DETERMINATION OF TRACE METALS IN SOME PETROLEUM PRODUCTS.

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DECLARATION

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for a higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.

Nwabueze Ogbuehi,

Date: 19/7/84

DEDICATION

This work is dedicated

To my parents

-Whose work and self-sacrifice
opened the path of learning to
their children

To my brother Chuks

For being what he is
- A real brother

To an engendered species

- those who still believe
in the acquisition of
knowledge.

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N. Ogbuehi

ABSTRACT

Petroleum and its products contain a high percentage of hydrocarbon in addition to sulphur, phosphorous and measurable quantities of metals. The metallic constituents are either indigenous to the oil or are present as additives. When intentionally added, these metals help to impart desirable properties (e.g. increase stability, improve combustion characteristic and act as film-strength improver) to the oil. Often the presence of these metals in oils may cause the finished product to have undesirable properties such as corrosion of refinery equipment, reduction of the activity of process catalyst and premature failures in engines due to excessive wear. Again, when these petroleum products are burnt in engines, these metals are lost to the environment as pollutants.

The quality of the air in large cities is now, more than ever before recognised (47) as an important factor in the standard of urban life. It impinges directly, but often subtly and unquantifiably, on public health, enjoyment of surroundings, plant life, property fabric and even local meteorology. As one one of the great conurbation of the world, Nigeria

is not exempted from most of the environmental pollution problems that are found elsewhere.

In view of the effects of metals discussed above, the present work presents a study of some trace metal levels in gear and brake fluids. The analysis of the entire commercially available product was not practical and therefore sample from the major marketings companies were studied and they include six brake fluids namely Agip SAE J1703, Mobil SAE J.1703C, National (Etonax B) SAE J1703, TEXACO SEA 1703, TOTAL SAE J1703C BP. Super SAE J1703 and four gear oils - Agip SAE 85W/140, Mobil HD140, TEXACO SAE 85W/90 and TOTAL,extreme pressure gear oil.

Two methods of sample preparation were used. In the first case, the oil was dried under an, infrared lamp and ashed with the aid of a muffle furnace using sulphuric acid as an ashing aid. In the second case, dithizone was used to extract lead and cadmium into 40% nitric acid.

Flame photometric technique was used for the determination of sodium,, potassium) calcium while atomic absorption spectrometric technique was

empxoyed for zinc, copper, lead, manganese, magnesium cadmium, Nickel, chromium and cobalt. Iron was spectrophotometrically estimated,

There were variations in results of sodium, potassium, calcium, zinc, manganese obtained for the different oils while copper, magnesium, cadmium, nickel, lead and iron gave results that show little or no variation from oil to oil.

Of the metals determined, nickel has the least value of 4.0 mg/kg and potassium the high value of 20956.0 mg/kg.

Chromium and cobalt were either absent or present in an amount that was below the detection limit of the instrument used.

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ABBREVIATIONS

FAO	=	Food and Agricultural Organization
IAEA	=	International Atomic Energy Agency.
WHO	=	World Health Organization
EDTA	=	Ethylenedramine tetraacetic acid disodium salt.
B.D.	=	Below Detection Limit
S.D.	=	Standard Deviation

CHAPTER ONE

I N T R O D U C T I O N

1.1 TRACE METAL IN OUR ENVIRONMENT.

By the word "trace" metal, we mean those metals that are present in very low concentrations, they may be present in either the elemental or combined form, more often the latter (1). According to the same author, in the past, trace was taken to mean a concentration that is below the limit of quantitative determination in the amount of sample taken for analysis. However, the use of more sophisticated instruments has changed this definition to what is given above.

Trace levels of potentially 'toxic' metal are appearing in our environment and accumulating in the atmosphere, water and plants in increasing significant amount (2). Recent research (3) has shown that the predominant source of phosphorus, sulphur, vanadium, chromium, manganese, copper, zinc and lead in the air seem to be anthropogenic. The same author is of the view that most of these metals can be extremely toxic to plants even in low concentration and as such air borne pollutants may be causing significant changes in the genetic structure of the plant population

exposed to them. The same is true of aquatic lives and man. For instance, it has been reported (4) that children between the ages of one and nine living around lead mine (in Kellog , Idaha USA) suffer from anemia - a desease that has been traced to the inhalation of lead dust. Again, the same authors have reported chromium to be potentially carcinogenic in man, though, the level that could cause this is not yet known.

It does not mean that all trace metals are toxic, some are essential and even those that are reported toxic, toxicity depends on the dose. Thus manganese and vanadium have been reported (7) to be essential for photosynthesis, while chromium is a nucronutrient for plants at ppb level but becomes toxic at higher concentrations.

1.2 OCCURRENCE AND COMPOSITION OF CRUDE OIL.

Crude oil or petroleum as it is often called is an exceedingly complex mixture and it comes from underground rock formations ranging in age from thousands to millions of years. Its origin dates back to time immemorial and little is known about it until the middle of the nineteenth century (5).

Crude deposits occur throughout the world, some of them in remote areas. The major producing areas include; United States, Alberta in Canada, Venezuela, the Middle east, Russia, North Africa and Nigeria in the West Coast of Africa.

Crude oil consists predominantly of hydrocarbons with sulphur, nitrogen, oxygen and metals as minor constituents. These minor constituents occur as organo compounds (6), however sulphur and at least one of the metals (mercury) have been reported (8). to occur in their elemental forms. These metals are often present in measurable quantities thus the determination of about twenty-eight elements from the ash of different domestic crudes have been reported (6). Also Filby (10), has reported the determination of thirteen metals from the ash of seven different oils. These studies have revealed the presence of such metals as; chromium, lead, mercury, molybdenum, nickel, selenium, tin, vanadium, zinc, sodium, potassium, calcium and others in crude oils.

The concentration of these metals in crude oils may be small but they are sources of environmental pollutants and the cause of corrosion (9) of equipment and poisoning of process catalyst-hence the need for quality control.

1.3 SOURCES OF METALS IN PETROLEUM PRODUCTS.

There are about three ways through which metals could enter petroleum products. In one case, the metals could be indigenous to the crude oil and could not all be removed during the refining processes. In cases such as this, the metals are usually present as oil soluble organometallic compounds, inorganic particulate, as colloids and/or filterable suspension (7, 10, 12) (e.g. nickel and vanadium are indigenous to crudes).

In the second case, the metals may be intentionally added to the products to secure some desirable properties (7, 10, 13). Examples in this case include zinc and barium that are introduced as an autioxidant and corrosion inhibitor respectively.

Lastly these metals could be added extraneously into these products either during the cause of refining, blending, handling and by interaction with storage facilities.

1.4 EFFECTS OF THE PRESENCE OF METALS IN CRUDE OILS AND PETROLEUM PRODUCTS.

The effects of the presence of metals in crude oils and petroleum products are dual in nature depending on whether the metals are indigenous to

the crude or are present as additives. If they are indigenous to the crude or its products or are introduced extraneously, they may impart undesirable properties to the finished products. For instance, they may cause corrosion of refinery equipment, reduce the activity of process catalyst, equipment detrioration and premature ~ ·ine failure (10). King et al (12), have identified vanadium and nickel as being capable of causing serious refining problems and may also give rise to detrimental properties in the finished commercial products.

Often, some of these metals are intentionally added to the oil. Such additives are helpful in stabilizing fuels, lubricants and enhancing performance of lubricants. They also could serve as combustion characteristic improver and promoting better ignition qualities in petrol. A time honoured example is the use of tetrdethyllead in motor and aviation fuels as an "anti-knock" agents. Again King, et al (12) are of the view that zinc, calcium and magnesium which are usually present in the crude as organometallic soaps have surface active properties and can act as emulsion stabilizer.

Appendix IA list some trouble areas in automobile and the corresponding metals to which their increase in oil can be related.

1.5 PHYSIOLOGICAL EFFECTS OF METALS.

The physiological effects of metals on all livingthings (plants and animals) can be considered from two perspectives; viz, dietary essential and toxic point of view. Of interest to an environmentalist are those that are important toxicologically (7) primarily because the dietary essential metals may become toxic at certain concentration levels.

Some of these trace metals are found in living things in quantities that reflect their contact with their environment. According to Smith et al (15), some researchers are of the view that internal mechanisms control the level of essential trace metals in tissue while the nonessential ones are distributed in a manner that reflects the environment.

It has also been reported that the toxicity of metals (15) is a function of its chemical form. Thus hexavalent chromium, pentavalent vanadium, divalent manganese and methylmercury are more toxic than other forms of the corresponding metal.

Metals deposited on soil are relatively imobile and their mobility depends on the pH of the medium. The contamination of plants grown on metal-contaminated soil depends on the plant variety and the soil (15) condition. Often, plants do not concentrate enough metals to pose a serious human and animal health problem.

Metals that find their way into surface waters pose hazard. In advance countries, water quality criteria (17) have been established to protect users. When introduced into surface waters, they are usually rapidly removed to the shores or sea beds where they settle out. Aquatic plants are usually good scavengers and through them most of these metals find their ways into other aquatic animals that feed on them, hence - man.

Those metals that are lost to the environment as air pollutant pose direct health problems if inhaled or ingested (7), otherwise they eventually enter soil or water where their movement is dictated by the medium concern.

TABLE 1.1*

PHYSIOLOGICAL EFFECTS OF METALS FOUND IN PETROLEUM PRODUCTS

METAL	EFFECTS ON HUMAN	EFFECTS ON ANIMAL	EFFECTS ON PLANTS	TOXICITY DATA
Barium	Baritosis, a banign pneumoconiosis. Soluble salts highly toxic orally. Soluble salts are skin and mucous membrane irritants	Full strength barium lubricant dispersant is a mild eye irritant. BaO and $BaCO_3$ cause paralysis.	Poisonous to most Plants. 0.1 ppm Ba^{2+} reduces heterotrophic active of freshwater microflora	LD_{50} diesel exhaust solids $>$ 10g/kg (animals). LD_{50} (oral) Barium sulphonates 3-10g/kg LD_{50} (oral Barium Phenolates 4-5g/kg. Fetal dose in humans $\geq$ 0.55g $BaCl_2$
Chromium	Dermatitis, ulceration of skin, perforation of nasal septum, chronic catarrh, emphysema carcinogenesis when inhaled. Cr(VI) extremely toxic. Not cumulative. Apparently essential in glucose metabolism.	100ppm recommended limit for fisheries	5ppm recommended limit for irrigation water. Soils containing 0.2-0.4% Cr are infertile. Toxic to some aerobic microbes at ppb level. A micronutrient.	Normal ingestion 0.05 mg/day. Toxic level 200mg/day. No ill effects from well water with 1.0-25.0 mg/litre. LD (oral) Potassium chromate in rabbits 1.9g within 2hrs.

TABLE 1.1 (cont'd)

METAL	EFFECTS ON HUMAN	EFFECTS ON ANIMAL	EFFECTS ON PLANTS	TOXICITY DATA
Iron	Siderosis (a pneumoconiosis due to Fe inhalation	- -	A micronutrient	- -
Cadmium	Cumulative poison. Pulmonary emphesema, hypertension, kidney damage. Cardiovascular desease. Interferes with Zn and Cu metabolism. Inhalation of 0.03-35mg/m^3 significantly reduced children's weight. GI sympotoms.	1ppm present in many plant and animal tissues. Caries, anemia and retarded growth in rat. Maximum concentration in earthwarms near a highway, 115 ppm.	Stunts growth of lettuce, radish, been and turnip plants. Tomatoes, barley and cabbage more tolerant leaves accumulate excessive amounts when solutions contain a few tenths ug/ml.	LD (oral) ffor rabbits 200-600mg. LD_{50} CdO fume 500mg/m^3 for rats to 1,500mg/m^3 for monkeys.
Cobalt	Goitrogenic. Lung effects disputed. Dermatitis. No injury from $CO_2(CO)_8$. Affects heart and GI tract 7ug/day beneficial. Liver and kidney damage.	Essential nutrient. Polycythemia. Bone hyperplasia, metaplasia in spleen, liver and kidneys. Hyperglycemia due to reversible pancreatic damage	Essentiality not established	Normal ingestion 0.002 mg/day toxic level 500mg/day. CO metal dust more toxic than salts in lung irritation. Lethal dose of either relatively high LD $CO_2(CO)_8$ in animal by inhalation 100 ppm.

TABLE 1.1 (cont'd

METAL	EFFECT ON HUMAN	EFFECTS ON ANIMAL	EFFECT ON PLANTS	TOXICTY DATA
Copper	Antagonistic to Zn toxicity Not cumulative. Require 1-2mg/day. Inhalation of Cu - containg dust causes lung and GI disturbances. Affects erythrocytes and liver. Skin and mucus membrane irritants.	Ingestion and inhalation caused hamochiomatosis and lung and liver injury. Limits irrigation water, salt water organisms and freshwater organisms 0.1, 0.05 and 0.02 ppm, respectively.	A micronutrient. Toxic to some aerobic microbes at ppb level 0.05M Cu^{2+} inhibits root growth and .1M stops germination of lettuce.	Normal ingestion 2-5mg/day; 65-130mg $CuSO_4$ dangerous and 648 - 972mg highly toxic. 29g $CuSO_4$ fetal.
Lead	Brain damage, convulsions, behavioral disorders, death.	Pb naphthenate kills rabbits by skin absorption (death due to pneumonia) cumulative poison in vertebrates renal and vescular poison.	0.1 ppm Pb^{2+} reduces heterotrophic activity in microfloral and vescular poison.	Oral toxicity of PB naphthenate 3.5 - 5.1 g/kg Normal Pb ingestion 0.4mg/**day.**

TABLE 1.1 (cont'd)

METAL	EFFECTS ON HUMAN	EFFECTS ON ANIMAL	EFFECTS ON PLANTS	TOXICITY DATA
Manganese	Chronic Mn Poisoning and/or Mn pneumonitis Reduces Fe absorption Requirement 3-9mg/day Primarily a nerve toxin. CNS symptoms often result in permanent disability.	Pathological effects on nerve cells and the liver. 1.9 - 9.9 mg is thyroid inhibitor in rats.	A key role in Photosynthesis	--
Nickel	Rarely gives systemic toxic effects even from therapeutic doses (65 - 195mg $NiSO_4$ and 324 - 454mg $NiBr_2$) Dermatitis, respiratory disorder, carcinogenesis (nose and lung).	Moderately toxic to aquatic organisms. Maximum Ni concentration in earthwarms near a highway 38ppm Inhibits enzyme system. Kidney damage (calf) 1-3mg/kg Ni compound causes intestinal disorders, convulsion and asphyxia in dogs.	Can be very toxic dependings on its chemical form. A micronutrient. 0.01 ppm redues the heterotrophic activity of freshwater microflora.	Normal ingestion 0.3 - 0.5mg/day 30-73mg $NiSO_4.6H_2O$ toxic in human.

TABLE 1.1 (cont'd)

METAL	EFFECTS ON HUMAN	EFFECTS ON ANIMAL	EFFECTS ON PLANTS	TOXICITY DATA
Vanadium	Cardiovascular disease carcinogenesis. Main toxic effect on respiratory system V_2O_5 residues from fuels irritating to those who clean oilfired burners, renew firebrick lining and clean heat exchanger tubes (dust contain 6 - 20% V)	Feeding 5mg/liter V^{4+} for life to rats gave no significant reduction in growth or longerity. Not carcinogenic rats and mice.	Essential for green algae. Stimulates higher green plants in small amount.	10mg/kg Fetal to rat. Sublethal doses 92 - 368 ppm 49µg/ml drinking water highly toxic. 0.205 mg/liter causes lung changes in animals LD (i.v.) in human 30mg V_2O_5 as tetravenadate.

TABLE 1.1 (cont'd)

METAL	EFFECTS ON HUMAN	EFFECTS ON ANIMAL	EFFECTS ON PLANT	TOXICITY DATA
Zinc	Dermatitis, hypertension, arteriosclerotic and heart diseases. 675 - 2,250 mg/liter is emetic. Causes mineral loss from bones. Most Zn compounds not particularly toxic at moderate concentration orally. Zn inhibit the teratogenic embryocidal and neo-plastic effect of Cd. Essential.	Zn dithiophosphates are severe eye irritants 0.1-1.0 ppm lethal to fish and other aquatic animals.	Essential 0.1ppm Zn^{2+} reduces heterotrophic activity of microflora.	LD_{50} (oral) Zn dithio phosphates 2.13 - 3.7g/kg. LD_{50} (skin) 11.3g/kg for rabbit (24-hr contact) mixed Mg - Zn phenolate LD_{50} (oral) 9.5mg/kg LD_{50} (oral) $ZnCl_2$ in guinea pigs, rats and mice 200 - 350mg/kg. Normal injection Zn 10 - 15mg/day.

*Taken from Reference (7)

Very few people seem to know that metals lost to our environments contribute to human health problem. Japanese Itai-itai decrease was traced (18) to the consumption of rice grown in cadmium contaminated irrigation water, while brain damage and incidences of lung cancer have been attributed to lead and nickel respectively (16). The physiological effects of some of the metals found in petroleum and its products are given in table 1.1.

1.6 BENEFICIAL EFFECTS OF METAL ADDED TO PETROLEUM PRODUCTS.

Despite all the ills associated with the presence of metals in petroleum products, there are still some advantages that the presence of some of these metals have in oils when they are intensionally added. Thus in petroleum product, additives are used for the purpose of gaining some performance advantage in the products. The amount of these additives used for any particular product depends (7) on the agreement between the manufacturer and the consumer. These additives usually used in small amounts have different objectives depending on the type of product. Some of them may be singly functional or multifunctional and they may

enhance or add to the oil (23) one of the qualities listed in the next paragraph.

i. Decrease oil oxidation and reduce the corrosion of certain types of sensitive bearing materials.

ii. Provide the oil with greater resistance to wear of main and connecting rods, bearing, particularly where full-film lubrication is lacking.

iii. Improves the dispersant-detergent qualities of the oil and thus promote engine cleanliness.

iv. Improves the viscosity-temperature relationship of an oil over the range of temperature at which it is to be used.

v. Reduce the pour point.

vi. Prevent foaming of the oil.

vii. Prevent rusting of engine and moving parts when water enters oil.

The surface-active materials (23) finding major use are oil-soluble metal soaps of specific types and ashless polar compounds, usually nitrogenous, based on polymeric materials or having long hydrocarbon chains. They are usually found in motor and aviation fuels, diesel fuel, heating oils and lubricants of all kinds. A time honoured example is the use of tetraethyllead in motor and aviation fuel as an anti-knock agent.

Of late, another line of application is being added to uses of these additives, thus according to Eliot, (21), emphasis is now being laid on the possible use of oil additives as a means of controlling air pollutants emission, mainly visible smoke, particulate, sulphur compounds and oxides of nitrogen.

Some of the types of metal containing additives that are now in use are outlined in appendix IB.

1.7 AIMS AND OBJECTIVES.

The present work is aimed at the determination of levels of trace metals in some commercial petroleum products; namely; brake and gear fluids. These trace metals are lost to the environment when there products are burnt in engines. While in the environment and since they do not decay, they impinge directly, but often subtly and unquantifiably, on public health, enjoyment of surroundings, plant and animal lives.

As one of the great conurbation of the world, Nigeria is not exempted from most of the environmental pollution problems that are found elsewhere. This becomes obvious if one observes that our roadside are littered with thousand and one mechanic workshops each contributing to environmental pollution with his used oils. Again, the number of vehicles on our roads is on the increase which also implies an increase in amount of emission product - pollutants.

It is in the light of this that the present work has been undertaken. It is hoped that in addition to the satisfaction that the work will offer, at the end, we will be able to say quantitatively the amount of trace metal lost to the environment when a quantity of a particular oil is used.

Again, it is hoped that it will increase the awareness of our policy makers on the need for clean environment. It is also hoped that the information that will be obtained, would form a platform for teaching our roadside mechanics and the general public about proper disposal of used oils.

In the pursuance of the above goals, the determination of the following trace metals will be carried out on ten commercial petroleum products (brake and gear fluids) sodium, potassium, calcium, zinc, copper, lead, manganese, magnesium, cadmium, nickel, iron chromium and cobalt.

CHAPTER TWO

MATERIALS AND METHODS

2.1 TECHNIQUES IN TRACE METALS ANALYSIS OF PETROLEUM PRODUCTS.

The assessment of the quality of petroleum products is of a major concern not only to the refiners and sellers but also the user (23) who may be a direct consumer or a manufacturer whose product incoporates petroleum products and also to an environmental scientist because of their contribution to pollution.

Sales of their products require product specifications and as consumer requirements change so do these specifications with consequent changes in quality control methods. One of the parameters sought for during quality control operations is trace metals because of its effects on process equipment, finished products and contributions to environmental pollution.

The oil industry is a dynamic one and consequently the analytical requirements for the determination of these trace metals are also ever changing. Many analytical techniques have been used for the

determination of trace metal in petroleum product though, at present, rather few find common application as could be seen shortly.

Mention has been made earlier on the need of quality control of petroleum and its products and it is on this basis that many quantitative analytical technique have been developed. Again, because of the low metal content of some petroleum and their products and their wide range of viscosity, some of these techniques utilize ashing methods to concentrate the metals.

Milner et al (33), Karchmer et al (34) and Milner (25) have discribed some quantitative chemical methods involving colorimetric methods for the analysis of microquantities of petroleum products for trace metals, such as iron, vanadium, nickel and copper. The methods are based on the reaction of aliquots of the solubilized ash with reagents more or less specific for the metal being sought for. However, according to Gunn et al (35), this method has a disadvantage of being laborious, time consuming and expensive when a large number of elements in a single sample are required. To eliminate these vices, for some determinarts, Gunn et al (35), and Barney II et a

(36) have described spectrographic methods that use the ash directly after mixing with lithium carbonate or calcium chloride respectively as base matrix. The method involves the direct excitation of the ash in electrode layer using dc arc. In the past, flame photometric technique was used mainly for the analysis of alkali and alkaline earth metals but with the introduction of new fuel system (e.g. nitrous oxide-acetylene system) most other metals in the periodic table can be analysed with a reasonable degree of accuracy (14). According to Buell (14), its use is still limited to the analysis of alkali and alkaline earth metals in the oil industries.

Some electroanalytical techniques have also been used in trace analysis in oil industries, thus cobalt, barium and copper have been determined by polarography (25). In all, separation from interfering cations is necessary.

Atomic absorption spectroscopy has become the single most widely used technique for the analysis of inorganic ash from petroleum and its products (25, 37) primarily because of its simplicity of operation, speed, high sensitivity and versatility, relative freedom from interference and low cost. According to Barrett et al

(37), well over sixty metals and metalloids are amenable to atomic absorption spectroscopic analysis at concentration levels ranging from mg/ml to picogram/ml levels. The most significant disadvantage of this method is its lack of simultaneous multi-element analysis capability (24, 25). Modified forms of this technique that does not use flame for atomization are now available. A time honoured example is Heated Vaporization Atomic Absorption. In this, electrically heated devices replace the flame in the conventional form. The modified forms of atomic absorption spectrometer make analysis elegant as the sample does not have to pass through the initial steps of samples preparation (7, 24). Other techniques such as X-ray fluorescence and neutron activation analysis which incorporate multi-element analysis as one of their advantages has also beeen introduced into the oil industries for trace metal analysis (7, 24).

Previous work done in our laboratory by Ojobor (39) used flame atomic absorption spectrometry and flame photometric techniques for the determination of trace metals **in** lubricating oils. In the present work, the same techniques will be used in addition to spectrophotometric technique for iron.

Other techniques that may be regarded as miscellaneous in petroleum trace analysis include gravimetric and titrimetric methods.

2.2 SAMPLES STUDIED.

Brake fluids and Gear oils were studied. These were bought from filling stations in Kaduna and Zaria. The analysis of the entire commercially available products was not practical and therefore samples from major marketing companies were studied in this work and they are as detailed in the table 2.1

TABLE 2.1

Brake Fluids

(i)	Agip	SAE J.1703
(ii)	Mobil	SAE J.1703C
(iii)	National(Donax B): brake and clutch fluid	SAE J.1703
(iv)	TEXACO	SAE 1703
(v)	TOTAL	SAE 1703C
(vi)	BP Super	SAE 1703

Gear Oil

(vii)	Agip	SAE 85W/140
(viii)	Mobil	HD 140
(ix)	TEXACO,Multi-gear lubricant	SAE 85W/90
(x)	TOTAL, extreme pressure gear oil.	

2.3 EXPERIMENTAL

Sample Preparation:

The aim of sample preparation is to convert the analytes of interest to a measurable form. Usually, it involves either the destruction of the sample matrix or dissolution and separation of analytes of interest and their concentration. There are so many ways of destroying the sample matrix. Milner (25) has discribed techniques of sample preparation suitable for petroleum and its product. Some of these techniques include; dry ashing, reagent aided ashing, dilution with solvent, wet oxidation and direct analysis. According to Hofstader et al (24), some of these techniques are only suitable for determinations at microgram/gram level for determinations at nanogram/gram levels, their suitability is questionable. This, the authors say, is particularly true with reagent-aided ashing, wet oxidation or fusion techniques where high reagent to sample ratio may introduce errors. The wet oxidation method actually involves digestion using various acids such as sulphuric, nitric, perchloric and others, either alone or as mixture usually in a Kjeldahl flask. Another disadvantage of this method (24) is that the final digest which is usually a strong acid solution may not be amenable to direct analysis by a particular technique - e.g. anodic stripping voltammetry..

The ashing technique (with or without ashing aid) involves drying the oil under an infrared light, heating the dried oil with Bunsen flame to char the carboneceous matter and finally ashing in a muffle furnace at a suitable temperature (usually between 450 and 550^{o}C). Some investigators (25, 26) have used this technique and found that most metallic elements (e.g. nickel, vanadium, antimony, arsenic and tin) are lost during the ignition through volatilization and mechanical entrainment and adsorption. However some investigators (33, 34) have eliminated such loses by pre-fixing the metals before igniting the oil. Also, according to Morgan et al (26), properly controlled combustion and igniting will yield ash samples representing quantitative recovery of metallic content.

Owing to these ills associated with ashing, the trend is now shifting to dilution of samples with solvent. Thus Joh C. Vanloon (27) have reported the determination of nickel and vanadium in oil by diluting with xylene while Burrows et al (28) have analysed for iron, copper, and chromium (present as wear metals) by diluting with 4-methylpentan-2-one. In all, the aim is to reduce the viscosity of the oil. These earlier

investigators used organometallic compounds as standards. Owing to the fact that these organometallic standard are costly and not always within reach, new investigators (27, 30, 31, 32) have developed solvent systems that utilizes inorganic standards Direct analysis (i.e. analysis without sample preparation) would have been the best technique but unfortunately, not all analytical techniques are amenable to this method when determinations are at nanogram/gram level (24). Other technique that have been used by some analysts include flame decomposition and extraction.

No one method of sample preparation could be said to be the best. The choice is usually that of the analyst and he has to balance convenience with degree of accuracy desired. Often he may be limited to the facilities and reagents at his disposal. Previous work in our laboratory by Ojobor (39), used ashing technique in the analysis of lubricating oils for trace metals. Sulphuric acid was used to pre-fix the metal before drying and ashing. The present investigation in addition to ashing used extractive technique to bring lead and cadmium into aqueous solution. The two methods are outlined below:

Reagents:

All reagents used were of analytical-reagent grade.

(1) Deionised Water,

(2) Xylene

(3) Dithizone (Powder)

(4) Sulphuric acid, 36N

(5) 1:1 Nitric acid

(6) 40% nitric acid;

prepared by diluting 350ml of 70% nitric acid to 500ml.

1% m/V lanthanum solution; prepared as in 2.4.

Apparatus.

(1) Silica crucible, 10.5cm internal diameter and 200ml capacity.

(2) Two infrared lamps with thermostat.

(3) Two hot plates with thermostat.

(4) A graduated 10ml pipette.

(5) 50-ml beakers (20)

(6) 4 Separatory funnel; 100-ml capacity.

(7) Mettler balance H8.

(8) Muffle furnace: Carbolite Sheffield England GLM3.

(9) Whatman Filter Paper No. 41.

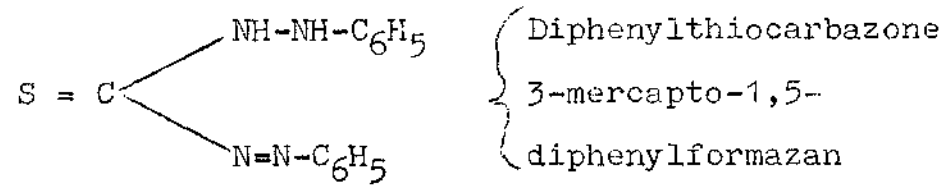
2.3.1 PROCEDURE I (ASHING) (25)

30.0g of the oil sample was weighed into a silica crucible and mixed with 15ml of 36N sulphuric acid (that is 0.5ml for every gram of sample used). The crucible with its content was then heated from top by means of an infrared lamp and with a hot plate from below. The heat from both heaters was gradually increased until the sample was reduced to a dry carbonaceous matter. This black carbonaceous residue was charred by heating on a Bunsen flame. This was then followed by ashing at 450 ± 25°C in a muffle furnace.

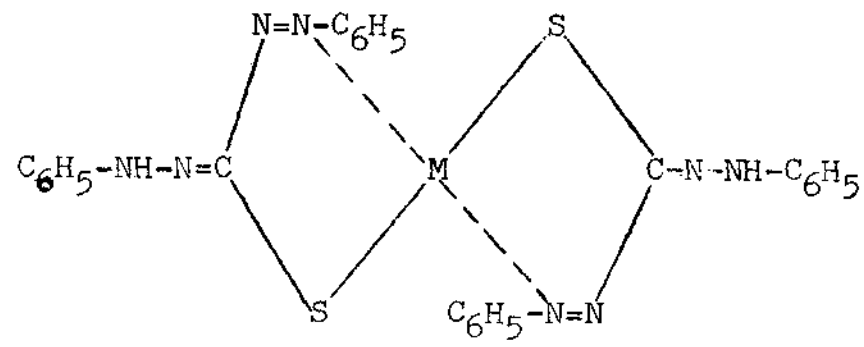
The ash so obtained was solubilized by treating with 10ml of 1:1 nitric acid followed by about 10 minutes digestion on a steam bath. The solution was diluted with deionised water and filtered into a 50-ml volumetric flask. 10ml of 1% lantanum solution was added and the volume made up to mark.

2.3.2 THE METAL DITHIZONATES (41)

Dithizone is an outstanding reagent for heavy metals having sulphurphilic properties. The structure is as follows.



Dithizone contains two active hydrogen atoms each of which can be replaced by an equivalent of metal. When one hydrogen of the dithizone molecule is replaced, a primary dithizonate is formed while the replacement of both hydrogen atoms gives a secondary dithizonate. All dithizone-reacting metals form primary dithizonates, but not all form secondary dithizonates. The structure of a primary dithizonate of the metal M(11) can be represented as follow



The dithizonate so formed is not stable under oxidizing conditions. Most oxidizing agents (e.g. nitric and perchloric acids) destroy the dithizonate structure with the metals being converted into its inorganic form.

2.3.3 PROCEDURE II (EXTRACTION)(25 ref)

(This procedure was used to bring lead and cadmium into aqueous solution) 10.0g of the sample was weighed into a 50-ml beaker. For the gear oils, 10ml of xylene was added to reduce their viscosity. Excess of solid dithizone (about 0.2g) was mixed with the sample. The mixture was later transfered to a separatory funnel 5ml of xylene was used for rinsing the beaker and the rinsing were also added to the separatory funnels. The metals were then extracted into 25ml of 40% nitric acid. The extracts were later digested on a hot plate until about 5ml was left. 10ml of deionised water was then added and boiled for about 2 minutes before it was filtered into a 25-ml volumetric flask and made up to mark.

2.4 FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM AND CALCIUM.

Principles of Flame Photometry.

Alkali and alkaline earth metals have low ionization potential and can thus ionize at low temperatures. This property is utilised in the flame photometric determination of these metals. When the solution of such a metal ion is aspirated into a

flame, the ground state atoms absorb thermal energy and some electrons are raised to a higher energy level. A proportion falls back to a lower state releasing energy as light of characteristic wavelength (e.g. yellow for sodium). In flame emission work, the flux of emitted light is measured and can be related to concentration in the solution. Evaluation is usually by the calibration curve metho

Instrument and Apparatus.

Flame photometer - Corning EEL scientific instrument. Evans Electroselemum Ltd England. 50-ml volumetric flasks.

Reagents.

All reagents used were of analytical reagent grade unless otherwise stated.

i. 1% m/V lanthanum solution: Prepared by dissolving 13.3579g of lanthanum chloride heptahydrate in 50-ml of nitric acid with gentle warming and making up to 500ml with deionised distilled water in a 500-ml volumetric flask.

ii. 1M nitric acid: Prepared by diluting 31.25ml of 16N nitric acid to 500ml.

iii. Hydrochloric acid 11.3N.

iv. 0.1M EDTA: Prepared by dissolving 37.224g of disodium dihydrogenethylene diaminetetra-acetate (dried at 80^{o}C for 2 hours) in water and making up to a litre. This was standardized with 0.1M zinc chloride solution.

v. Eriochrome Black T indicator: Prepared by dissolving 0.2g in 15-ml of triethanolamine.

Standard Solutions.

Sodium:

1000 ppm stock solution of sodium was prepared by dissolving 2.542g of sodium chloride (dried at 140^{o}C for an hour and cooled in a desiccator) in wate: and making up to a litre with deionised water. This was stored in a plastic bottle.

The intermediate standard solution was prepared from the stock by diluting 10ml aliquote to 100ml t·

give 100ppm sodium. From this, 1 to 5ppmNa working standards were prepared by appropriate dilution with water. The calibration curve for this is shown in figure 2.1.

Potassium:

A 1000ppm stock solution of potassium was prepared by dissolving 1.901g of potassium chloride (dried at 110°C) in water and making up to a litre.

The intermediate standard was obtained from the stock by diluting 10ml aliquot to 100ml to give 100 ppm potassium. From this, 2 to 10 ppm working standards were obtained by appropriate dilution with water. The calibration curve for this metal is given in figure 2.2.

Calcium:

100ppm calcium stock solution was prepared by adding 2.4972g calcium carbonate to about 50ml of water in a litre volumetric flask. Concentrated hydrochloric acid was then added dropwise to effect complete dissolution. The resulting solution was made up to mark with water.

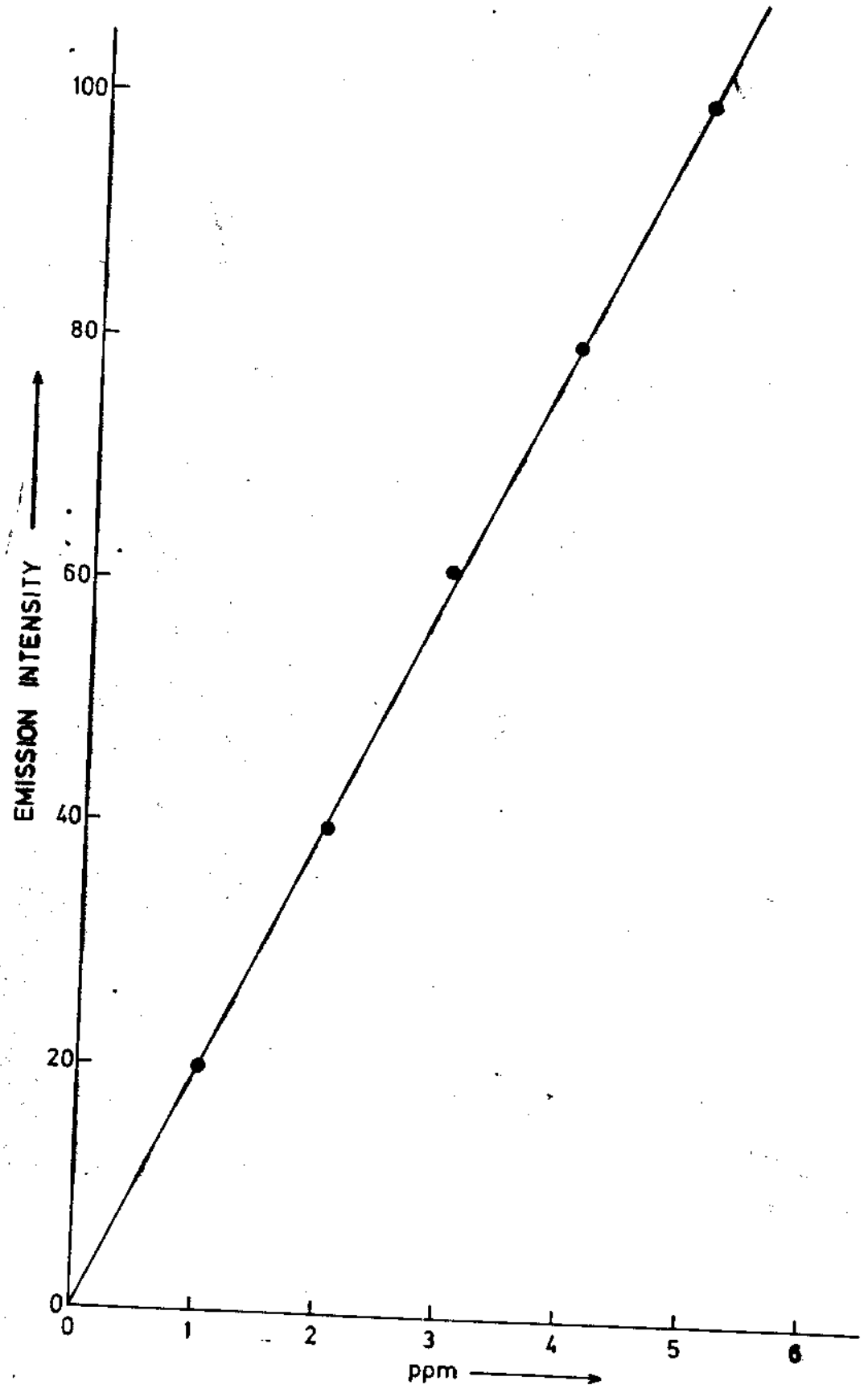


FIGURE 2.1 CALIBRATION CURVE FOR SODIUM.

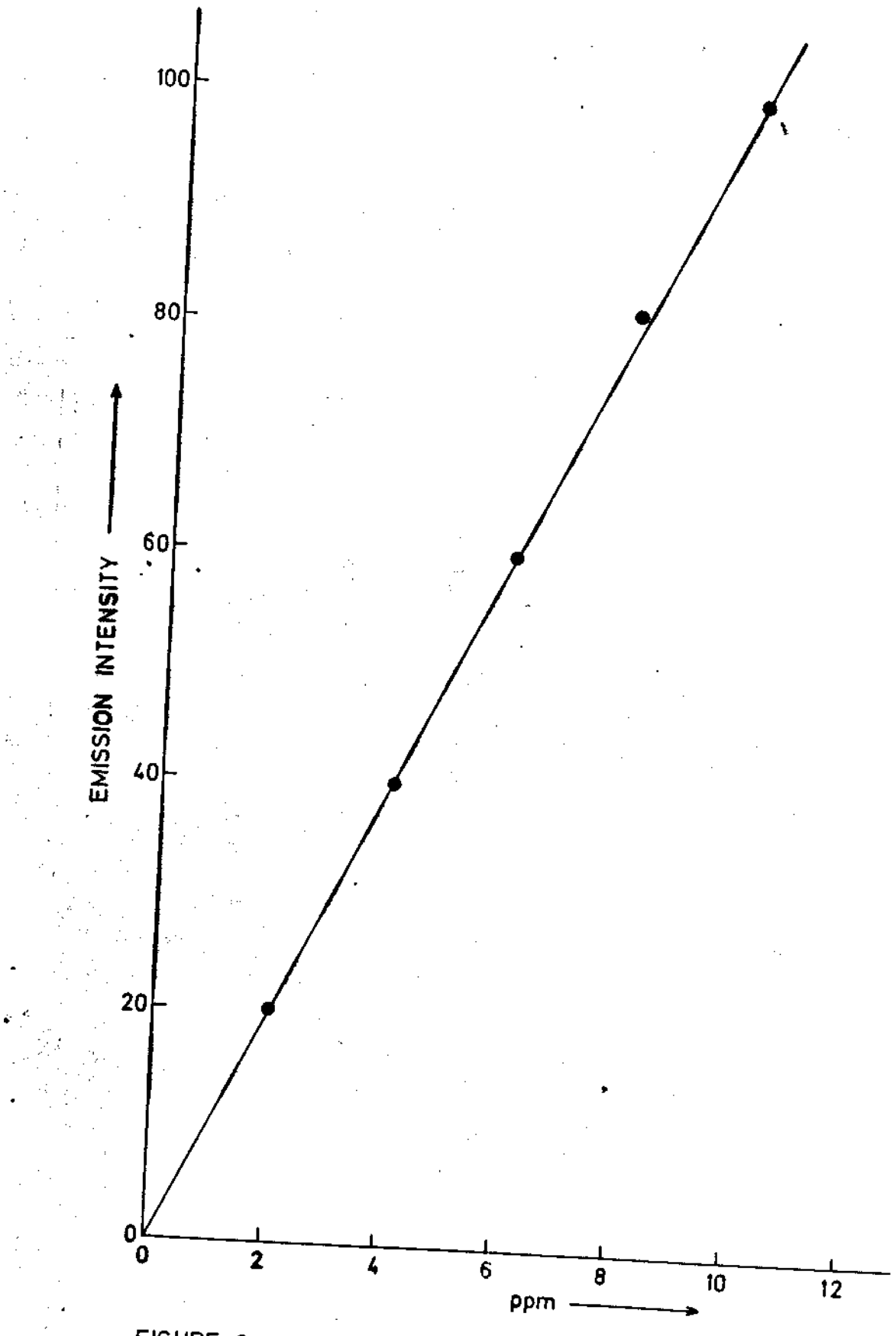


FIGURE 2.2 CALIBRATION CURVE FOR POTASSIUM.

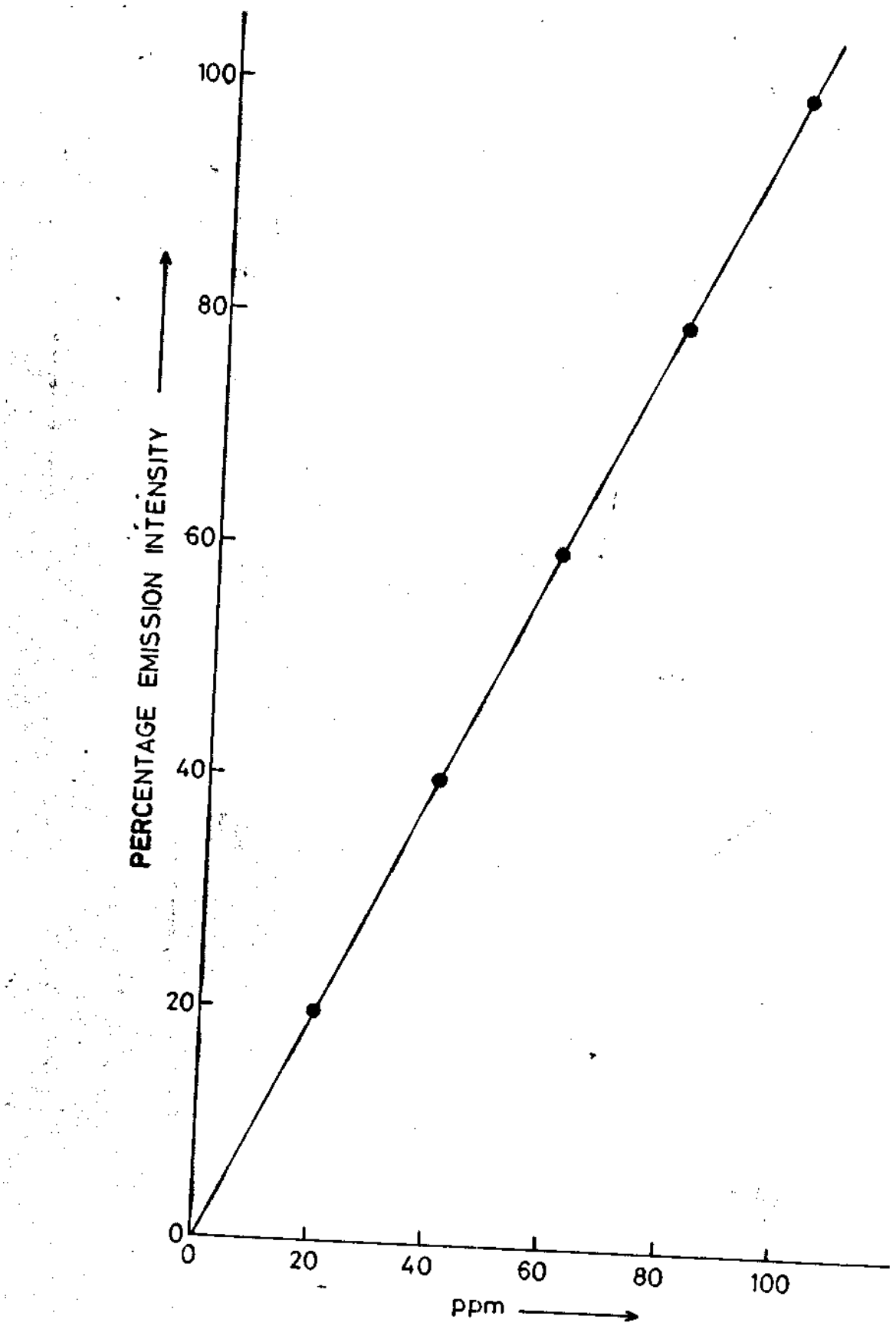


FIG. 2.3 CALIBRATION CURVE FOR CALCIUM.

The solution was standardized with 0.1M EDTA solution using Eriochrome Black T as an indicator (46). 20 to 100ppm calcium working standards were prepared by the appropriate dilution from the stock with water. 10ml of each standard solution was mixed with 2.5ml of 1% lanthanum solution before aspiration into the flame. The calibration curve for the metal is given in figure 2.3.

2.4.1 PROCEDURE:

Samples were prepared as in 2.3.1. The metals are excited by spraying their solution into the flame of the burner of the flame photometer. Before the instrument is used for the analysis of any of the metals, the highest concentration of the metal (usually 5ppm for sodium, 10ppm for potassium and 100ppm for calcium) was used to standardize the instrument (i.e. setting it at 100% intensity). After this, other concentrations of the standard were aspirated into the flame and their intensity measured. The instrument is flushed with deionized water before aspirating the samples. The instrument is again flushed between analysis of each sample. Duplicate determinations were carried out for each sample. Calibration curve

were constructed from the reading obtained from the standards. The results of the analysis are given in tables 3.4, 3.5, 3.6 for sodium, potassium and calcium respectively while figure 2.1 to 2.3 give their respective calibration curve.

2.5 ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF ZINC, COPPER, LEAD, MANGANESE, MAGNESIUM, CADMIUM, NICKEL, CHROMIUM AND COBALT (37, 42, 45, 46)

Principles of Atomic Absorption Spectroscopy:

If a solution containing metallic species is aspirated in a flame (such as air - acelylene or air-nitrous oxide systems) an atomic vapour will usually be formed with some of the metal atoms being excited to higher energy state. The proportion excited is usually small (37) but the ground state atoms have a highly specific and very sharp absorption spectrum. If light of one of these wavelengths is generated outside and passed through the flame, then absorbance follows the Beer-Lambert law. It is proportional to the path length and concentration (in the flame). Evaluation is usually by calibration curve method why?

Apparatus.

SP 1900 Pye Unicam Atomic Absorption Spectrometer. (flame was air-acetylene) Individual Cathode lamps.

Reagents.

All the reagents used were of analytical reagent grades unless otherwise stated.

Deionised water.

i. 0.1M EDTA: Prepared as in 2.4.

ii. Eriochrome Black T: Prepared by dissolving 0.2g of the dye stuff in 15ml of triethanolamine with the addition of 5-ml of 99% enathol to reduce viscosity.

iii. Xylenol Orange: Prepared by dissolving 0.5g of the compound in 100ml of water

Starch solution.

iv. 0.1M Sodium thiosulphate: Prepared by dissolving 24.818g of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$, in a litre of water.

Murexide.

This was prepared by shaking 0.5g of the powder with water and using the supernatant liquid for titration.

Standard solutions of the metal ions were prepared as outlined under preparation of standards.

PREPARATION OF STANDARDS FOR THE INDIVIDUAL METAL IONS.

Zinc:

A 1000ppm stock solution of zinc was prepared by dissolving 4.3980g of zinc sulphate heptahydrate ($ZnSO_4.7H_2O$) in water and making up to a litre. The solution was standardized with 0.1M EDTA solution using Eriochrome Black T as indicator (46).

10ppm intermediate standard solution of zinc was prepared by diluting 1 ml aliquot of the stock to 100ml. 1 to 5 ppm working standards were prepared by appropriate dilution of the intermediate with water the calibration curve is given in figure 2.5.

Copper:

1000ppm stock solution of copper was prepared by dissolving 3.9282g of copper sulphate pentahydrate

($CuSO_4.5H_2O$) in a small quantity of water and making up to one litre. The solution was standardized using 0.1M sodium thiosulphate solution using starch indicator (46). 10ppm intermediate copper standard was prepared by diluting 1 ml of the stock to 100ml with water. From this 1 to 5 ppm copper working standards were prepared as usual. Figure 2.4 shows the calibration curve for copper.

Lead:

1000ppm stock solution of lead was prepared by dissolving 1.584g of lead nitrate in 10ml of 40% nitric acid, and the volume made up to a litre. The solution was standardized using 0.1M EDTA solution with xylenol orange indicator. An intermediate 10ppm lead solution was prepared by diluting 1 ml of the stock to 100ml with water. From this 1 to 5 ppm lead standards were obtained as usual. Calibration curve of lead is given in figure 2.5.

Manganese:

A 1000ppm stock solution of manganese was prepared by dissolving 3.076g of manganous sulphate monohydrate ($MnSO_4.H_2O$) in water containing 1.5ml concentrated nitric

acid and the volume made up to one litre. The solution was standardized using 0.1M EDTA solution with Eriochrome Black T indicator (46). An intermediate 10ppm manganese solution was prepared by diluting 1ml of the stock solution to 100ml. From this, 1 to 5ppm working standards were prepared as usual. The calibration curve for this metal is given in figure 2.4.

Magnesium:

The stock solution for this metal was prepared by dissolving 10.0135g of magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) in water and making up to one litre to give a 1000ppm solution. This solution was standardized using 0.1M EDTA with Eriochrome Black T as indicator (46). A 10ppm magnesium intermediate stock solution was prepared by diluting 1 ml of the stock to 100ml. From this the working standard in 0.5 to 2.5 ppm range was obtain by appropriate dilution of the intermediate. The calibration curve for this analyte is given in figure 2.6.

Cadmium:

1000ppm cadmium stock solution was prepared by dissolving 2.1071g of cadmium nitrate in water and making up to a litre. The solution so obtained was

standardized using 0.1M EDTA with xylenol orange as the indicator (46). 10ppm cadmium intermediate standard was obtained from the stock by diluting 1 ml of the stock to 100ml. 1 to 5 ppm cadmium working standard was obtained from the intermediate stock by appropriate dilution. The calibration curve for this metal is given in figure 2.7.

Nickel:

The stock solution of this metal was prepared by dissolving 4.953g of nickel nitrate hexahydrate in a little water containing 1.5ml of concentrated nitric acid and the volume finally made up one litre to give 1000ppm nickel. The solution was standardized using 0.1M EDTA with murexide as the indicator. 10ppm intermediate standard was obtained by diluting 1 ml of the stock to 100ml with water. No calibration curve is given for this metal as determination was by standard addition method.

Chromium:

1000ppm stock solution of chromium was prepared by dissolving 2.828g of dried potassium dichromate in a little quantity of water containing 1.5 ml of concentrated sulphuric acid. The volume was then made up to one litre.

A 10ppm intermediate standard was prepared by diluting 1 ml of the stock to 100ml. From this, the working standard ranging from 1 to 5ppm was prepared as usual. No calibration was given for this metal as it was not detected in all the samples.

Cobalt:

The stock solution for this metal was prepared by dissolving 3.1016g of cobalt nitrate in water and making up to one litre. This gives a solution of 1000 ppm cobalt. This solution was standardized using 0.1M EDTA solution with xylenol orange as indicator. 10ppm cobalt intermediate standard was prepared from the stock by diluting 1 ml of 100ml. The working standard in the range of 1 to 5ppm were obtain from this by appropriate dilution. This element was not detected in all the sample and as such the calibration was not given.

2.5.1 PROCEDURE.

The samples were prepared as in 2.3.1 and 2.3.2. All necessary dilutions was made with deionised water.

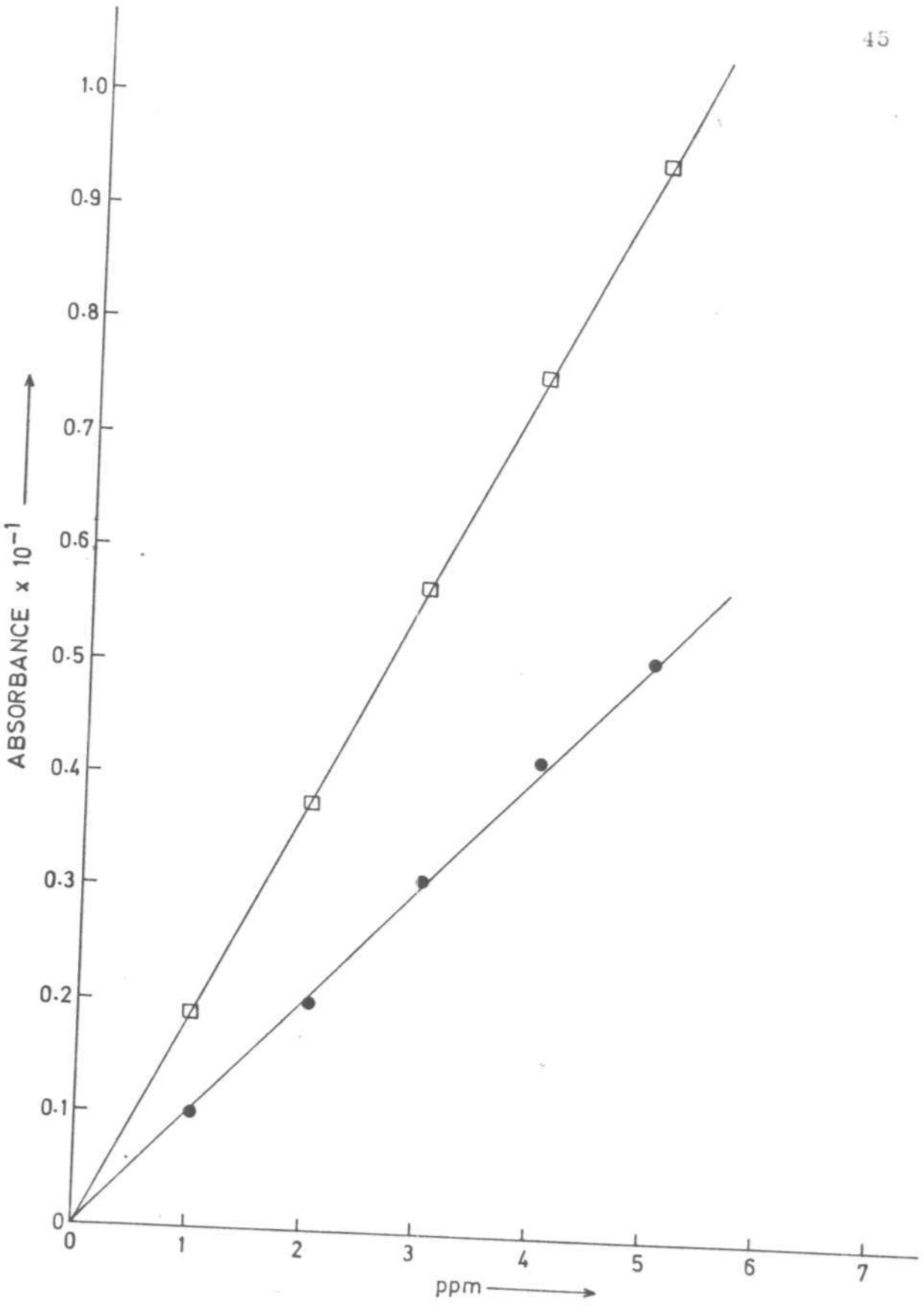


FIG. 2.4 CALIBRATION CURVES FOR MANGANESE AND COPPER
● MANGANESE, □ COPPER.

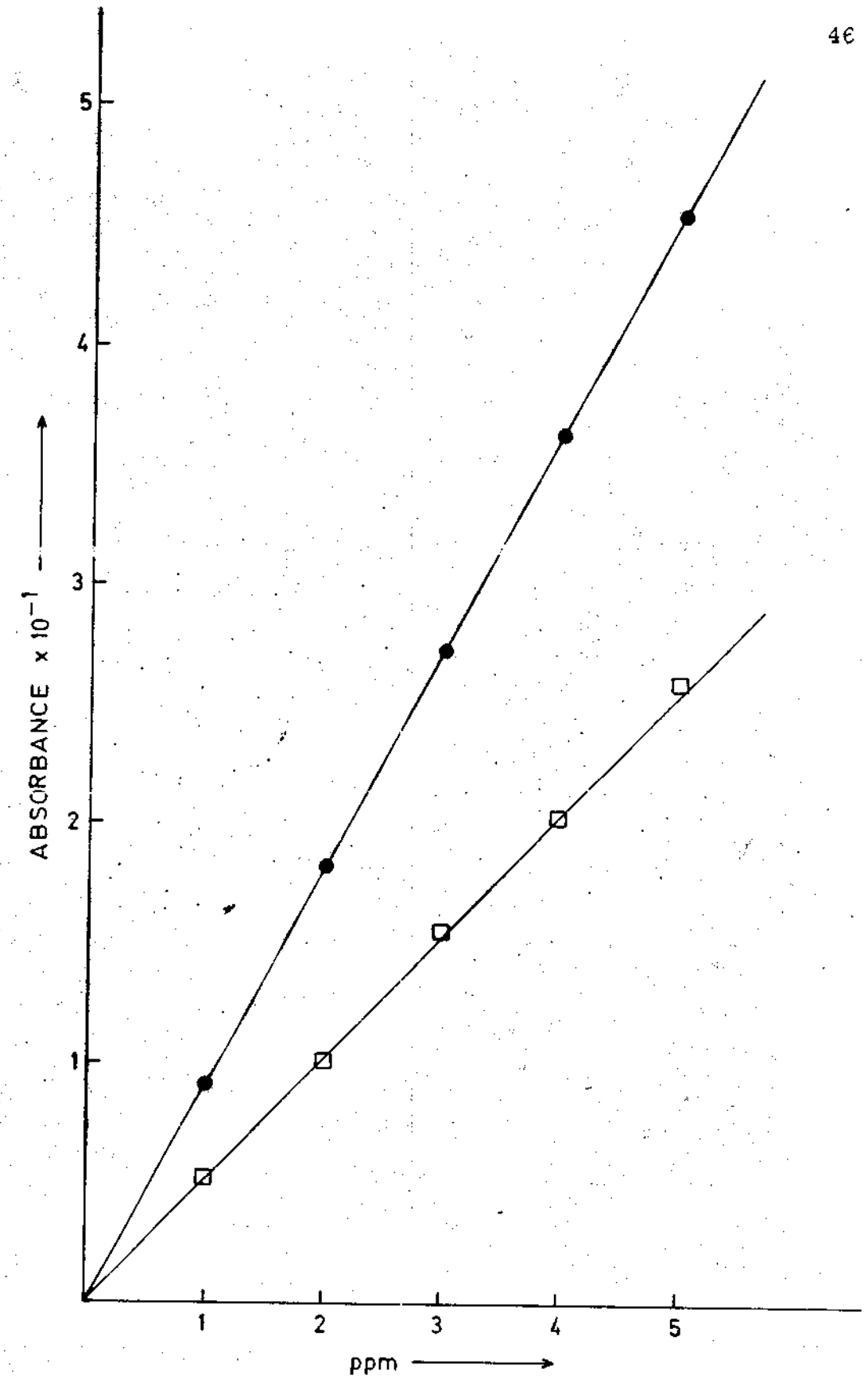


FIG. 2.5 CALIBRATION CURVES FOR ZINC AND LEAD. ●ZINC, □LEAD.

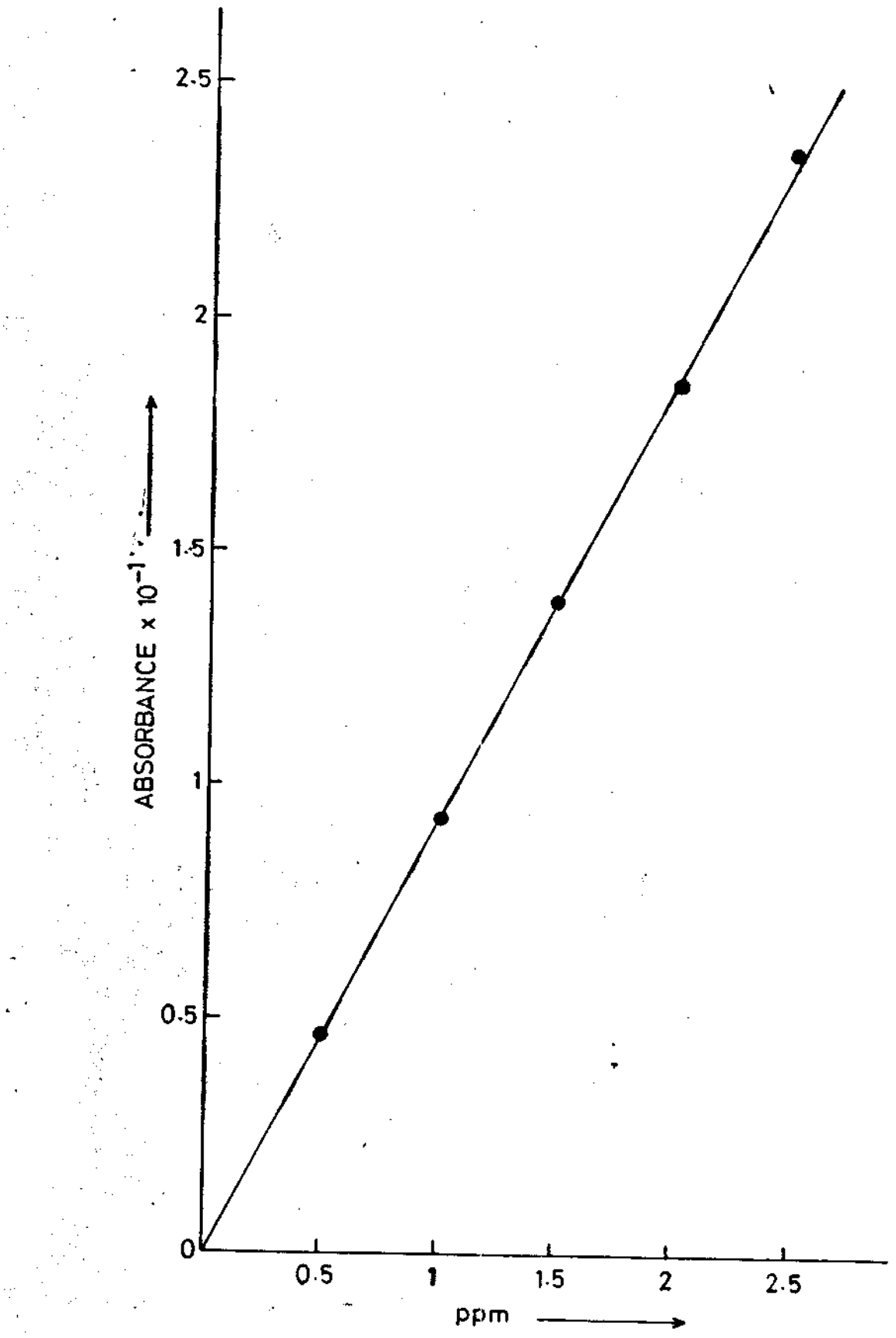


FIG. 2.6 CALIBRATION CURVE FOR MAGNESIUM

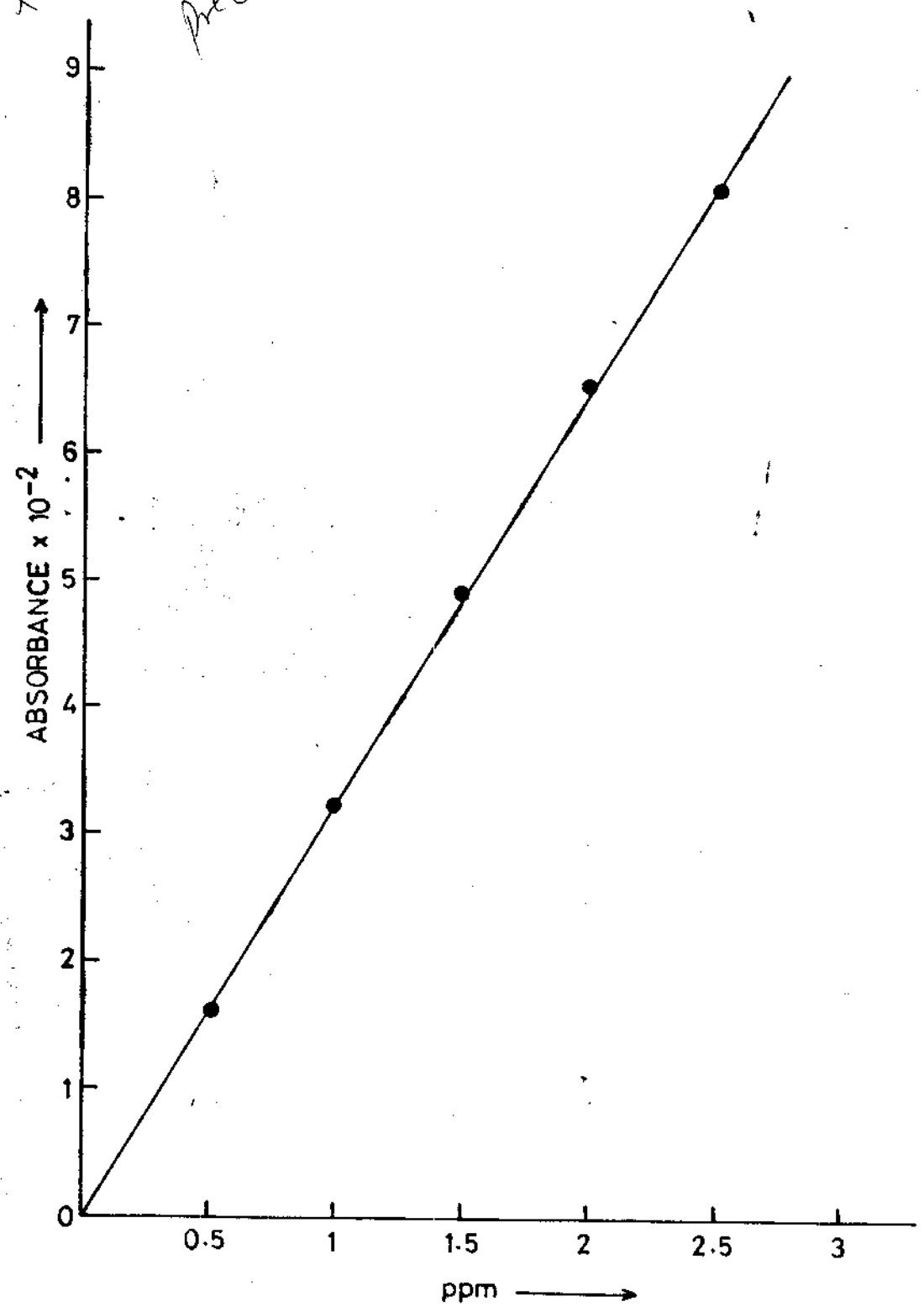


FIGURE 2.7 CALIBRATION CURVE FOR CADMIUM.

INSTRUMENTAL OPERATION AND SAMPLE ANALYSIS

The instrument was switched on and allowed to warm up for about 5 minutes with the cathode lamps of the metals in place. The instrumental, conditions for the determination of each metal is given in table 2.2. Air-acelylene system was used.

The different metal contents of the sample was determined by first aspirating the standard solutions into the flame to obtain their absorbance. The samples were then aspirated and the absorbance for the different metals noted and compared with that of the standards by way of calibration curve.

Standard addition method was used in the determinati of nickel. In this 10ml of the sample solution was placed in each of 3 25-ml volumetric flasks. 1.25, 2.5 and 3.75ml of the intermediate standards was added to the three flasks in that order. The volumes were made up to mark to give solutions containing 0.5, 1, 1.5ppm nickel plus the unknown concentration of nickel in the sample. The solution were aspirated in the flame of the atomic absorption spectrophotometer and their absorbance versus concentration was plotted to give nickel concentration on interpolation (27). The results of these analysis are given in appendix IIID to IIIK.

TABLE ...45

TYPICAL OPERATING CONDITIONS OF THE ATOMIC ABSORPTION SPECTROPHOTOMETER

	Silver	Copper	Lead	Manganese	Magnesium	Cadmium	Nickel	Strontium	Cobalt
Analytical wavelength (nm)	328.06	324.75	217.0	279.48	285.21	228.8	232.0	307.8	240.7
Slit Width	0.1-0.15	0.15-0.2	0.15-0.2	0.15	0.15-0.2	0.15-2.0	0.10	0.10-0.15	0.1-0.15
Flame	A	A	A	A	A	A	A	A	A
Air ($l\,min^{-1}$)	9	9	9	9	9	9	9	9	9
Acetylene ($l\,min^{-1}$)	0.7-1.1	0.8-1.0	0.8-1.0	0.8-1.0	0.9-1.1	0.8-1.0	0.8-1.1	1.1-1.2	0.8-1.0
Current setting (mA)	10	5	6	12	4	6	15	10	15
Best precision (mA)	5 - 10	4 - 5	5 - 6	10 - 12	4	5 - 6	12 - 15	8 - 10	12 - 15
Best Sensitivity	1 - 2	3 - 4	3 - 4	6.0	2 - 3	3 - 4	7 - 11	5 - 7	7 - 15

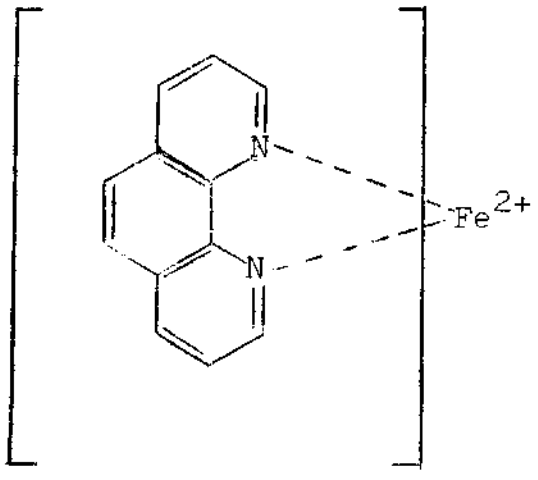
A = Air-acetylene

Taken from Reference 45.

2.6 SPECTROPHOTOMETRIC DETERMINATION OF IRON.

This technique was used for the determination of iron instead of atomic absorption spectrometric technique because the signals obtained from the latter instrument were not consistent.

This determination is based upon the formation of the orange-red ferrous-orthophenanthroline complex when iron (11) is treated with o-phenanthroline. The structure of this complex is given as



The coloured complex obeys Beer-Lambert law at 510nm. In forming this complex, iron must be in the reduced state (Iron(II)) and this is achieved with the aid of hydroquinone or hydroxylamine hydrochloride.

Intrument and Apparatus.

Spectrophotometer EEL Spectra Evans Electro-seleium Ltd., 25-ml volumetric flasks (10), Graduated 10-ml pipette, 50-ml burette.

Reagents.

All reagents used were of analytical reagent grades.

Deionised water was used throughout.

Standard Iron Solution 100ppm.

This was prepared by dissolving 0.702g of ferrous ammonium sulphate hexahydrate. ($FeSO_4.(NH_4)_2SO_4.6H_2O$) in 50ml of water containing 1 ml of concentrated sulphuric acid and making up to 1 litre in a volumetric flask. This was standardised using 0.1M EDTA with N-phenylanthranilic acid as the indicator (46). The intermediate standard of 10 ppm was prepared by diluting 10ml of the stock to 100ml.

i. 0.1M EDTA: Prepared as in 2.4.

ii. N-phenylanthrolic acid.

iii. O-phenanthroline solution 0.1%: Prepared by dissolving 0.1g of 1,10-phenanthroline monohydrate in 100ml of water by warming at 70 - 80°C.

iv. Hydroxylamine hydrochloride 10%: Prepared by dissolving 10.0g in 100ml of water.

v. 2M Sodium acetate: Prepared by dissolving 16.2g in 100ml of water.

vi. Bromophenol blue solution.

2.6.1 PROCEDURE (25).

The sample was prepared as in 2.3.1. 10ml aliquot was placed in a 25-ml volumetric flask. Another 10ml aliquot was also placed in a small Erlenmeyer flask. Three drops of bromophenol blue indicator was added to the latter and then titrated with 2M sodium acetate until a blue end point was obtained. The volume of sodium acetate used in the titration was noted to be 7.5ml.

0.2ml of 10% hydroxylamine hydrochloride solution was added to the aliquot contained in the volumetric flask, followed by 2ml of 0.1% 1,10-phenanthroline solution. This was swirled and 7.5ml of 2M sodium acetate solution was then added. After about 15 minutes, the volume was made up to mark and the absorbance of iron measured at 510nm in a 1-cm cell. The instrument was set using a blank that contains all reagent without the sample.

Preparation of Calibration Curve.

Calibration curve for iron was prepared by treating 1 - 10ml portions of the intermediate standard solution as in the sample except that instead of adding a determined quantity of sodium acetate 1ml was added in each case. The absorbance was also measured at the same wavelength after about 15 minutes. The calibration curve is given in figure 2.8. The concentration of iron in the samples was evaluated from the calibration curve and is given in table 3.14.

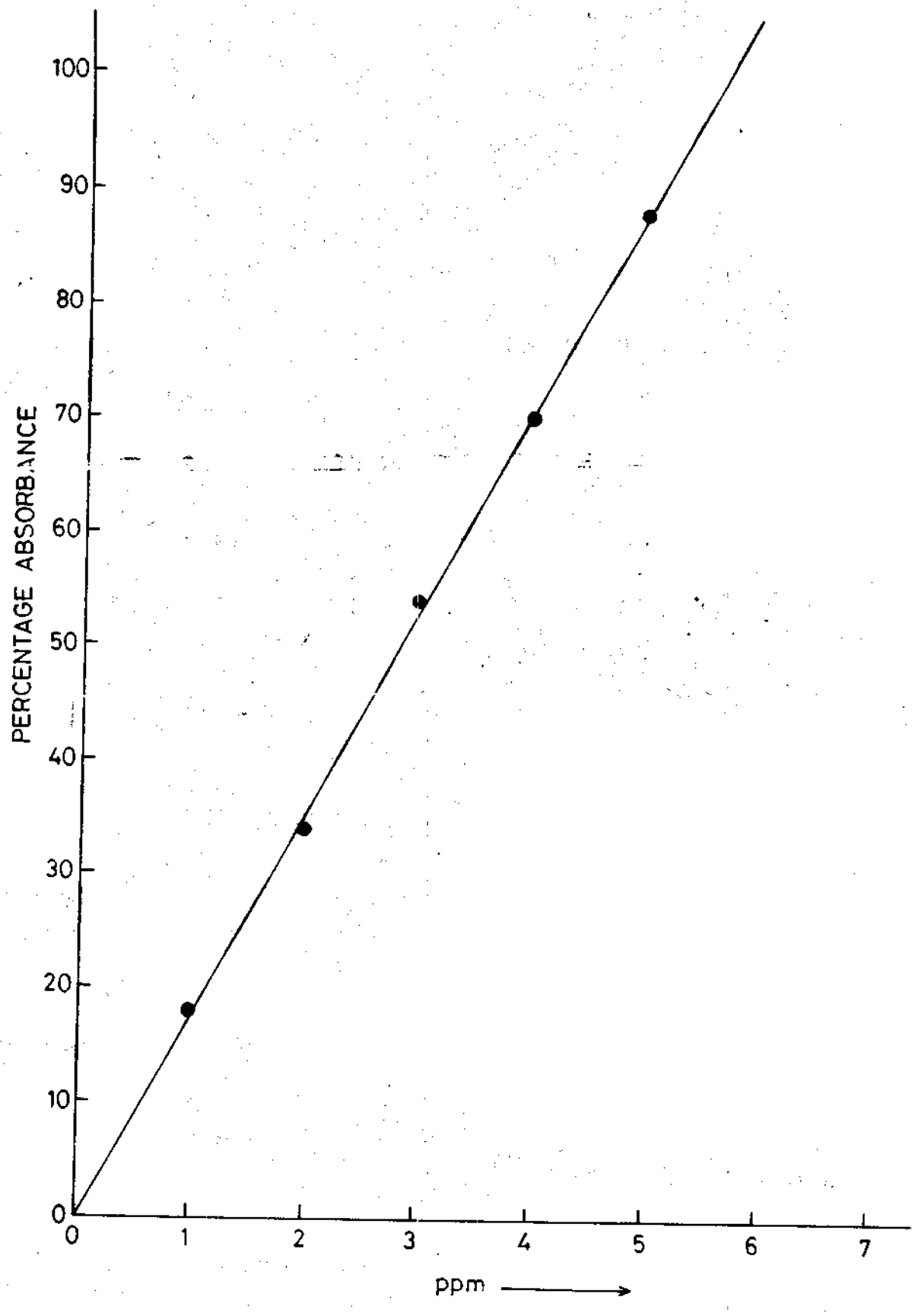


FIG. 2.8 CALIBRATION CURVE FOR IRON

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 RESULTS.

For the purpose of discussion of results, the samples are coded A, B, C to F for brake fluids and G to J for the gear oils as outlined in table 3.1.

TABLE 3.1

Sample	Code
Brake Fluid	
Agip	A
Mobil	B
National (Donax B)	C
TEXACO	D
TOTAL	E
BP Super	F
Gear Oil	
Agip	G
Mobil	H
TEXACO	I
TOTAL	J

Atomic Absorption Spectrometric technique was used in the determination of zinc, copper, lead, manganese, magnesium, cadmium, nickel, chromium and cobalt in the ash of six different brake fluids and four gear oils. Sodium, potassium and calcium determinations were by flame photometric technique while iron was analysed with the aid of a spectrophotometer. Seven determinations were carried out for each analyte except for lead for which eight determinations were used for calculations. The results obtained were statistically treated to get the mean and standard deviations. These are summarised in tables 3.2 and 3.3. The detailed results are given in Appendices III(A) to III(K).

3.2 DISCUSSION OF RESULT.

From the result of the analyses given in tables 3.2 and 3.3 it could be seen that wide variations exist for metals like sodium, potassium, calcium, zinc and manganese. Thus for sodium a maximum mean value of 1944.7 $\pm$ 137.4 mg/kg and a minimum mean value of 94.0 $\pm$ 9.4 mg/kg were recorded among the brake fluids. The result obtained for potassium ranged from a mean value of 35.4 $\pm$ 4.4 to 20956.0 $\pm$ 612.9 mg/kg of sample.

The values obtained for these two metals in gear oils did not vary much. They are in the range of 84 to 97 mg/kg for sodium (except for sample F that has a mean value of 65.7 $\pm$ 4.1) and 23 - 29 for potassium.

The variation in values of calcium affected both brands of oil. Thus, for brake fluids, it ranges between 139 - 483 mg/kg of sample and 54 - 299 mg/kg of gear oil sample. Zinc did not vary much among the brake fluids. Except for samples A and C that have mean values of 62.8 $\pm$ 5.2 and 37.5 $\pm$ 5.6 respectively, others are within the range 41 - 47 mg/kg of sample. The real variations were observed among the gear oils where the values ranged from 179 - 3665 mg/kg of sample. The variations in the value of manganese were general. It ranged from 36 to 60 mg/kg for the brake fluids and 37 to 59 for the gear oils.

TABLE 3.2

SUMMARY RESULT OF ANALYSIS OF BEARD FLUIDS

Samples	Sodium	Potassium	Calcium	Zinc	Copper	Lead	Manganese	Magnesium	Cadmium	Nickel	Iron	Chromium	Cobalt
A	1767.0± 94.2	20737.0±130.7	463.0±35.0	62.9±5.2	21.3±2.0	27.0±1.8	44.5±3.2	20.6±1.6	18.6±2.9	5.3±0.3	39.7±3.3	BD	BD
B	1712.0±111.0	20856.0± 68.0	483.3±20.9	44.3±3.3	24.2±2.2	27.6±2.0	46.0±3.0	20.5±1.4	20.6±3.8	5.8±0.8	34.7±1.5	BD	BD
C	1833.0±137.1	20708.0±683.0	362.0±35.0	37.5±5.6	21.8±1.7	27.5±2.3	36.7±4.1	16.2±1.4	23.0±2.3	6.1±0.6	42.9±6.0	BD	BD
D	1947.0± 9.4	4241.0 ±173.0	222.6± 7.5	43.8±5.2	22.0±1.2	25.2±2.6	52.2±3.2	20.6±2.4	21.4±3.0	5.8±0.6	100.5±8.2	BD	BD
E	94.6± 9.4	31.6 ± 6.4	242.0±18.7	47.4±3.8	21.4±1.6	29.8±2.2	60.2±3.6	19.3±1.5	20.3±3.2	4.7±0.7	38.9±1.9	BD	BD
F	85.7± 7.2	35.4 ± 4.5	139.3± 4.4	41.3±5.2	22.7±1.5	31.6±2.6	46.3±3.6	21.0±2.4	19.4±2.6	4.0±0.4	47.4±6.0	BD	BD

BD = Below Detection Limit.

TABLE 3.3

SUMMARY OF RESULTS OF ANALYSIS OF GEAR OILS

Samples	Sodium	Potassium	Calcium	Zinc	Copper	Lead	Manganese	Magnesium	Cadmium	Nickel	Iron	Chromium	Cobalt
G	97.5±7.1	29.7±4.1	233.9±7.1	2053.0±137.0	42.0±4.1	29.9±2.3	44.2±4.2	38.5±3.8	21.7±1.9	4.7±0.7	29.5±2.6	BD	BD
H	84.8±7.6	21.8±2.3	54.1±6.9	188.0±15.9	41.0±4.6	29.7±3.1	59.0±2.8	17.8±2.3	26.0±2.2	5.0±0.6	40.6±2.7	BD	BD
I	89.1±5.2	28.5±3.4	299.2±10.5	3663.0±125.8	42.0±2.6	30.8±1.6	48.2±5.2	18.6±2.0	30.4±3.1	5.1±0.7	44.9±4.6	BD	BD
J	65.7 4.1	23.2 0.9	67.0 4.9	179.1 100.0	41.8 3.0	29.6 2.0	37.9 3.5	14.3 2.1	30.0 3.4	5.9 0.7	43.6 3.7	BD	BD

BD = Below Detection Limit

According to Hurcombe (40), there are no reference standards or tolerance limit for these metals in petroleum products. The practice among the producers is to operate an internal and confidential quality control for their product. In the light of this, it was impossible to make a comparative study on the results. In the absence of any reference standard, the variations in values of some of the metals studied could be explained in two ways. First the difference in value could be due to contamination that might have arisen during handling, storage or transportation.

In the second case, some of these metals are usually present in petroleum products as additives that serve to supplement their natural characteristics and improve their performance or broaden the area of their suitability. Some of the additives serve (23) as antirust agent, oxidation inhibitors, corrosion preventives, detergent and dispersant agent, oiliness improver film-strength additive, viscosity-index improver, and foam inhibitor.

Often, one metal could be used to produce different additives with different functions, for instance zinc could be used to produce such additives as (7) zinc diorgano

dithiophosphates, zinc dithiocarbamates and zinc phenolates. Occationally, these petroleum products could be fortified (13) with different additives to impart the desirable properties to the product. It is possible for these additives to contain the same metal or different metals, depending on the goals of the consumer oil companies. When this is the case, variation in concentrations of trace metals present in these product should not be unexpected.

There were generally little or no variations in values obtained for copper, lead, cadmium, nickel, magnesium and iron in both brands of oil. Values of magnesium among the gear oils fall in the range 14 - 18 mg/kg of sample with exception of sample G were a value of 38.5 $\pm$ 3.7 was recorded. Again the values of iron among the brake fluids are in the range of 34 - 47 mg/kg with an exception value of 106.5 $\pm$ 8.2 mg/kg being recorded with sample D. The range of this metal for the gear oils is 40 - 44mg/kg, however, a very low value of 29.5 $\pm$ 2.6 mg/kg was obtained from sample G.

These exceptional value might be due to the differential requirements of the metals by the consumer oil companies. Where the metal contents of the oils are within the same range, it is probably

because the metals are indigenous to the refined feed stock. This could also be the reason why results that are perculiar with brands of oil are obtain for copper. (see tables 3.2 and 3.3).

It is also noticeable in tables 3.4 to 3.14 that there are variations in result for even a set of determinations. This is not unexpected as errors were likely to have been introduced during the sample preparation stages through such means as volatilization of the inorganic components during ignition. This is more pronounced in cadmium analysis where the instrument failed to detect the metal from the solubilized ash until extraction technique was employed to bring the metal into aqueous solution. Losses of ash matter could also have arisen through mechanical entrainment and production of fly ash due to rapid heating. The problems become compound when one considers the open atmosphere in which drying and ashing were done.

However, these problems were minimised during drying and ashing be increasing heating rate of the infrared lamp and muffle furnace gradually with time.

Chromium and cobalt were not found in the sample. They were either absent or present in an amount that was below the detection limit of the instrument used.

3.3 SUMMARY AND CONCLUSIONS.

In addition to hydrocarbons, petroleum and its products often contain sulphur, phosphorus and measurable quantities of metals. The metallic constituents are either indigenous to the oil or are deliberately added to the oil because of the beneficial effects they have on the properties of the oil. For instance, such additives could improve the property of the oil by acting as one of the following (13); viscosity index improver, antioxidant, antifoam agent, detergent inhibitor, film strength improver and corrosion inhibitor. Often, the presence of these metals in oil may have some harmful effect on the quality of the oil, such that, they may not function properly when used in engines.

The petroleum products are sources of pollutents in our environment. The standard of public health, enjoyment of surroundings, plant life depend on the quality of the air or generally the environment. As our country is growing so is the number of vehicles

on our roads growing, each contributing to the level of metal pollutant of the environment by way of emission and disposal of used oils. One fact is obvious, metals do not decay, thus the possibility of accumulation of "toxic" metals in our environment exists and this might get to a level that would spell danger for us.

The present work evaluated the level of metals in brake and gear oils, namely; Agip, Mobil, National, TEXACO, TOTAL and BP Super brake fluids and Agip, Mobil, TEXACO and TOTAL gear oils. The sample were prepared by drying under an infrared lamp and ashing in a muffle furnace. Losses by volatilaization were minimised by prefixing the metals with 98% sulphuric acid before drying. The sample for the analysis of lead and cadmium were prepared by extracting the metals into 40% nitric acid using dithizone.

Atomic absorption spectrometric technique was used to determine, zinc, copper, lead, manganese, magnesium, cadmium, nickel, chromium and cobalt while sodium, potassium and calcium were evaluated using flame photometric technique. Iron was estimated spectrophotometrically. The concentration ranges of the metals determined in the two brands of oil are given as:

CONCENTRATION RANGE OF METALS DETERMINED mg/kg^{-1}

Metal	Brake Fluid	Gear Oil
Sodium	94.0 - 1947.0	65.7 - 97.5
Potassium	31.7 - 20956.0	23.2 - 29.7
Calcium	139.3 - 62.9	54.1 - 299.2
Zinc	37.5 - 62.9	179.1 - 3665.0
Copper	21.3 - 29.2	41.0 - 42.0
Lead	25.2 - 31.6	29.6 - 30.8
Manganese	36.7 - 60.2	37.9 - 59.0
Magnesium	16.2 - 21.0	14.3 - 38.5
Cadmium	18.0 - 29.3	21.7 - 30.4
Nickel	4.0 - 6.1	4.7 - 5.9
Iron	34.7 - 106.5	29.5 - 44.9
Chromium	BD	BD
Cobalt	BD	BD

The level of metals detected appears low with exception of sodium, potassium and zinc which were present in relatively high concentration in some samples. The levels found for other metals may not be harmful after they have been distributed in the

environment, but it must be remembered that metals do not decay and that the number of vehicles on our roads is on the increase and as such the level of these metals in our environment may accumulate to a stage where it would precipitate danger. Care must be taken to educate our roadside mechanics on the need of proper disposal of waste oils to control polluting our environment.

SUGGESTIONS.

Selemium, arsenic, molybdenium, antimony, barium and silver have also been reported (10) to be present in crude oils from which the base stock of there petroleum products are usually produced. These metals have also been reported (10, 16) to be toxic to all forms of life. It is therefore recommended to include the analysis of these metals in a similar study in future.

A study of soil and water samples from areas around some roadside mechanic workshops could be undertaken to determine the extent of pollution caused by disposal of such used oils.

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APPENDIX IA*

METALS ANALYSED IN LUBRICATING OILS AND AREAS ASSOCIATED WITH POSSIBLE TROUBLE.

ELEMENT	AIRCRAFT	RAIL; ROAD DIESEL ENGINES.
Aluminium	Lubricating Pump	Bearings
Cadmium		Water Leaks. Bearing
Chromium	Cr-plated parts	Water leaks
Copper	Bearings	Bearings
Iron	Excess Wear→ Various	Part ← Excess wear
Magnesium	Gearbox Housings	
Sodium	Saltwater leak.	
Nickel		Alloy constituent
Lead	Bearings	Bearings
Zinc		Absence[a] (< 10ppm)
oil Additives		Depletion

[a]The Zinc additives used in some oils corrode Silver bearings.

*From reference 14.

APPENDIX IB

LUBRICANT ADDITIVES*

METAL	REPRESENTATIVE COMPOUNDS	PURPOSE
Antimony	Sb dialkyl dithiocarbamates	Antiwear, extreme pressure, and antioxidant additives in conventional and low-ash-type automotive crankcase oils, industrial and automotive gear oils, greases amount 1 - 3%
Barium	Ba diorgano dithiophosphates Ba petroleum sulphonate, Ba phenolate Ba phosphates orthiophosphates.	Corrosion inhibitors, detergents, rust inhibitor automatic transmission fluids, greases.
Boron	Borax, boric acid esters	Antiwear agents, autioxidant deodorant cutting oils greases, brake fluid
Cadmium	Cd dithiophosphates	Steam turbine oils
Lead	Pb naphthenate	Extreme pressure additive, greases, gear oils
Mercury	Organo mercury compounds	Bactericide, e.g. cutting oil emulsions
Molybdemum	MoS_2 - Mo dibutyl dithiocarbamate and phosphate.	Greases, extreme pressure additive
Nickel	Cyclopentadienylnickel complexes	Antiwear agents, minimize carbon deposits improv lubrication and combustion.

APPENDIX IB (cont'd)

METAL	REPRESENTATIVE COMPOUNDS	PURPOSE
Selenium	Selenides	Oxidation and bearing corrosion inhibitors
Tin	Organotin Compounds	Antiscuffing additive, metal deactivators.
Zinc	Zn diorgano dithiophosphates Zn dithiocarbamates Zn phenolates.	Antioxidant, corrosion inhibitors, antiwear additives, detergent, extreme pressure additives, in crankcase oils, hypoid gear lubricants, greases, aircraft Piston-engine oils, turbine oils, automatic transmission fluids, railroad diesel engine oils, differential and wet brake lubricants.

*Taken from Reference 15.

APPENDIX IIIA

SODIUM (Concentration in mg/kg)

A	B	C	D	E	F	G	H	I	J
1852.00	1900.00	1900.00	2080.00	92.00	90.00	108.00	84.00	84.00	70.00
1667.67	1666.67	2083.33	1833.33	86.67	86.67	90.00	71.67	83.33	61.00
1840.00	1866.67	2066.67	2000.00	80.00	89.00	85.67	76.67	85.67	65.00
1653.00	1666.67	1866.67	2016.67	105.00	100.00	103.33	93.67	90.00	65.33
1766.67	1666.67	1720.06	1666.67	105.00	106.67	96.67	85.00	94.67	62.67
1906.67	1600.00	2026.67	1960.00	86.67	94.00	98.67	86.67	98.33	73.33
1683.33	1620.00	1866.67	2070.00	102.00	103.33	100.00	94.00	87.33	62.33
Mean	1767.0	1712.	1933.0	1946.8	94.0	95.8	97.5	84.5	89.1	65.7
STD Div.	94.2	111.1	122.2	137.4	9.4	7.2	7.1	7.6	5.2	4.1

APPENDIX III(B)

POTASSIUM (Concentration in mg/kg)

A	B	C	D	E	F	G	H	I	J
21592.00	21066.00	20666.67	4080.00	32.00	32.00	32.00	22.00	32.00	24.00
22333.33	20000.00	20000.00	4333.33	23.33	28.00	27.33	26.33	32.00	23.33
18600.00	21666.67	21866.67	4266.67	23.33	36.67	26.67	24.00	23.33	24.67
21416.67	20426.67	20666.67	3966.67	32.00	36.67	25.00	22.33	32.00	23.33
20460.00	21866.67	21533.33	4200.00	40.00	40.00	28.33	28.33	25.00	21.67
19093.33	20666.67	20000.00	4294.33	30.00	32.67	38.33	23.33	27.33	23.33
21666.67	21000.00	20273.33	4546.67	40.67	41.67	30.33	27.33	22.67	22.33
Mean	20737.4	20956.1	20709.1	4241.0	31.6	35.4	29.7	24.8	28.2	23.2
Std. Div	1306.7	612.5	682.9	172.5	6.5	4.4	4.1	2.3	3.4	0.9

APPENDIX III(C)

CALCIUM (Concentration in mg/kg)

	A	B	C	D	E	F	G	H	I	J
	482.00	460.00	356.00	230.00	260.00	140.00	240.00	46.67	300.00	60.00
	490.00	500.00	326.00	216.67	266.67	143.33	233.33	53.33	310.67	66.67
	476.67	466.67	333.33	210.33	233.33	133.33	236.67	60.67	286.67	63.33
	466.67	493.33	316.67	218.00	233.33	133.33	236.67	62.67	306.67	70.00
	420.00	506.67	393.33	223.33	223.33	139.00	222.33	60.00	313.33	66.67
	400.00	503.33	406.67	226.67	260.00	146.00	243.33	51.67	287.33	76.67
	503.33	453.33	400.67	233.33	215.67	140.00	225.00	43.33	290.00	65.33
Mean		462.7	483.3	361.9	222.6	241.8	139.3	233.9	54.1	299.2	67.0
SD		35.3	20.9	35.1	7.5	18.7	4.4	7.1	6.9	10.5	4.9

APPENDIX III(D)

ZINC (Concentration in mg/kg)

A	B	C	D	E	F	G	H	I	J
40.00	45.60	36.00	44.80	48.00	34.00	2320.00	166.00	3920.00	3120.00
66.67	50.00	46.67	46.67	46.67	43.33	1866.67	193.33	3500.00	3333.33
60.00	43.33	33.33	33.33	40.00	35.00	2083.33	173.33	3666.67	3200.00
63.33	40.67	43.33	50.00	48.33	40.00	2133.33	216.67	3600.00	3133.33
70.00	40.00	30.00	48.33	46.67	45.00	1933.33	180.00	3733.33	3000.00
66.67	47.33	40.00	43.33	53.33	50.00	2000.00	200.00	3666.67	3200.00
53.33	43.33	33.33	40.00	50.00	41.67	2033.33	186.67	3566.67	3266.67
Mean	62.9	44.3	37.5	43.9	47.6	41.3	2052.9	188.0	3664.8	3179.6
SD	5.2	3.3	5.6	5.2	3.8	5.2	136.8	15.8	125.8	100.0

APPENDIX III(E)

COPPER (Concentration in mg/kg)

A	B	C	D	E	F	G	H	I	J
25.00	26.67	23.33	21.67	21.67	22.33	40.00	46.67	43.33	46.67
21.67	25.33	21.67	21.67	23.33	25.00	46.00	39.33	40.00	43.33
19.33	26.00	19.33	20.00	20.00	23.33	46.67	46.67	43.33	39.00
23.33	21.67	23.33	23.33	24.00	20.67	37.67	36.00	38.67	38.67
20.67	20.00	24.00	22.67	19.33	22.00	36.67	43.33	39.33	41.67
20.00	25.00	20.00	20.67	20.00	21.33	40.00	40.67	46.67	46.67
19.00	24.67	20.67	23.67	21.33	24.33	46.67	34.00	42.67	38.33
Mean 21.3	24.2	21.8	22.0	21.4	22.7	42.0	41.0	42.0	41.8
SD 2.0	2.2	1.7	1.2	1.6	1.5	4.1	4.6	2.6	3.0

APPENDIX III(F)

LEAD (Concentration in mg/kg)

A	B	C	D	E	F	G	H	I	J
25.21	28.00	24.80	26.40	28.40	32.01	28.60	24.60	30.00	28.70
26.00	25.01	28.60	28.10	30.40	35.00	25.70	26.40	31.10	31.20
25.36	30.00	23.01	22.00	26.60	26.09	33.01	38.10	30.20	26.30
29.40	26.06	30.10	26.20	27.80	33.01	32.20	34.10	28.40	33.00
25.20	24.70	28.20	25.70	33.00	34.00	27.80	28.60	32.20	31.00
26.60	30.00	30.01	26.80	32.00	32.00	32.10	30.26	31.10	30.20
28.01	28.00	27.08	19.90	29.10	29.50	30.00	28.40	34.00	27.70
30.00	29.01	28.20	26.40	32.10	32,10	30.00	32.10	29.60	28.60
Mean 27.0	27.6	27.5	25.2	29.9	31.6	29.9	30.3	30.8	29.6
SD 1.8	2.0	2.3	2.6	2.2	2.6	2.3	4.1	1.6	2.0

APPENDIX III(G)

MANGANESE (Concentration in mg/kg)

	A	B	C	D	E	F	G	H	I	J
	40.00	50.00	43.33	56.67	60.00	42.00	41.67	60.00	56.67	41.33
	46.67	44.67	33.33	53.33	55.33	51.67	50.33	56.00	53.33	33.33
	40.00	41.67	35.00	53.33	64.00	46.67	49.67	63.33	49.33	38.33
	48.00	50.33	30.00	48.33	63.33	50.67	46.33	61.67	46.67	32.00
	43.33	46.67	38.33	49.33	64.67	46.67	42.00	56.67	53.33	40.00
	45.00	45.00	40.00	51.67	55.67	45.00	40.00	55.33	41.67	38.33
	48.33	43.33	36.67	57.33	58.33	41.67	39.67	60.00	43.33	41.67
Mean	44.5	46.0	36.7	52.9	60.2	46.3	44.2	59.0	49.2	37.9
SD	3.2	3.0	4.1	3.2	3.6	3.6	4.2	2.8	5.2	3.5

APPENDIX III(H)

MAGNESIUM (Concentration in mg/kg)

	A	B	C	D	E	F	G	H	I	J
	19.00	20.80	16.00	19.60	18.00	20.00	40.4	16.00	14.00	16.00
	21.67	20.00	15.00	23.63	21.00	24.00	37.33	21.00	20.00	15.00
	23.33	18.33	16.67	20.00	20.00	20.00	41.67	16.67	16.33	13.33
	20.00	22.17	14.67	24.00	18.33	16.67	45.00	15.00	14.67	16.67
	21.67	18.67	16.67	17.67	16.67	23.33	36.67	20.00	21.67	14.00
	18.67	21.33	19.33	17.67	20.67	22.67	33.33	16.00	16.67	16.00
	20.00	22.0	15.33	21.67	20.33	20.00	35.00	20.00	18.67	15.33
Mean	20.6	20.5	16.2	20.6	19.3	21.0	38.5	17.8	18.0	14.3
SD	1.6	1.4	1.4	2.4	1.5	2.4	3.8	2.2	2.0	2.1

APPENDIX III(I)

CADMIUM (Concentration in mg/kg)

A	B	C	D	E	F	G	H	I	J
15.00	24.00	24.00	18.00	25.00	17.00	22.00	24.00	30.00	36.00
22.00	27.00	25.00	20.00	32.00	22.00	20.00	28.00	34.00	32.00
20.00	19.00	19.00	22.00	26.00	16.00	24.00	24.00	28.00	24.00
21.00	16.00	26.00	17.00	35.00	24.00	19.00	23.00	26.00	31.00
14.00	23.00	24.00	26.00	29.00	20.00	24.00	30.00	35.00	28.00
16.00	18.00	21.00	23.00	30.00	18.00	20.00	27.00	28.00	30.00
18.00	17.00	22.00	24.00	28.00	19.00	23.00	26.00	32.00	29.00
Mean	18.0	20.6	23.0	21.4	29.3	19.4	21.7	26.0	30.4	30.0
SD	2.9	3.8	2.3	3.0	3.2	2.6	1.9	2.3	3.1	3.4

APPENDIX III(J)

NICKEL (Concentration in mg/kg)

A	B	C	D	E	F	G	H	I	J
5.67	6.00	6.67	5.33	5.00	4.33	4.67	6.33	4.67	5.67
4.33	6.33	5.33	5.00	4.33	3.67	5.00	5.00	4.67	4.67
5.00	5.33	6.00	6.33	4.33	3.33	3.67	4.67	5.00	6.67
5.33	4.00	6.67	5.67	4.00	4.00	6.00	5.00	4.00	6.33
6.33	6.67	5.33	6.33	5.67	4.00	4.33	4.33	5.33	6.00
4.33	6.00	6.67	5.33	5.67	4.67	4.00	5.00	5.67	5.33
6.33	6.32	6.00	6.67	4.00	3.67	5.00	4.67	6.33	6.67
Mean	5.3	5.8	6.1	5.8	4.7	4.0	4.7	5.0	5.1	5.9
SD	0.8	0.8	0.6	0.6	0.7	0.4	0.7	0.6	0.7	0.7

APPENDIX III(K)

IRON (Concentration in mg/kg)

	A	B	C	D	E	F	G	H	I	J
	44.33	36,00	40.33	107.33	42.33	44.33	28.00	40.33	50.00	48.33
	44.33	32,67	33.33	93.33	37.33	48.33	33.00	36.67	43.00	49.33
	37.67	36.00	45.00	112.67	37.33	58.33	26.33	40.00	36.67	39.33
	36.33	33.00	46.67	117.00	38.67	40.00	30.00	43.33	50.67	42.00
	40.33	35.00	48.33	113.33	40.00	45.00	28.33	45.00	43.67	39.00
	39.33	36.67	50.33	96.67	36.67	53.33	33.67	38.00	47.67	42.33
	35.33	33.33	36.00	105.33	40.00	42.67	27.33	41.00	42.67	45.33
Mean	39.7	34.7	42.9	106.5	38.9	47.4	29.5	40.6	44.9	43.6
SD	3.3	1.5	6.0	8.2	1.9	6.0	2.6	2.7	4.6	3.7