INVESTIGATING INTO THE EFFECT OF pH ON THE AVAILABILITY OF TRACE ELEMENTS IN SOIL

By
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DECLARATION

This thesis is my original work and has not been presented for a degree in any other University.

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Dedicated to

My son Kevin, my wife Sheila, my sister Jane and my Parents Mr. & Mrs. I.J. Kamugi

ABSTRACT

The hydrogen ion concentration (pH) changes in soil can be very important in determining the yield of plants. Linear relationships have been found between the soil- and the plant-available trace elements.

Induced ion-chlorosis has been associated with excess (toxic) levels of cobalt and copper in soils and consequently in plants. "Bronzing" disease in rice has been associated with high iron levels while both an excess and deficiency of molybdenum and zinc lead to stunted plant growth. Manganese disorder leads to necrosis of young leaves and stunted root growth. To observe the effect of pH on the availability of these trace elements in soil, liming and acidification of both the acidic and the basic soils respectively were done. The available contents were then obtained after pH analyses, extraction using 0.1M HCl, complexation using both APDC (pH 2) and NaDDTc (pH 6) and irradiating following the EDXRF analysis technique.

Total contents of the elements in different soils were obtained by pelletilization. Two binding agents (PVP and starch) were tried out and compared for the low organic-matter soils.

While no obvious relationships were observed between the total and available contents of these elements, the available contents changed, though not linearly with the pH variation. Thus one can predict and pick out the pH at which a higher or lower elemental concentration may be obtained as desired

hence a way of varying its amounts in soils and plants.

PVP was found to be a good substitute for starch while making pellets of very dry, low organic-matter soils (eg. sands).

EDXRF technique was found to be a fast, precise and accurate method of soil analysis.

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Abbreviations used in the text.

Abbrev.	Meaning
COHb	Carboxyhaemoglobin
BOD	Biochemical Oxygen Demand
PV	Permanganate Value
COD	Chemical Oxygen demand
EDXRFS	Energy Dispersive X-Ray Fluorescence Spectroscopy
MCA	Multi-Channel Analyser
Si/Li	Lithium drifted silicon detector
Ge/Li	Lithium drifted Germanium detector
DDW	Double distilled water
APDC	1% (by weight) Ammonium pyrrolidine dithiocarbamate
NaDDTc	2% (by weight) sodium diethyl dithiocarbamate
HCl	Hydrochloric acid
PVP	Polyvinyl pyrrolidone
IAEA	International Atomic Energy Agency
MDL	Minimum Detection Limit
D.f.	Dilution factor

CHAPTER ONE

INTRODUCTION

1. Environmental Pollution

1.0 General

As a result of the high industrialization in our technologically based society, waste disposal has become one of the world's chief environmental concerns. Most of the industrial wastes are hazardous to living things and pose potential dangers as pollutants to human health and plant life. These may be toxic chemicals, flammable, radioactive, and explosive or biological in nature and take the form of solids, sludges, slurries, gases and liquids - and they all pose a mounting disposal problem.

1.1 Air Pollution

Air pollutants include any natural or artificial composition of matter capable of being airborne. They may occur as solid particles, liquid droplets, gases or in various admixtures of these forms. The other class of pollutants occurs as radioactive materials.

(a) Gaseous materials.

These include carbon monoxide, carbon dioxide, nitrogen oxides, hydrocarbons, sulphur oxides and ozone. Carbon monoxide is a very serious local pollutant which is formed whenever carbon is burned with insufficient oxygen. It competes with oxygen for haemoglobin forming COHb leading to arterial wall lesions in humans. Its main agent is tobacco smoking.

As a pollutant, NO (and hence NO_2) is produced largely by fuel combustion in automobiles and through photochemical reactions by the sun. NO oxidizes to NO_2 and then forms O_3 (ozone). Both ozone and nitrogen dioxide form nitrated organic compounds, peroxides, aerosols and other pollutants.

Sulphur oxides especially sulphur dioxide (SO_2) are mainly produced during the burning of fossils and coal. They are widely used in the manufacture of fungicides and bacteriocides and are toxic in high concentrations. Both nitrogen and sulphur oxides combine with rain water in the atmosphere to form acid rain. Other toxic gases include hydrocarbons, ammonia, halogens (F_2, Cl_2, Br_2, I_2) and compounds like vinyl chloride monomer (VCM), which is linked with causing augiosarcoma (a form of liver cancer in humans). Freons are also important because of their potential in destroying the ozone layer.

The depletion of the stratospheric ozone layer, the increase in tropospheric ozone (ozone near the ground), the rise in carbon dioxide and methane concentrations, higher levels of acidity in rain and changes in the radiative balance of the earth atmospheric energy system, all of these changes, directly reflect the increasing influence of human activity on the global atmosphere, the life-support system of the planet earth.

Atmospheric pollution has other serious consequences in society:- An International Chess Federation President was quoted in a local daily (standard newspaper of 7.9.89) to have said in New Zealand that Wellington, which was making a bid to host the 1990 World Chess Championships is the closest inhabited

country to the "ozone hole" over the antarctica i.e. the Antarctical Ozone Layer which lets its dangerous radio-activity and thus is dangerously radioactive and on no account should the chess grandmasters play the match there (to avoid skin cancer). The ozone layer in the south of south Island has thinned so much that glaciers have started melting and risks of skin cancer are very high.

(b) Particulate (Solid) Wastes

These pollutants are in the form of sludges slurries, aerosols, fumes, dusts and soot. These may be the non-viable or viable type. Non viable types include those which are toxic in nature eg. mercury and lead which affect human body causing body cancer, mental retardation and other serious problems. Others include the carcinogenic Polycyclic Aromatic Hydrocarbons (PAH) which are present in the atmosphere due to combustion processes especially of coal and to an extent, vehicle emissions. Polynuclear aromatic compounds found in oil refineries are carcinogenic/mutagenic and react with other common air pollutants to produce hazardous compounds (Josephson, 1981). Other pollutants whose toxicities are under scrutiny include asbestos, beryllium and cadmium. The viable ones include pollen grains, microorganisms and insects.

(c) Radioactivity

Atmospheric radioactivity originates from both natural and artificial sources.

(i) Natural Radioactivity

This results from the presence of radionuclides originating from radioactive minerals in the earth's crust or from the

interaction of cosmic rays with the gases of the atmosphere. The presence of this radioactivity is dependent on the mode of decay and the half-life of the nuclide. Alfa, beta, gamma and X-rays are some of the products of such fission and the last two are especially dangerous to the body cells since they are deep penetrating. The radio-nuclides contribute to atmospheric radioactivity by forming noble gases (^{222}Rn and ^{220}Rn) which emanate from the earth's crust.

Another source of natural atmospheric radioactivity is the combustion of fossil fuels where a number of radionuclides, including radium isotopes, originate from traces of ^{238}U and ^{232}Th.

Induced radioactivity is the type that is induced by cosmic rays. When the latter interacts with atmospheric gases, a number of radioactive species [(tritium - ^{3}H, carbon-14 (^{14}C), berylium-7 (^{7}Be), berylium-10(^{10}Be)] and sodium, phosphorus and chlorine isotopes.

(ii) Artificial Radioactivity

This is the production of radionuclides from nuclear reactors, thermonuclear or nuclear bombs or from a plant reprocessing spent reactor fuel. These radionuclides occur as either fission products or activation products. Strontium-90 (^{90}Sr) which is a fission product is the most dangerous of the fission products because (i) it is abundantly formed during fission of uranium and plutonium; (ii) it is long lived ($\tau_{\frac{1}{2}}$ = 28y) and it is chemically similar to calcium and is thus readily absorbed by living things and hence passes through

the food chains to man. It is deposited in the skeleton with calcium where it presents the potential hazard of bone cancer, or injury of the bone marrow).

1.2 Water Pollution

Water is the most important natural resource in the world without which life cannot exist and industries cannot operate. Water plays a vital role in the development of communities and its suitability must be monitored through water quality control measures. This would help in eradicating waterborne diseases and other forms of environmental pollutants and hence safeguard public health.

Drinking water must obviously be fit for human consumption and should also be suitable for other domestic uses such as washing clothes etc. It is therefore the responsibility of a water engineer to provide a water that is free from:

Visible settlable and suspended matter, excessive colour, taste and odour, objectionable dissolved matter, aggressive constituents and bacterial pollution.

-suspended and settlable matter may include soil and sand particles, insoluble solids like fibres and organic materials - all of which are indicative of water pollution.

-colour may be due to suspended solids and may render the water unacceptable for certain industrial uses eg. production of high-grade art paper.

-taste and odour may be due to dissolved impurities, often organic in nature (eg. phenols).

-dissolved matter includes the total dissolved solids

(TDS) which may be due to many soluble materials which also affect the electrical conductivity of a water sample.

-dissolved oxygen (DO), is necessary in order to maintain biological life in the water (the planktons) and the fish. However organic wastes in polluted water rapidly remove this DO giving the water an insipid taste and making it difficult to support life.

(a) Oxygen Demand

Organic compounds are generally unstable and may be oxidized biologically or chemically to stable relatively inert end products such as carbon dioxide, nitrates and water. Thus by measuring the amount of oxygen required for the stabilization of a waste, one can get an indication of the organic content pollution of waste in the water.

(i) Biochemical oxygen demand (BOD) - is a measure of the oxygen required by micro-organisms whilst breaking down organic matter.

(ii) Permanganate value (PV) - chemical oxidation using potassium permanganate solution.

(iii) Chemical oxygen demand (COD) - chemical oxidation using boiling potassium dichromate and concentrated sulphuric acid.

(b) Nitrogen

Since biological reactions only proceed in the presence of sufficient nitrogen, the concentration of a different form of nitrogen gives a useful indication of the nature of the sample, and its strength. The four forms of nitrogen are:

(i) organic nitrogen - in form of proteins, amino acids & urea.

(ii) ammonia nitrogen - as ammonium salts or as free ammonia.

(iii) nitrite nitrogen - an intermediate stage.

(iv) nitrate nitrogen - final oxidation product of nitrogen.

High organic nitrogen and ammonia nitrogen with little nitrate and nitrite nitrogen indicate recent pollution while a sample with no organic nitrogen and ammonia nitrogen and some substantial nitrate nitrogen, would be considered safe as nitrification had occured and thus pollution could not have been recent.

Most natural waters contain many microorganisms some of which are harmless to man while others are responsible for many diseases posing a major health problem. These include viruses, bacteria, fungi, algae and protozoa.

(c) Heavy metals

Many biogeochemical studies have been done in many countries on effects of smelting activity impacts on river and lake water. Nriagu (1984) reported that lakes in Ontario, USA showed varying degrees of acid precipitation leading to accumulation of metals in the layers of sediment. It is known that lake sediments preserve a good historical record of changes in the fluxes of heavy metals in the lake basin (MARC, 1985) and have thus become the prime focus of many studies.

Presence of calcium ions in solution reduces the toxicity effect of heavy metals such as lead and zinc. High concentrations of sodium, calcium and magnesium prevent the toxic effects of heavy metals by forming complexes. For example 1 mg/l of lead in soft water may be rapidly fatal to fish, but in hard water

of say 150 mg/l calcium hardness, 1 mg/l of lead will be harmless.

1.3 Soil Pollution

The major terrestrial zone of interaction in which life has evolved and adapted to the inorganic environment at the earth's surface, is soil. Pollution of soil is mainly due to pesticides applied to the vegetation and/or organisms found on a certain soil or heavy metals inherent in the soil or from surrounding areas like smelting works. The pesticides include herbicides (such as paraquat, atrazine), insecticides, fungicides and rodenticides. Although pesticides are mainly used to protect plant crops grown for food and in animal treatment, being applied either in form of spray, dusts, granules, creams or shampoos, they may also cause injury to man, plants and animals. In man ingestion or inhalation may suppress the central nervous system or cause dermatitis and allergies. Ingestion of organo-chlorines from fat of animals which have been fed on plants treated with the pesticide has been shown to lead to production of infertile eggs by birds of prey.

Pesticide residues may accumulate in the food chain by resisting removal from the crops (in the fatty tissue). Some may have phytotoxic action on the crops to which they are applied. Pesticide residues may harm microorganisms in the soil and may also affect the taste of milk or meat of animals fed on crops which have these residues on them.

1.4 Soil Trace Elements

The importance of inorganic chemical elements to the growth and development of living organisms, has in the recent years been demonstrated by soil scientists and agronomists to be of fundamental

significance. The inorganic portion of the soil comprises of elements, most of which occur in concentrations of less than 1% and are referred to as minor or trace elements. Their concentrations are expressed in µg/g of dry matter (Epstein, 1965). Others are required in larger amounts and are referred to as major nutrients. Their concentrations are usually expressed in percentage of dry matter.

Trace element relationships with life processes have been revealed through various biochemical investigations in various countries. They have become increasingly prominent as elements which are indispensable to the health of plants, animals and man, and to the overall agricultural productivity. They help to maintain productivity of land already under cultivation, and as components of fertilizers, they help restore fertility to already exhausted and infertile soil thus enabling new tracts of land to be developed for crop production (Sanchelli, 1969). Among the essential trace elements are:- boron, chlorine, copper, iron, manganese, molybdenum, sodium, zinc and cobalt. Apart from these essential ones, other elements are found present in both plant and animal tissues but whose functions are not yet fully understood. They are therefore considered non-essential. Some of them are: bromine, iodine, strontium, titanium and lithium (Kabata-Pendias, 1984).

In general, although most of these elements play a great role as growth stimulating factors, all trace elements become toxic to plants and animals if present in the soil in concentrations appreciably higher than normal. The required amounts

differ from plant to plant but will generally fall within a certain range for most plants [Davis et al.,1978; Gough et al.,1980; Kabata-Pendias, 1979; and Kitagishi & Yamane, 1981].

Table 1a: Shows appropriate trace element concentration ranges in mature leaf tissues (generalized for various species in µg/g dry weight).

Element	Deficient if less than the stated amounts of essential elements	Sufficient or Normal	Excess or Toxic
As	-	0.5	>5
B	5-30	10-50	>50
Ba	-	<500	>500
Cd	-	0.05-0.2	>5
Co	-	0.02-1	>15
Cr	-	0.1-0.5	>5
Cu	2-5	5-30	>30
F	-	5-30	>50
Hg	-	-	>1
Mn	15-25	30	>30
Mo	0.1-0.3	0.3-1.0	>10
Ni	-	0.1-5	>10
Pb	-	5-10	>30
Se	-	0.01-2	>5
V	-	0.2-1.5	>5
Sn	-	<60	>60
Zn	10-20	27-150	>150
Zr	-	<15	>15

Trace elements of the transition metal group are known to activate enzymes or to be incorporated into metalloenzymes as electron transfer systems (Cu, Fe, Mn and Zn) and also to catalyse valence changes in the substrate (Cu, Co, Fe and Mo). Some particular roles of several elements (Al, Cu, Co, Mo, Mn and Zn) which seem to be involved in the protection mechanism of frost-dry and draught resistant plant varieties have been reported by Muriutian, 1972. These elements are however not present in their native form in the plants but as complexes.

Table (1b) below shows the forms and principle functions of some trace elements that are essential to plants (Bowen 1979, Clarkson & Hanson, 1980).

Table (1b)

Element	Constituent of	Involved in
B	Phosphogluconates	Metabolism of carbohydrates, nucleic acid and flavonoid synthesis.
Co	Cobamide coenzyme	Symbiotic N_2 fixation, synthesis of chlorophyll and proteins.
Cu	Plastocyanins, oxidases, and ceniloplasmin	Oxidation, photosynthesis, protein and carbohydrate metabolism.
Fe	Hemo-proteins and non-hemeiron proteins	Photosynthesis, N_2 fixation, and valence changes.
Mn	Many enzyme systems	Photoproduction of O_2 in chloroplasts, NO_3^- reduction.
Mo	Nitrate reductase, oxidases and molybdoferredoxin	N_2 fixation, NO_3^- reduction and valence changes.
N_2	Enzyme urease	Translocation of N.
Zn	Anhydrases, proteinases, peptidases and dehydrogenases	Carbohydrate and protein metabolism.

1.5 Deficiencies and toxicities of essential elements

Metabolic disorders of plants are effected by both micronutrient deficiencies and their excesses. If there is inadequate supply of an essential trace element (i.e. a deficiency), plant growth becomes abnormal or stunted and its further development is disordered. Similarly, an excess of such an element may lead to serious problems in the plant (toxicity).

Table 1(c) below shows general effects of trace element deficiency and toxicity on some common cultivars (Bergmann & Cumakov, 1977; Mengel & Kirkby, 1978).

Element	Deficiency symptom	Toxicity symptom
B	Chlorosis and browning of young leaves, killed growing points and distorted blossom development	Margin or leaf-tip chlorosis, wilting and drying-off of older leaves. Browning of leaves points.
Cd	Data not available	Brown margined leaves, curled leaves, and brown stunted roots; chlorosis.
Co	Data not available	Interveinal chlorosis in new leaf, followed by induced Fe-chlorosis, damaged root tips.
Cu	Wilting, melanism, white twisted tips, disturbance of lignification	Dark green leaves, followed by induced Fe-chlorosis, thick, short or barbed wire roots.
Fe	Interveinal chlorosis in young organs	Dark green foliage, stunted growth of tops and roots, dark brown leaves of some plants (eg. "bronzing") disease in rice.
Mn	Chlorotic spots and necrosis of young leaves	Chlorosis on old leaves, blackish-brown or red necrotic spots, accumulation of MnO_2 particles in epidermal cells; drying tips and stunted root growth.
Mo	Chlorosis of leaf margins, distorted curding of cauliflower, deformation of leaves due to excess NO_3	Yellowing of leaves, depressed root growth
Zn	Interveinal chlorosis (mainly in monocots) stunted growth, violet-red points on leaves	Chlorotic and necrotic leaf tips, retarded growth of entire plant, and injured roots resemble barbed wire

1.6 TOTAL AND AVAILABLE TRACE ELEMENT CONTENTS

1.6.1 Total Contents

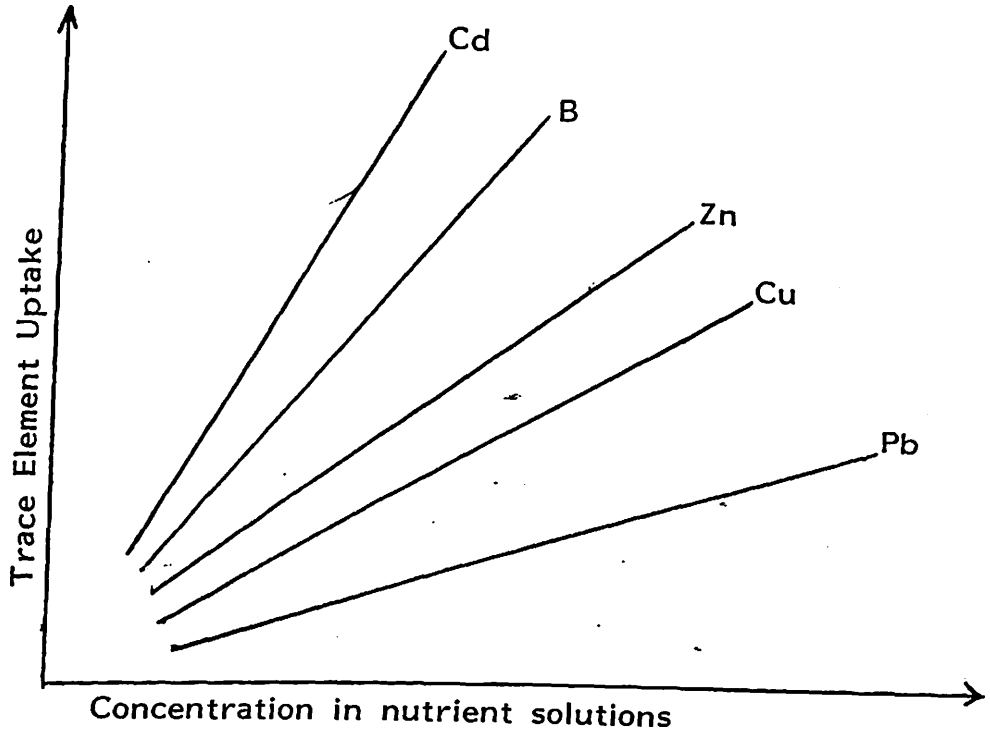
The total trace element content of soils usually reflects the composition of the materials from which they have been derived (Wells, 1960). These comprise of the parent rocks which constitute the reserve and the primary source of the elements. The results are usually given in %, mg/kg and ppm of dry soil. The total amounts of trace elements depend on the type and intensity of weathering, climatic and other factors predominating during the process of soil formation.

1.6.2 Available Contents

Plant 'available' element contents are much less than the total amounts in the soils. These are the elements available mainly in the soil solution and whose amounts depend on many factors. Some of these factors are: pH, organic matter content, texture, moisture content, clay minerals, pore size, redox potential and interelement interaction (FAO, 1972; Sanchelli, 1969). These contents are also expressed in ppm of dry soil.

There is a linear response of trace elements absorption by several plant species in increasing their tissue concentrations of nutrients and soil solution as shown in Fig. 1 below.

Fig. 1: Trace element uptake by plants as a function of their concentrations in nutrient solutions.



These responses by plants indicate that the plants absorb the trace elements in the dissolved form and the amount of absorbed elements increase with solubility. This further suggests that methods based on element concentrations in the soil solution are reliable in diagnosing the available trace element status of soils.

Some of the factors affecting availability of trace elements have been subject of numerous studies and considerable information about them has been reported on such factors as pH, texture and organic matter. Contradicting information has been given by various authors with respect to the pH effect on the availability (FAO, 1972).

It is against this background that this project was intended to investigate into the effect of pH on the availability of

trace element in soils and to establish the relationship, if any, between this available content and the total contents.

1.7 SOIL pH

The solubility and uptake of aluminium, cobalt, copper, iron, nickel, tin and zinc and partly of manganese is reduced by reducing the acidity while that of sulphur and molybdenum increases (Mitchell, 1957; Neelakantan & Mehta, 1961; Radhawa & Broadbent, 1965; and Singh et al., 1969). A summarised table of the effect of soil pH on the availability of a number of elements (iron, cobalt, zinc and manganese) to plants has been given by Truog, 1948).

In general the availability of manganese is more dependent on pH than is the case for other trace elements. For example, Christensen et al., 1950 reported a reduction of exchangeable manganese content down to 0.02-0.05 due to liming; while in some cases the uptake of copper was affected only slightly or not at all by pH (French et al., 1957; Lucas & Davis, 1961).

Contradicting results on the pH effect on the extractability of trace elements with chemical solvents has been reported by Brown, 1961; Hodgson, 1963. There are also differences in the influence of pH on the native and applied trace elements, the latter being more affected (Leyden & Toth, 1960 and Wear 1956). Availability of molybdenum is said to increase with increased pH.

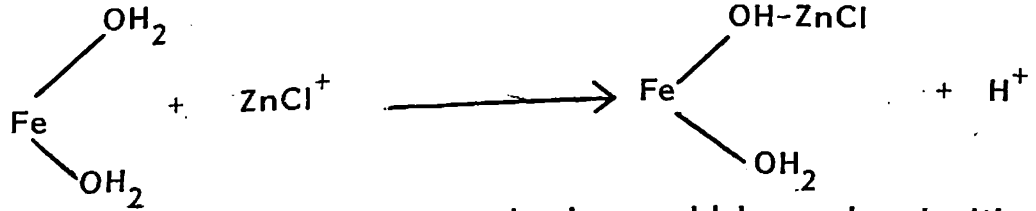
Soil iron(II) and iron(III) ions are soluble and available to the plants in the pH range between 3 and 8. Absolute iron deficiency is rare-but may occur where the pH level is greater

than 8 mainly due to physiological causes. Availability of iron for plant use increases with acidity but is lowered by phosphates and lime. A heavy concentration of iron(III) ions in the soil solution can be toxic to plants (Sauchelli, 1969). Iron(II) ions contribute very little to the total soluble inorganic iron in well aerated soils except under high soil pH. The soluble iron level reaches a maximum in the alkaline pH range. Acid soils are higher in soluble inorganic iron than are neutral or calcareous soils (Lindsay, 1979).

pH effects are thought to be related to the competitive exchange of H^+ with heavy metals occluded by hydrous oxides and the effect of pH on the dissolution - precipitation and oxidation of iron and manganese oxides (Kings, 1988). His work revealed that although the soil properties related to metal retention varied among metals, sorbed copper, zinc, cadmium, nickel and cobalt were better related to pH than to any of the other properties measured.

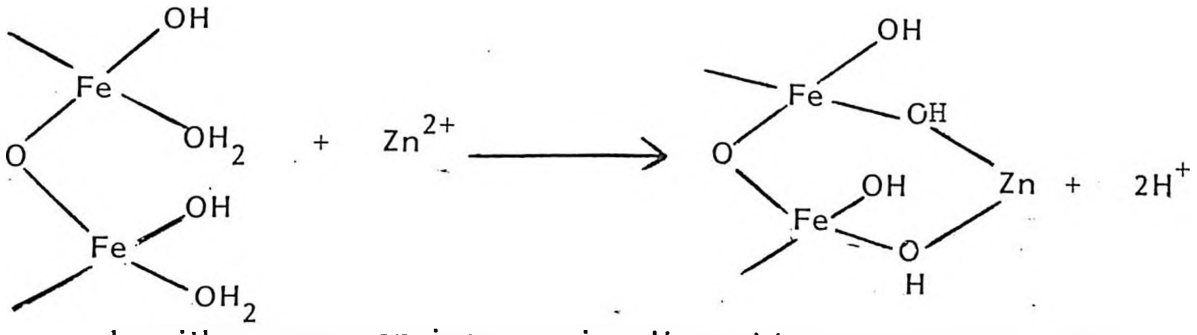
In his study of zinc-sorption on aluminium and iron oxides; Kalbas et al. postulated two mechanisms for retention of metals, as follows:

1. Zinc plus a monovalent anion (say chloride) sorption involve only aquo groups.



Zinc sorbed by this mechanism could be replaced with Ba^{2+} ion.

2. Zinc sorbed as Zn^{2+}. In this case Zn would not be replaced with Ba^{2+}. It was therefore thought to be held by a strong chemical bond



In either case, an increase in pH would cause deprotonation of the OH group, thus facilitating the reaction. A hypothesis by Leeper, (1979) was that pH increase results in hydrolysis of metals (M) and since the hydration shell of $M\text{-}OH^{+}$ is less than that of M^{2+}, the metal is held more directly on the sorbed surface.

Molybdenum behaviour in soils has been widely studied because of its unique position among other micronutrients. This is so because it is the least soluble in acid soils and is readily mobilized in alkaline soils (Lindsay, 1979).

Solubility of copper compounds is pH independent. McBride & Blasiak, 1979 reported that due to the affinity of copper for organic complexing, soluble copper-organic forms appear to compromise most of the copper solution over a wide pH range. Organic complexing of copper has a prominent practical implication in governing the bioavailability and migration of copper in the soil.

Solubility of manganese is of significance since the plant supply of manganese depends mainly on the soluble manganese pool in the soil. In well drained soils, the solubility of manganese always increases with increase in soil acidity.

Toxicity of some field crops has been reported on acid soils of pH around 5.5 or lower. Toxicity is also known to occur at higher pH ranges in poorly drained (poorly aerated) soils (Reuter, 1975).

Mobility of cobalt is also highly related to the kind of organic matter contents in soils. Soils with high organic matter have low cobalt content. Co-organic chelates may become readily available to plants even at high pH and low organic matter (Bloomfield 1981). Factors that contribute to cobalt deficiency for grazing animals are mainly associated with alkaline (calcareous) soils, light leached soils and soils with high organic matter-content. Cobalt sorption by manganese oxides increases greatly with pH in the soil (Kabata-Pendias, 1984).

From the foregoings, it is evident that pH has been considered by soil and plant scientists to be a major parameter in determining the availability of trace elements in soils. The investigators have, however not dealt with the trace element problem in an african environment and more so in Kenya where no such work has reportedly been done.

1.8 THE OBJECTIVES of this research work were therefore :

(i) to investigate into various ways of determining the availability of trace elements in soils;

(ii) to investigate the effect of pH on the availability of trace elements in soils;

(iii) to establish the relationship, if any, between the total and available trace elements in soils ; and

(iv) to carry out the precision experiments for the technique above.

CHAPTER TWO

2A. ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY TECHNIQUE

2.0 General

In contrast to wavelength-dispersive X-ray spectroscopy which uses a crystal spectrometer to separate the characteristic lines of different elements spatially at different reflection angles according to their wavelengths, energy dispersive X-ray fluorescence radiation (undispersed secondary beam) spectroscopy is done by measuring its energy. The spectrometer normally operates by measuring the consequence of interactions of the incident X-rays in the detector medium.

Energy dispersive X-ray fluoresence technique plays a very important role in analysis mainly due to its ability to analyse multielements simultaneously.

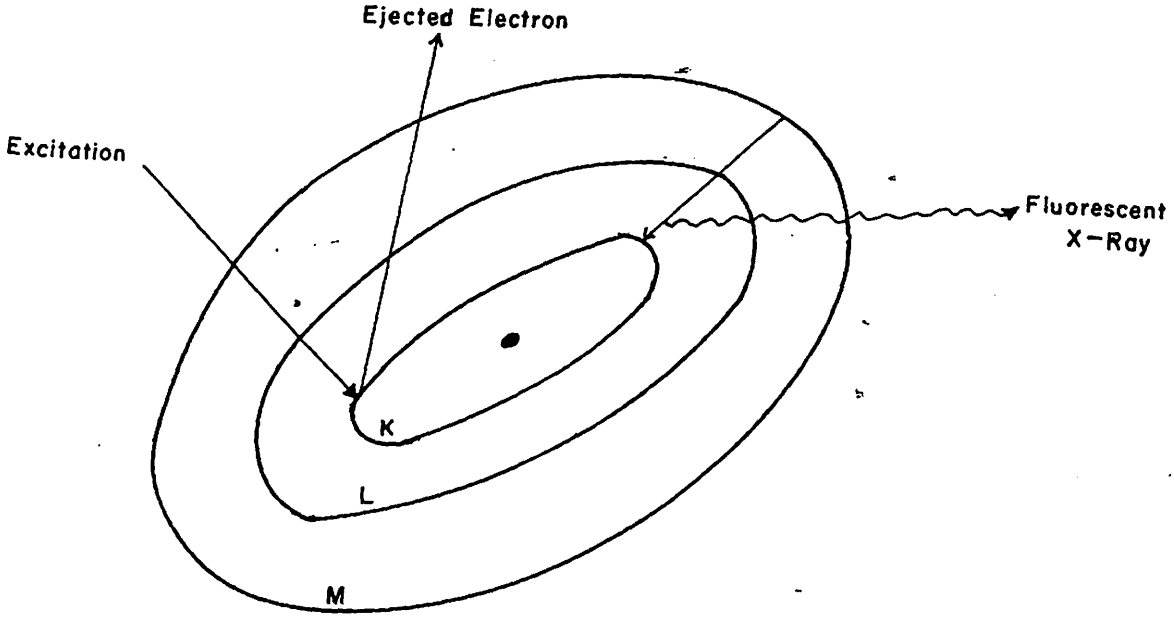
2.1 BASICS OF THE METHOD

Interaction of X-rays with matter

Two main effects that take place during X-ray interaction with matter are scattering and photoelectric absorption. The latter is responsible for characteristic radiation which is produced when an excited atom deexcites by transition of electrons from outer orbitals to inner levels to regain stability. This occurs when an atom is bombarded by particles of sufficient energy exceeding the electron-binding energy in a given shell ejecting an electron filling the subshells. Transition of outer orbital electrons to inner shells retains the original atomic configuration with the emission of energy (in form of X-radiation), of wavelengths

depending on (i) the excited and (ii) final orbitals in which the electron rests.

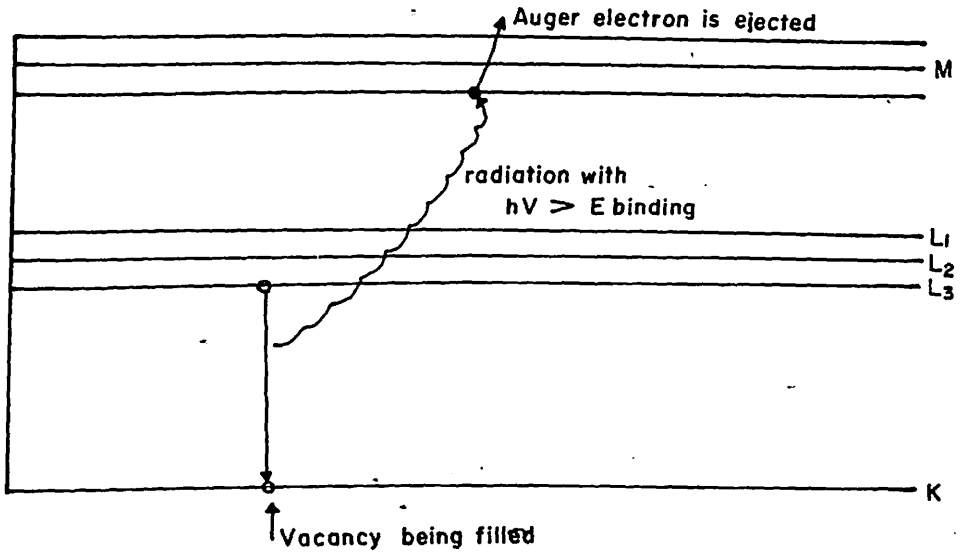
Fig. 2a below shows the excitation, ejection of electron and re-filling of atomic orbitals with emission of X-rays in this photoelectric effect.



2.2 AUGER ELECTRON EFFECT

This is a competing effect to the photoelectric effect whereby deexcitation proceeds by emission of an outer-shell electron in a radiation-less process instead of an inner X-ray photon. This is the more likely process in elements of low atomic number, Z, where the fraction of vacancies producing X-ray emission is less than 10% (Burhop & Asaad, 1972).

Fig. 2b below shows the production of the auger electron.



2.3 FLUORESCENT YIELD

The K-fluorescent yield or K-characteristic photon yield, w_k, is the number of photons of all lines in the K series emitted in unit time divided by the number of k-shell vacancies formed during the same time.

$$w_k = \frac{\Sigma (n_k)_i}{N_k} = \frac{n_{k_{\alpha 1}} + n_{k_{\alpha 2}} + n_{k_{\beta 1}}}{N_k}$$

where

w_k = k-fluorescent yield

N_k = rate at which K-shell vacancies are produced

$(n_k)_i$ = rate at which photons of a spectral line i are emitted.

For L and M shells, fluorescent yield w_L and w_M are similarly defined. Fluorescent yield is therefore the probability that the filling of a vacancy in a specified shell will result in emission of a characteristic X-ray photon regardless of whether the vacancy arose from primary or secondary excitation (Bertin, 1975).

2.4 EXCITATION SOURCES

In X-ray fluorescence spectroscopy, the excitation source used depends on the fundamental physical processes, the cost and its availability. The available options are: electrons, protons, and photons (X-rays or γ -rays).

Although electrons and protons have the advantage of being easy to generate, they have the disadvantages that the sample must be enclosed in the same vacuum as the source and that there is a large amount of continuum bremsstrahlung produced in the sample which reduces the fluorescent signal to background ratio (Herglotz, 1978). Bremsstrahlung is produced by energetic secondary electrons resulting from collisions of the incident ions with electrons in the sample.

Photon-excited X-ray fluorescence analysis has been widely used with excellent performance and convenience. Unlike charged particles, photons do not undergo continuous energy-loss processes and therefore obey the exponential attenuation law

$$I = I_o e^{-(\mu/\rho)\rho x}$$

where

I_o = initial intensity of the beam in photons/sec.

I = intensity of radiation transmitted through a thickness x cm,

ρ = density of material in g/cm^3

μ/ρ = mass attenuation coefficient expressed in cm^2/g, and which is a function of wavelength of incident radiation and atomic number of the absorber. If the absorber has more than one element,

$$\mu/\rho = W_1 \frac{\mu_1}{\rho_1} + W_2 \frac{\mu_2}{\rho_2} + \ldots\ldots$$

which is the sum of the weight fractions (W_i) multiplied by their individual mass absorption coefficients (μ_i / ρ_i).

In energy dispersive X-ray fluorescence analysis, the portion associated with photoelectric absorption is the important part as far as excitation of characteristic X-rays is concerned.

2.5 SCATTERING

Photons also interact by scattering with the sample. There are two forms of scattering namely: Coherent (Rayleigh) and Incoherent (Compton).

(a) Rayleigh scatter

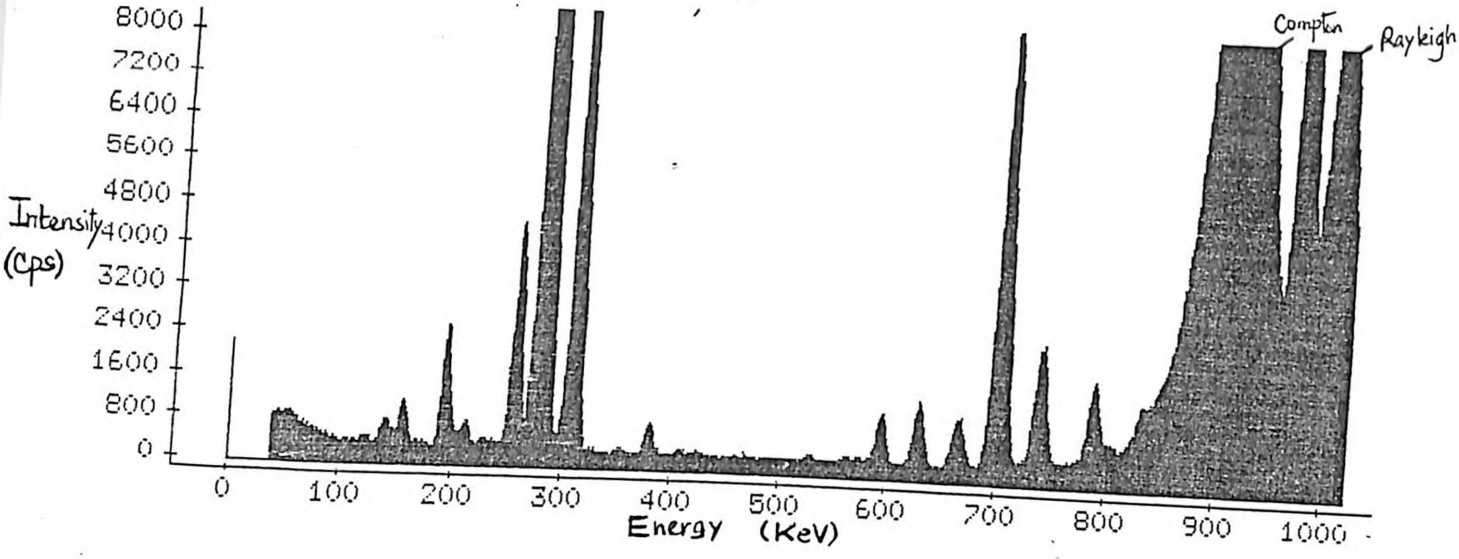
Here, an incident photon interacts with a tightly-bound atomic electron and is elastically scattered without loss of energy. This coherent scatter increases with atomic number. It is the cause of diffraction of X-rays by crystals.

(b) Compton scatter

This is the interaction that takes place with a loosely bound electron resulting in an energy-loss in the scattered photon. In an X-ray spectrum, compton scatter is shown as a diffuse peak of wavelength slightly greater than the lines caused by the tube target (Rayleigh Scattered radiation).

A typical EDXR spectrum is shown in the figure 2c below.

Fig. 2c



2.6 PAIR-PRODUCTION

Apart from the true photoelectric absorption and scattering, a third phenomenon that contributes to the total mass absorption is pair-production. Here, photons passing close to atomic nuclei give their energy to creating and imparting kinetic energy (KE) to two charged particles, an electron (e^-) and a positron (e^+) i.e.

X or γ photon ——— $e^- + e^+$

Thus the total mass absorption coefficients are the result of the three phenomena

$$\mu/\rho = \tau/\rho + \sigma/\rho + \pi/\rho$$

where τ, σ and π are photoelectric, scatter and pair-production effects respectively. In the wavelength region of X-ray spectrochemistry, pair production does not occur and photoelectric absorption predominates over scatter (Bertin, 1975). Consequently, μ/ρ is largely determined by τ/ρ.

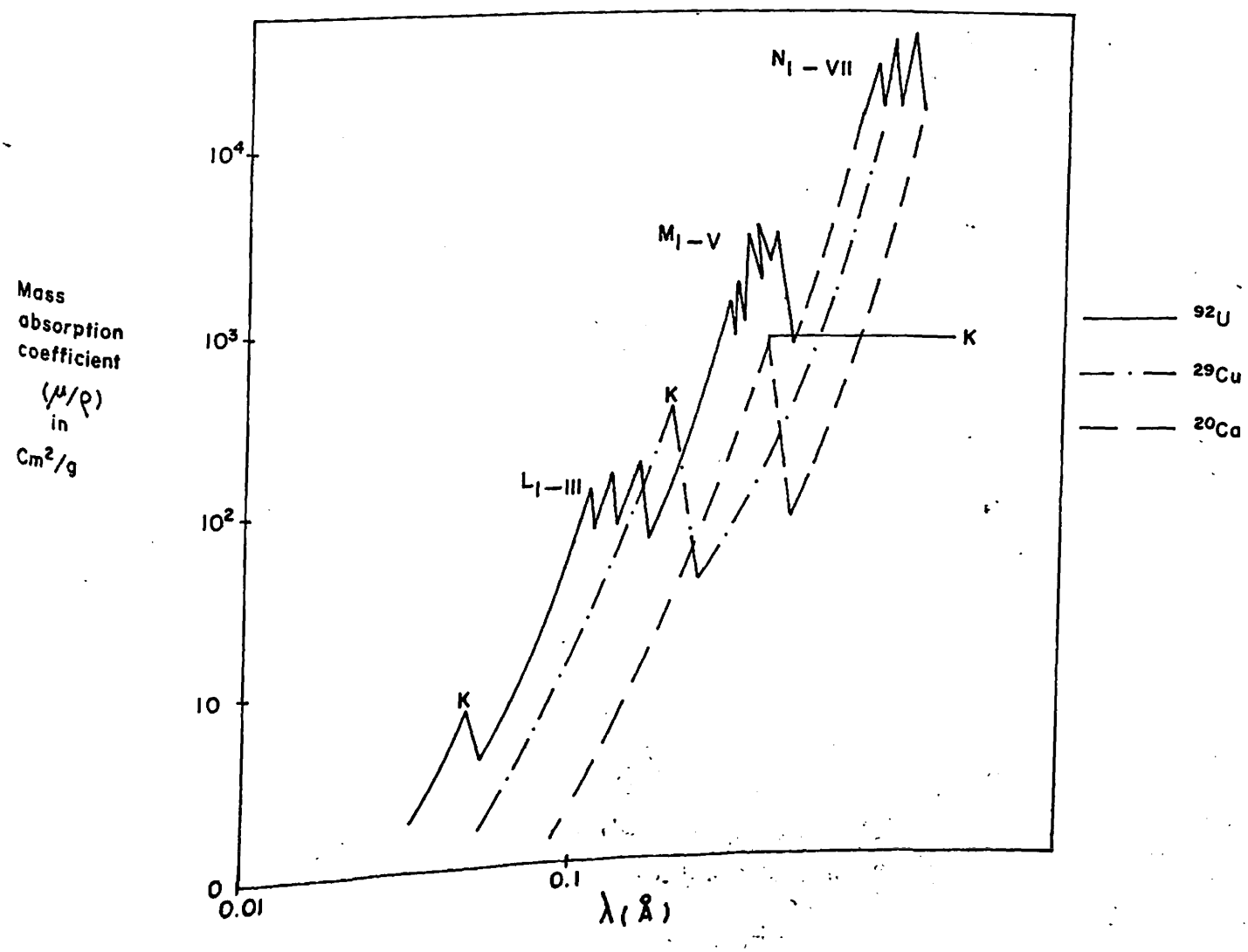
2.7 ABSORPTION EDGES

In an X-ray absorption curve the X-ray absorption coefficient of an element i.e. the 'stopping power' - decreases with X-ray wavelength. This is so because the shorter the

wavelength the greater the energy and hence the penetrating power. The maximum wavelength (minimum photon energy) that can expel an electron from a given atomic level of an element is known as the absorption edge of that level of the element. These absorption edges are represented as abrupt discontinuities on the absorption curves. Each element has as many absorption edges as it has excitation potentials - one K(λ_{Kab}); three L (λL_{Iabs}, λL_{IIabs}, λL_{IIIabs}); five M, seven N etc.

Fig. 2(d): Shows a typical X-ray absorption curve.

Fig. 2d



Explanation:

Consider a monochromatic primary radiation beam of wavelength λ incident on a secondary target of atomic number, Z. At $\lambda > \lambda.zk_{ab}$, the photons have lower energy than required to expel a Z_k electron, therefore no Z_k line appear. As λ decreases the photons become more energetic and the absorption coefficient decreases. At $\lambda\, zk_{abs}$, the photons have the exact energy required to expel Z_k electrons and the absorption increases abruptly. This is the photoelectric absorption and the expelled electron is a photoelectron. At $\lambda <<< \lambda\, zk_{ab}$ the photon energy is more than enough to expel Z_k electrons. However, they may not be absorbed, or else before being absorbed, they may penetrate the target to a depth from which Z_k radiation cannot emerge. At $\lambda < \lambda\, zk_{abs}$. photons have more than enough energy to expel Z_k electrons but each photon that is absorbed by an electron is wholly absorbed. The surplus energy imparts Kinetic Energy to the photoelectron so that the shorter the λ, the higher the velocity of the photoelectrons.

2B. INSTRUMENTATION

The type of Energy-Dispersive X-Ray Fluorescence Analysis (EDXRFA) instrument used here has been described by Muriithi, 1982. Like in all other conventional X-Ray spectrometers, the instrument has three basic parts:-

the primary source unit, the spectrometer itself and the measuring electronics (Jenkins, 1982).

The actual parts are:

(i) a radioisotope source (^{109}Cd, ^{55}Fe or ^{241}Am) to act as the primary beam source.

(ii) the sample compartment

(iii) a lithium-drifted silicon or Germanium detector [Si/Li or Ge/Li].

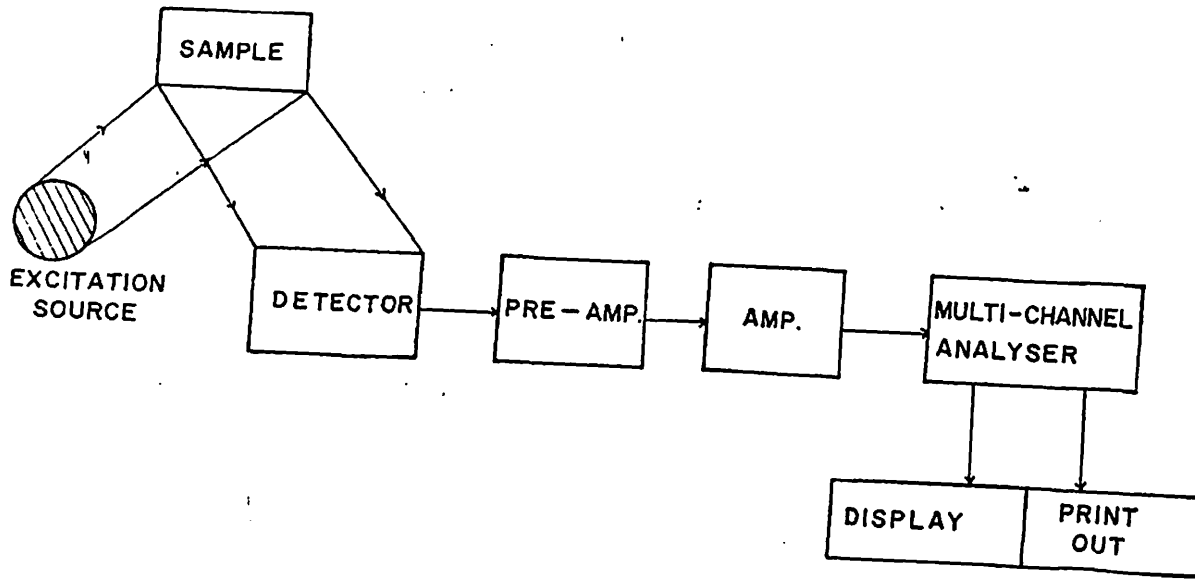
(iv) a preamplifier

(v) an amplifier

(vi) the multichannel analyser (MCA); and if desired,

(vii) a micro-computer.

Fig.2(e) below shows a diagramatic representation of an EDXRF Spectrometer.



2.8 EXCITATION

For energy dispersive work, excitation may be done with high or low power X-ray tubes OR radioisotope sources. X-ray tubes, particularly low-power tubes have certain advantages over radioisotopes. Among these are:

-the effective intensity and λ of excitation radiation can be varied much more widely with tubes than with isotopes; the latter being limited by the specific isotope and its activity (Ci).

-intensity from low-power tubes is higher than that from practical radioisotope sources, and accordingly, analysis time is shorter.

(eg. over a four-day period ^{55}Fe and ^{109}Cd sources decay by 0.29% and 0.59% respectively whereas low-power tubes may remain stable within 0.25% for one to two weeks (Dyer, 1972).

-X-ray tubes are safer than radioisotopes since they can be turned off when not in use or when changing samples.

Radioisotopes on the other hand have their advantages over tubes:-

-they are small, light, inexpensive and easily portable.

-reduction of radiation pathlength results in low analyte photon between specimen and detector.

Table 2 below shows some commonly used radioisotopes for X-Ray fluorescence excitation.

		Useful Radiation	
Radioisotope Source	Half-Life	Type	E(Kev)
^{55}Fe	2.7y	Mn K x-rays	5.9
^{57}Co	270d	Fe K x-rays γ	6.4 14,122,136
^{109}Cd	1.3y	Ag K x-rays γ	22.1 87.7
^{125}I	60d	Te K x-rays γ	27 35
^{153}Gd	326d	Eu K x-rays γ	42 97,103
^{210}Pb	22y	Bi L x-rays γ	11 47
^{238}Pu	89.6y	U L x-rays	15-17
^{241}Am	470y	Np L x-rays γ	11-22 26,59.6

y = years
d = days

2.9 DETECTION

The detector is normally collimated to accept X-rays which originate at the sample and have sufficient energy to penetrate the thin detector window. The most significant of the detectors for X-ray intensity measurements are the semiconductor detectors which have an advantage of improved energy resolution among others. These are Si(Li) and Ge(Li). The detector must be maintained at liquid nitrogen temperature (-196°C) to reduce noise and to ensure optimal resolution; and also to reduce the diffusion of lithium which is usually very high at room temperature.

2.10 SIGNAL-PROCESSING ELECTRONICS

These include the pre-amplifier, amplifier and the pulse-height analyser.

The pre-amplifier stage is mounted with the detector and maintained at low temperature in the cryostat. It integrates each detector charge signal to produce a voltage set up proportional to charge. The pulse is then amplified and shaped in a series of integrating and differentiating stages to achieve the optimum shape to maximise the signal-to-noise ratio.

The resulting pulse is then processed and encoded in a multichannel pulse-height analyser which accumulates the X-ray spectrum. From this spectrum of intensity versus X-ray photon energy, both qualitative (identification/detection of elements in the sample) and quantitative (determination of elemental concentrations) analyses may be done.

2.11 QUALITATIVE AND QUANTITATIVE ANALYSES

2.11.1 Qualitative analysis

This is a comparative technique where various elements in a specimen are identified by comparing their spectral peaks with those of known elements. An XRF analysis energy chart for the elements and their respective characteristic energies is internationally available and may be used to identify the particular elements present in the sample.

2.11.2 Quantitative analysis

Standard calibration method

As stated before, the analyte-line intensity in a specimen is not simply a weight fraction of the analyte and the line-intensity from pure analyte. This is because of other factors which influence the count rate. These are called absorption enhancement effects or matrix effects which must be corrected for when doing quantitative analysis.

Most of the methods used in correcting for matrix effects during measurements involve the use of calibration standards, where the intensity data is converted to analytical concentration by use of calibration curves or mathematical relationships derived from the measurements on standards.

Among these methods are:

1. Standard addition and dilution methods where the sample is subjected to quantitative increments in concentrations or dilutions of the analyte.
2. Making very thin specimens so that absorption-enhancement effects are very much reduced.

3. Standard comparison method - where the analyte-line intensity from the sample is compared with that from standards having the same form and matrix as the sample. Here, analysis is done by measurement of analyte line-intensity from the sample and application of this intensity to the calibration curve obtained from known standards, to derive analytical concentrations graphically. Alternatively, a mathematical calibration factor may be derived from the data and used on the sample.

4. Internal standardization - which involves the quantitative addition to all specimens of an internal standard element having excitation and absorption-enhancement characteristics similar to those of the analyte in the particular matrix.

5. Matrix-dilution method - where the matrix of all specimens is levelled or diluted to a composition such that the matrix effect is determined by the diluent.

6. Mathematical correction - which involves the use of experimentally derived parameters for correction.

2.12 THE FUNDAMENTAL PARAMETER METHOD (FPM)

This method requires no calibration standards. It permits the calculation of analytical composition from the measured analyte-line intensity and the tabulated values of three fundamental parameters, namely:-

(i) the primary spectral distribution,

(ii) absorption coefficient, and,

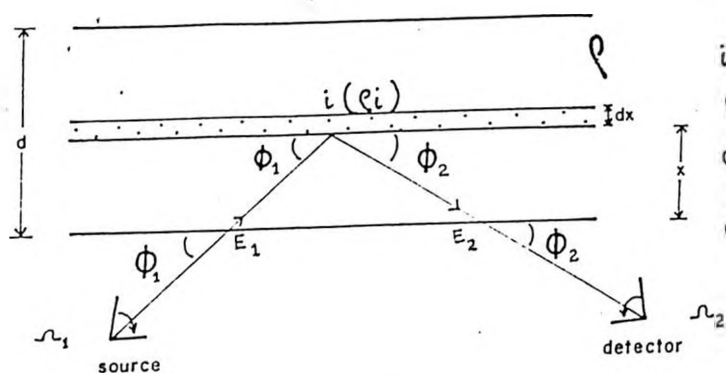
(iii) fluorescent yield.

The method has been shown to agree reasonably with the standard method using certified Reference Materials of soils and biological samples (Holynska et al., 1986).

2.12.1 The Basic fluorescent intensity equation

This is derived from the basic excitation equation and from the geometry shown here below:

Fig. 2f



i = atom of element in the sample

ρ = specimen density

ϕ_1 = incident angle of primary beam seen from the source

ϕ_2 = take off angle of secondary bea as seen from the detector.

E_1 = energy of incident primary radiation of intensity, I_o

E_2 = energy of fluorecent radiation of intensity, I_i.

This derivation is based on three assumptions (Birks, 1969):-

1. The sample is homogeneous where the density of any element i is constant throughout the sample volume.
2. The primary X-radiation is monochromatic, and,
3. A fixed geometry is maintained during measurements and enhancement is regarded as negative absorption.

Excitation and detection of K_α X-rays of energy, E_i of element i in the sample is a product of three probabilities:-

1. Probability that the primary radiation will penetrate through depth X of the sample upto layer dx,

$$P_1 = I_o \Omega_1 \exp - \left[(\mu/\rho)(E_1)\, \rho x \operatorname{cosec} \phi_1 \right] \quad \text{-----} \quad (i)$$

where $(\mu/\rho)_{\Omega_1}$ = mass absorption coefficient of the specimen for the incident energy, E_1.

ρ = density of sample

2. Probability that the element i will totally absorb the primary radiation in the layer of thickness, dx and emit its characteristic X-rays of energy, E_i is given by:

$$P_2 = \sigma_i^{Ph}(E_i).\ \rho_i\ dx\ \csc\phi_1 (1-1/J_k^i).w_k^i\ f_\alpha^i \quad \ldots\ldots \text{(ii)}$$

where:

σ_i^{Ph} = Probability of photoelectric effect

J_k^i = Magnitude of the absorption edge

$$f_\alpha^i = \frac{I_{k\alpha}}{I_{k\alpha} + I_{k\beta}},$$

ρ_i = partial density of element i in the sample

3. Probability that the k- X-rays of E_i will penetrate out of the sample and be detected is given by:

$$P_3 = \Omega_2 \exp-\left[(\mu/\rho(E_i)\ \rho x\ \csc\phi_2\right] .\ \Sigma(E_i) \ldots\ldots\ldots \text{(iii)}$$

where

Σ = Detection efficiency of the detector

As at the detector, the fluorescent intensity, dI_i is given by the product $P_1 \times P_2 \times P_3$.

$$dI_i = I_o \Omega_1 \Omega_2 \csc\phi_1\ \rho_i\ \sigma_i^{Ph}(E_1)(1-1/J_k^i).w_k^i f_\alpha^i .\Sigma(E_i)\exp(-a\rho x)dx$$

$\ldots\ldots$(iv)

a = total mass absorption of the primary and fluorescent radiations in the sample.

ie. $a = \mu/\rho(E_1)\ \csc\ \phi_1 + \mu/\rho(E_i)\ \csc\phi_2$

Since $[I_o \Omega_1 \Omega_2 \csc\phi_1\ \rho_i\ \sigma_i^{Ph}(E_1)(1-1/J_k^i).w_k^i f_\alpha^i .\Sigma(E_i)]$ is a constant, say c, then

$$dI_i = C \exp(-a\rho x)\, dx \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (v)$$

On integration with limits $x=o \longrightarrow x=d$, equation (v) yields:

$$I_i = C(\rho_i d) \left[\frac{1-\exp(-a\rho d)}{a\rho d}\right] \quad \ldots\ldots\ldots\ldots (vi)$$

which can be re-written as:

$$I_i = I_o \Omega_1 \Omega_2 \csc\phi_1 \sigma_i^{Ph}(E_1)(1-1/J_k^i).w_k^i\, f_\alpha^i\, .\, \Sigma(E_i)\, \rho_i d \left[\frac{1-\exp(-a\rho d)}{a\rho d}\right]$$

$\ldots\ldots (vii)$

OR

$$I_i = G_{o(t)}\, K_i\, (\rho_i d) \left[\frac{1-\exp(-a\rho d)}{a\rho d}\right]$$

where $G_{o(t)} = \Omega_1 \Omega_2 \csc\phi_1$ and is the geometry constant in (c/s) and which depends on the activity of the source and thus changes with time.

$G_{o(t)}$ is the geometry at time t.

$K_i = \sigma_i^{Ph}(E_1)\, f_\alpha^i\, w_k^i (1-1/J_k^i).\, \Sigma(E_i)$ and is the relative excitation-detection efficiency in cm^2/g where;

$\sigma_i^{Ph}(E_1)$ = photoelectric cross-section for element i and primary radiation, say, of Ag Kα (22.1 KeV).

w_k^i = fluorescence yield of i for the k-shell

$$f_\alpha^i = \frac{I_{k\alpha}}{I_{k\alpha} + I_{k\beta}} \quad \text{or} \quad \frac{I_{L\alpha}}{I_{L\alpha} + L_{L\beta}}$$

J_k^i = absorption jump at the k-edge of the photoelectric absorption of element i.

$\Sigma(E_i)$ = detection efficiency for X-rays of energy, E_i.

$\frac{1-\exp(-a\rho d)}{a\rho d}$ is called the absorption correction factor and may be written as A_{corr}

This factor helps in correcting for:

(i) absorption of primary radiation within the sample which renders it less effective in exciting atoms of elements located deeper in the sample.

(ii) absorption of the fluorescence radiation within the sample and along their way out in the direction of the detector.

A_{corr} is determined experimentally by the use of a thick multielement target made from an admixture of chemical salts, of, say, Ti, Mn, Zn, Br and Nb of high purity. Three measurements are made viz:-

(i) Intensity of element of interest to give I_1^i

(ii) Intensity of target elements when the target is placed on the sample to give I_2^i, and

(iii) Intensity of target elements alone to give I_o^i

The $a\rho d$ for the target elements are then calculated on the basis of the attenuation law using the equation;

$$a\rho d = \log \frac{I_o^i}{I_2^i - I_1^i}$$

and from a plot of $a\rho d$ values of these target elements against their characteristic energies on a log-log scale, it is possible to obtain the approximate $a\rho d$ values of elements of interest in the sample by interpolation.

*For transparent samples, $0.1 < a\rho d < 2$ and therefore A_{corr} must be determined.

*For thick samples, d is big and $\rho d \rightarrow \infty$. The equation thus becomes

$$I_i = G_o K_i (\rho d)_i \cdot \frac{1}{a\rho d}$$

$$= G_o K_i \alpha_i \cdot \frac{1}{a} \quad \text{where } a = a(\alpha_i)$$

and $(\rho d)_i = \alpha_i$

*For thin samples, d is very small making

$$\frac{1-\exp(-a\rho d)}{a\rho d} \simeq 1$$

Thus the equation now becomes:

$I_i = G_o K_i (\rho d)_i$ where $(\rho d)_i$ is the uncorrected concentration of element i in the sample.

The intensity of radiation of element i is now proportional to the concentration of i and therefore there are no absorption and interelement effects. The uncorrected concentration for the thin sample (eg. liquid sample) is then obtained from the equation as

$$(\rho d)_i = \frac{I_i}{G_o K_i}$$

and the value obtained is then divided by the mass per unit area of the pellet, ρd in case of solid samples.

Therefore $(\rho d)_i^{corr} = \frac{I_i . \text{area of pellet}}{G_o K_i . \text{mass of sample}}$

If any dilution has been done, the final value is multiplied by the dilution factor to obtain the actual element concentration in the sample.

2.13 TYPICAL APPLICATION OF XRFA

-analysis of cements

-metals and alloys

-air particles in pollution

-forensic studies

-trace element analysis

-radiation protection and monitoring

2.14 ADVANTAGES OF XRF SPECTROMETRY OVER OTHER TECHNIQUES

-the spectra are easy and regular as compared with optical emission spectra and are independent of chemical state.

-non-destruction of specimen during analysis enables other tests and repeat analyses to be done when desired.

-the technique can deal with a variety of specimen forms (solid, powder, paste, liquid or gas), which may be distributed on filter paper, mylar film, cellulose tape, ion-exchange resin etc.

-qualitative and quantitative analyses may be performed easily.

-operations can be carried out by less skilled manpower.

-small selected areas can be analysed in place so that contamination and loss by chemical or physical separation are avoided.

-X-ray spectroscopy is very rapid and convenient measuring many elements at a time eg. MCA analysing 20 or 30 elements in a minute or less.

2.15 LIMITATIONS

-the sensitivity of the commercially available spectrometers decreases with decreasing atomic number such

that they are substantially useless for elements of $Z<9$.

-the method is sensitive to surface texture (only a thin surface layer) and gives average bulk composition only for homogeneous substances.

-the initial cost of an X-ray spectrometer - especially an automatic one - is high although the operation costs are low.

CHAPTER THREE

EXPERIMENTAL

REAGENTS AND MATERIALS

1. Stock solutions of the elements manganese, iron, cobalt, copper, zinc and molybdenum prepared from the analytical grade salts.
2. Double Distilled Water (DDW).
3. 1% Ammonium pyrrolidine dithiocarbamate (APDC) [1-Pyrrolidinecarbodithioic acid, ammonium salt)- prepared by dissolving 1.00g of the salt into 100 cm^3 solution in a volumetric flask and used when fresh.
4. 2% Sodium diethyl dithiocarbamate (NaDDTc). [Diethyldithiocarbamic acid, sodium salt trihydrate].
5. Ammonium hydroxide - analar.
6. Nitric acid - analar.
7. Lime.
8. 1M magnesium chloride solution at pH 7 prepared from analytical grade salt.
9. Hydrochloric acid - analar.
10. Buffer solutions made for pH 2.6-12.
11. Sulphuric acid - analar.
12. 0.45 µm millipole filter membranes.
13. Whatman No. 2 filter papers.

3.0 ACCURACY

In order to determine the accuracy of the EDXRFA instrument (the Multi-Channel Analyser), recovery experiments were performed. These were done for both solid and liquid samples/standards.

3.0.1 Solids

Thin pellets were prepared using IAEA certified Referenc Materials following the method described in section 3.2.1 below. The results obtained after irradiation with the X-rays were compared with the ones available for each element from the CRM certificate. The CRM samples analysed were soil-7 and SY-3.

3.0.2 Liquids

To obtain the elemental concentrations in a liquid using EDXRF analysis, co-precipitation technique was adopted. This method involved the formation of insoluble chelates via coordination with either ammonium pyrrolidine dithiocarbamate (APDC) or sodium diethyl dithiocarbamate (NaDDTc).

3.0.2.1 Standard Preparation and Treatment

Standard stock solutions of known concentrations for the elements manganese, iron, copper, zinc, cobalt and molybdenum were prepared from their pure analytical grade salts. From these, mixed standards were prepared and their pH values were varied using dilute solutions of ammonia and/or nitric acid. For APDC, the pH was varied between pH 1 and pH 8 in units of one, while for NaDDTc pH values ranged from pH 3 to pH 9.

3.0.2.2 Co-precipitation

To 100 cm^3 of the pH-adjusted standard solution in a 250 cm^3 beaker, 10 cm^3 of freshly prepared 1% APDC or 2% NaDDTc solutions in water (by weight) were added and allowed to stand with intermittent stirring for 30 and 15 minutes respectively. The resulting precipitate was then filtered through a 0.45 μm millipole filter membrane (previously soaked in dilute nitric acid and rinsed thoroughly with double distilled water to remove any metal contamination) under pressure. The filter was air-dried and placed in a clean petri-dish awaiting XRF analysis. From the recovery results obtained after X-ray irradiation, pH for best recovery was selected for each reagent and noted down.

3.0.3 Minimum Detection Limit

The minimum limit of detection was determined for all elements of interest (manganese, iron, cobalt, copper, zinc and molybdenum) using the formula:

$$MDL = \frac{3}{m} \{ I_b / T_b^2 \}^{\frac{1}{2}}$$ [Jenkins et al., 1981]

where

m = gradient of calibration graph (in counts/μg)

I_b = intensity of the background

and

T_b = analysis time

In all the analyses, T_b was maintained between 2000 and 20,000 seconds using the ^{109}Cd radioisotope source.

To achieve this, mixed (multielement) standards were prepared as in sec. 3.0.2.1 but with a pH of 2 for APDC and pH 6 for NaDDTc (as obtained from the results of 3.0.2.2).

A blank containing only a single element and the co-precipitating reagent was prepared to be used in obtaining net counts in the calibration and in any other analyses.

The calibration curves were obtained from a plot of the measured net counts (intensity) of a single element's characteristic line versus the mass of each standard element (in μg). From the graph, the gradient, m, (in counts/μg) and the background, b, were calculated using the least square method. The general calibration equation for the calibration line is $y = mx + b$. MDL for soil elements were determined by pelletilization followed by irradiation (Jenkins et.al. 1981).

3.0.4 Precision

This term refers to the distribution of reproducibility of replicate results (or measurements). By defination, precision, P_i, quantitatively is the difference between the individual measurement, m_i, and the mean $\bar{m}$ of a large set of independent replicate measurements of analysis, usually expressed relative to the mean as a percent:

i.e. $$P_i = \frac{m_i - \bar{m}}{\bar{m}} \times 100\%$$

In this work the precision of the experimental technique was obtained by preparing and irradiating eight different pellets of approximately the same weight from the same soil sample following the preparation method described in section 3.2.1 below. Irradiation was done using the ^{109}Cd radioisotope source on a Si/Li detector for 10,000 seconds and then the elemental concentrations were calculated. The standard deviation was also calculated for the elements of interest using the general formula:

$$S = \sqrt{\frac{1}{n}\sum_i (X_i - m)^2 \, f(x_i)} = \sqrt{\frac{1}{n}\sum_i x_i^2 \, f(X_i) - m^2}$$

where

n = sample size

$f(x_i)$ = frequency of occurrence of value x_i in the sample

m = mean

3.1 SOIL SAMPLING

Batches of soil samples in both the basic and the acidic pH ranges were collected in black polythene bags and given code-numbers. The sample weight was approximately 3 kg. Among the sampling places were Nyeri, Kabete, Murang'a, Kibirigwi irrigation scheme, Kajiado and Rongai.

These soil samples were then air-dried followed by grinding at the National Agricultural laboratories to a size that could pass through a 0.2 mm sieve. They were then stored in a cool, dry place.

3.2 SAMPLE PREPARATION FOR EDXRF ANALYSIS

3.2.1 Pelletization

In order to obtain the total concentrations of elements in the soil bulk, pellets were made as follows: Small amounts of a homogenised mixture of the fine soil and a pure binding material (starch or cellulose) were spread on a 2.5 cm diameter steel disc in a hydraulic press and pressed at a pressure of about 5K Pa. The process was repeated in order to make at least four pellets of about 0.2g each. These pellets were weighed (by difference method) in order to determine the mass per unit area of the

sample to be irradiated. The dilution factor was calculated from the mixing ratios of the sample weight to that of the dilutant. This process was repeated for all the soil samples obtained from different areas.

3.2.2 pH readings

All the pH readings were taken using a Pye Unicam Model 292 pH meter. To get the soil pH, 20g of air-dry soil was scooped and transferred into a 100 cm^3 plastic shaking bottle. A blank containing only distilled water was also set alongside the sample. 50 cm^3 of distilled water was added to the bottles (to give a 1: $2\frac{1}{2}$ soil: water suspension) and shaken for two hours in a reciprocal shaker. The suspension was then homogenised by short but vigorous manual shaking followed by pH reading as pH H_2O (Hesse, 1971). missing in the list of references.

3.2.3 Available Trace Elements

To get the available content of trace elements manganese, zinc, copper, iron, molybdenum and cobalt in the soil, soil extractions using: A- a freshly prepared 0.1M HCl solution and B- buffer solution were done.

3.2.4 Preparation of Extracting Reagents

A. 0.1M HCl

0.1M HCl was prepared by first diluting 88.5 cm^3 of concentrated hydrochloric acid (11.3M) of s.g. 1.18 into 1000 cm^3 using distilled water to make a 1M HCl solution and then diluting this solution ten times. This was done by aliquoting 100 cm^3 of 1.0M HCl in a 1000 cm^3 volumetric flask and making to the mark with the distilled water. This was used the same day while the remainder was discarded to ensure freshness.

B. Buffer solution of pH range 2.6-12

A mixture of the following analytical grade salts was made using distilled water in a 1000 cm^3 volumetric flask.

6.008g citric acid,

3.893g potassium dihydrogen phosphate,

1.769g boric acid, and

5.266g barbitol (Diethylbarbituric acid).

100 cm^3 of this mixture added to known volumes (X) of 0.2M NaOH solution gave the following pH values at 18°C.

Table 3

X cm^3	pH	X cm^3	pH	X cm^3	pH
2.0	2.6	36.5	5.8	74.0	9.2
4.3	2.8	38.9	6.0	74.9	9.4
6.4	3.0	41.2	6.2	77.6	9.6
8.3	3.2	43.5	6.4	79.3	9.8
10.1	3.4	46.0	6.6	80.8	10.0
11.8	3.6	48.3	6.8	82.0	10.2
13.7	3.8	50.6	7.0	82.9	10.4
15.5	4.0	52.9	7.2	83.9	10.6
17.6	4.2	55.8	7.4	84.9	10.8
19.9	4.4	58.6	7.6	86.0	11.0
22.4	4.6	61.7	7.8	87.7	11.2
24.8	4.8	63.7	8.0	89.7	11.4
27.1	5.0	65.5	8.2	92.0	11.6
29.5	5.2	67.5	8.4	95.0	11.8
31.8	5.4	69.3	8.6	99.6	12.0
34.2	5.6	71.0	8.8		
		72.7	9.0		

3.2.5 Extraction Procedure

After each pH analysis on a soil, extraction of trace elements was done as follows:

50 cm^3 of either 0.1M HCl or buffer solution of the same pH value as the soil being extracted, was added to 5g of a soil in a shaking bottle and the bottle was then stoppered. A blank was also set up similarly but without soil and both bottles and their contents were shaken on a reciprocal shaker for one hour. The suspension was then filtered through a pre-washed filter paper (Whatman No. 2) and the filtrate (now containing the trace elements) was stoppered awaiting X-ray analysis. This was repeated for all the batches of soil being analysed.

3.3 pH VARIATION IN SOILS

3.3.1 Lime Analysis

Total and available trace element analyses were carried out on lime to ascertain its effect on these trace elements' levels on soils being incubated with it. This was done by pelletization as in section 3.2.1 (for the total elements) and extraction with 0.1M HCl for the available elements as in sec. 3.2.5 above.

3.3.2 Acid Soil Reclamation

Two acid soils (S1 and K1B) were selected and incubated in clean perforated plastic containers using varying amounts of lime following the procedure by Ssali & Nuwamanya (1980). The incubation period was $3\frac{1}{2}$ months within which, periodic wetting, mixing and breaking of large crumbs into fine particles were done. At the end of this period, the samples were air-dried, re-ground and sieved. 0.1M HCl and buffer solutions were used

for extraction of the heavy metals on the various samples after doing their pH analyses.

3.3.3 Basic Soil Reclamation

Two basic soils (Kaj and Ron) were also selected for acidification. The pH was determined using the pH-meter after which the pH was lowered using varying amounts of dilute sulphuric acid in two large buchner funnels (leaching). After the first acid washing, a certain amount of the soil would be scooped out, allowed to dry, ground in a motor and weighed for pH analysis and for acid (0.1M HCl) extraction. A more concentrated acid solution would then be added to the remaining soil and the process of scooping followed by pH analysis and extraction repeated. This yielded varying pH ranges and varying amounts of the extracted heavy metals.

3.4 USE OF POLYVINYL PYRROLIDONE (PVP) AS A BINDER

Starch as a binding agent was found to be poor for samples whose organic matter content was very low as is the case with Rongai and Kajiado soils. In such cases, large amounts of starch was required which had the disadvantage of eclipsing the low concentration elements rendering them undetectable. This necessitated the use of an alternative binding agent - the PVP- which was used even at low dilution factors. The results using both starch and PVP were then compared.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 PREPARATION OF STANDARDS AND ANALYSIS

Starting with 1000 µg stock solutions of the elements manganese, iron, cobalt, copper, zinc and molybdenum which had been previously prepared from their salts, 10 µg standard solutions were prepared separately after succesive dilutions. Mixed standards were then prepared and their trace elements precipitated using both NaDDTc and APDC at various pH values. From the results obtained here, the pH for best recovery was established and also the accuracy of the technique was determined. Minimum limits of detection were also calculated from these results.

^{109}Cd source with a runtime of 10,000 seconds was used for irradiation in the XRF instrument.

Table 4a: (i) Trace element recoveries using NaDDTc (in ppm)

		pH 4.0		pH 5.0	
Element	Expected (Theoretical)	Observed (Experimental)	% Recovery	Experimental	% Recovery
Mn	50	46.7±1.9	93.4	48.6±0.7	97.2
Fe	40	37.8±1.2	94.5	37.3±1.0	93.3
Co	6	4.8±0.4	80.0	6.3±0.3	105.0
Cu	10	10.3±0.4	103.0	9.6±0.2	96
Zn	10	11.0±0.3	110.0	10.3±0.2	103.0
Mo	12	0	0	0	0

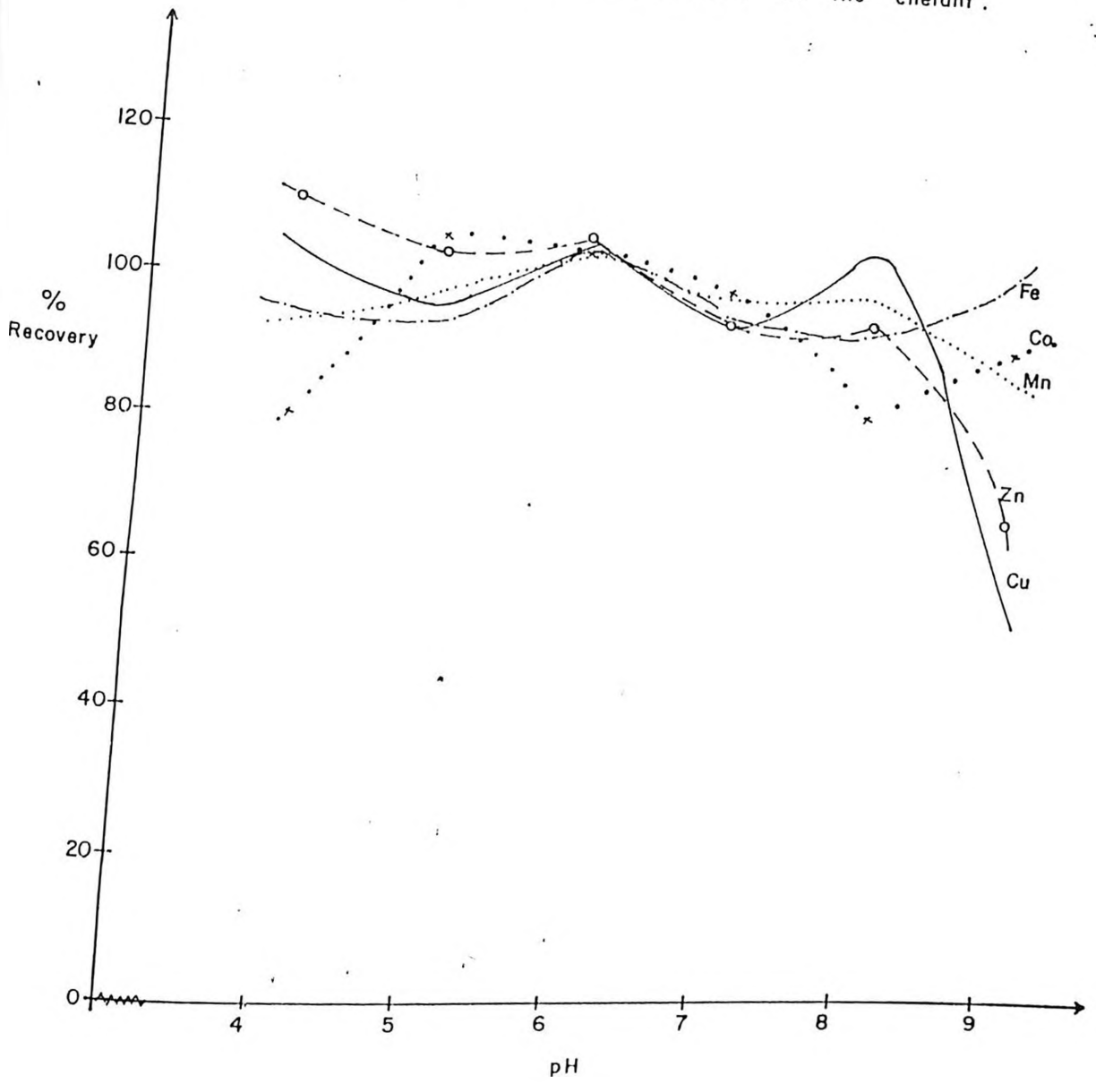
Table 4a (i) Trace element recoveries using NaDDTc (in ppm) cont'd

Element	pH 6.0		pH 7.0	
	Experimental Recovery	% Recovery	Experimental Recovery	% Recovery
Mn	51.4±1.3	102.8	48.7±1.7	97.4
Fe	41.5±1.1	103.75	38.0±1.9	95.0
Co	6.2±0.6	103.3	5.9±0.9	98.3
Cu	10.5±0.6	105.0	9.4±0.5	94.0
Zn	10.6±0.5	106.0	9.4±0.5	94.0
Mo	0	0	0	0

Element	pH 8.0		pH 9.0	
	Experimental Recovery	% Recovery	Experimental Recovery	% Recovery
Mn	49.4±1.3	98.8	43.9±1.4	87.8
Fe	37.3±1.5	93.3	40.9±1.8	102.3
Co	4.9±0.9	81.7	5.5±0.5	91.7
Cu	10.5±0.5	105.0	5.6±0.5	56.0
Zn	9.5±0.5	95.0	6.7±0.5	67.0
Mo	0	0	0	0

From the results in table 4a (i) above, it was observed that although the recovery was generally good in the entire pH range 4-9, it is evident that the optimum pH is 6 when using NaDDTc. This is observed more clearly from the plot of percentage heavy metal recoveries versus pH of the standards (Fig. 4a).

Fig. 4a : Plot of percentage recoveries of elements Mn, Fe, Co, Cu, Zn, and Mo pH of the standards using NaDDTC as the chelant.



It was further observed that molybdenum was not recovered at all using NaDDTc as the complexing agent. An attempt was made to complex it using APDC for the same elements but at different concentrations. The molybdenum concentration was increased to 20 µg as suggested by Herglotz and Birks (1978). pH variation using APDC was done between pH 2.0 and pH 8.0 as shown in Table 4a(ii) below.

4a(ii) Trace element recoveries using APDC (in ppm)

Element	Mn		Fe		Co	
Expected Concent-ration	50		20		5	
at	Observed Conc.	% Recovery	Observed Conc.	% Recovery	Observed Conc.	% Recovery
pH 2.0	-	0	20.6±1.4	103.0	5.2±0.5	104.0
pH 3.0	0.26±0.14	0.52	19.4±0.7	98.0	5.2±0.4	104.0
pH 4.05	0.4±0.2	0.8	19.5±0.6	97.5	5.1±0.3	102.0
pH 5.0	0.4±0.24	0.8	19.5±0.7	97.5	5.3±0.6	106.0
pH 6.1	0.42±0.24	0.84	19.7±0.9	98.5	5.5±0.5	110.0
pH 7.0	0.42±0.31	0.84	18.4±0.9	92.0	5.0±0.3	100.0
pH 8.0	4.9±0.5	9.8	19.9±0.5	99.5	5.3±0.3	106.0

4a(ii) Trace element recoveries using APDC (in ppm) cont'd

Element	Cu		Zn		Mo	
Expected Concent-ration	20		20		20	
at	Observed Conc.	% Recovery	Observed Conc.	% Recovery	Observed Conc.	% Recovery
pH 2.0	19.6±0.7	98.0	21.5±0.8	107.5	19.8±0.5	99.0
pH 3.0	18.4±0.6	92.0	20.3±0.7	101.5	16.7±0.4	83.5
pH 4.05	18.4±0.5	92.0	20.2±0.7	101.0	0.4±0.05	2.0
pH 5.0	18.7±0.5	93.5	20.7±0.6	103.5	0.3±0.05	1.5
pH 6.1	17.3±0.9	86.5	20.5±0.5	102.5	0.4±0.1	2.0
pH 7.0	14.3±0.5	71.5	17.3±0.7	86.5	0.3±0.1	1.5
pH 8.0	14.3±	71.5	15.5±0.5	77.5	0.07±0.02	0.35

From the results in the table 4a(ii), it is quite evident that APDC is a suitable complexing agent for iron, cobalt, copper and zinc over the whole pH range of pH 2-7. The recoveries of copper and zinc however decrease at pH 8.0 suggesting that probably at pH > 8.0 APDC is not a suitable complexing agent. This is supported by the IAEA technical document (1983) which suggested that the suitable ranges for this complexing agent are below pH 8. pH 2 was found to be the most suitable for molybdenum recovery while manganese was not recovered in any appreciable amounts over the whole pH range using APDC.

In conclusion, it is clear that whenever analyses of these heavy metal element's levels are to be done as liquids (as in the case of available contents), both APDC (at pH 2) and NaDDTc (at pH 6) should be used as complexing agents - the former chiefly used for molybdenum determination.

Fig. 4b below shows the recovery of molybdenum in relation to the pH using APDC.

4.2 Trace element recovery using NaDDTc at pH 6.

In order to confirm the general applicability of pH 6 when using NaDDTc during heavy metal complexation, another set of metal standards was prepared and the process of complex formation and irradiation done on them.

Average results of five determinations using NaDDTc at pH 6 (concentration in ppm) are given in table 4b below.

Fig. 4b – Plot of Molybdenum recovery against p^H of the Mo – standard while using APDC as the Chelant.

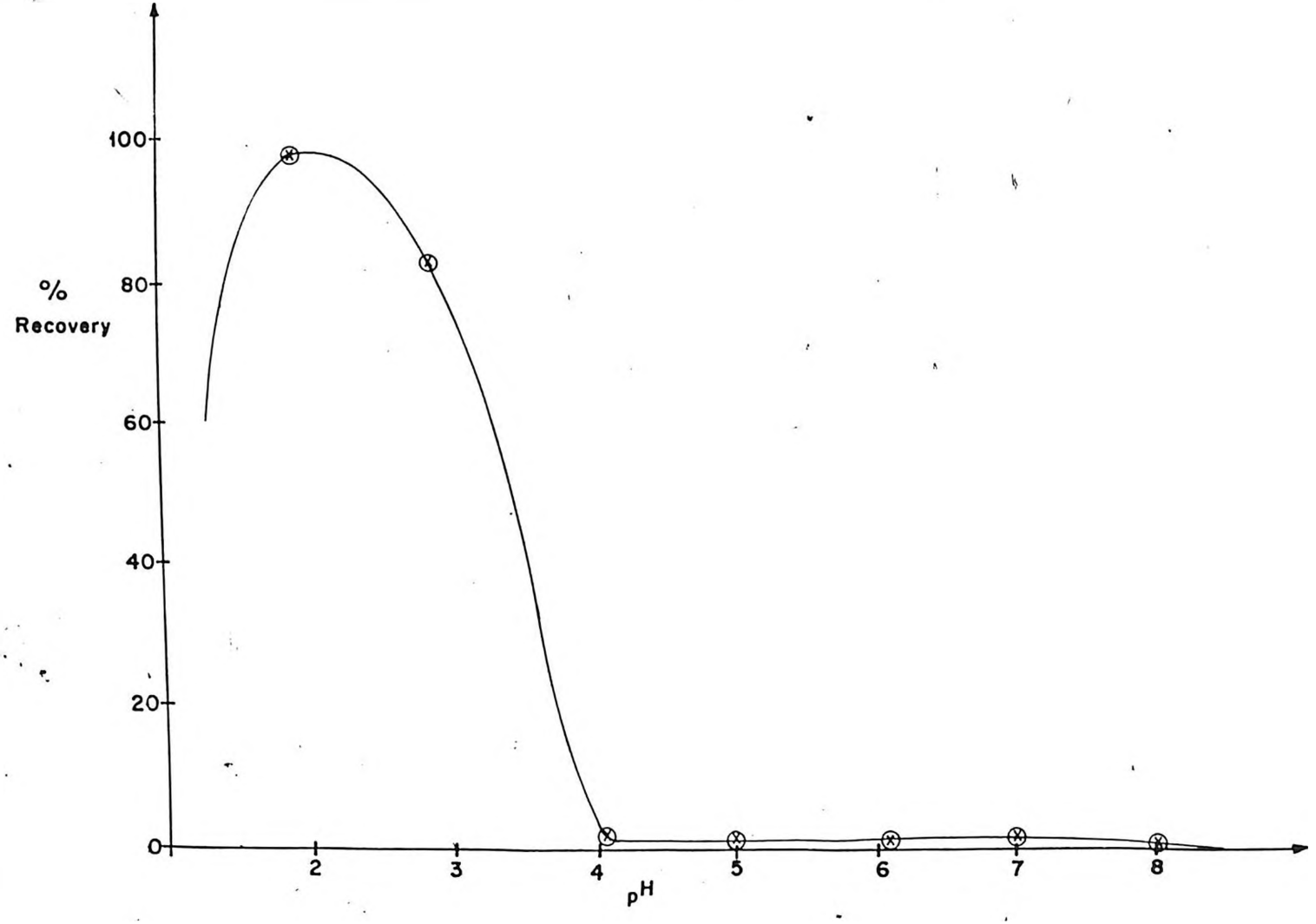


Table 4b

Element	Std 1				Std 2		
	Expected Conc.	Experimental value	% Recovery	Element	Expected Value	Experimental value	% Recovery
Mn	10	9.6±0.9	96.0	Mn	20	19.8±0.6	99.0
Fe	60	57.6±2.6	96.0	Fe	30	30.0±0.7	100.0
Co	2	2.0±0.7	100.0	Co	8	7.9±0.6	100.0
Cu	2	1.9±0.5	95.0	Cu	8	8.6±0.6	107.5
Zn	25	25.1±0.6	100.4	Zn	40	36.0±1.0	90.0
Mo	10	0	0	Mo	2	0	0

Table 4b Cont'd

Element	Std. 3			Element	Std. 4		
	Expected Conc.	Experi-mental value	% Recovery		Expected Value	Experi-mental value	% Recovery
Mn	30	28.8±0.9	96.0	Mn	40	41.5±1.3	103.8
Fe	40	38.0±1.8	95.0	Fe	30	31.1±1.2	103.7
Co	6	5.5±0.6	91.7	Co	4	4.2±0.7	105.0
Cu	10	9.7±0.5	97.0	Cu	20	20.4±1.1	102.0
Zn	10	9.3±0.5	93.0	Zn	5	5.3±0.8	106.0
Mo	4	0	0	Mo	6	0.14±0.06	2.3

Table 4b Cont'd

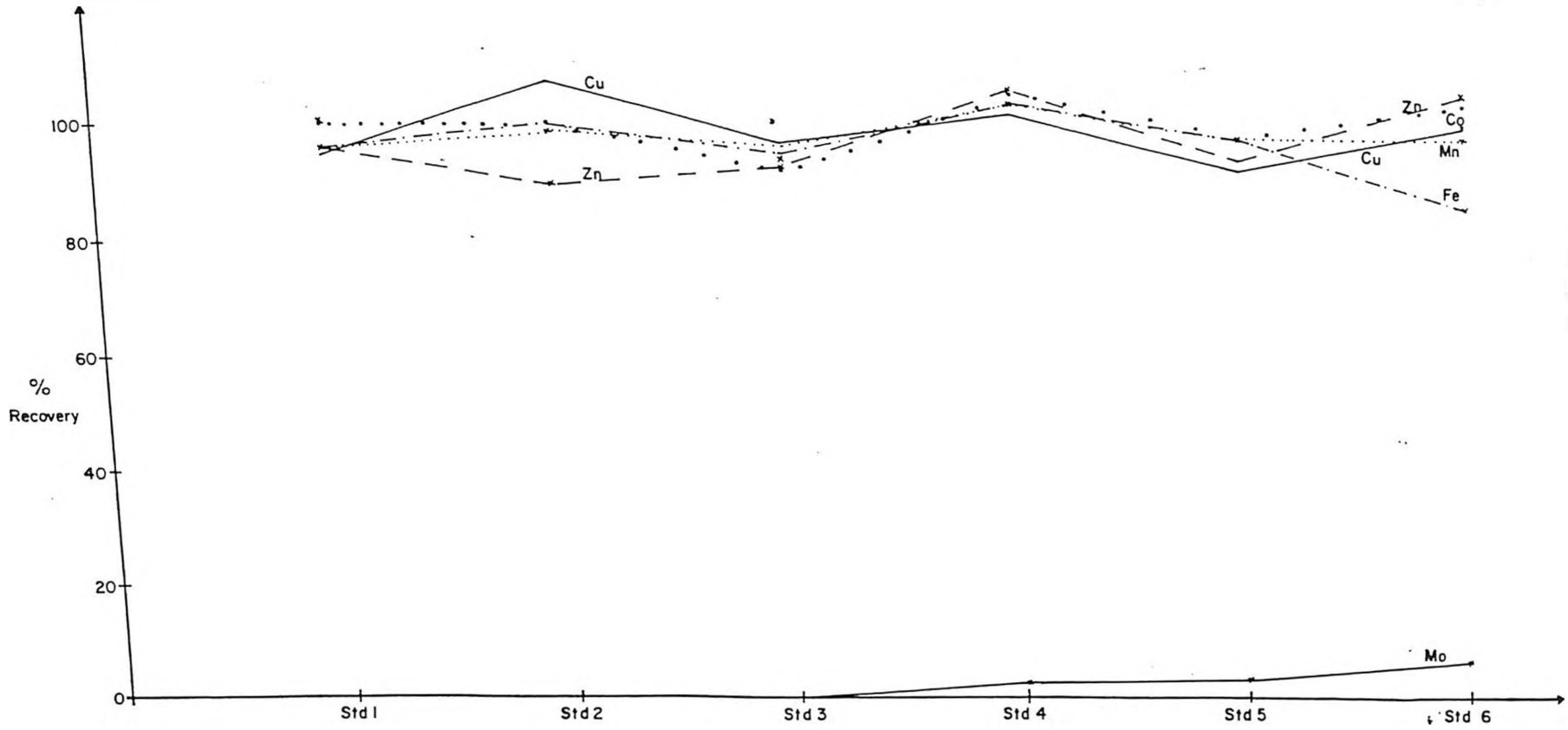
Element	Std. 5			Element	Std. 6		
	Expected Conc.	Experi-mental value	% Recovery		Expected Value	Experi-mental value	% Recovery
Mn	50	48.9±1.7	97.8	Mn	60	58.6±2.8	97.7
Fe	20	19.6±1.1	98.0	Fe	10	8.5±1.1	85.0
Co	5	4.9±0.2	98.0	Co	10	10.4±1.1	104.0
Cu	15	13.8±0.4	92.0	Cu	4	4.0±0.8	100.0
Zn	15	14.1±0.6	94.0	Zn	30	31.8±0.7	106.0
Mo	12	0.36±0.1	3.0	Mo	8	0.5±0.2	6.3

Fig. 4c below shows graphically these metal recoveries at pH 6 for different standard concentrations.

From these results, it is clear that with the exception of molybdenum, the recoveries of all the other elements (iron, cobalt, zinc, manganese and copper) at pH 6 with NaDDTc, are almost 100%. This means that at pH 6, NaDDTc is a good complexing agent for these five elements while, as was found out earlier, APDC at pH 2 is good for molybdenum.

These two complexing agents at their respective pH ranges for best recovery were then used to precipitate these elements in various soil extracts.

Fig. 4c: % Recoveries of elements using NaDDTc at pH 6



4.3 RESULTS OF THE IAEA CERTIFIED REFERENCE MATERIALS (AN AVERAGE OF FIVE DETERMINATIONS)

Table 4c 1. Soil-7

Element	Concentration (range) from CRM certificate µg/g	Average concentrations obtained µg/g
Ti	2600-3700	2840
Cr	ND	21.3
Mn	604-650	639.2
Fe	2520-2630	2727
Co	ND	453.1
Cu	9-13	9.54
Zn	101-113	105.4
Br	3-10	4.18
Rb	47-56	49.8
Sr	103-114	112.0
Y	15-27	20.6
Nb	7-17	15.6
Pb	55-71	88.3
Zr	180-201	197.6

Table 4d

2. Soil-5Y3

Element	Concentration (range) from CRM certificate µg/g	Average concentrations obtained µg/g
Ti	900	ND
Mn	2600	2640.2
Fe	49000	49656.2
Co	12.0	13.2
Cu	17	18.0
Zn	250	254
Br	–	–
Rb	210	213.8
Sr	300	283.8
Y	740	727.8
Zr	340	340.8
Nb	145	146.8
La	1400	1404
Ce	2000	2240
Th	980	970.5
U	640	628

With the exception of iron and lead in Soil-7, all the other elements have their concentrations falling within the ranges given in the CRM certificate. The higher iron concentration may be due to contamination since iron is the most abundant of the heavy elements.

Lead has other close L-lines whose intensity may add to that in the L_α ones leading to higher values of concentration. A lower K_i value may also lead to higher concentration of lead.

There is also very close agreement between the observed and the expected concentration values in the soil SY-3. This in effect suggests that the XRF technique in use in this research work is accurate and reproducible as had earlier been confirmed using liquid standards.

The following standard deviation tables serve as proof of the accuracy of this technique due to their low % st. dev. values.

Table 4e Soil-7

Element	CRM Certificate Range (µg/g)	Expected Average, m	Observed Average, $\bar{m}$	Calculated St. deviation, s	% S.D.
Ti	2600-3700	3150	2840	310	9.8
Mn	604-650	627.0	639.2	12.2	1.9
Fe	2520-2630	2575	2727	152	5.9
Co	ND	-	453.1	-	-
Cu	9-13	11.0	9.54	1.46	13.3
Zn	101-113	107.0	105.4	1.6	1.5
Br	3-10	6.5	4.18	2.32	35.7
Rb	47-56	51.5	49.8	1.7	3.3
Sr	103-114	108.5	112.0	3.5	3.2
Y	15-27	21.0	20.6	0.4	1.9
Nb	7-17	12.0	15.6	3.6	8.3
Pb	55-71	63.0	88.3	25.3	40.2
Zr	180-201	190.5	197.6	7.1	3.7

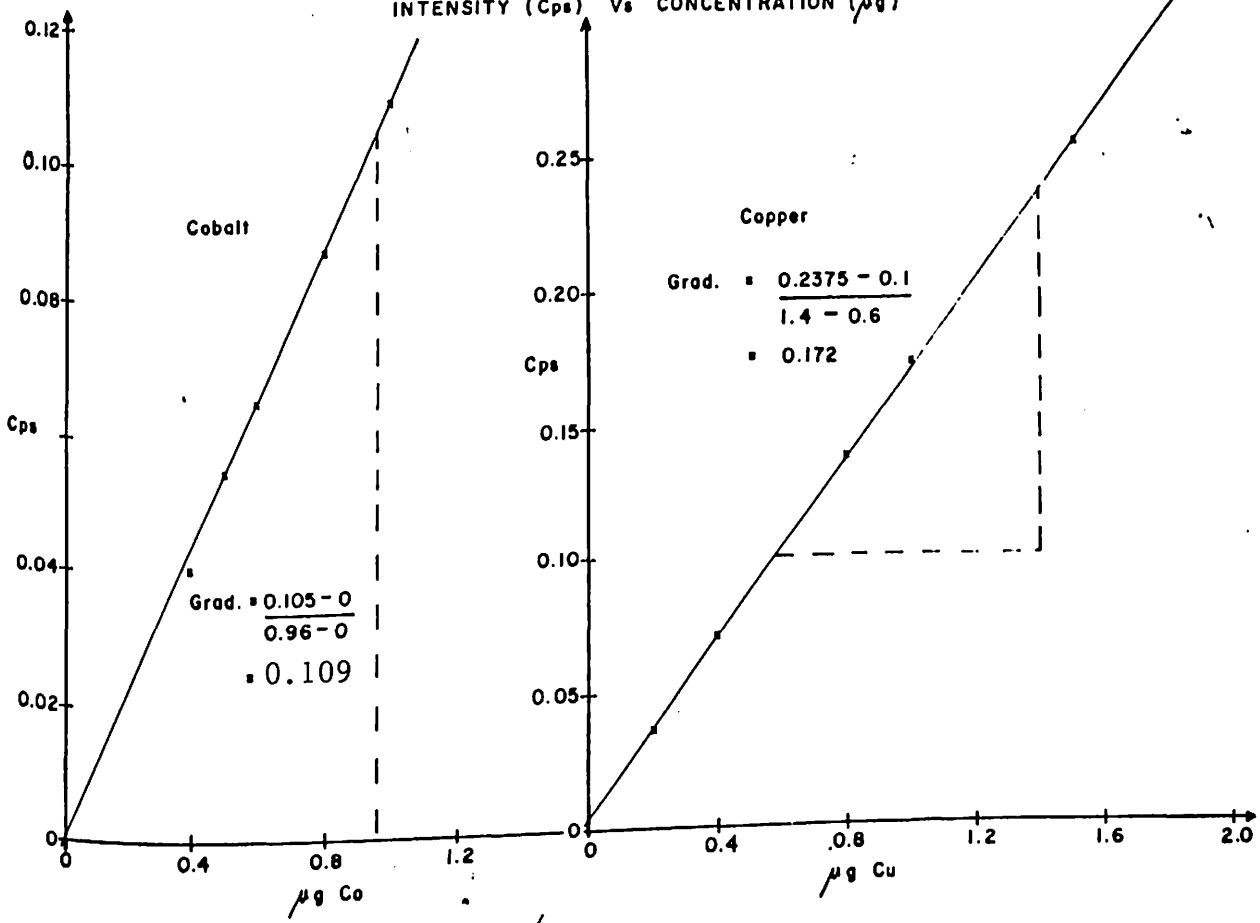
Table 4f

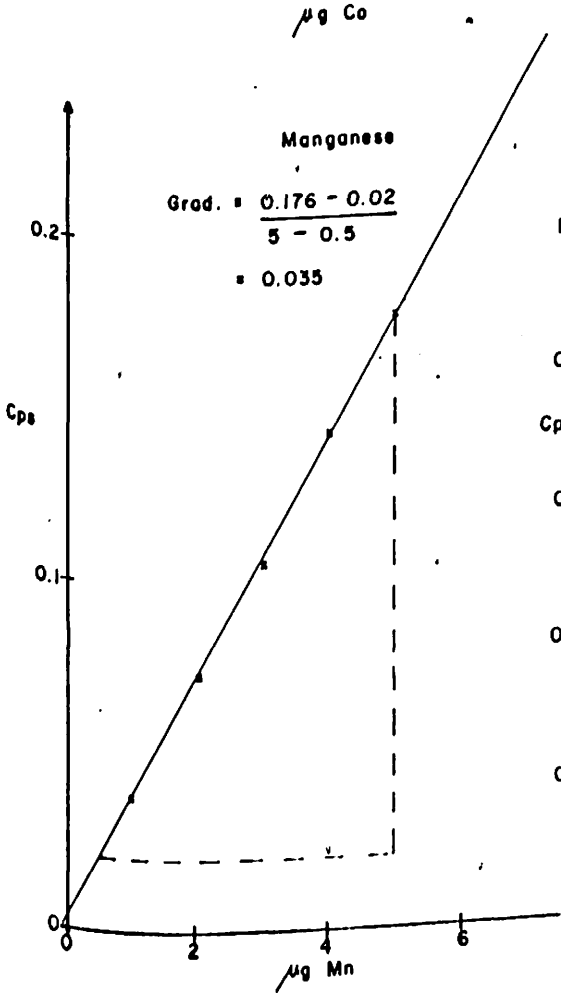
Soil SY-3

Element	Expected Conc.	Observed Conc.	Calculated Standard Deviation	% Standard Deviation
Ti	900	-	-	-
Mn	2600	2640.2	40.2	1.5
Fe	49000	49656.2	656.2	1.3
Co	12	13.2	1.2	(10)
Cu	17	18	1.0	5.9
Zn	250	254	4	1.6
Br	-	-	-	-
Rb	210	213.8	3.8	1.8
Sr	300	283.8	16.2	5.4
Y	740	727.8	12.2	1.6
Zr	340	340.8	0.8	0.2
Nb	145	146.8	1.8	1.2
La	1400	1404	4.0	0.29
Ce	2000	2240	240	12
Th	980	970.5	10.5	1.07
U	640	628	12.0	1.9

FIG. 4d : MINIMUM DETECTION LIMIT GRAPHS

INTENSITY (Cps) Vs CONCENTRATION (μg)





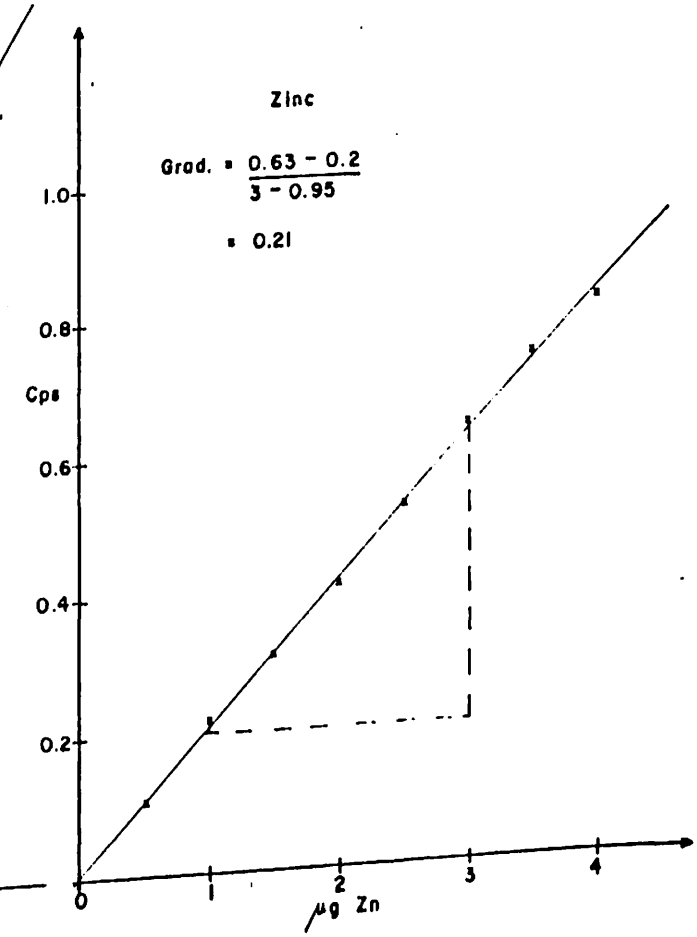
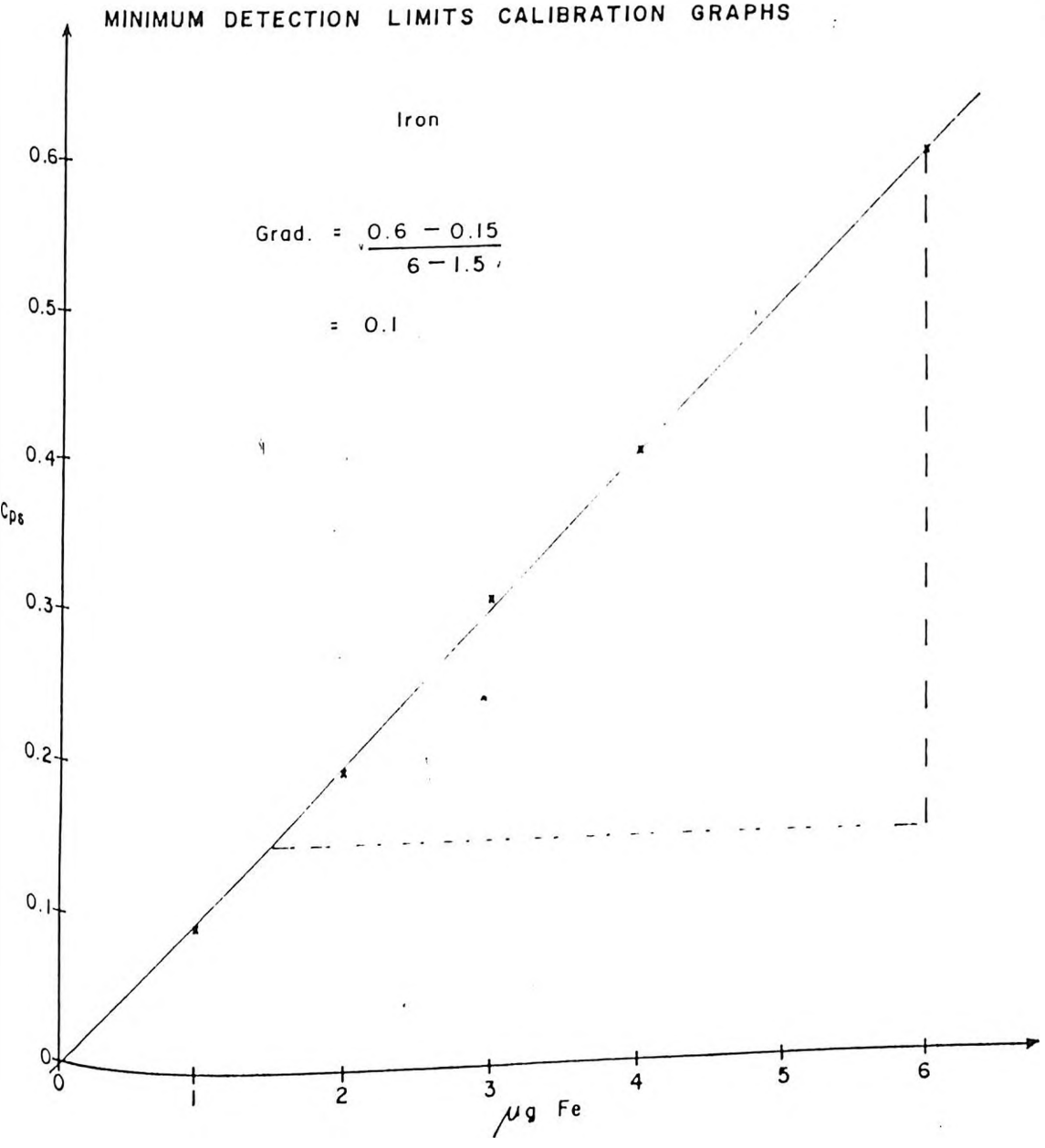


Fig. 4d: Cont'd


MINIMUM DETECTION LIMITS CALIBRATION GRAPHS
Iron
Grad. = 0.6 − 0.15 / 6 − 1.5
= 0.1
0.6
0.5
0.4
0.3
0.2
0.1
0
C_{p6}
0
1
2
3
4
5
6
µg Fe

4.4 MINIMUM DETECTION LIMITS (MDL)

The minimum detection limits for all the elements of interest were determined using the formulae given below:-

For liquid samples:

$$MDL = \frac{3}{m}\sqrt{I_b/T_b^2}$$

where m = the gradient of the calibration graph which was calculated as shown in figs. 4d below.

I_b = intensity of the background

T_b = analysis time

Table 4g below shows the minimum detection limits (MDL) values and the calculating parameters.

Element	Gradient (m)	I_b in (Counts)	Count time T_b (in sec.)	MDL
Fe	0.10	674	5,000	0.16
Mn	0.035	3042	20,000	0.24
Co	0.109	528	5,000	0.13
Cu	0.172	370	5,000	0.07
Zn	0.21	7336	20,000	0.06
Mo	0.054	3515	10,000	0.30

For solid samples (Pellets):

$$MDL = \frac{3 \times \text{std. conc.}}{I_{net} \times A_{corr}}\sqrt{\frac{N_{Bg}}{T^2}}$$

where

$$A_{corr} = \frac{1/(1-\exp(a\rho d)}{a\rho d}$$

and

Std. Conc. = Concentration of the standard element

N_{Bg} = Number of background counts

T = Time in seconds

I_{net} = Total intensity of ($K\alpha_1$ + $K\alpha_2$) or ($L\alpha_1$ + $K\alpha_2$) lines

Ref: Jenkins et al. (1981)

4.5 PRECISION

Precision (repeatability of measurements) was obtained by irradiating 8 pellets of the same soil and calculating the deviation from the mean as

$$P_i = \frac{m_i - \bar{m}}{\bar{m}} \times 100\%$$

where P_i = precision

$\bar{m}$ = mean measurement

m_1 = individual measurement

The table below represents the replicate results of a soil analysed as pellets for precision determination.

Table 4h below shows the minimum detection limits of elements in a soil-7 pellet

Element	Conc. of element in the std.	Net intensity	Back-ground Counts	apd	Time (sec.)	Calcu-lated A_{corr}	Calcu-lated MDL (ppm)
Ti	3150	1.6083	7709	5.6	2000	5.62	45.9
Mn	627	1.83639	10312	2.75	"	2.938	17.7
Co	453.1°	2.00423	****	1.83	"	2.18	-
Cu	11.0	0.102027	4060	1.21	"	1.72	5.99
Zn	107.0	1.02556	7750	1.55	"	1.968	7.0
Rb	51.5	1.33654	4340	0.66	"	1.37	2.78
Y	21.0	1.00292	10541	0.33	"	1.174	2.75
Zr	190.5	10.8451	21360	0.29	"	1.152	3.34
Nb	12.0	0.83323	9980	0.55	"	1.300	1.66
Pb	63.0	0.898463	7986	1.12	"	1.66	5.66

°Value not certified.

MDL - Calculated minimum detection limit.

* - The background intensity is too high for any detection to take place.

Table 4i: Replicate results of total trace element analysis of 8-soil pellets prepared using starch (in %).

Element \ Test #	1	2	3	4	5	6	7	8	Mean
K	3.0404	2.7181	2.8618	2.9896	2.9074	2.6354	3.0967	3.0448	2.9118
Ca	2.0452	1.8871	1.9496	1.8222	1.9928	2.0750	2.239	2.2889	2.0375
Ti	1.8958	1.8822	1.8098	1.8164	1.8601	1.8374	1.8717	2.0338	1.8934
V	0.1286	0.1467	0.1573	0.1461	0.1456	0.1420	0.1549	0.1438	0.1456
Mn	0.8118	0.8027	0.7931	0.8176	0.8337	0.8172	0.8257	0.8208	0.8116
Fe	8.7459	9.2507	8.871	9.1294	9.1644	9.3613	8.7366	9.3109	9.0713
Co	0.1459	0.1454	0.1480	0.1493	0.1471	ND	0.1477	0.1468	0.1472
Cu	0.00332	0.00335	0.00329	0.0032	0.00329	0.00322	0.00323	0.00345	0.00329
Zn	0.0178	0.0170	0.0167	0.0164	0.164	0.0165	0.01757	0.0171	0.0170
Ga	0.00221	0.00213	0.00212	0.00223	0.00211	0.00218	0.00218	0.00213	0.00216
As	0.00128	0.00121	0.00122	0.00125	0.00127	0.00122	0.00133	0.00127	0.00126
Br	0.00065	0.00075	0.00062	0.00062	0.00063	0.00061	0.00077	0.00074	0.00067
Rb	0.0102	0.0109	0.0109	0.00962	0.0102	0.0107	0.01045	0.01055	0.01044
Sr	0.0107	0.0113	0.0113	0.0105	0.0108	0.01115	0.0108	0.0106	0.0109
Y	0.00731	0.00758	0.0069	0.00667	0.00675	0.0075	0.00752	0.00705	0.00716
Zr	0.0770	0.07812	0.07834	0.0787	0.0756	0.0789	0.0794	0.0751	0.0776
Nb	0.0175	0.0181	0.0180	0.0165	0.0168	0.0174	0.0173	0.0170	0.0173
La	0.3791	0.3582	0.3721	0.3474	0.3627	0.3550	ND	0.3606	0.3622

The general equation for calculating the precision is

$$p_i = \frac{\text{experimental value - mean}}{\text{mean value}} \times 100\%$$

say Iron p_1 $\frac{8.7459-9.0713}{9.0713} \times 100\% = 3.6\%$

p_2 $\frac{9.2507-9.0713}{9.0713} \times 100\% = 1.98\%$

$p_3 = -2.21\%$ $p_6 = 3.2\%$

$p_4 = 0.64\%$ $p_7 = -3.7\%$

$p_5 = 1.0\%$ $p_8 = 2.6\%$

Cobalt $p_1 = -0.88\%$ $p_5 = -0.068\%$

$p_2 = -1.2\%$ $p_6 = ND$

$p_3 = 0.54\%$ $p_7 = 0.34\%$

$p_4 = 1.4\%$ $p_8 = -0.27\%$

Copper $p_1 = 0.91\%$ $p_5 = 0\%$

$p_2 = 1.8\%$ $p_6 = -2.1\%$

$p_3 = 0\%$ $p_7 = -1.8\%$

$p_4 = -2.7\%$ $p_8 = 4.9\%$

Zinc $p_1 = 4.7\%$ $p_5 = -3.5\%$

$p_2 = 0\%$ $p_6 = -2.9\%$

$p_3 = -1.76\%$ $p_7 = 3.35\%$

$p_4 = -3.5\%$ $p_8 = 0.59\%$

Manganese $p_1 = 0.02\%$ $p_5 = 2.7\%$

$p_2 = -1.1\%$ $p_6 = 0.69\%$

$p_3 = -2.28\%$ $p_7 = 1.74\%$

$p_4 = 0.74\%$ $p_8 = 1.13\%$

The low % precision values (<5%) obtained imply that the difference between one value and another for the same element is very small. This suggests high degree of reproducibility and hence high reliability of the method.

4.6 AVERAGE TOTAL ELEMENTAL CONTENTS OF VARIOUS SOILS PREPARED AND ANALYSED AS PELLETS USING STARCH AS THE BINDING AGENT (IN %).

The total trace element concentrations were obtained by preparing and irradiating 4 thin pellets of each soil or lime and taking the average concentration of each element as shown in tables 4j and 4k below.

Table 4j:

Element \ Sample code	S1	S2	S3	S4
Ti	0.09102	0.337	0.530	0.255
Cr	ND	0.00617	ND	ND
Mn	0.4842	0.2500	0.142	0.464
Fe	10.3524	4.860	6.802	8.694
Co	0.1847	0.0927	0.216	0.1936
Cu	0.0007	0.00464	0.0008	0.00094
Zn	0.0195	0.0165	0.027	0.0102
Br	-	0.0004	0.00084	-
Rb	0.01088	0.01031	0.00178	0.00112
Sr	0.00222	0.03216	0.00197	0.00101
Y	0.01189	0.00907	0.00184	0.00741
Zr	0.184	0.01912	0.0109	0.096
Mo	-	0.00069	-	0.00027
Nb	0.04198	0.01705	0.022	0.051
La	ND	ND	0.340	ND
Pb	0.01541	ND	0.00546	0.01967

ND = not determined

Total Heavy metal contents cont'd (%)

Sample Code / Element	LR352	K15	UF, UL	MM
Ti	0.9153	0.974	1.1203	0.965
Mn	0.4065	0.397	0.1704	0.2801
Fe	10.167	9.490	10.1985	9.860
Co	0.269	0.125	0.1496	0.1538
Cu	-	0.00167	0.00267	0.00233
Zn	0.01098	0.017	0.01223	0.00888
Br	0.00088	0.000271	0.00085	0.000393
Rb	0.00055,	0.00205	0.00206	0.00041
Sr	0.00317	0.028	0.02089	0.00484
Y	0.00457	0.00813	0.00631	0.00412
Zr	0.0514	0.080	0.0591	0.04052
Nb	0.00914	0.0174	0.0119	0.00834
La	ND	0.626	0.6938	0.5507
Pb	0.00145	0.0038	0.00309	0.00298

ND = not determined

Total Heavy metal contents cont'd (%)

Sample Code / Element	RONI	KIB	KAB	RON2
Ti	0.9783	1.8175	0.6216	1.7361
Mn	0.5957	0.7860	0.2998	0.7945
Fe	8.0867	13.808	7.6991	8.7504
Co	0.1255	0.2259	0.06421	0.1242
Cu	0.00323	0.00356	0.00204	0.00331
Zn	0.0192	0.02345	0.01364	0.0177
Br	0.0009	0.00075	0.00047	0.00063
Rb	0.0120	0.00566	0.108	0.0107
Sr	0.0129	0.03508	0.00301	0.0109
Y	0.00779	0.01183	0.00701	0.00775
Zr	0.0848	0.0874	0.1672	0.0794
Nb	0.0197	0.01993	0.0350	0.0175
La	0.2109	0.5203	0.1593	0.3092
Pb	0.00021	-	0.00451	ND

ND = not determined

4.7 AVERAGE TOTAL HEAVY METAL CONTENT IN LIME-ANALYSED AS THIN PELLETS PREPARED USING STARCH AS A BINDING AGENT.

Table 4k

Element	Average elemental concentration in µg/g
Sc	15600
Mn	45.0
Fe	0.40
Co	30.8
Cu	30.2
Zn	26.8
Sr	1393
Zr	54.4
Pb	21.48

4.8 AVAILABLE CONTENTS

After air-drying the soil samples that had been collected, they were later ground and sieved. pH analysis was then done using 1:2½ soil-water ratio. Extraction was also done using 0.1M HCl.

Table 4l below represents the available metal element concentrations in µg/g from different soils and their corresponding pH values. Precipitation of the elements was done using both NaDDTc at pH 6 and APDC at pH 2.

Table 4 l.

Soil Code	Soil pH H_2O	Element					
		Mn	Fe	Co	Cu	Zn	Mo
S1	5.4	225±8.1	35.5±4.6	-	3.2±0.7	5.1±1.3	-
S2	8.1	94±1.0	11.5±2.2	-	1.6±0.2	1.4±0.1	-
S3	6.9	133±3.8	119.7±5.0	1.6±0.6	2.4±0.5	57.3±2.5	-
S4	6.4	329±6.5	341.1±10.3	5.5±0.7	3.6±0.5	70.7±1.4	0.8±0.04
LR352	4.8	245.8±11.4	193.2±3.4	3.5±0.8	7.6±0.5	13.6±0.5	-
MM	4.4	80.9±3.0	191.9±3.2	2.1±0.7	7.8±0.5	24.7±0.8	-
UF,UL	5.1	88.3±3.1	1054.4±3.0	8.2±1.5	6.2±0.6	19.8±1.1	-
KI5	5.4	86.8±2.2	328.5±3.4	-	3.4±0.6	18.5±0.8	-
KIB	4.3	87.5±1.2	344.4±2.9	1.1±0.6	4.6±0.02	18.5±0.5	-
RON	7.3	353.3±24.2	126.5±13.6	-	7.2±2.5	14.5±2.5	-
KAJ	8.3	127.2±4.1	3.0±2.1	-	1.2±0.4	1.6±0.5	-

Soil samples S1 and S4 were extracted at pH 7.0 using 1M $MgCl_2$. NaDDTc at pH 6 and APDC at pH 2 were used as the heavy element precipitants.

Table 4m: Results - concentrations in µg/g

Soil Code	Soil pH H_2O	Element					
		Mn	Fe	Co	Cu	Zn	Mo
S1	5.4	624.7±15.4	55.7±12.9	-	-	3.5±2.5	-
S4	6.4	28.6±1.9	4.3±0.4	-	0.5±0.1	1.0±0.1	0.03±0.01

From the table on available heavy metal elements it is easy to observe that soil samples from different geographical locations have different trace element levels. In the table of total elemental contents, cobalt occurs in higher concentrations than copper in all but one soil sample. One would expect the same trend in the available contents if there were a linear relationship between the total and the available contents. This however does not happen and infact cobalt is largely unavailable in most of the soils using 0.1M HCl, 1M $MgCl_2$ and the buffer solutions as the extractants. It is therefore true that there is no obvious relationship between the total and available trace elements contents in a soil other than the more expected one - that the available contents cannot exceed the overall total concentration of the particular element in a soil.

Further, it is clear that other than pH, other factors come into play in influencing the total and available contents (as seen in S1 and K15 which have the same pH but different available contents.

4.9 AVAILABLE HEAVY METAL CONTENT IN LIME EXTRACTED USING 0.1M HCl (and precipitated using NaDDTc at pH 6.0 and APDC at pH 2).

Table 4n

Element	Available concentration in ppm
Mn	0.82
Fe	-
Co	0.40
Cu	0.24
Zn	0.06
Mo	-
Pb	0.21

The above results show that lime has very little of the available heavy metals of interest. It thus has negligible effect on the soil in which it may be incubated when liming (to raise the soils pH).

4.10 LIMED SOIL ANALYSIS

Two acidic soils (S1 and KIB) were limed using varying amounts of lime for an incubation period of 3½ months. pH analyses of the various samples followed by 0.1M HCl extraction were done. One of the soils (S1) was also extracted using buffer solution of the corresponding pH value.

Table 4o: Results

4.10(i) S1

Concentration in µg/g after 0.1M HCl Extraction

pH / Element	5.4	6.2	6.5	7.5	7.8
Mn	222.1±7.8	50.7±1.5	57.9±1.8	123.4±0.2	190.3±4.9
Fe	36.5±4.4	38.3±3.1	30.8±2.0	48.3±1.5	62.1±2.1
Co	-	-	-	-	-
Cu	3.2±1.1	0.6±0.2	1.6±0.5	2.3±0.6	2.3±0.8
Zn	5.1±0.9	12.8±1.0	5.7±0.6	10.2±0.7	12.6±0.9
Mo	0.1±0.01	0.2±0.02	0.21±0.13	-	-
Pb	0.5±0.05	1.3±0.4	-	-	1.2±0.2

Table 4o , Cont'd

Concentration in µg/g Cont'd

pH / Element	7.9	8.05	8.25	8.4
Mn	200.9±5.1	138.7±3.7	60.0±1.2	72.3±1.5
Fe	59.7±1.4	55.5±2.7	56.6±2.2	54.9±3.3
Co	-	-	-	-
Cu	2.6±0.7	1.4±0.5	0.8±0.4	1.0±0.6
Zn	12.7±1.1	10.3±0.9	7.4±0.8	8.3±0.9
Mo	-	-	-	-
Pb	1.0±0.01	0.7±0.4	0.4±0.3	-

4.10ii S1

Table 4p: Concentration (µg/g) after buffer extraction

pH / Element	5.4	6.2	7.0	7.9	8.1
Mn	979.6±12.4	575.8±8.3	214±4.6	84.2±6.0	46.4±2.9
Fe	633.4±7.9	565.1±8.2	316±6.1	899.6±6.5	146.5±4.6
Co	-	2.9±2.1	-	3.5±2.4	-
Cu	0.8±0.3	1.0±0.3	0.9±0.2	-	2.0±1.3
Zn	10.6±0.9	6.0±0.6	4.3±0.7	3.4±0.8	3.1±0.9
Mo	0.4±0.2	-	0.4±0.3	0.6±0.2	-
Pb	1.1±0.6	1.0±0.5	1.2±0.6	1.4±0.5	1.1±0.4

Table 4p Cont'd

Concentrations in µg/g

pH / Element	8.25	8.4	8.7	8.8
Mn	26.5±4.0	38.3±2.3	40.6±2.5	24.1±1.9
Fe	209.2±4.4	370.2±4.0	150.0±6.2	52.6±1.9
Co	-	-	-	1.8±1.1
Cu	1.3±0.5	0.9±0.3	1.4±0.6	0.5±0.4
Zn	3.0±0.9	2.1±0.6	1.5±0.4	1.4±0.5
Mo	0.3±0.2	0.2±0.1	-	-
Pb	1.6±0.9	1.4±0.4	-	0.6±0.3

From tables 4(o) and 4(p), the element manganese keeps on fluctuate in level as the pH of the soil increases. In general, manganese level is highest at a soil pH range of about 7.2-8.05. Iron increases and then falls out as the pH is raised.

Cobalt is unavailable even at high pH values while copper and zinc are reversely affected by pH alteration. Copper level decreases as pH is raised while zinc increases.

From table 4(p), the buffer extracts high amounts of manganese at low pH which decrease drastically as pH is raised above 7.0. The iron decreases from pH 5.4 to 7.0 and then rises at pH 7.9. It falls gradually after pH 8.1.

Zinc decreases gradually over the whole pH range while copper remains relatively unaffected. Molybdenum availability using the buffer solution is reduced to nil after pH 8.4

Molybdenum increases in availability as the pH is raised by liming upto pH 7.9 beyond which it decreases at higher lime amounts, may be due to its adsorption by $CaCO_3$ (Takker, 1982).

4.10 (iii) KIB soil incubated for $3\frac{1}{2}$ months with lime and extracted with 0.1M HCl

Table 4g: Results

pH / Element	4.3	4.6	5.1	6.2	7.2	7.5	7.9
Mn	87.5±1.2	166.5±3.4	84.5±1.7	117.0±3.8	504.2±6.9	307.4±3.8	179.7±2.3
Fe	344.4±2.9	189.8±1.3	189±2.4	151.5±3.1	149.7±2.7	70.7±2.6	10.8±1.4
Co	1.1±0.6	-	-	-	-	-	-
Cu	4.6±0.02	2.7±0.6	2.8±0.6	5.6±1.1	2.2±0.6	1.6±0.4	2.1±0.5
Zn	18.5±0.5	26.3±0.6	26.5±1.1	29.8±1.0	23.0±0.7	32.9±0.7	22.3±0.7
Mo	-	-	-	0.7±0.3	-	-	-
Pb	0.4±0.3	0.58±0.24	-	-	-	0.18±0.15	-

4.11 BASIC SOIL RECLAMATION

Basic soils were acidified by acid-washing using dilute H_2SO_4 of varying concentrations in buchner funnels. This was accomplished by washing-off the ions responsible for alkalinity in the soil (ie. Ca^{2+} and Mg^{2+}) and replacing them with H^+ according to the following general equation.

$$\underbrace{\left.\begin{matrix}Ca\\Mg\end{matrix}\right\}Soil}_{Basic} + H_2SO_4 \longrightarrow \underbrace{\begin{matrix}Ca^{2+}\downarrow\\Mg^{2+}\end{matrix} + H\ Soil}_{acidic}$$

Table 4r: Results - concentrations in µg/g

4.11(i) : Kaj soil at initial pH of 8.3

pH / Element	8.3	7.6	7.1	6.8	5.7	5.4
Mn	127.2±4.1	40.1±0.7	14.4±0.5	21.8±0.9	8.0±1.2	7.8±0.9
Fe	3.0±2.1	7.2±2.5	12.8±1.2	18.2±1.7	5.9±0.3	5.4±0.4
Co	-	1.1±0.3	-	-	-	0.3±0.1
Cu	1.2±0.4	2.6±0.8	0.8±0.4	-	0.7±0.2	1.9±0.5
Zn	1.6±0.5	3.4±0.4	4.5±0.6	2.9±0.5	2.5±0.4	1.3±0.1
Mo	-	-	-	-	-	-
Pb	-	0.37±0.15	0.45±0.23	0.31±0.26	0.36±0.10	0.49±0.21

Table 4 s: Concentrations in µg/g

4.11(ii): Ron soil at initial pH of 7.3

pH / Element	7.3	6.7	6.1	5.6	5.2	4.5
Mn	353.3±24.2	1184±26.4	1318.5±21.7	1042.1±12.4	863.1±6.7	837±11.0
Fe	126.5±13.6	484.7±10.1	504.3±15.4	487.3±9.1	462.5±6.2	1196±10.0
Co	-	-	-	-	2.1±2.0	6.0±3.0
Cu	7.2±2.5	6.8±3.0	6.0±2.1	3.1±0.8	0.6±0.3	-
Zn	14.5±2.5	12.6±1.6	23.8±1.5	18.4±1.9	6.1±0.6	9.3±0.6
Mo	-	-	-	-	-	-
Pb	-	-	-	-	-	-
Y	18.0±1.6	18.6±1.7	21.0±1.5	17.7±1.4	19.6±0.2	18.9±0.4

Table 4s: Concentrations in µg/g Cont'd

pH / Element	3.6	3.0	2.8	2.5	2.0	1.8
Mn	1053.4±17.2	3011.5±46.7	3153.7±66.2	2928.6±57.4	1042.7±26.4	3385.9±132.6
Fe	6871.0±62.3	4735.7±35.6	1345.3±109.2	15304.8±142.8	19619.7±86.8	19768.4±748.1
Co	38.3±13.7	20.8±15.4	82.5±29.3	104.3±20.0	132.7±50.0	377.5±84.4
Cu	2.3±1.0	0.85±0.67	4.3±1.9	-	13.5±4.3	5.2±2.8
Zn	22.7±3.0	21.6±2.2	32.3±4.1	36.5±4.4	67.8±6.6	80.6±12.4
Mo	0.3±0.2	-	0.53±0.35	-	-	-
Pb	-	-	-	-	-	-
Y	ND	23.4±2.0	38.5±2.8	24.9±2.2	20.6±1.7	28.5±3.5

ND = Not Determined

4.12 RESULTS OF A DRY RONGAI SAMPLE RUN AS PELLETS PREPARED USING A-STARCH (DILUTION FACTOR 2) AND B-PVP (DILUTION FACTOR 1.11).

Table 4 t: 6.13A. Starch (D.f. 2) Units-%

Test # / Element	1	2	3	4	Mean
K	0.9291	0.9869	0.9506	0.9645	0.9578
Ca	0.8669	0.8534	0.8697	0.9177	0.8769
Ti	0.9569	0.9319	0.9644	1.0599	0.9783
V	0.0412	0.0344	0.04082	0.04088	0.03933
Mn	0.7073	0.4848	0.5233	0.5367	0.5621
Fe	7.1670	7.0812	7.2829	7.9075	7.3597
Co	0.1098	0.1145	0.0954	0.1191	0.1097
Cu	0.00297	0.00324	0.0038	0.0032	0.0033
Zn	0.01764	0.01817	0.01808	0.0193	0.0183
As	0.00097	0.00148	0.00125	0.00143	0.00128
Br	0.00096	0.00069	0.00063	0.00099	0.0082
Rb	0.0111	0.0110	0.0119	0.0125	0.0116
Sr	0.0125	0.0119	0.0134	0.01395	0.0129
Y	0.00731	0.00696	0.00786	0.00782	0.0075
Zr	0.08128	0.0802	0.0869	0.09092	0.0848
Nb	0.01887	0.01812	0.02075	0.02036	0.0195
Pb	0.00014	-	0.00030	-	0.00022
La	0.1933	0.2110	0.2246	0.2147	0.2109

Table 4u: 6.13 B.PVP (D.f. 1.11) Units - %

Element \ Test #	1	2	3	4	Mean
K	1.2883	1.2493	1.1624	1.2942	1.2486
Ca	1.0683	1.0542	0.9736	1.1104	1.0516
Ti	1.0795	0.9997	1.0646	0.9937	1.0344
V	0.0513	0.0548	0.0503	0.0507	0.0518
Mn	0.5587	0.5928	0.5025	0.6139	0.5670
Fe	7.8316	7.4837	7.3456	7.2988	7.4899
Co	0.1276	0.1337	0.1225	0.1233	0.1268
Cu	0.00323	0.003135	0.00339	0.003207	0.00324
Zn	0.01745	0.01843	0.01785	0.01814	0.01797
As	0.0009	0.00109	0.0011	0.0013	0.0011
Br	0.00087	0.00090	0.00084	0.00094	0.00089
Rb	0.0118	0.01148	0.0110	0.01126	0.01139
Sr	0.0125	0.0124	0.0119	0.01144	0.01206
Y	0.00764	0.00743	0.00726	0.00717	0.00738
Zr	0.08171	0.08111	0.07982	0.07974	0.08062
Nb	0.01802	0.01845	0.01838	0.1784	0.01817
Pb	0.000180	-	0.000189	-	0.000185

From the results in the two tables above (4t and 4u), it is evident that the data in both tables agree to a high degree (taking the difference in methods and dilution errors into consideration). This suggests that these two binding agents may be used complementarily or interchangeably. However for

dry soils such as the above sample from such areas as Rongai, Kajiado and the Coast regions where the organic matter is low, binding the soil using starch was found to be very difficult and at times impossible. PVP came in as a fast binder which is easy to handle and which has improved specimen homogeneity since it is made in paste form.

Table 4v showing the various sampling locations, sample codes, no. of samples collected per location, soil classification and other related remarks.

Sampling Site	Sample Code	# of samples collected	Soil Classification	Remarks
Kajiado	S2 Kaj	15 15	VERTISOLS and orthic RENDZINAS (Imperfectly drained, moderately deep, very dark grey to black, firm, slightly calcareous, craking clay with a gravelly calcareous subsoil).	These soils are developed on Tertiary basic igneous rocks (olivine basalt and nepheline phonolites).
Nyeri	S4	15	humic NITISOLS (well drained, extremely deep, dusky red to dark reddish brown, friable clay, with an acid humic topsoil).	"
Muranga	S3	15	mollic ANDOSOLS (well drained deep to very deep, very dark greyish brown, friable and smeary, clay loam, with a thick humic topsoil).	This soil is developed on ashes and other pyroclastic rocks of recent volcanoes.
Ongata Rongai	RON1 RON2	15 15	VERTISOLS (Imperfectly drained, very deep dark grey to black, firm bouldery and stony, cracking clay which is calcareous).	This soil is developed on Tertiary basic igneous rocks (olivine basalt and nepheline phonolites).
Kibirigwi Irrigation Scheme	LR352 K15 MM	5 5 5	humic NITISOLS (well drained, extremely deep, dusky red to dark reddish brown, friable clay with an acid humic topsoil)	"

Table 4v Cont'd

Sampling Site	Sample Code	# of samples collected	Soil Classification	Remarks
Kibirigwi Irrigation Scheme	UF/UL	5	ferralic CAMBISOLS with rhodic or orthic FERRALSOLS and rocky outcrops	This soil is developed on undifferentiated, Basement System rocks - predominantly gneisses.
Karatina Town	K1B	5	humic NITISOLS (well drained extremely deep, dusky red to dark reddish brown, friable clay with an acid humic topsoil).	This soil is developed on Tertiary basic igneous rocks (olivine basalts and nepheline phonolites).
Chiromo Kabete (N.A.L.)	S1 Kab	5 10	eutric NITISOLS; with nitro-chromic CAMBISOLS and chromic ACRISOLS, (partly pisoferric or petroferric phase) (well drained, extremely deep, dusky red to dark reddish brown, friable clay, with inclusions of well drained, moderately deep, dark red to dark reddish brown, friable clay over rock, pisoferric or petroferric material)	This soil is developed on Tertiary basic igneous rocks (olivine basalts and nepheline phonolites).

All the samples were collected from a depth of upto 30 cm.

Total # of samples collected = 130.

Ref: Exploratory Soil Map and agro-climatic Zone map of Kenya, 1980. By W.G. Sombrock, H.M.H. Braun and B.J.A. van der Pouw.

CHAPTER FIVE

5. CONCLUSION

The Energy dispersive X-Ray Fluorescence technique is a fast, accurate and precise one which enables its operator to analyse many results in a short period of time. The operation of the instrument is simple and doesn't really require alot of expertise. Simultaneous multielement analysis is a further advantage of the method.

The technique gives concentrations of the elements of interest in as low as a few ppm by precipitation methods.

NaDDTc at pH 6 has been found very effective as a coprecipitant for manganese, iron, cobalt, copper and zinc while APDC at pH 2 has been proved best for molybdenum. It is therefore necessary to use both reagents whenever one is precipitating these elements for X-ray analysis.

From the precision results, it is evident that the whole technique from the sample preparation to the actual X-ray analysis, the method is simple, accurate, precise and reproducible.

Available elements have been found to have no direct and linear relationship with the total elements.

pH has been confirmed to be of great influence on the available heavy metal elements in the soil. However there cannot be a good graphical representation of the trends of these heavy metals with pH changes since there is no linearity. One can only pinpoint certain increments in metal concentration at a certain narrow pH range or at an exact pH value. It has however been well established that by varying the pH of either the basic or the acidic soils, heavy metals such as manganese,

iron, cobalt, copper, zinc and molybdenum increase or decrease in their available concentrations. Thus, regions which have a low availability of one or all of these elements (but where the element is inherent in the totals), this availability may be increased by varying, among other parameters, the pH.

Polyvinyl-pyrrolidone (PVP) has been shown to be more effective and easier to handle and use, as a binding agent during pellet formation than starch. It thus can be used for dry, low-organic soils and sandy soils where starch cannot be used.

Further work recommended

Apart from 0.1M HCl, 1M $MgCl_2$ (pH 7) and the buffer solutions; further work should be done in order to obtain more soil extracting reagents for the available trace elements. It is also necessary to look for a multielement extractant other than this 0.1M HCl conventionally used extractant. Further work is needed in the activity and range of usefulness of 1M $MgCl_2$ and the buffer solutions in the extractions.

Apart from the soil-pH-variation done in the laboratory in various containers, the same pH alterations should be done in the field and the available metal contents done on them then comparison of the available contents in the soils to those in the actual crops grown on the soil should be done to support the general hypothesis that this relationship is linear.

The pH alteration vs availability of trace elements relationship should also be coupled with such other relations as with depth, soil texture and organic matter contents of the soils.

A more universal complexing reagent for the elements in the soil filtrate or suitable co-precipitation conditions may be sought in order to lessen the amount of work, time and reagents used while using NaDDTc (for manganese, iron, cobalt, copper and zinc) and APDC (for molybdenum only)!

Referencing is mixed!

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APPENDIX I

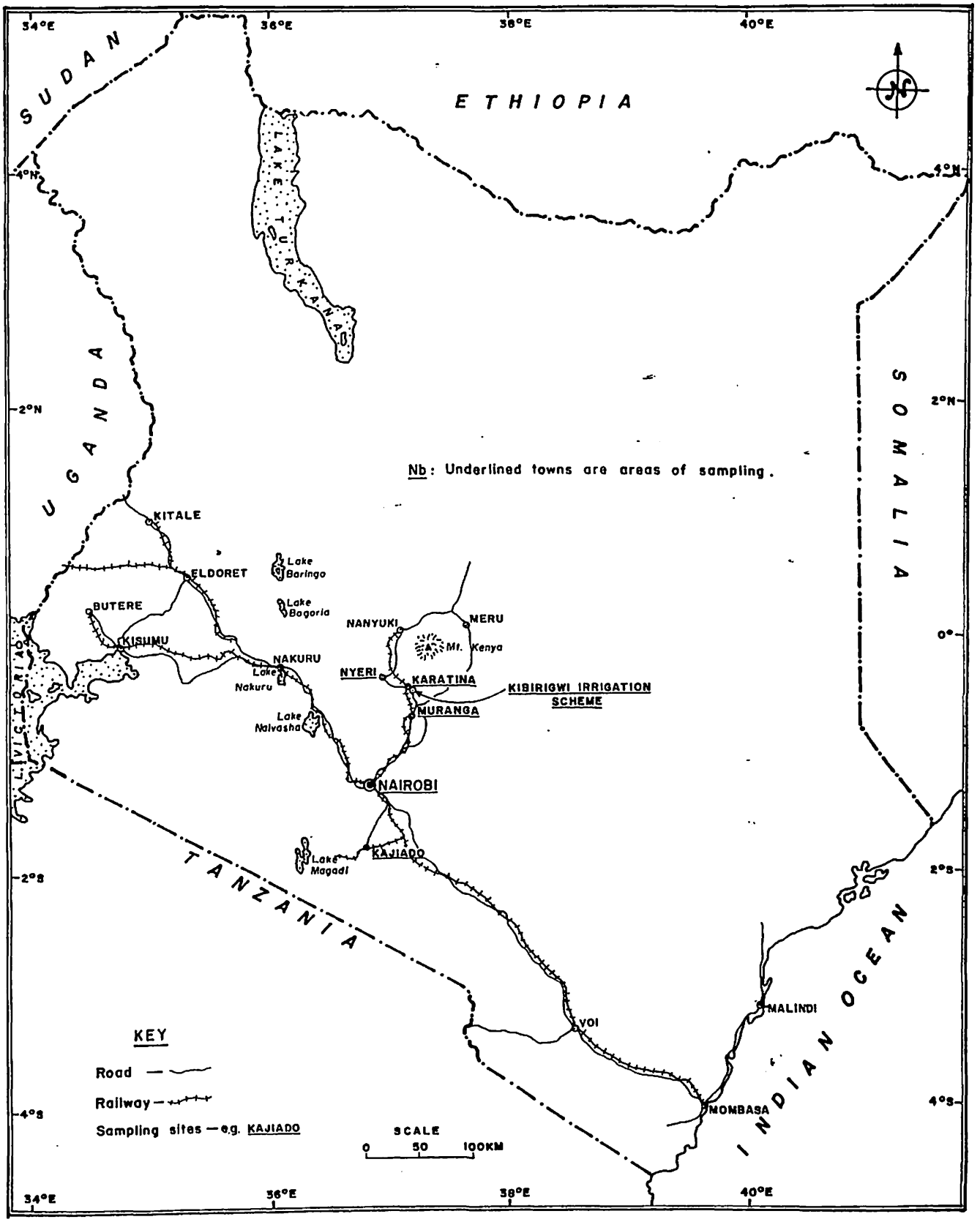

FIGURE 1 – MAP OF KENYA SHOWING SAMPLING SITES

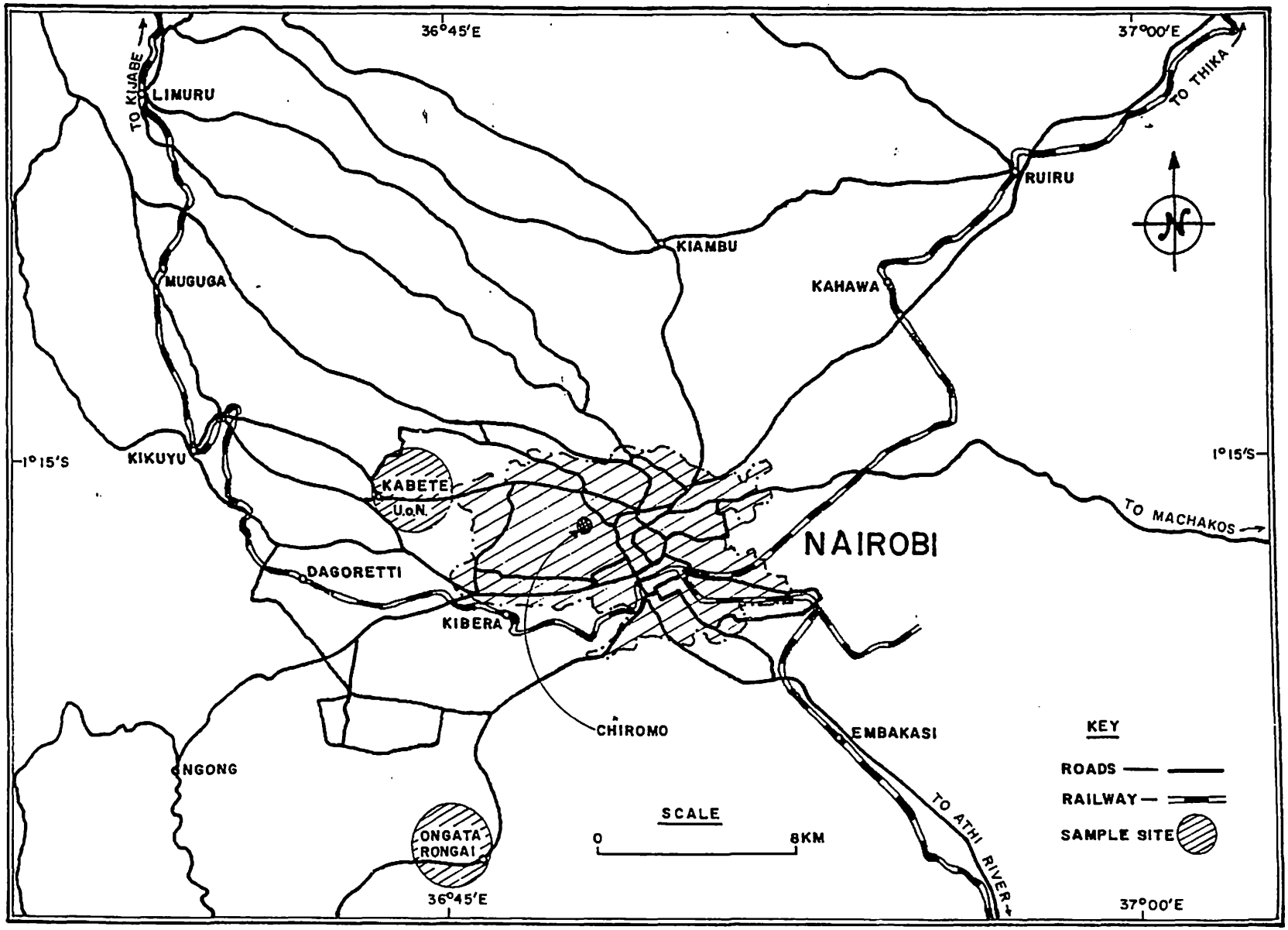

FIGURE 2 — MAP SHOWING SAMPLING SITES WITHIN NAIROBI AND ITS ENVIRONS