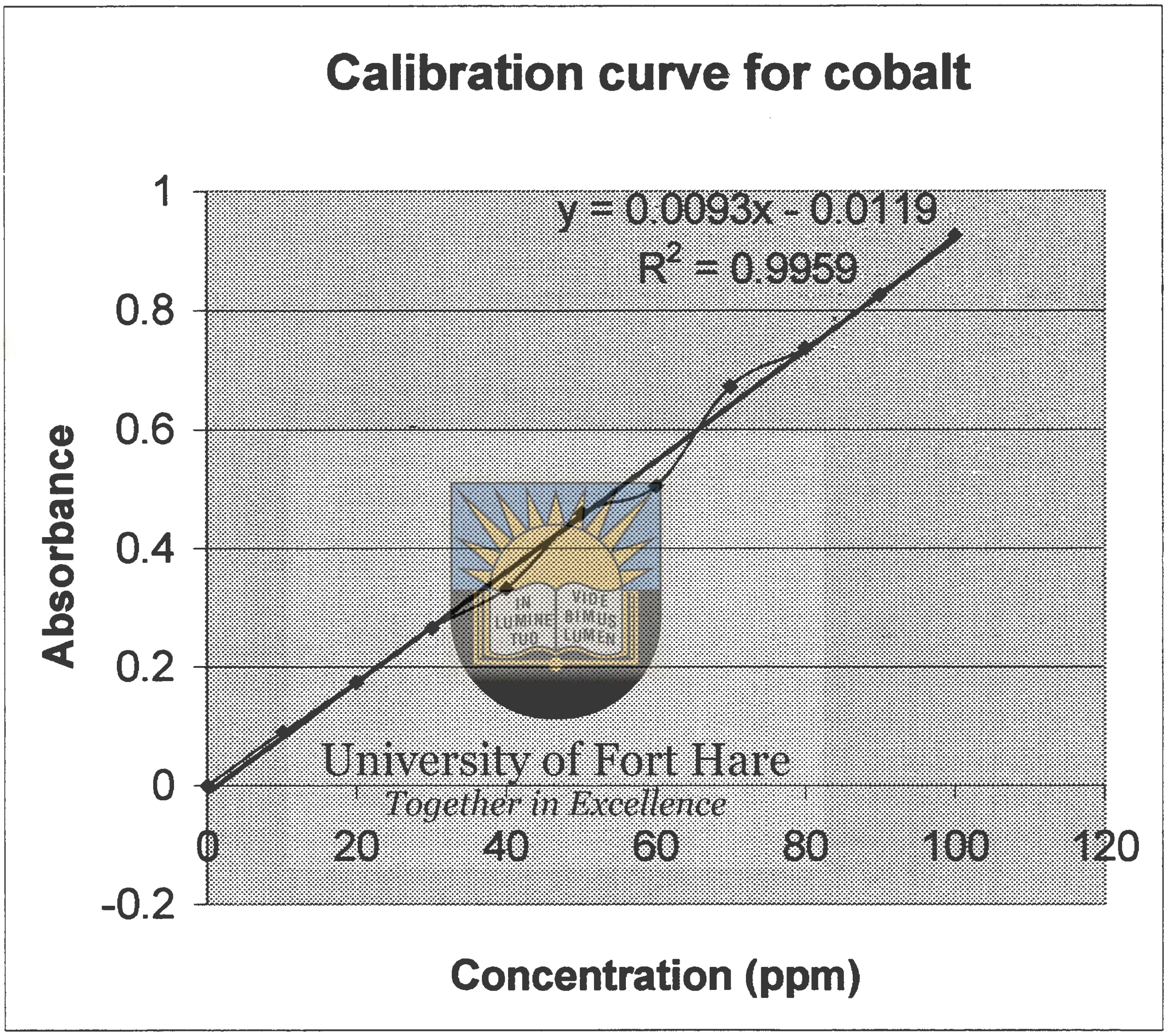


Figure 2.2 : Plot of concentration vs absorbance for cobalt

Table 2.4 : Concentration vs absorbance for titanium

Concentration (ppm)	Absorbance
0	0
10	0.0802
20	0.1718
30	0.2306
40	0.3210
50	0.4010
60	0.4812
70	0.6222
80	0.6416
90	0.7218
100	0.8020

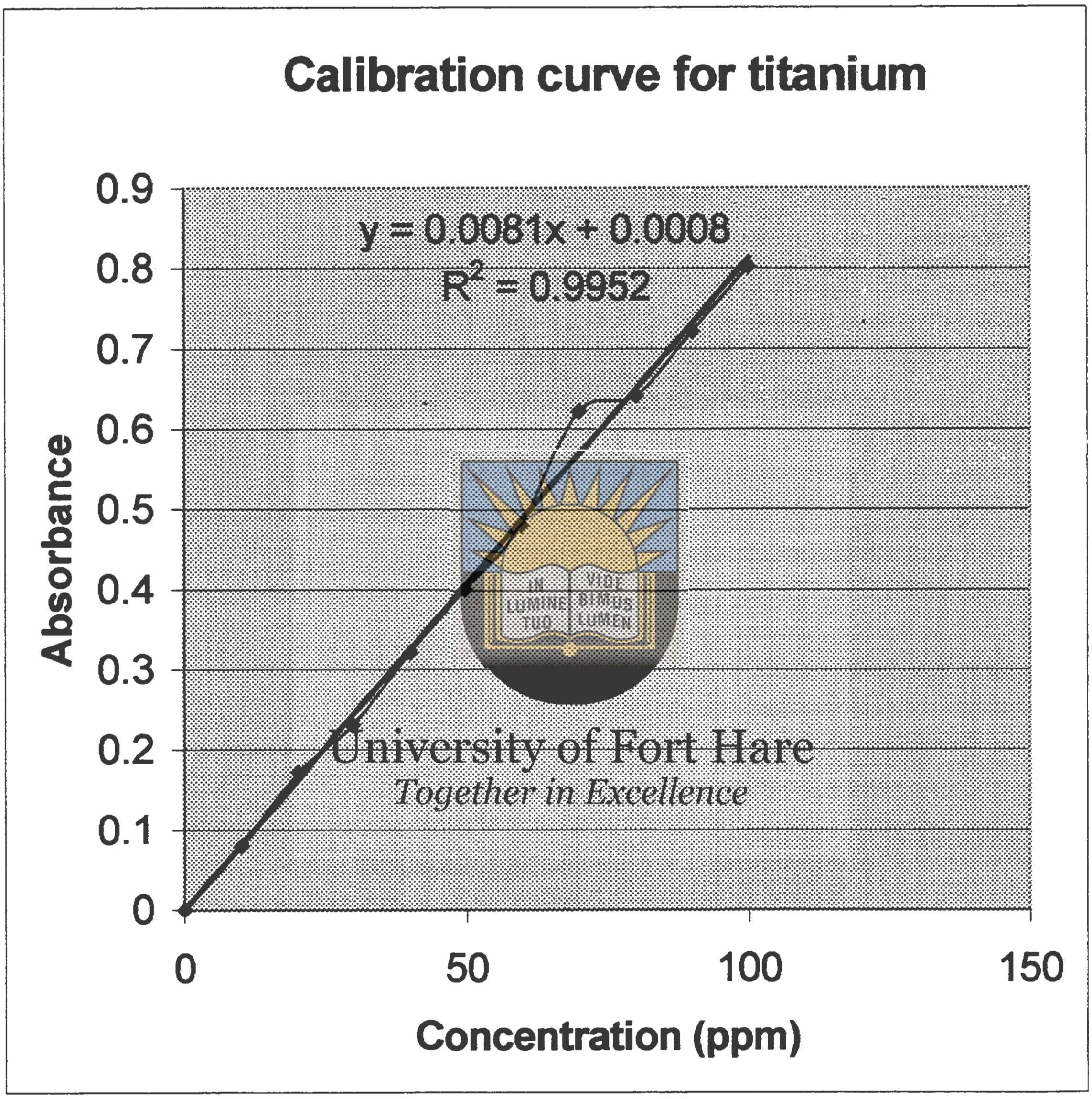


Figure 2.3 : Plot of concentration vs absorbance for titanium

Table 2.5 : Concentration vs absorbance for vanadium

Concentration (ppm)	Absorbance
0	0
10	0.0094
20	0.0189
30	0.0275
40	0.0378
50	0.0500
60	0.0571
70	0.0665
80	0.0756
90	0.0901
100	0.0944

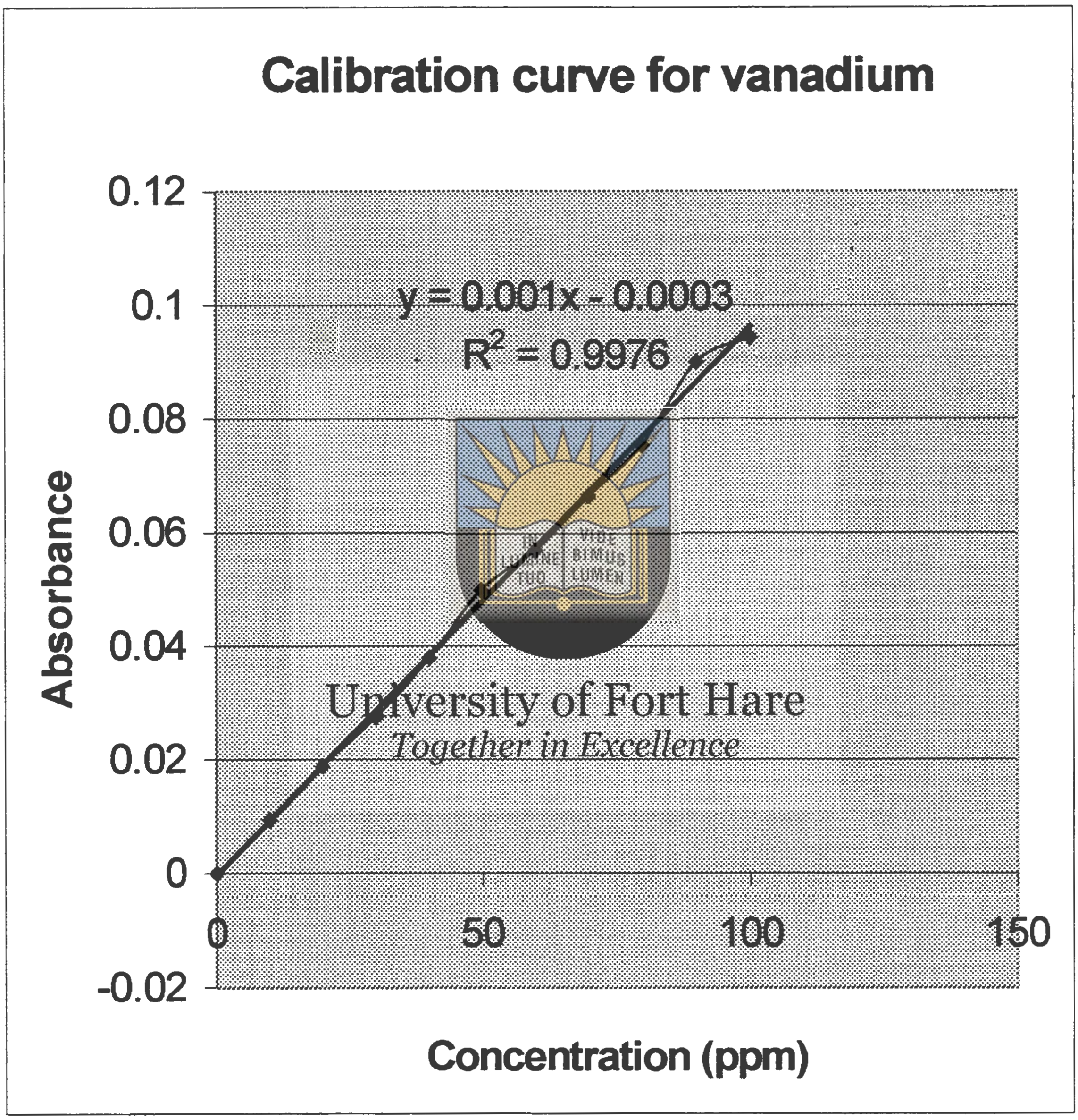


Figure 2.4: Plot of concentration vs absorbance for vanadium

Table 2.6 : Concentration vs absorbance for chromium

Concentration (ppm)	Absorbance
0	0
10	0.0162
20	0.0324
30	0.0504
40	0.0611
50	0.0789
60	0.0972
70	0.1134
80	0.1331
90	0.1458
100	0.1587

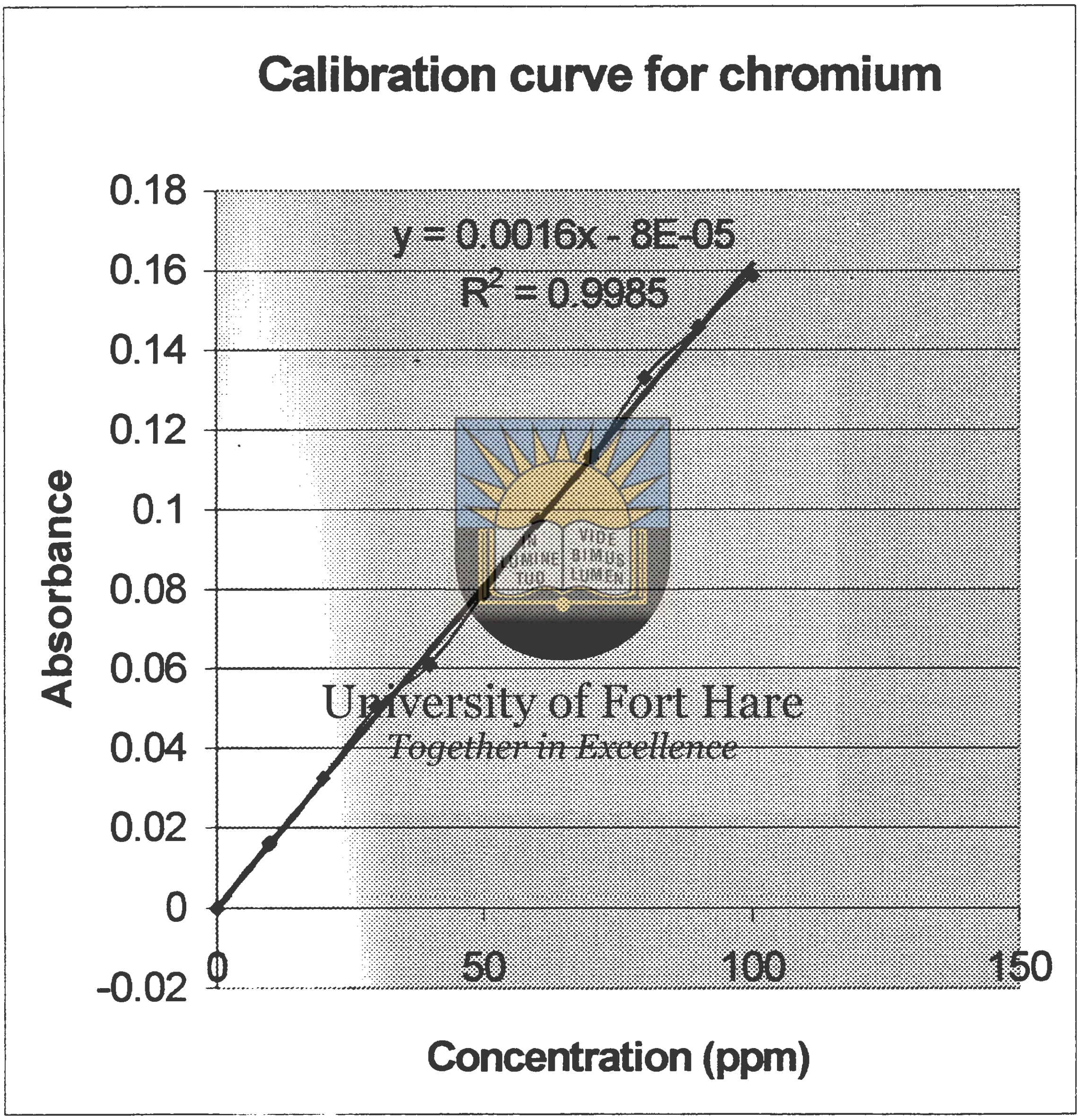


Figure 2.5 : Plot of concentration vs absorbance for chromium

Table 2.7: Concentration vs absorbance for manganese

Concentration (ppm)	Absorbance
0	0
10	0.0788
20	0.1575
30	0.2363
40	0.2985
50	0.4105
60	0.4725
70	0.5537
80	0.5931
90	0.7088
100	0.7875

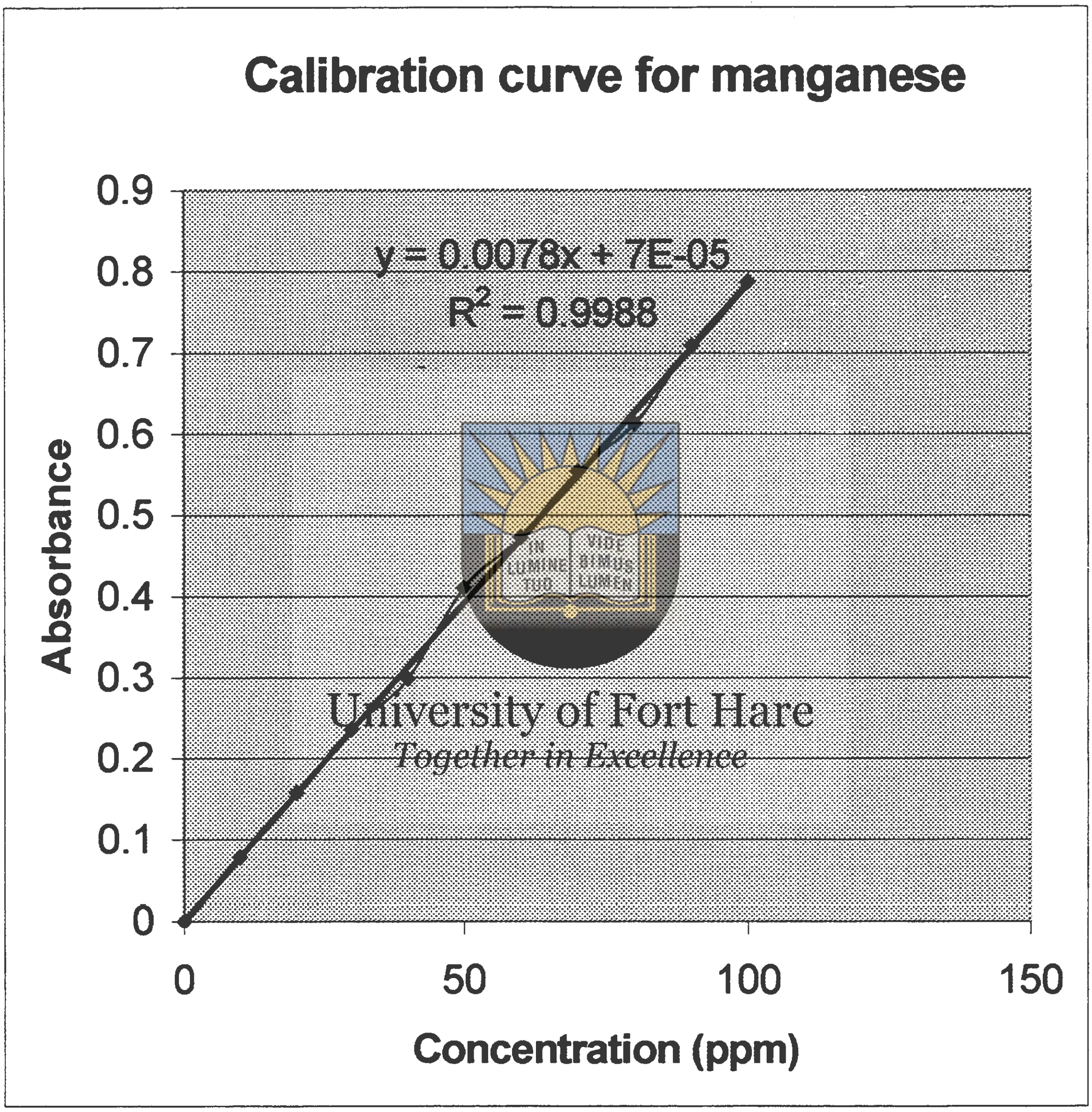


Figure 2.6 : Plot of concentration vs absorbance for manganese

Table 2.8: Concentration vs absorbance for iron

Concentration (ppm)	Absorbance
0	0
10	0.0614
20	0.1229
30	0.1843
40	0.2874
50	0.2992
60	0.3686
70	0.4201
80	0.4914
90	0.5529
100	0.5982

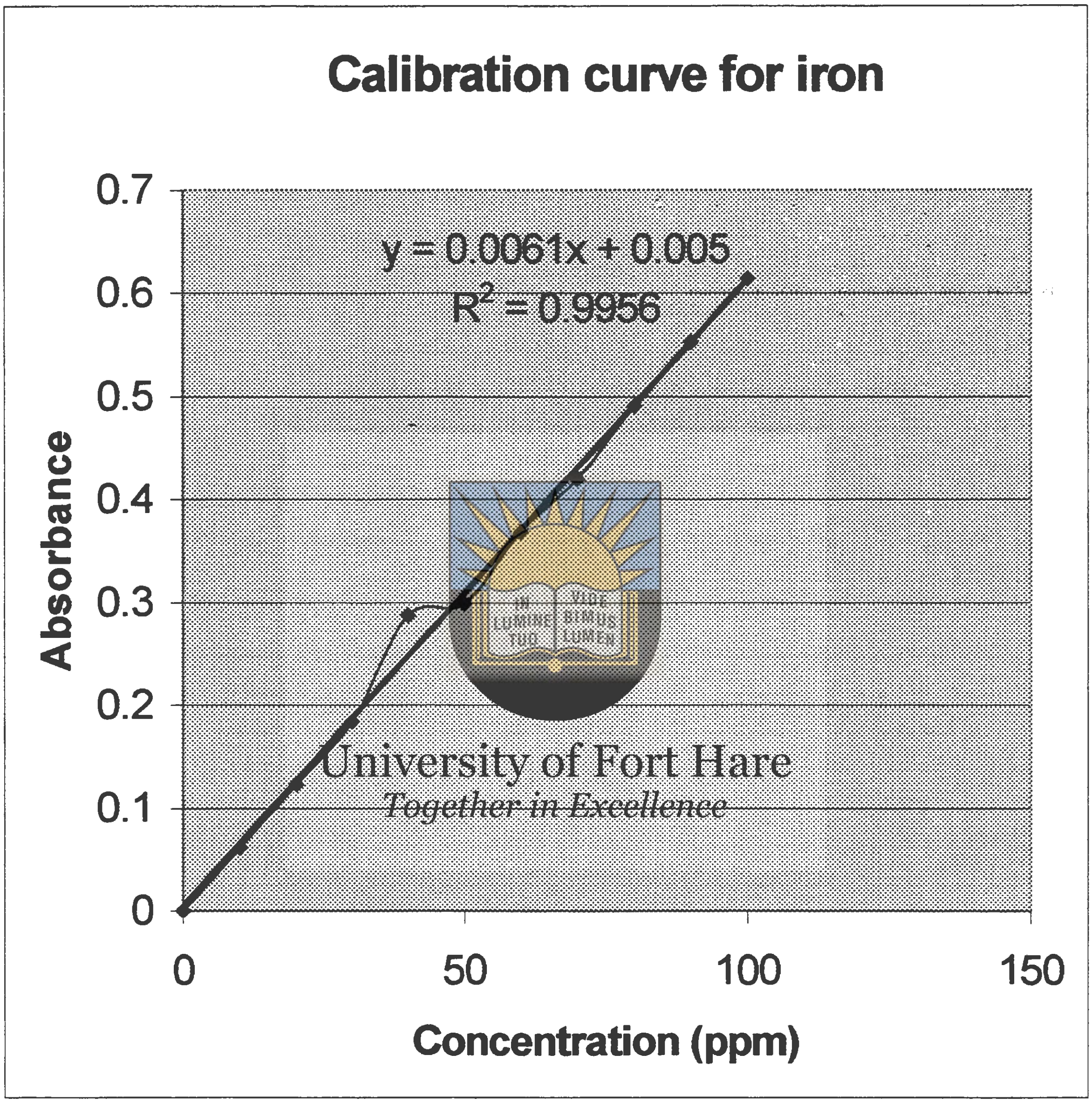


Figure 2.7: Plot of concentration vs absorbance for iron

Table 2.9 : Concentration vs absorbance for nickel

Concentration (ppm)	Absorbance
0	0
10	0.0990
20	0.1980
30	0.3100
40	0.3870
50	0.4954
60	0.5760
70	0.7292
80	0.8010
90	0.8731
100	0.9900

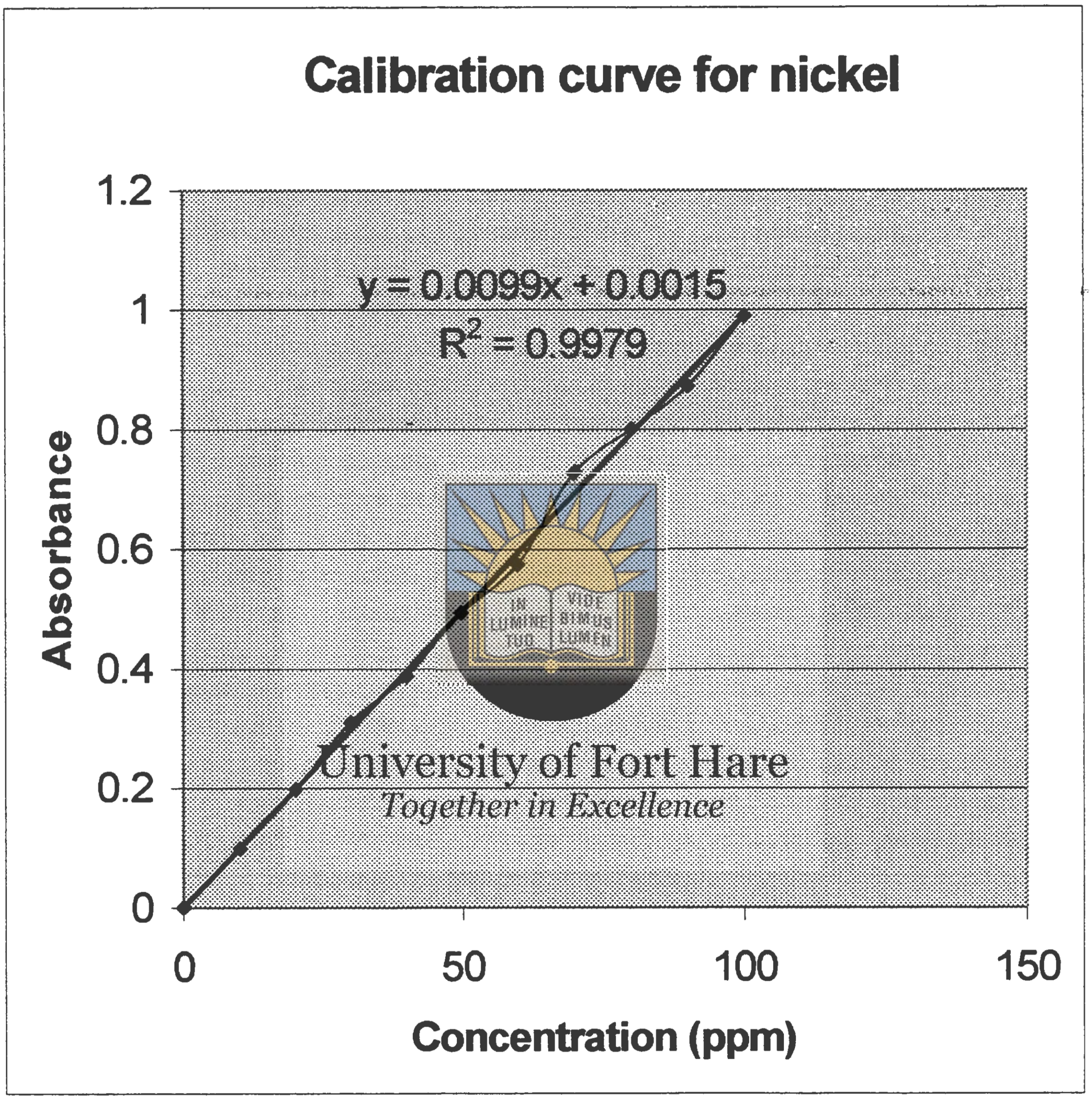


Figure 2.8 : Plot of concentration vs absorbance for nickel

Table 2.10 : Concentration vs absorbance for zinc

Concentration (ppm)	Absorbance
0	0
10	0.1067
20	0.2133
30	0.2997
40	0.4132
50	0.5533
60	0.6677
70	0.7789
80	0.8456
90	0.9671
100	1.0066

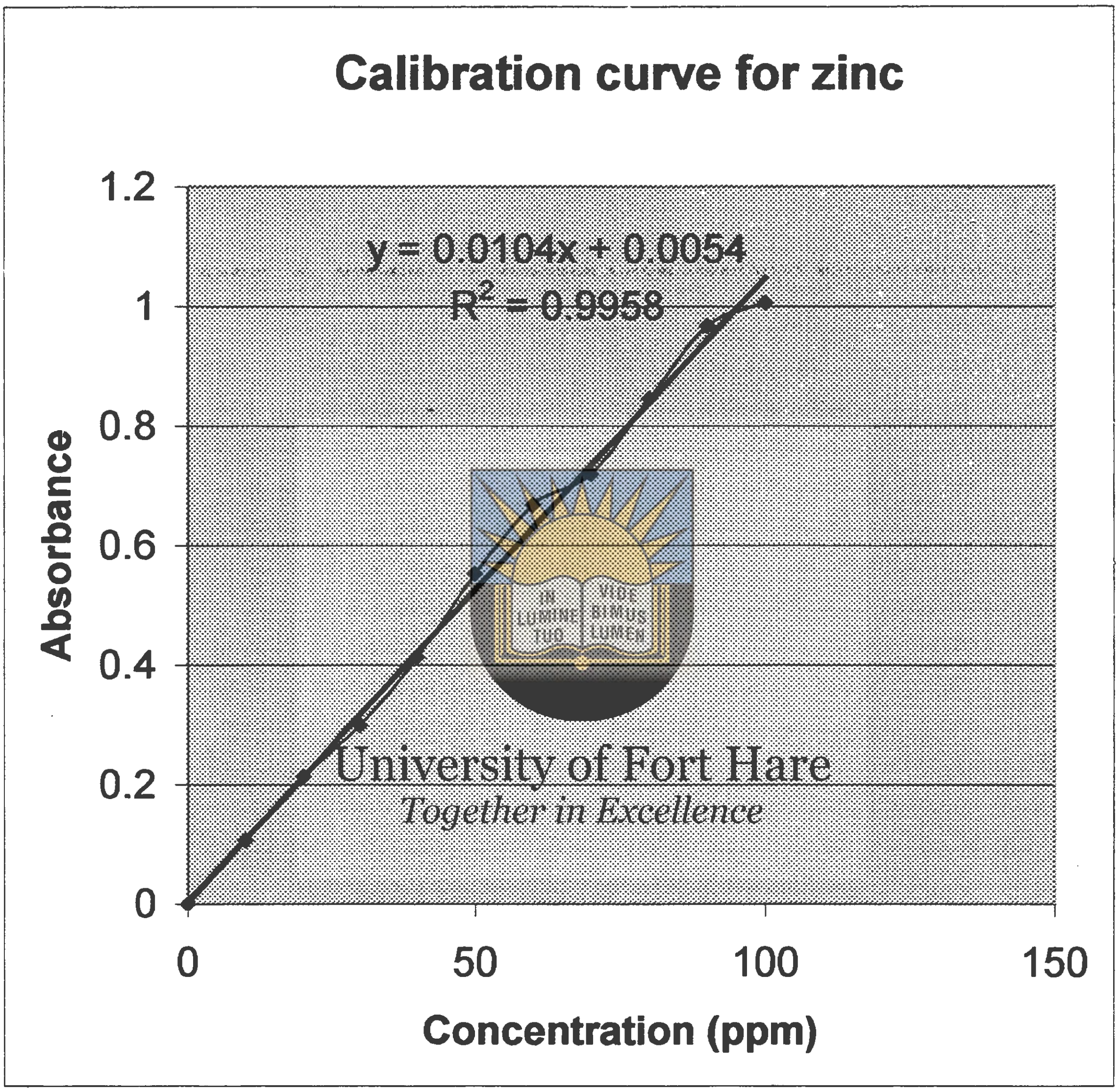


Figure 2.9 : Plot of concentration vs absorbance for zinc

Table 2.11: Concentration vs absorbance for molybdenum

Concentration (ppm)	Absorbance
0	0
10	0.1000
20	0.1790
30	0.2881
40	0.4010
50	0.4811
60	0.6101
70	0.6912
80	0.7932
90	0.9172
100	1.1002

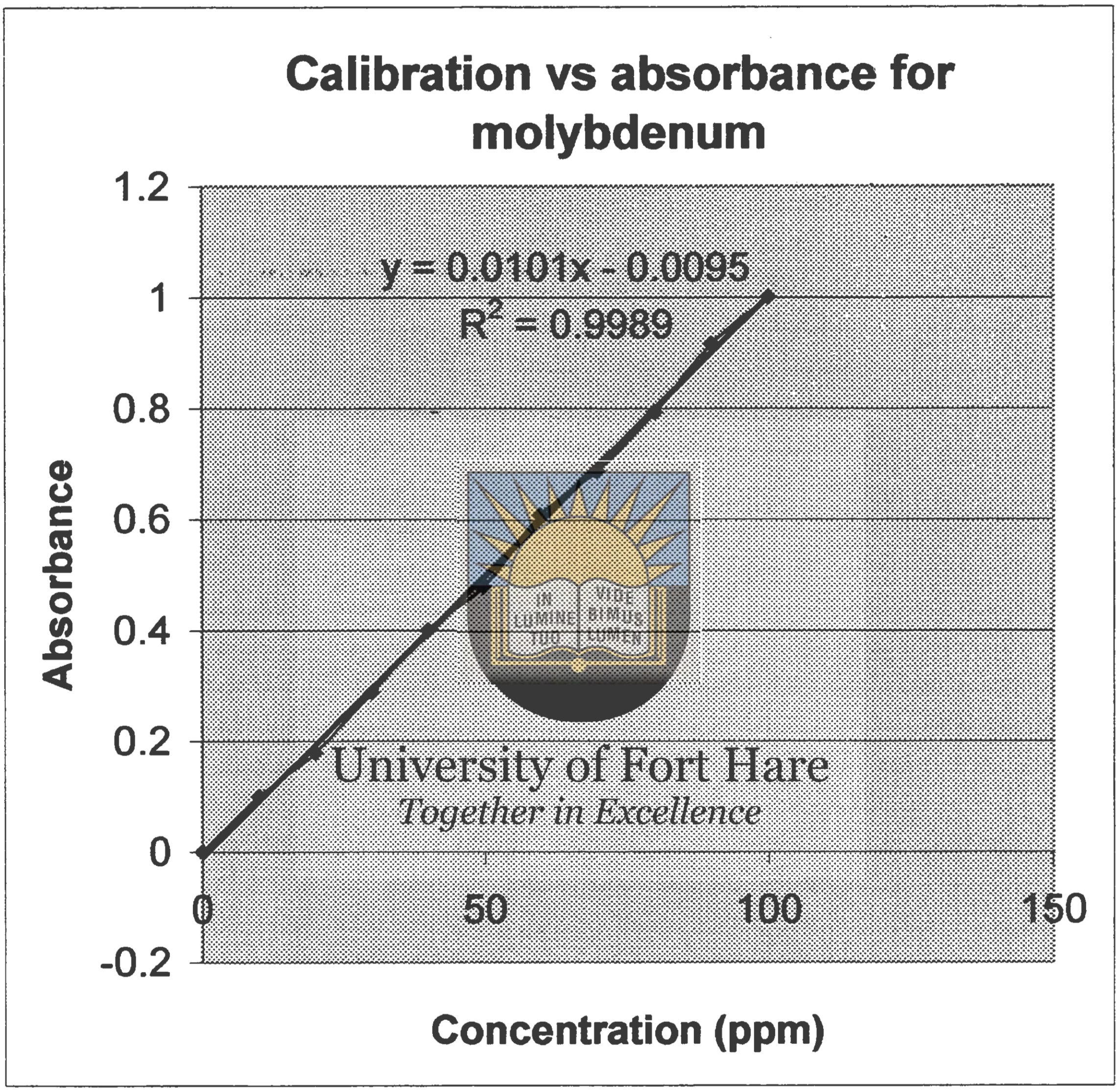


Figure 2.10: Plot of concentration vs absorbance for molybdenum

Table 2.12 : Concentration vs absorbance for silver

Concentration (ppm)	Absorbance
0	0
10	0.0345
20	0.0800
30	0.1151
40	0.1552
50	0.2000
60	0.2381
70	0.2761
80	0.3210
90	0.3576
100	0.4020

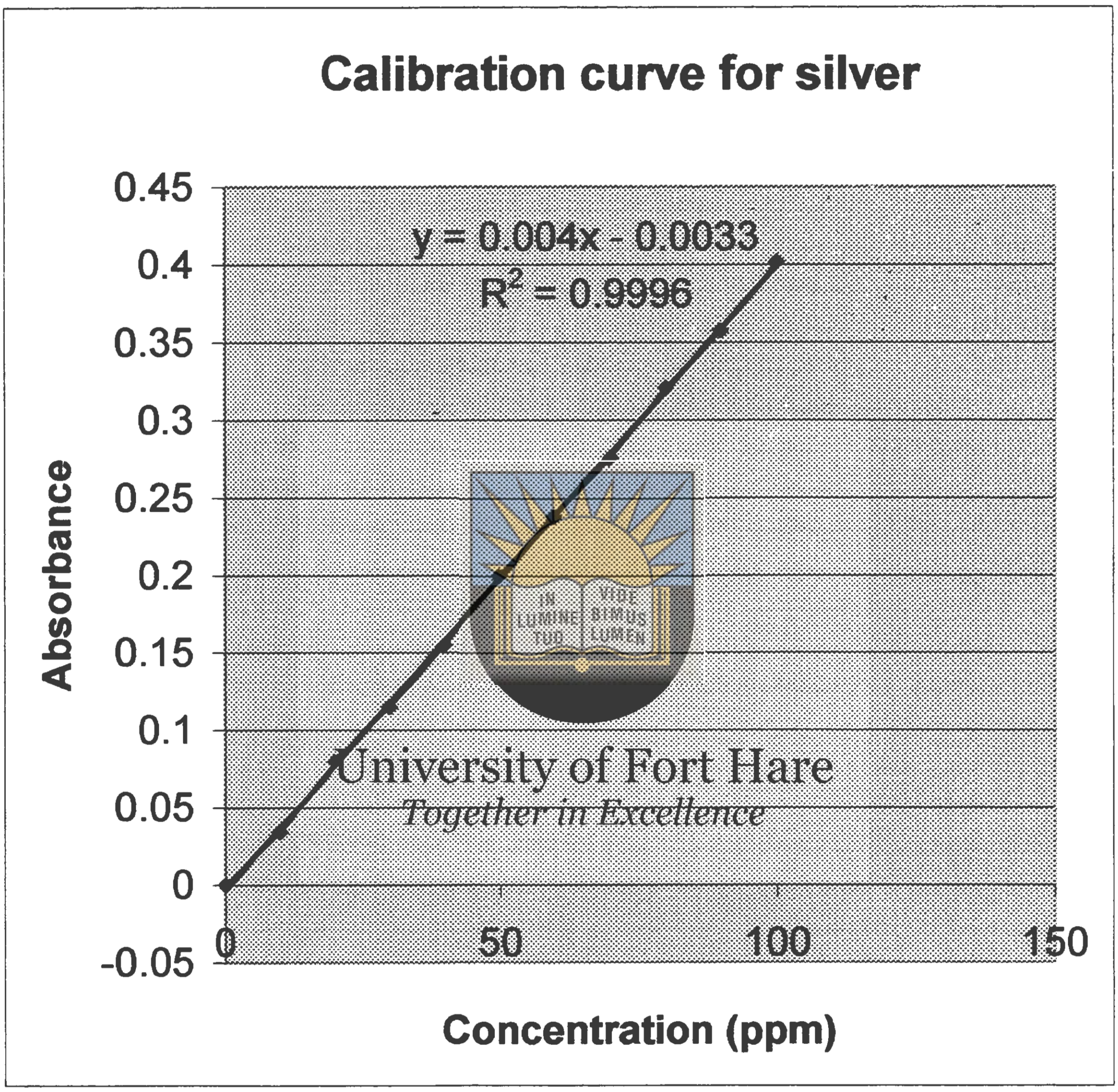


Figure 2.11: Plot of concentration vs absorbance for silver

Table 2.13 : Concentration vs absorbance for cadmium

Concentration (ppm)	Absorbance
0	0
10	0.0960
20	0.1700
30	0.255
40	0.3124
50	0.4250
60	0.5100
70	0.5950
80	0.6689
90	0.7986
100	0.8509

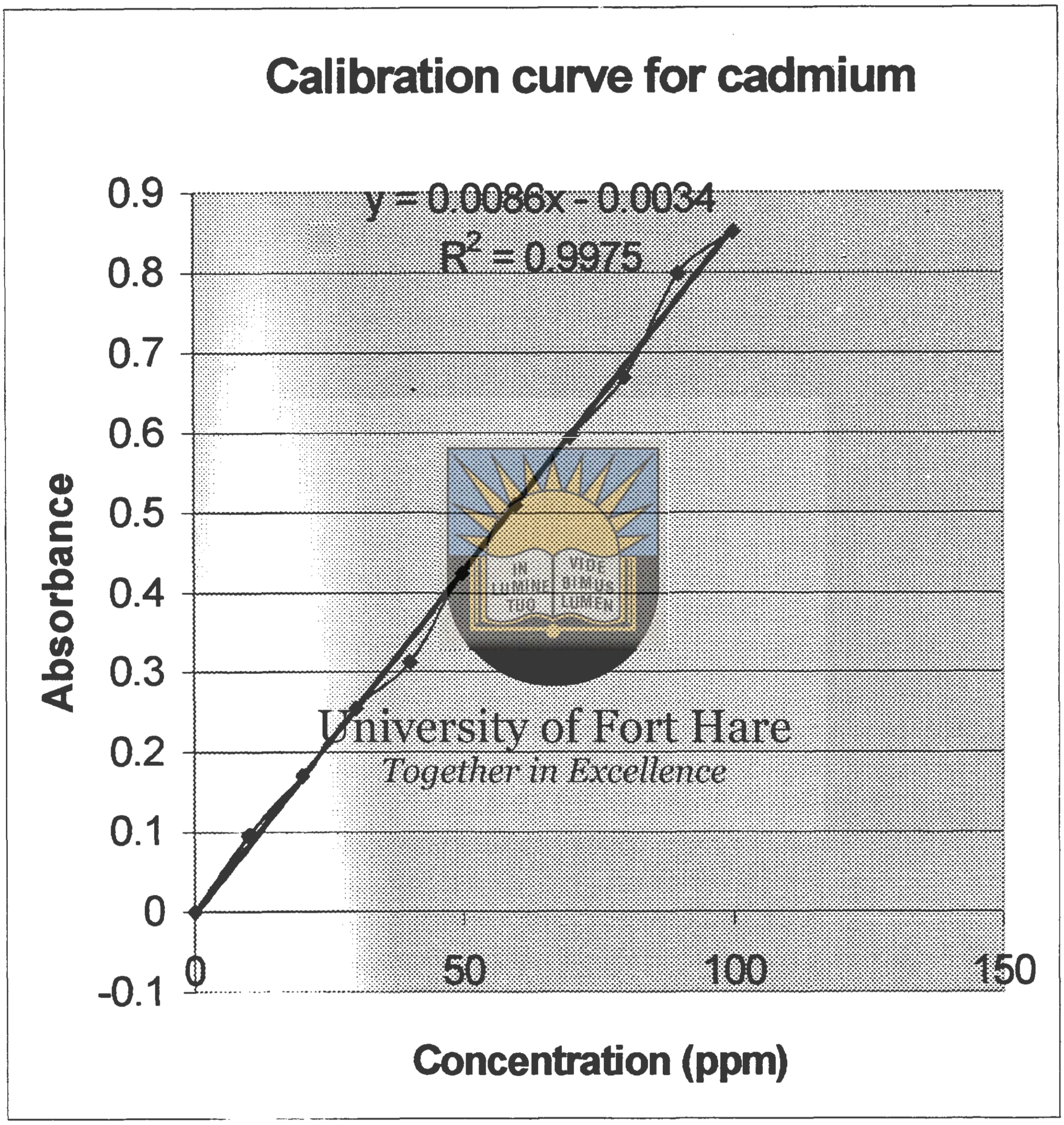


Figure 2.12: Plot of concentration vs absorbance for cadmium

Table 2.14 : Concentration vs absorbance for bismuth

Concentration (ppm)	Absorbance
0	0
10	0.0457
20	0.1000
30	0.1567
40	0.1997
50	0.2432
60	0.3001
70	0.3321
80	0.4121
90	0.4564
100	0.5106

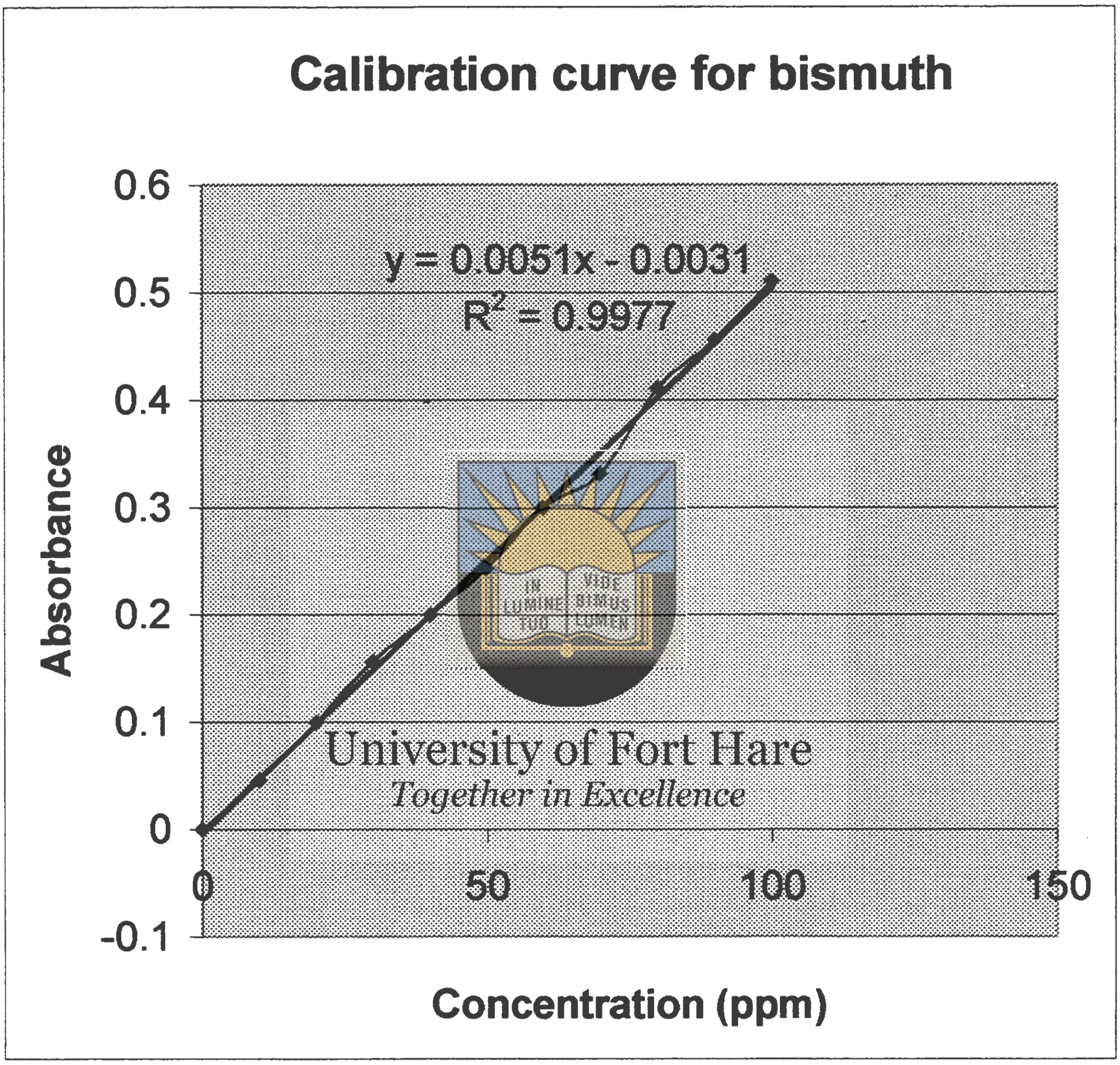


Figure 2.13 : Plot of concentration versus absorbance for bismuth

Table 2.15 : Concentration vs absorbance for selenium

Concentration (ppm)	Absorbance
0	0
10	0.0314
20	0.0627
30	0.0941
40	0.1123
50	0.1568
60	0.1882
70	0.2202
80	0.2509
90	0.3011
100	0.3378

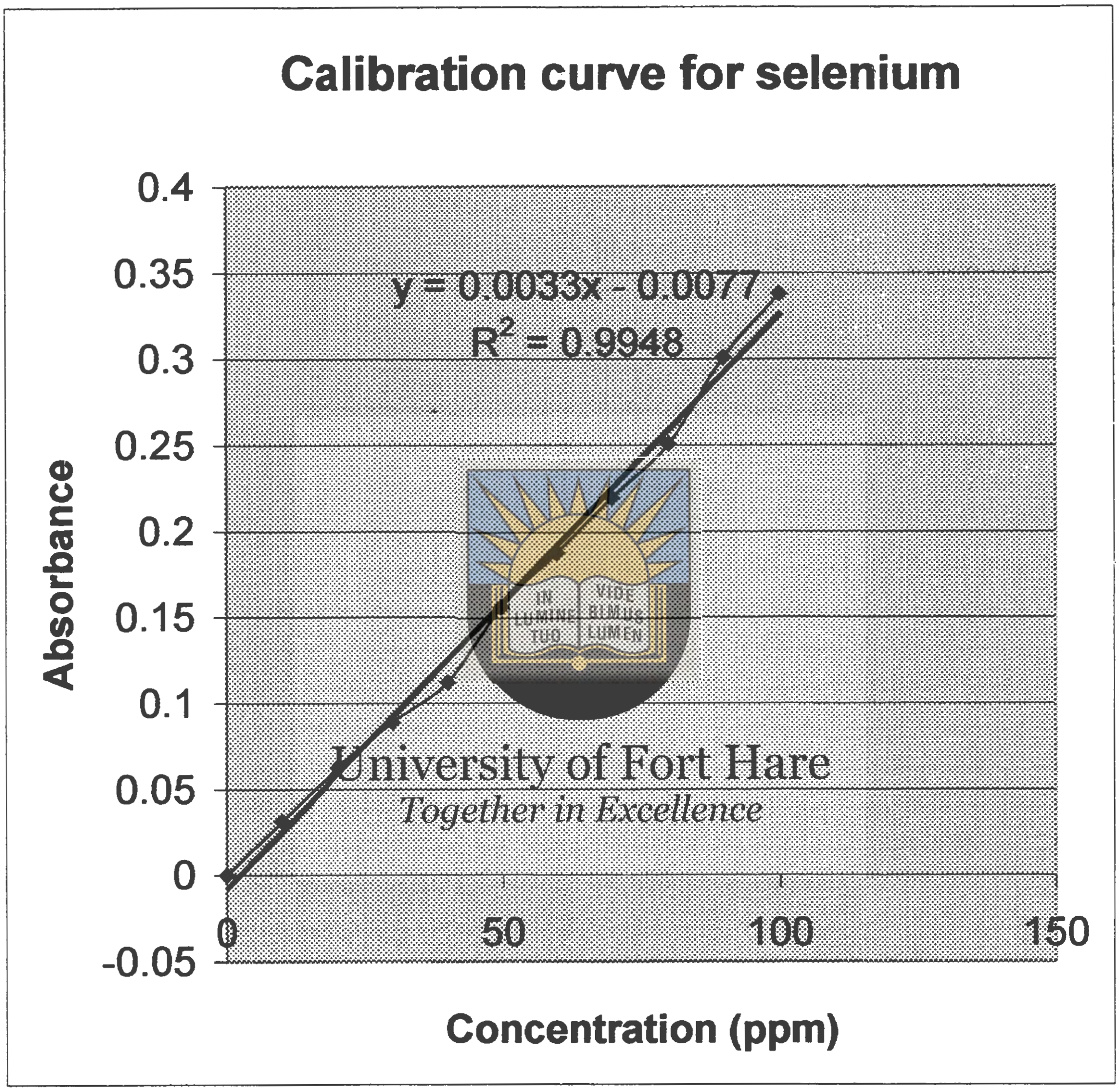


Figure 2.14 : Plot of concentration vs absorbance for selenium

Table 2.16 : Concentration vs absorbance for lead

Concentration (ppm)	Absorbance
0	0
10	0.0221
20	0.0442
30	0.0563
40	0.0776
50	0.1105
60	0.1326
70	0.1499
80	0.1688
90	0.1989
100	0.2210

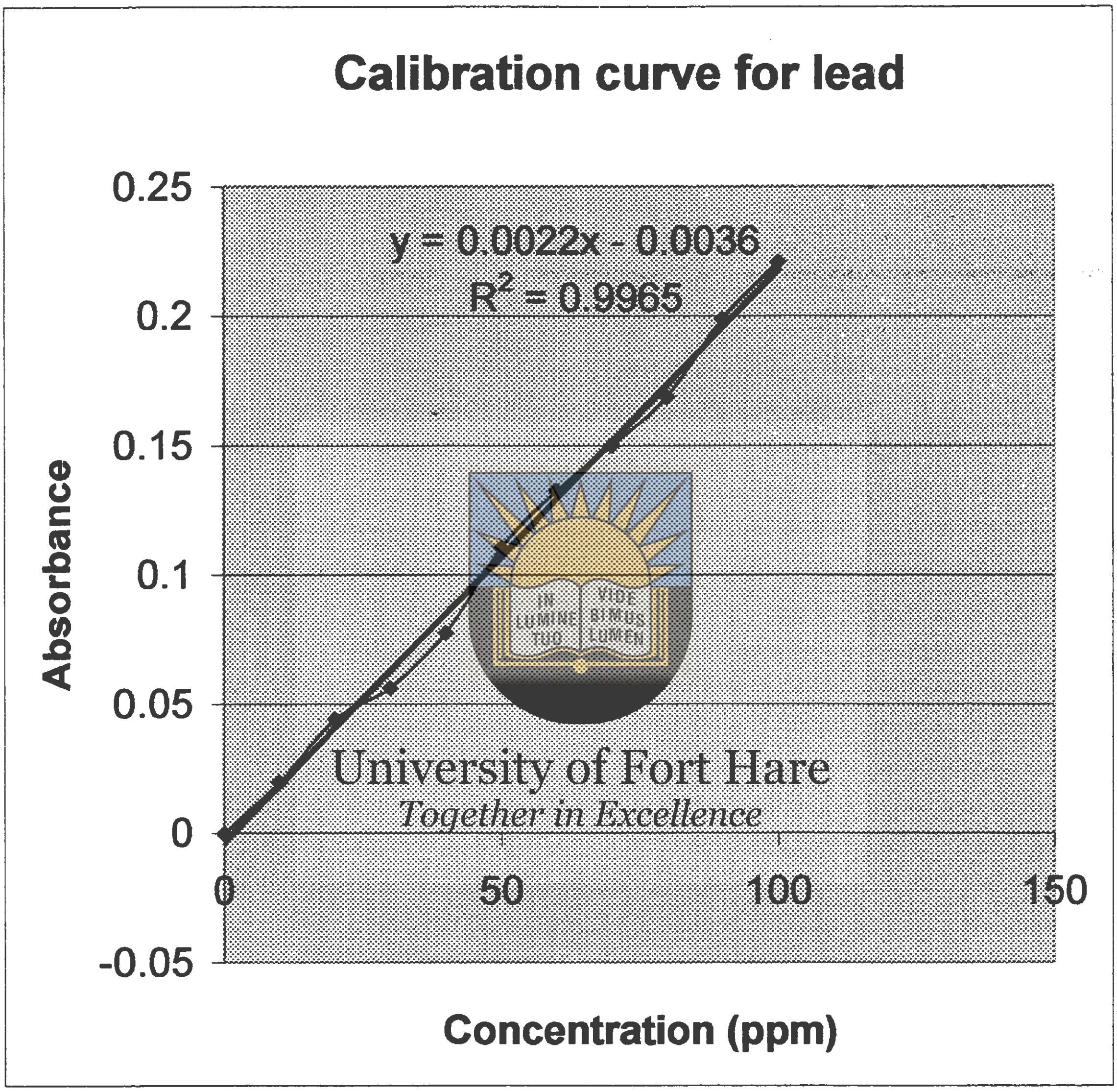


Figure 2.15 : Plot of concentration vs absorbance for lead

Table 2.17 : Concentration vs absorbance for calcium

Concentration (ppm)	Absorbance
0	0
10	0.0418
20	0.0839
30	0.1352
40	0.1672
50	0.1978
60	0.2508
70	0.2926
80	0.3344
90	0.2991
100	0.3971

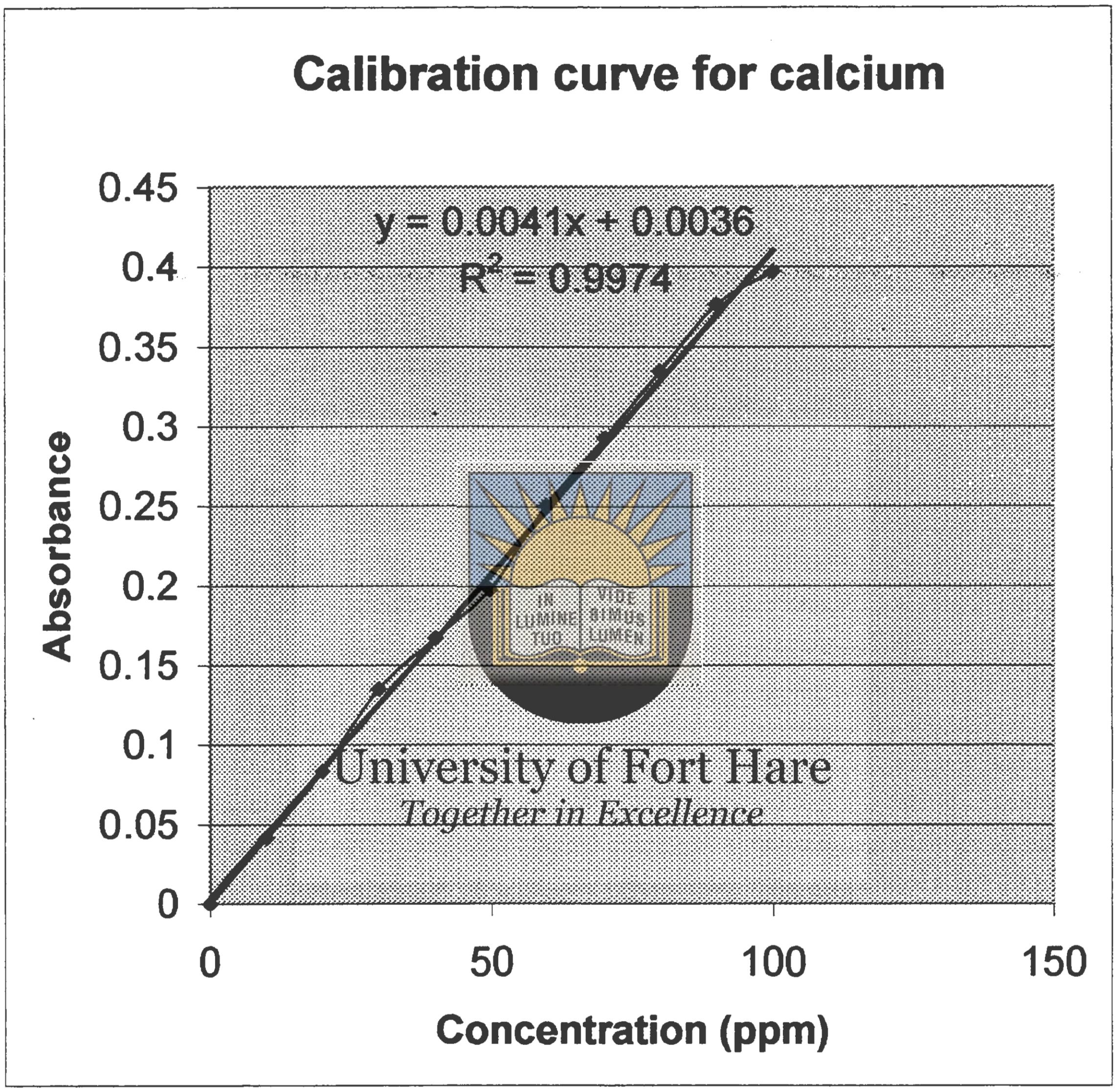


Figure 2.16 : Plot of concentration vs absorbance for calcium

Table 2.18: Concentration of elements in soil samples before separation by AAS

Element	Sample I mg/L	Sample II mg/L	Sample III mg/L	Mean	Variance	Standard deviation
1.Bismuth	3.97	3.43	3.15	3.51	0.174	1.410
2.Calcium	21.16	23.98	22.54	22.56	1.9882	0.417
3.Cadmium	0.117	1.67	0.765	0.851	0.608	0.779
4.Cobalt	16.01	20.78	30.98	22.59	58.484	7.648
5.Chromium	89.79	66.33	77.12	77.75	137.89	11.74
6.Copper	32.46	37.09	40.61	36.72	16.709	4.088
7.Iron	455.76	387.1	351.23	398.02	2821.21	53.12
8.Manganese	174.76	201.34	187	187.7	176.99	13.30
9.Molybdenum	0.901	0.352	0.699	0.651	0.07595	0.276
10.Nickel	75.13	80.76	90.11	82.00	57.255	7.567
11.Lead	13.79	16.99	20.01	16.93	9.6748	3.11
12.Selenium	0.585	0.112	0.976	0.558	0.187	0.432
13.Tin	0.511	0.967	1.212	0.897	0.127	0.356
14.Titanium	0.136	0.678	0.961	0.592	0.176	0.420
15.Vanadium	72.51	65.9	69.09	69.17	10.928	3.3058
16.Zinc	10.86	8.15	9.63	9.55	1.8412	1.357

Calculation of the mean, variance and standard deviations are shown in the following equations:

$$\text{Mean} = X = \frac{\sum_{1}^{n} X_i}{n},$$

$$\text{Variance} = S^2 = \frac{\sum_{1}^{n} (X_i - \bar{X})^2}{n-1}$$

$$\text{Standard deviation} = S = \sqrt{\frac{\sum_{1}^{n} (Xi - \overline{X})^2}{n-1}}\ .$$

2.7. General procedure for the separation of the multicomponent mixtures.

An aliquot (50 mL) of solution mixture (Bi, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn Ti, V and Zn) was taken into a 250 mL flask and its pH was first adjusted to 0.5 with dilute nitric acid and ammonium hydroxide. The solution was then transferred quantitatively into a 250 mL separatory funnel and 10 mL of thenoyltreiflouroacetone (TTA) was added before shaking with benzene for approximately one minute. The two phases were allowed to separate. The sixteen elements listed were then separated into four smaller groups on the basis of their ability to form complexes at different pH's which are soluble into different organic solvents. These groups are shown below.

Separation of elements into hypothetical groups (1-4)

Group 1 (Se, Mo, Ti and Sn)
(pH = 0.5 – 2.5)

Group 2 (Fe, Bi, Cu, V and Cd)
(pH = 3.00 – 4.90)

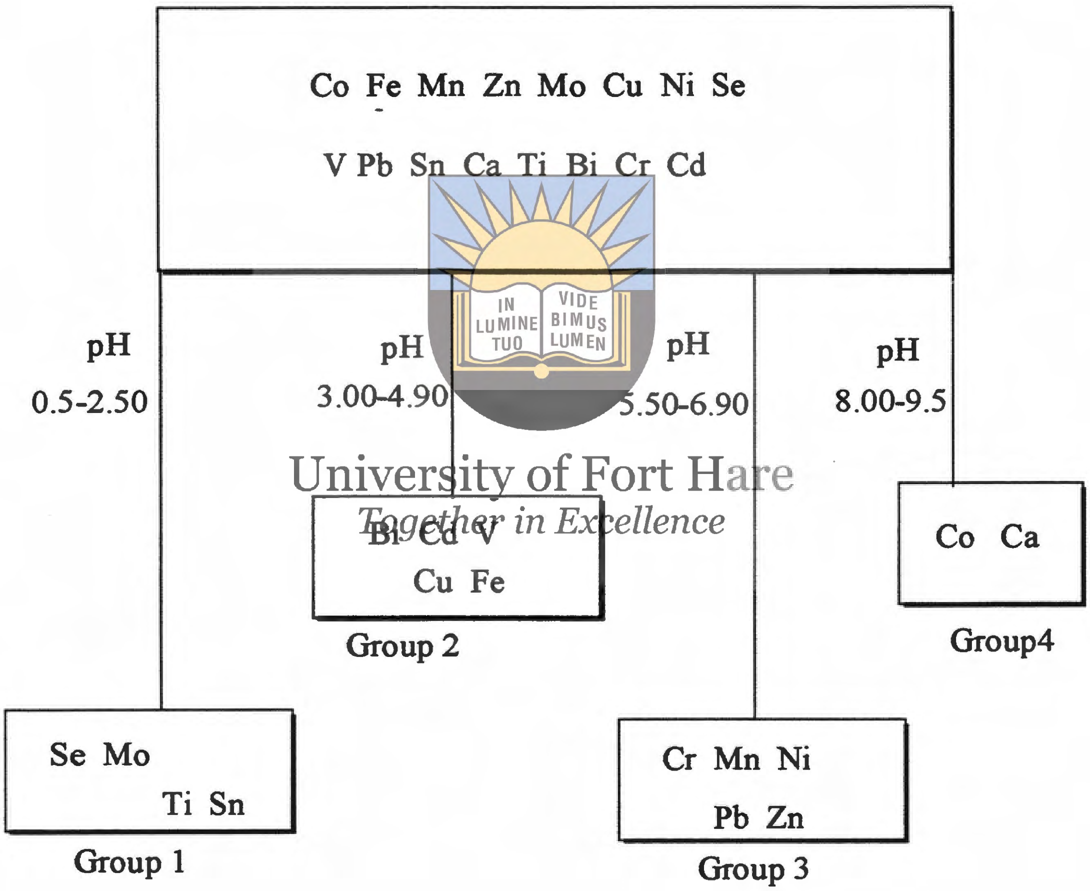
Group 3 (Cr, Mn, Pb, Zn and Ni)
(pH = 5.50 – 6.90)

Group 4 (Co and Ca)
(pH = 8.00 – 9.50)

Separation of the multi-component mixtures of complexes into four groups are summarized in scheme 1:

General scheme for the separation of the sixteen elements in four groups by varying the pH values.

Scheme 1



2.7.1 Separation procedure of the group 1 elements (Mo, Ti, Sn and Se)

An aliquot (50 mL) of solution containing Mo, Ti, Se and Sn was taken into a 100 mL flask and its pH was adjusted to 0.8. The solution was then transferred quantitatively into a 125 ml separatory funnel. Ascorbic acid was added as a masking agent to prevent any interferences from Ti, Sn and Se. On addition of 5 mL TTA in benzene, the separatory funnel was shaken for a minute and the two layers were allowed to settle then a molybdenum complex was precipitated which was 98% extracted into 3 × 10 mL benzene.

The pH of the aqueous solution was raised to 1.7 and a greenish-yellow precipitate of a Ti complex was formed which was then extracted into 3 × 10 mL benzene up to 96%. The optimum pH for the maximum [illegible]on of tin was found to be 2.5 with little interferences from selenium which was prevented by the addition of tartaric acid solution. The Sn-complex was extracted 98% in MIBK leaving Se in solution which was determined directly from the aqueous solution of this group and the concentration was found to be 98-99%. The separation by solvent extraction of this group of elements are shown in scheme 2. The extent of extraction are also given in table 2.19 and the pH vs %E curves are in figure 2.17

Scheme 2 : Separation chart of Group I elements (Mo, Se, Ti and Sn)

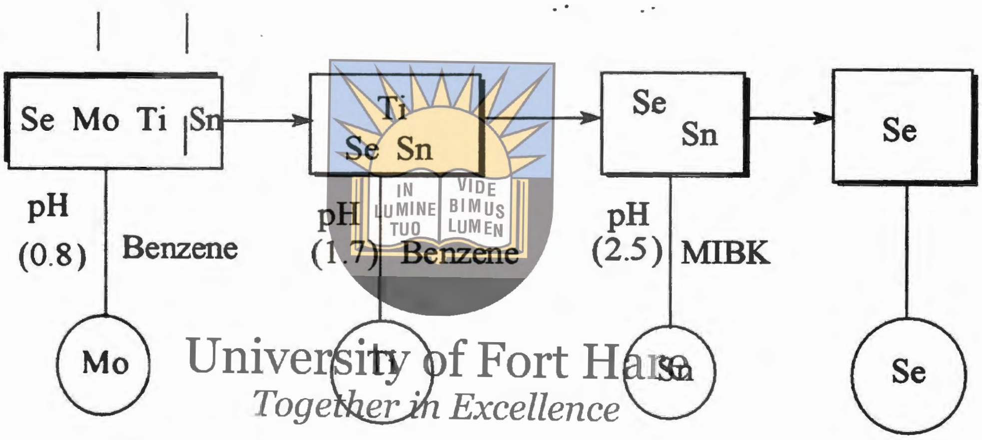


Table 2.19: Concentration (ppm) of elements after separation by AAS

Element	SampleI (ppm)*	% E**	SampleII (ppm)	%E	SampleIII (ppm)	%E
Mo	0.883	98(0.901)	0.345	98(0.352)	0.685	98(0.699)
Ti	0.131	96(0.136) -	0.651	96(0.678)	0.923	96(0.961)
Sn	0.501	98(0.511)	0.948	98(0.967)	1.188	98(1.212)
Se	0.576	98.5(0.585)	0.110	98(0.112)	0.961	98(0.976)

* These results are from three repetitions which showed excellent agreement

** figures in the parentheses are those obtained before extractions

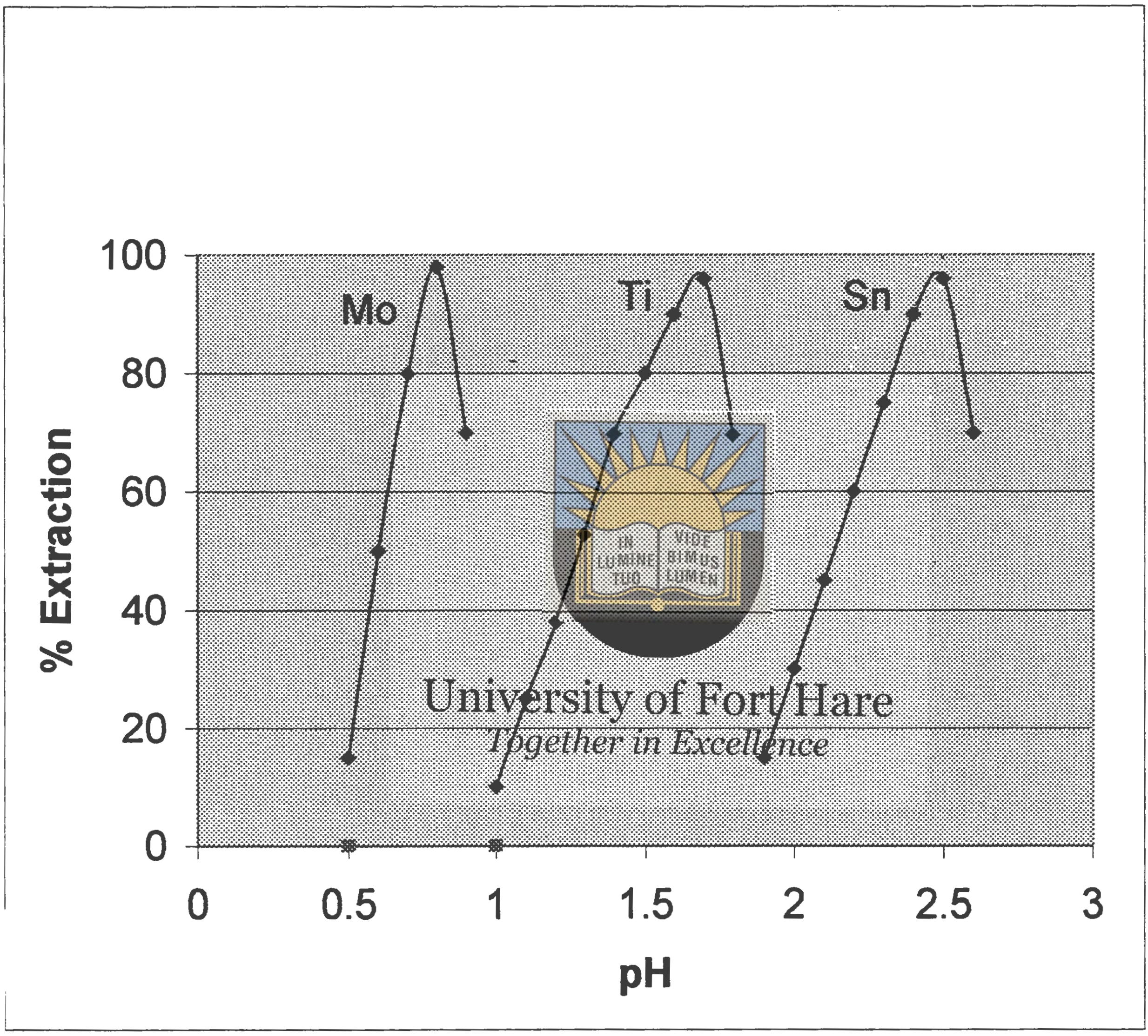


Fig 2.17 : pH vs % Extraction curves for Mo, Ti and Sn

2.7.2. Separation procedure of the group II elements (Fe, Bi, Cu, V and Cd)

Here, at pH 3.10, both Fe and Bi are precipitated where Bi was extractable almost completely (99%) in CCl_4 without any interference from Fe which was extracted into benzene to $\geqslant$ 95%. The pH of the aqueous solution was then increased to 3.7 which was found to be the most optimum for Cd which was readily extracted to 99% in chloroform.

Copper is the next element to be extracted in this group. A solution of mannitol was added to avoid interferences from vanadium. Raising the pH of the aqueous solution further to 4.5 resulted in the formation of a solid copper complex which was extracted to nearly 96% in benzene. Further raising the pH to 4.9, a coloured complex of vanadium reappeared which was 97 % extracted into n-butanol.

Separation of this group was achieved by using different extracting solvents which is summarized in scheme 3. Results of the extent of extraction are given in table 2.20 and the pH vs %E curves in figure 2.18

Scheme 3 : Separation chart for group 2 elements (Fe, Cu, V, Bi and Cd)

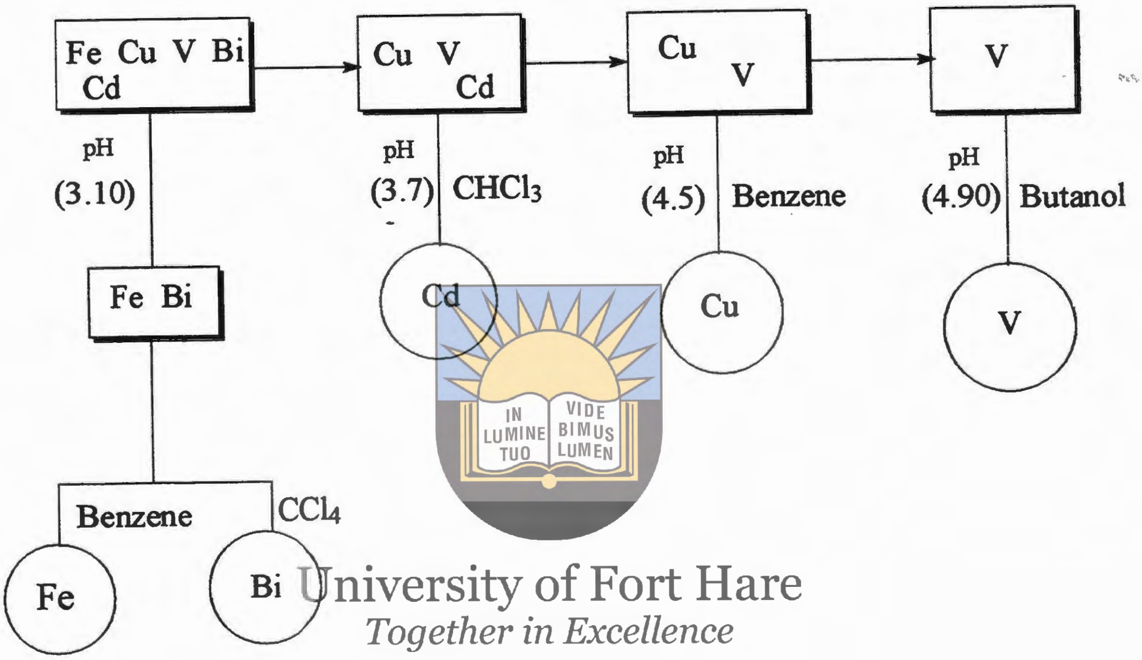


Table 2.20: Concentration (ppm) of elements after separation by AAS

Element	SampleI (ppm)*	%E**	SampleII (ppm)	%E	SampleIII (ppm)	%E
Fe	435.25	95(455.76)	369.68	95(387.1)	335.43	95(351.23)
Bi	3.93	99(3.97)	3.40	99(3.43)	3.12	99(3.15)
Cu	31.16	96(32.46)	35.61	96(37.09)	38.99	96(40.61)
V	70.33	97(72.51)	63.92	97(65.9	67.02	97(69.09)
Cd	0.116	99(0.117)	1.653	99(1.67)	0.758	99(0.765)

* These results are from three repetitions which showed excellent agreement

** figures in parentheses are those found before extractions for all four tables

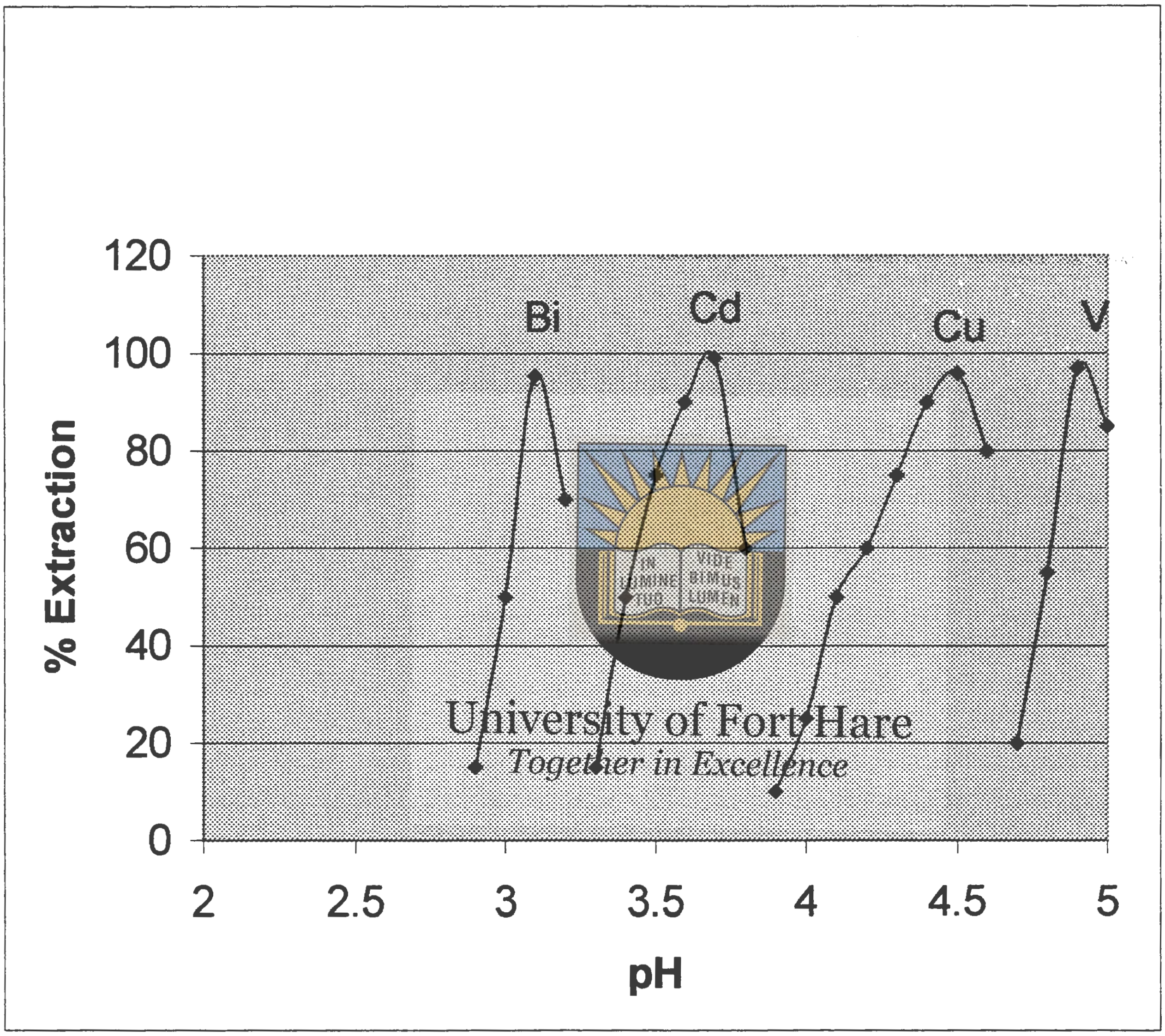


Fig 2.18 : pH vs % Extraction curves for Bi, Cd, Cu and V

2.7.3 Separation procedure of group III elements (Zn, Mn, Pb, Cr and Ni)

This group constitutes chromium, manganese, lead, zinc and nickel and their separation is marked by the interference of each other. On adjusting the pH of the solution to 5.50, adding EDTA to prevent interference the zinc-complex was precipitated out which was extracted approximately 97% into benzene. Raising the pH of the mixed solution to 6.10, both manganese and lead were precipitated which was extracted into benzene. Lead and manganese were separated by stripping off lead with 3 × 5mL of 1M nitric acid and manganese remained in the organic solution.

Chromium was the next element in this [illegible] separated and it required a weakly acidic medium. Firstly potassium cyanide was added as a masking agent for nickel and the pH was gradually increased to 6.85. When an insoluble orange complex of chromium was formed and was extracted to a maximum of 95.6% into 3 × 5mL benzene After extracting chromium with benzene, silver chloride solution was added to demask nickel which was recovered up to 96% of the original. Separation scheme for this group is summarized in scheme 4. Results of the extent of extraction are given in table 2.21 and the pH vs %E curves are given in figure 2.19.

Scheme 4 : Separation chart of group 3 elements (Cr, Ni, Zn, Mn and Pb)

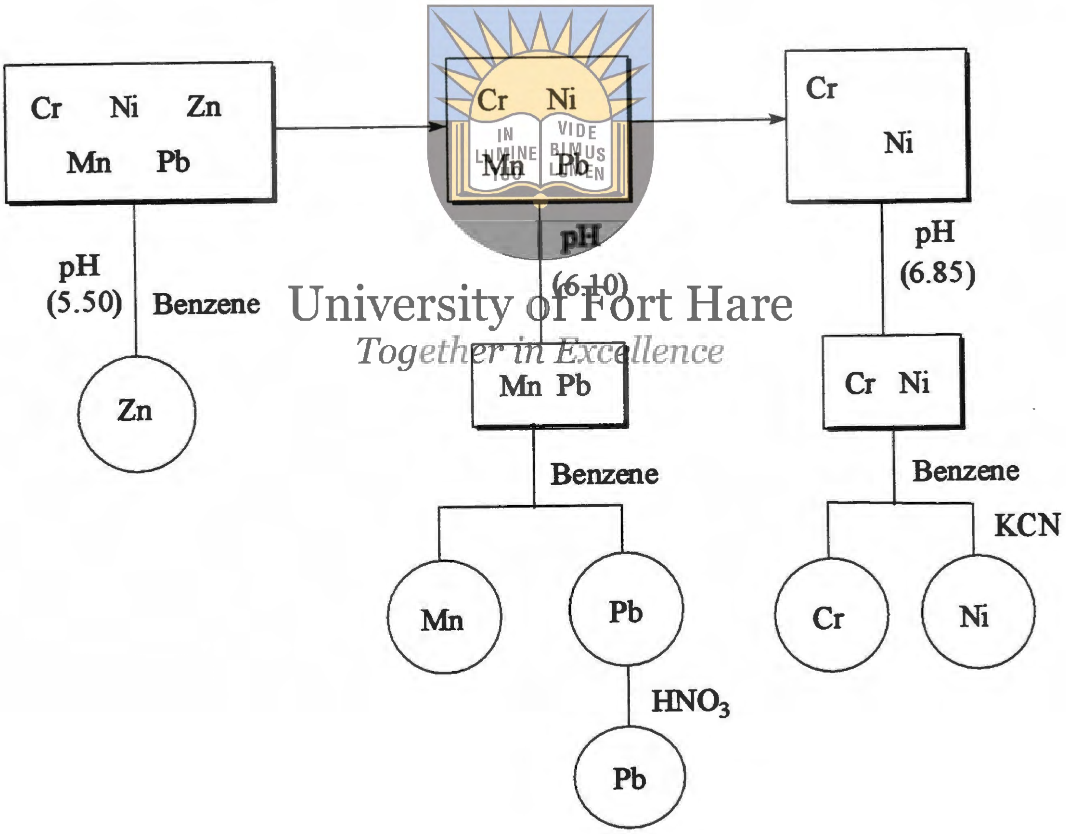


Table 2.21: Concentration (ppm) of element after separation by AAS

Element	SampleI (ppm)*	%E**	SampleII (ppm)	%E	SampleIII (ppm)	%E
Zn	10.43	96(10.86)	7.91	96(8.15)	9.34	96(9.63)
Mn	167.77	96(174.76)	193.29	96(201.34)	179.52	96(187)
Pb	13.51	98(13.79)	16.55	98(16.99)	19.61	98(20.01)
Cr	85.84	95.6(89.8)	63.41	95.6(66.33)	73.73	95.6(77.12)
Ni	72.13	96(75.13)	78.34	96(80.76)	87.41	96(90.11)

* These results are from three repetitions which showed excellent agreement

** figures in the parentheses are those found before extractions

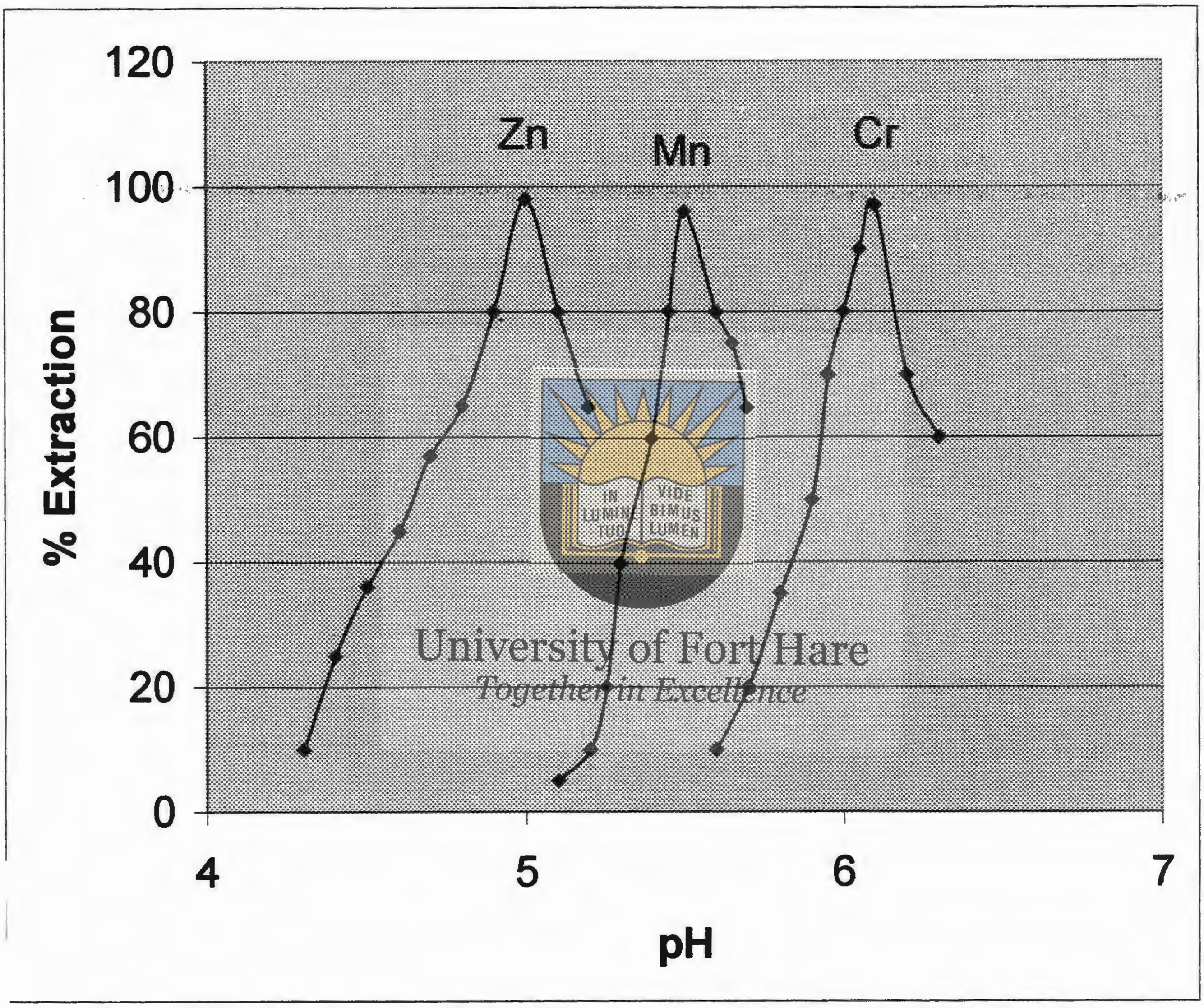


Fig 2.19: pH vs % Extraction curves for Bi, Cd, Cu and V

2.7.4 Separation procedure of group IV (Co and Ca)

Co and Ca were both extracted under alkaline media using the same ligand, TTA. The solubility of the complexes of Co and Ca was found to be completely different and this was used to our advantage during their separation. EDTA was added in the solution to eliminate any interferences from calcium. The pH of the aqueous solution was adjusted to 8.0 with ammonium hydroxide when Co-complex precipitated out which was extracted to 92% in isobutyl alcohol.

By raising the pH to 9.2, an insoluble complex of calcium was extracted to approximately 89% into benzene. Scheme 5 shows the separation chart of group 4, results of the extent of extraction in table 2.20 and the pH vs %E curves in figure 2.20

Scheme 5 : Separation chart for group 4 (Co and Ca)

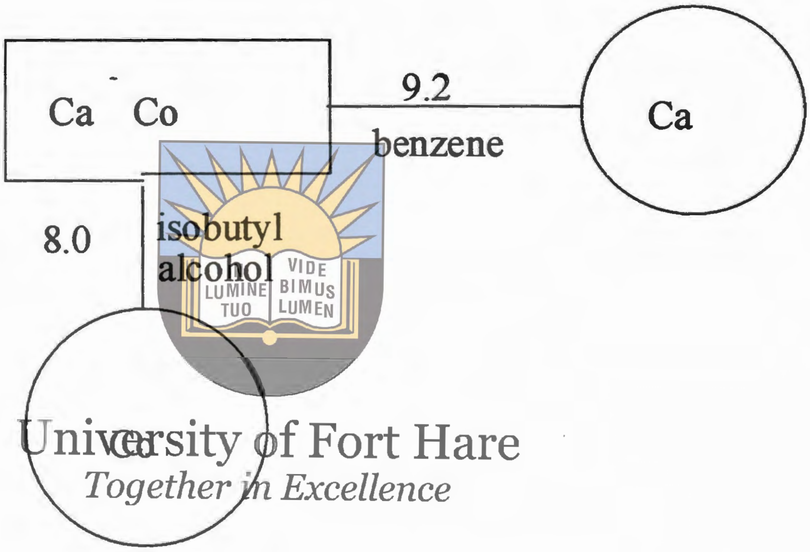


Table 2.22: Concentration (ppm) of elements after separation by AAS

Element	SampleI (ppm)	%E	SampleII (ppm)	%E	SampleIII (ppm)	%E
Co	14.73	92(16.01)	19.12	92(20.78)	28.50	92(30.98)
Ca	18.83	89(21.16)	21.34	89(23.98)	20.06	89(22.54)

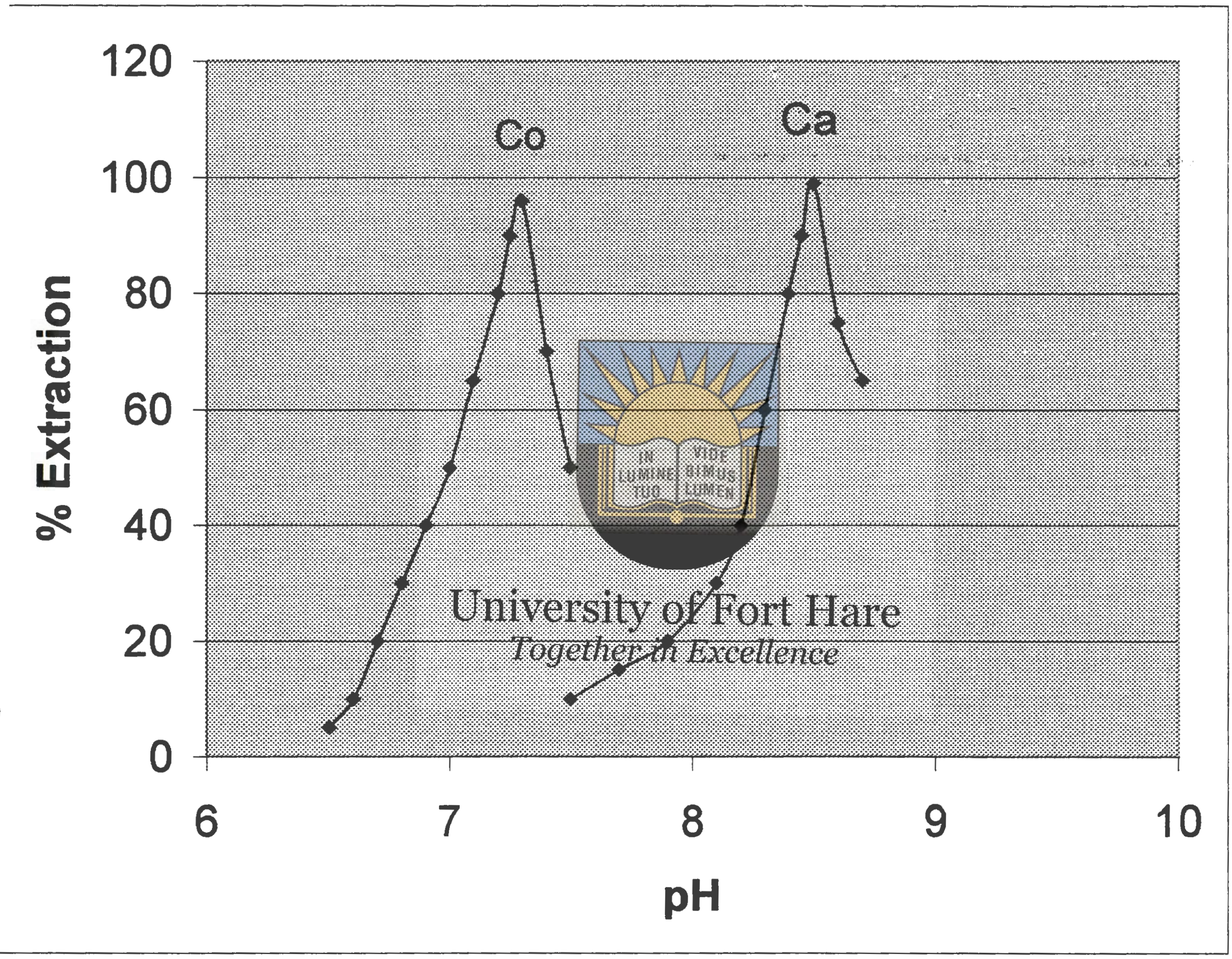


Fig 2.20 : pH vs % Extraction curves for Ca and Co

Table 2.23: Summary of results after extraction

Element	Sample I (ppm)	Sample II (ppm)	Sample III (ppm)
Bismuth (Bi)	3.93	3.40	3.12
Calcium (Ca)	18.83	21.34	20.06
Cadmium (Cd)	0.116	1.653	0.7574
Cobalt (Co)	14.75	19.12	28.50
Chromium (Cr)	89.79	66.33	70.03
Copper (Cu)	31.16	35.61	38.99
Iron (Fe)	387	455.76	351
Manganese (Mn)	174.76	201.78	187
Molybdenum (Mo)	0.883	0.345	0.685
Nickel (Ni)	72.13	78.34	87.41
Lead (Pb)	13.51	16.65	19.61
Selenium (Se)	0.576	0.110	0.961
Tin (Sn)	0.501	0.948	1.188
Titanium (Ti)	0.131	0.651	0.923
Vanadium (V)	72.51	65.9	69.09
Zinc (Zn)	10.43	7.91	9.34

Chapter 3

3. Results and Discussion

3.1 Preparation of soil samples for analysis

After removal of rocks, clays, leaves, grass etc by sieving, the soil organic matters were subjected to mixed oxidizing agents.

3.1.1. Destruction of organic matter by oxidation

The term 'soil organic matter' embraces the whole range of non-mineral fraction of soil including any vegetable or animal matters. The destruction of organic matter for trace element determination was first described by Fresenius and Von Babo[97]. Prior to the determination of metal ions in soil materials, the organic constituents were oxidized or removed to avoid interferences during analysis. Many method[98-99] have since been described for this purpose and most of these fall into two distinct classes: dry ashing and wet digestion. Dry ashing is usually accomplished by heating the sample to a relatively high temperature, generally between 400 and 700°C, in the presence of atmospheric oxygen which serves as the oxidant. Wet digestion means the removal of unwanted matters from the samples by sieving followed by oxidation of organic matters using a mixture of oxidizing acids containing $HClO_4$, HF, HNO_3 and H_2SO_4 at elevated temperatures. However, there are much differences of opinion as to the most preferred method. It has been emphasized[100] that there is no single procedure for wet ashing which will effectively oxidise a variety of biological materials. The combination of acids to be used should be carefully selected to avoid appreciable loss of volatile elements particularly Se, Cr and Mn. Selenium is quite volatile and cannot be dry ashed. It is lost even during wet digestion so perchloric acid had to be used[101-104]. Quantitative recovery of Cr was achieved by digesting the samples at lower temperatures (<100°C) in the presence of HF for 12 to 20 hours. Total recovery of Mo was achieved using the standard methods[105-106] such as oxidation in a combination of mixed acids, such as HCl, HF and HNO_3 , HCl, HNO_3 and $HClO_4$ or in 1:1 mixture of HNO_3 and $HClO_4$.

According to Christian and Feldman[107], the most commonly used acid mixture for wet digestion is a combination of nitric, [illegible] and perchloric acids in the ratio of 3:1:1.

3.2 Qualitative analysis of elements in the soil samples.

The electron microscopy and the AAS were used for this purpose and the following elements such as Co, Cu, Ca, Ti, Mn, Fe, Bi, Se, Ni, Zn, Pb, Cr, Cd, Sn, V and Mo were positively identified by both the techniques. However in the case of electron microscopy, Na, K and Mg were also detected.

3.3 Quantitative analysis before separation by AAS

As mentioned earlier that due to the limitations of hollow cathode lamps and other logistical problems, this investigation has been limited to only sixteen elements. Elemental concentrations (ppm) in 1 gram soil samples as determined by the AAS are compiled once again in table 3.1. A comparison of the observed values with those of the reported ones[108] (see table 3.2) clearly indicates that the elemental concentration of these soil samples fall well within the recommended ranges. A comparative study of the theoretical and actual values is summarized in table 3.3

Table 3.1 : Concentration (ppm) of the elements in the soil samples before separation

Element	**Sample I**	**Sample II**	**Sample III**
1.Bismuth	3.97	3.43	3.15
2.Calcium	21.16	23.98	22.54
3.Cadmium	0.117	1.67	0.765
4.Cobalt	16.01	20.78	30.98
5.Chromium	89.79	66.33	77.12
6.Copper	32.46	37.09	40.61
7.Iron	455.76	387.1	351.23
8.Manganese	174.76	201.34	187
9.Molybdenum	0.901	0.352	0.699
10.Nickel	75.13	80.76	90.11
11.Lead	13.79	16.99	20.01
12.Selenium	0.585	0.112	0.976
13.Tin	0.511	0.967	1.212
14.Titanium	0.136	0.678	0.961
15.Vanadium	72.51	65.9	69.09
16.Zinc	10.86	8.15	9.63

Table 3.2 : Theoretical values[108] of elemental concentrations (ppm) in soils

Element	**Theoretical values (ppm)[108]**
1. Bismuth	2 – 35
2. Calcium	10 – 100
3. Cadmium	0.1 – 2
4. Cobalt	1 – 40
5.Chromium	4 – 1000
6. Copper	0.5 – 130
7. Iron	> 75
8. Manganese	100 – 5000
9. Molybdenum	0.5 – 10
10. Nickel	0.1 – 150
11. Lead	10 – 200
12. Selenium	0.1 – 10
13. Tin	0.05 – 5
14. Titanium	0.05 – 2
15. Vanadium	10 – 100
16. Zinc	0.5 – 130

Table 3.3 : A comparative study of the theoretical and actual elemental concentrations (ppm) in soil samples

Element	**Theoretical values (ppm)**[108]	**Observed values (ppm)**
1. Bismuth	2 – 35	3 – 4
2. Calcium	10 – 100	20 – 25
3. Cadmium	0.05 – 2	0.1 – 2
4. Cobalt	1 – 40	15 – 35
5.Chromium	4 – 1000	50 – 90
6. Copper	0.5 – 130	31 – 41
7. Iron	> 75	350 – 460
8. Manganese	100 – 5000	170 – 202
9. Molybdenum	0.5 – 10	0.3 – 2
10. Nickel	0.1 – 150	70 – 91
11. Lead	10 – 200	12 – 25
12. Selenium	0.1 – 10	0.1 – 2
13. Tin	0.05 – 5	0.5 – 1.5
14. Titanium	0.05 – 2	0.1 – 1.0
15. Vanadium	10 – 100	60 – 75
16. Zinc	0.5 – 130	7 – 12

It has been reported that the pH of the soil has a large impact on the distribution of elements in soil as most of these remain insoluble at higher pH. The pH of the three soil samples in the non-arid land was found to be slightly alkaline and these are summarised in table 3.4.

Table 3.4 : The observed pH values for the three soil samples

Identity of the soil sample	**pH**
Sample I	7.45
Sample II	7.03
Sample III	7.87

3.4 Solvent extraction

Liquid-liquid extraction is a process of transferring a chemical compound from one liquid phase into another one which are immiscible. In such analysis, one phase is usually water and the other is a suitable organic solvent such as benzene, chloroform, carbon tetrachloride or some other organic solvents which are water-immiscible. When such a liquid is added to water, two layers are formed. Whether the organic liquid would be in the upper or lower layer depends on its density being lighter or denser than water. Sample mixtures with ligand are shaken vigorously with an immiscible organic solvent and the mixture is allowed to stand until the two solvent layers were separated out. If the complex of any particular element has a greater affinity for one of the organic solvent than water, it will readily be transferred from aqueous into organic media.

In the current investigation, we extensively applied this versatile technique for the separation of sixteen elements that have been qualitatively identified in soil samples using thenoyltriflouroacetone (TTA) as a single ligand. Separation and isolation of individual components was obtained from the mixtures by using the influences of the following parameters:

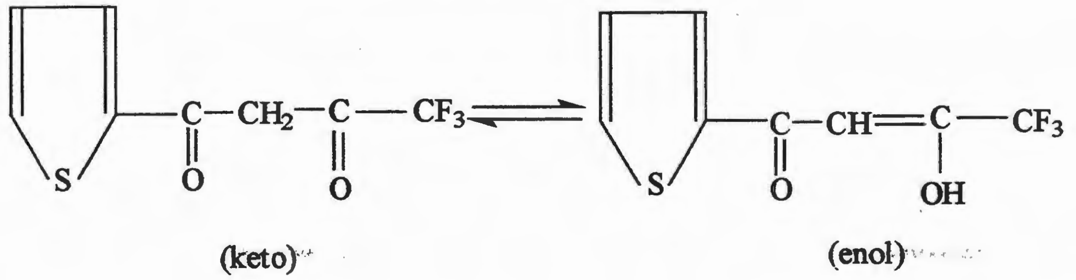
a. pH values
b. extracting organic solvent
c. complexing reagent (ligand)
d. masking and demasking agents

There are also other factors that are critical in enhacing the selectivity, such as the shaking and waiting time and the concentration of the complexing reagent.The results of the concentrations (ppm) of the elements after extraction are summarized once again in table 3.5 :

Table 3.5 : Summary of results after extraction

Element	Sample I (ppm)	Sample II (ppm)	Sample III (ppm)
Bismuth (Bi)	3.93	3.40	3.12
Calcium (Ca)	18.83	21.34	20.06
Cadmium (Cd)	0.116	1.653	0.7574
Cobalt (Co)	14.75	19.12	28.50
Chromium (Cr)	89.79	66.33	70.03
Copper (Cu)	31.16	35.61	38.99
Iron (Fe)	455.76	387	351
Manganese (Mn)	174.76	201.78	187
Molybdenum	0.883	0.345	0.685
Nickel (Ni)	72.13	78.34	87.41
Lead (Pb)	13.51	16.65	19.61
Selenium (Se)	0.576	0.110	0.961
Tin (Sn)	0.501	0.948	1.188
Titanium (Ti)	0.131	0.651	0.923
Vanadium (V)	72.51	65.9	69.09
Zinc (Zn)	10.43	7.91	9.34

3.4.1 Nature of the ligand used



Thenoyltriflouroacetone (TTA) was introduced as an analytical reagent by Calvin and Reid[109] in 1947. Many β-diketones containing the triflouromethyl group [RCOCH(R')COCF$_3$] have been synthesized by the Claisen condensation[110] method of ethyltriflouroacetone with a series of alkyl or aryl methyl ketones. Thenoyltriflouroacetone is a white crystalline solid (m.w. = 222.2, m.p. = 42.5-43.2 C) practically insoluble in water, but readily soluble in organic solvents. Because of the presence of the triflouromethyl group it has high acidity in the enol form, which is useful in for the extraction of many metals at low pH's. With metal ions, it forms chelates which are extractable into water-immiscible organic solvents. In alkaline solution, it is partly converted into the enol form, which lowers the distribution ratio. This is supported by the fact that in this investigation, the percentage extraction of the metal ions under alkaline media was low compared to those in the acidic media. For example, Co and Ca were extracted only about 92% and 89% at pH 8.00 and pH 9.50 respectively. This reagent has an acid dissociation constant of 6.7×10^{-7} at 25°C which enables larger amount of extraction.

Studies of TTA equilibria in solution show that the principal species in the aqueous phase is the hydrate which is supported by Connick and Mcvey[111], and in benzene 85% of the TTA occurs in the enol form. King and Reas[112-113] found that the activity coefficient of 0.01 M reagent in benzene to be less than unity. Above pH 8, TTA may be converted completely into the enol form[114] and that was found to be the case for Co and Ca as the concentration of these two elements in basic media were found to be significantly lower. However, this reagent possesses certain advantages over other β-diketones, especially acetylacetone such as

a. pK_a for TTA is 6.2, compared with 9.7 for acetylacetone, therefore TTA is less basic and its anionic concentration is much larger at any higher pH's, facilitating complexation by TTA
b. TTA chelates are stable in acid media and are non-volatile at room temperature;
c. TTA chelates are soluble in non-polar solvents and aromatic hydrocarbons;
d. many of its compounds that are intensely coloured, which favoured usefulness of spectrophotometric determination of the less common and heavy metals. These are supported by the works of Rangnekar and Khopkar[115-116].

This reagent is widely used and its concentration in extraction procedures is in the range 0.10-0.50 M in benzene, toluene, xylene and MIBK[117-118]. With more dilute solutions, separation is possible but the process is slow and extraction was often incomplete[119]. The properties and the application of TTA in extraction processes have been widely studied[120-122].

3.4.2 Co-extraction

The method for separation of the mixture of sixteen elements identified was developed here, however the method suffered from some limitations such as co-extraction of commonly associated ions. For example, during the separation of group 2 elements (Fe, Cu, V, Bi and Cd) at different pH values, Fe and Bi were co-extracted into benzene and these were to be separated by taking advantage of the solubilities of the complexes into different solvents. These co-extracted complexes were separated by dissolving Bi-TTA complex into CCl_4. Also in group 3, at pH 6.10, Mn and Pb were both extracted simultaneously from the organic solvent. Further raising the pH to 6.85, Cr and Ni were also found to be co-extracted into benzene and had to be separated by using cyanide ion as a masking agent for nickel.

The effect of co-extraction in the extractive isolation of elements as chelates was observed by Alimarin, Zolotov and Shakhova[123-124]. It was found that, with beta-diketones as a ligand, calcium co-extracts with elements such as Sc, Nd or Th and not with Al and Fe.

3.4.3 Effect of the extractant concentration

Lower concentrations of TTA ranging from 0.15 – 1 M in benzene were used in the current study for the extraction of these elements. With 0.05M TTA, the extraction of most elements was < 50%. However, with the increase in the concentration of the extractant to 0.25 M, the extraction was found to be quantitative as supported by the results of this study (see table 3.1). Most of the extractions performed were well above 95%. Mansell[73] reported that no extraction was possible, for example, over the pH range of 1 – 10 when 1 mL of 1% APDC solution was added to 80 mL of 0.5 ppm manganese solution. He investigated the effect of APDC concentration on the extraction by using a minimum of 2.25 mL of 5% APDC solution and maximum extraction of the manganese was obtai

3.4.4 Effect of the various stripping agents

After co-extraction of lead and manganese with TTA in benzene, various mineral acids were used for stripping lead. It was quantitatively stripped with 0.5-5M hydrochloric, nitric, sulfuric and perchloric acid. With 2.5 M hydrochloric acid the stripping was more than 94.2%, with 0.5 M sulfuric acid it was 85.7%, or 1.5 M perchloric acid it was 95%. With 2 M nitric acid the stripping was quantitative because at this concentration the optimum conditions of extraction were reversed. Hence 2 M nitric acid was used as the stripping agent for lead so as to separate it completely from manganese.

3.4.5 Effect of the masking agent

Masking occurs when the complexes formed in a particular media is sufficiently stable to resist further chemical change in the presence of a competing species. For example, during the separation of group 2 elements which comprises Fe, Bi, Cd, Cu and V, cadmium was masked by glycol during the extraction of Fe and Bi because of its interferences, while mannitol was found to suppress copper and vanadium during the extraction of cadmium into chloroform. For group 3 (chromium, manganese, lead, zinc and nickel) zinc was extracted at pH 5.50 after addition of EDTA to prevent any interferences from Cr, Mn, Pb and Ni. After raising the pH to 6.85 and adding potassium cyanide which effectively masked nickel, an insoluble-orange complex of chromium was extracted into benzene.

It is to be noted that the best reagents for masking would be those which form strong, colourless complexes with the ions to be masked but from relatively weak complexes with other cations. A reagent suitable under one set of conditions may not be good enough when conditions change, i.e., varying the pH or concentration of the metal ion for example in group 1, that is Mo, Ti, Se and Sn, addition of ascorbic acid facilitated the quantitative extraction of Mo-complex at pH 0.8 with little interference from the remaining elements in the group. Addition of tartaric acid as a masking agent for selenium in the Mo-free solution allowed the precipitation of Sn which was extracted at pH 2.5.

There are two ways in which selectivity can be achieved. Firstly by developing the reagents that are highly selective and secondly by the use of masking agents which, by suppressing the effects of interfering species will make the reaction specific under the chosen conditions. The effectiveness in preventing the reaction of a metal ion with an extracting agent increases with the increasing concentration of the masking agent.

3.4.6 Period of equilibration

The period of equilibration was found to vary from 1 – 10 minutes when extracting and separating these elements with TTA and maximum extraction was achieved in five minutes. Therefore, the equilibr[illegible]d of six minutes was maintained during all extractions.

3.4.7 Solvent effect

The different solvents such as benzene, MIBK, isobutyl alcohol, chloroform, carbon tetrachloride and n-butanol with varying dielectric constants were used for the extraction of these elements after separating them into four groups. In group 1, Mo and Ti were quantitatively extracted into benzene while Sn was extracted 98% into MIBK. In group 2, the difference in solubility of metal ion complexes in various solvents was extensively used to separate these elements. With CCl_4 as a solvent, the extraction of Bi complex was found to be almost complete (99%). At pH 3.7, a

TTA-Cd complex was extracted into chloroform. Vanadium was the last element to be extracted in this group with TTA in n-butanol.

In group 4, solubilities of Ca and Co were found to be different in different solvents and their extraction was found to be almost quantitative with benzene and isobutyl alcohol respectively. It was however, observed that other solvents such as chloroform, CCl_4 and MIBK, extraction of these metals never exceeded 75%. Polar solvents gave % extractions below 40% and this clearly illustrates the fact that non-polar solvents are more effective in extracting complexes at higher pH's. This is because in polar solvents the association of cationic species resulted in minimum extraction, while in non-polar solvents, absence of repulsive process gave maximum extraction. In the present s[illegible]as found that benzene being non-polar have the better ability of separation with much higher % extraction of M-TTA complexes.

The effect of the non-polar solvents on the extent of extraction of these complexes are summarized in table 3.6 and the % extractions are given in table 3.7

Conditions for the separation of the complexes of each element from the multi-component mixtures are summarized in table 3.6 :

Table 3.6 : Extraction conditions for various complexes with TTA

Element	pH	solvent	ligand	masking /demasking agent	stripping agent
1. Bismuth	3.10	CCl_4	TTA		
2. Calcium	9.2	benzene	TTA		
3. Cadmium	3.70	$CHCl_3$	TTA		
4. Cobalt	8.0	isobutyl alcohol	TTA	EDTA	
5. Chromium	6.85	benzene	TTA	KCN	
6. Copper	4.50	benzene	TTA	mannitol	
7. Iron	3.10	benzene	TTA		
8. Manganese	6.10	benzene	TTA		
9. Molybdenum	0.80	benzene	TTA	ascorbic acid	
10. Nickel	6.10	benzene	TTA	silver chloride	
11. Lead	6.10	benzene	TTA		1 M HNO_3
12. Selenium	2.50		TTA		
13. Tin	2.50	MIBK	TTA	Tartaric aicd	
14. Titanium	1.71	benzene	TTA		
15. Vanadium	4.9	n-butanol	TTA		
16. Zinc	5.50	benzene	TTA	EDTA	

Table 3.7 : Concentrations (ppm) of the elements in the soil samples before and after separation.

Element	**sample I before**	**sample I after***	**sample II before**	**sample II after***	**sample III before**	**sample III after***
1.Bismuth	3.97	3.93(99)	3.43	3.40(99)	3.15	3.12(99)
2.Calcium	21.16	18.83(89)	23.98	21.34(89)	22.54	20.06(89)
3.Cadmium	0.117	0.116(99)	1.670	1.653(99)	0.765	0.757(99)
4.Cobalt	16.01	14.75(92)	20.78	19.12(92)	30.98	28.50(92)
5.Chromium	89.8	85.84(96)	66.33	63.41(96)	77.12	73.73(96)
6.Copper	32.46	31.16(96)	37.09	35.61(96)	40.61	38.99(96)
7.Iron	455.76	435.25 (95.5)	387.1	369.68 (95.5)	351.23	335.43 (95.5)
8.Manganese	174.76	167.77 (96)	201.34	193.29 (96)	187	179.52 (96)
9.Molybdenum	0.901	0.883(98)	0.352	0.345(98)	0.699	0.685(98)
10.Nickel	75.13	72.13(96)	80.76	78.34(96)	90.11	87.41(96)
11.Lead	13.79	13.51(98)	16.99	16.65(98)	20.01	19.61(98)
12.Selenium	0.585	0.576 (98.5)	0.112	0.110 (98.5)	0.976	0.961 (98.5)
13.Tin	0.511	0.501(98)	0.967	0.948(98)	1.212	1.188(98)
14.Titanium	0.136	0.131(96)	0.678	0.651(96)	0.961	0.923(96)
15.Vanadium	72.51	70.33(97)	65.90	63.92(97)	69.09	67.02(97)
16.Zinc	10.86	10.43(97)	8.15	7.91(97)	9.63	9.34(97)

* Figures in the parentheses represent the percentage extraction after separation.

3.5 Conclusion

From tables 3.6 and 3.7 it is evident that the separation of these elements in general was satisfactory except in the case of Ca and Co where the % extraction was < 95%. As mentioned earlier that TTA, when in alkaline solution, it is partly converted into the enol form, which lowers the distribution ratio. This is supported by the fact that in our investigation, the % extraction of the metal ions under alkaline media was low compared to those in the acidic media. For example in the current work, Co and Ca were 89% and 92% extracted at pH 8.00 and pH 9.50 respectively. This is attributed to the fact that the reagent has an acid dissociation constant of 6.7×10^{-7} at 25°C.

It was however observed that the results obtained from 3 repetitions of each sample showed excellent agreement. The complex of Mn in benzene is very unstable and needs to be analysed within an hour of extraction. The manganese complex appears unstable even in MIBK[72] and extracted solutions should be analysed immediately to prevent the loss of Mn. Because of the desire to find a method of separation which possesses high sensitivity, vast specificity and rapidity of operation, interest has been directed to the combination of all the parameters for solvent extraction such as ligand, solvent, pH, period of equilibration etc for the successful isolation of the metal ions. It is also unfortunate that due to lack of facilities such as a titrator, the fixng of pH values became so cumbersome and no anions could be determined quantitatively.

Nevertheless, the proposed method is simple, selective and reproducible and provides quantitative extraction which permits a systematic separation path for the sixteen elements identified in soils. The experimental set up here are consistent enough to be useful as a technique for the trace element analysis.

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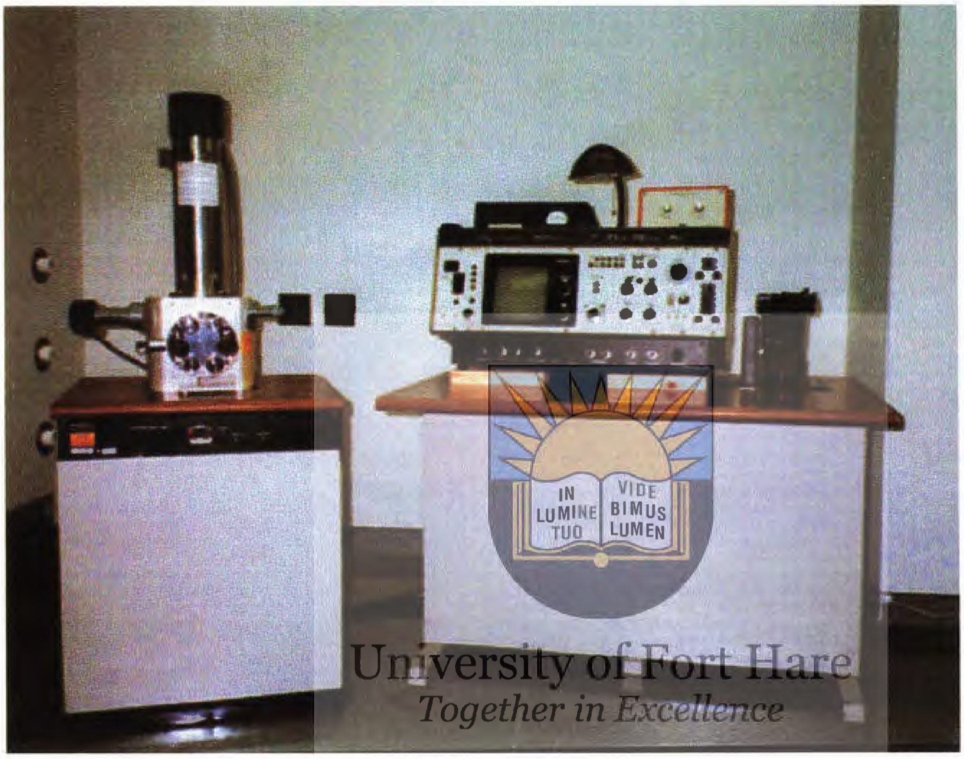
3.7. Appendices

3.7.1. Hitachi S-450 Scanning Electron Microscope

The Hitachi S-450 SEM is a conventional SEM equipped with a tungsten hairpin filament. This instrument can achieve resolutions in the order of 15 nm and provides adequate imaging to magnifications up to 15,000-20,000 times, although on rare occasions magnifications up to 70,000 times have been achieved. Accelerating voltages can range from 5 to 20 kV. The stage can accept specimens from the size of single cells to those of organs ranging up to mm in size. Working distances of up to 35 mm can be achieved and the stage is capable of full rotation and x-y translation in the order of 2.5-3.[illegible]aroid type 55 P/N or type 52 is used for recording images. The photographic picture of the instrument is shown in figure 3.1.

Figure 3.1 : Hitachi S-450 Scanning Electron Microscope



3.7.2. Atomic absorption spectrophotometer

Introduction

The basic components of any type or brand of atomic absorption spectrophotometer include the following:

A- Light Source

B- Burner/Nebulizer

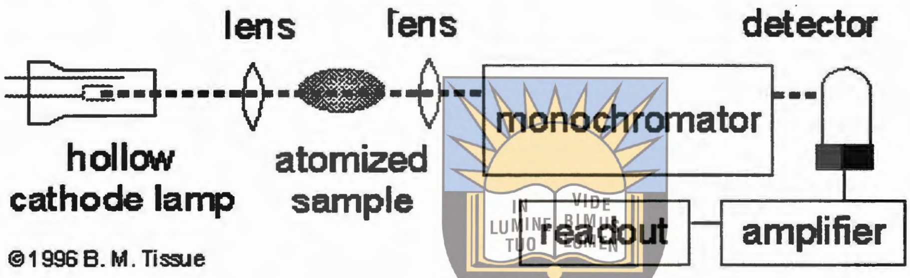
C- Monochromator

D- Photomultiplier Detector

E- Output Device

The primary sources of radiation in atomic absorption are hollow cathode lamps. These lamps are composed of a cathode and an anode sealed in a tube with an inert gas (argon or neon). The cathode is made of the element to be determined. When a high voltage is applied the atoms of the inert gas are ionized and attracted by the cathode. These ions hit the cathode and excite the atoms of the elements used to make the cathode. Once the atoms are excited radiation is emitted at the characteristic wavelength of the element. The light from the hollow cathode lamp passes through the flame (Burner/nebulizer) where the sample is atomized. This fine mist of the sample is sprayed into the nebulizer. Atoms of the elements are formed from the sample mist and are able to absorb some of the light from the lamp at the wavelength set for that particular element. The light passed through the flame is received by the monochromator, which is set to accept and transmit radiation at the specified wavelength. The light emerges from the monochromator exit slit and falls on the photomultiplier detector. At this point an output current, proportional to the incident light, is intensified, amplified, processed electronically and finally presented to a readout device (i.e. printer, digital display).

Schematic of an atomic-absorption experiment



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Instrumentation

Light source

The light source is usually a hollow-cathode lamp of the element that is being measured. Lasers are also used in research instruments. Since lasers are intense enough to excite atoms to higher energy levels, they allow AA and atomic fluorescence measurements in a single instrument. The disadvantage of these narrow-band light sources is that only one element is measurable at a time.

Atomizer

AA spectroscopy requires that the analyte atoms be in the gaseous phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source such as a flame or graphite furnace. Flame AA can only analyze solutions, while graphite furnace AA can accept solutions, slurries, or solid samples.

Flame AA uses a slot type burner to increase the path length, and therefore to increase the total absorbance. Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame.

The graphite furnace has several advantages over a flame. It is a much more efficient atomizer than a flame and it can directly accept very small absolute quantities of sample. It also provides a reducing environment for easily oxidized elements. Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms.

Light separation and detection

AA spectrometers use monochromators and detectors for uv and visible light. The main purpose of the monochromator is to isolate the absorption line from background light due to interferences. Simple dedicated AA instruments often replace the monochromator with a bandpass interference filter. Photomultiplier tubes are the most common detectors for AA spectroscopy. Photographic pictures of the instrument are shown in figures 3.2 and 3.3.

Figure 3.2 : Photographic picture of a flame atomic-absorption spectrometer

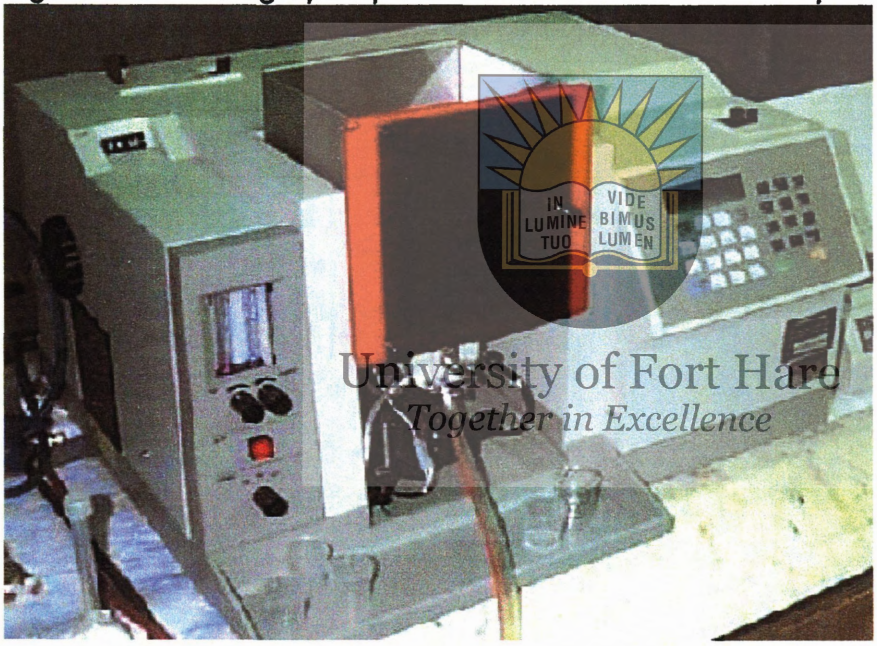

Fig 3.3 : Photographic picture of a graphite-furnace atomic-absorption spectrometer