

ANALYSIS OF SOME LUBRICATING OILS  
FOR TRACE METALS  
BY ATOMIC ABSORPTION SPECTROMETRY  
USING ASHING PROCEDURES

BY

PIUS FRANCIS OGWUCHE OJOBOR  
N.C.E.; B.Sc. ED (A.B.U.)

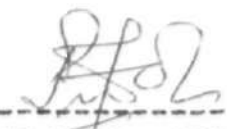
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DECLARATION

I hereby declare that this thesis "Analysis of Some Lubricating Oils for Trace Metals by Atomic Absorption Spectrometry Using Ashing Procedures" 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 specially acknowledged by means of references.

  
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PIUS F. O. OJOBOR

Date: 6/5/1983

DEDICATION

TO THE LOVING THOUGHTS I HOLD

FOR

MY MOTHER, INO-EKPA

MY WIFE, CECILIA

AND

MY CHILDREN, JOHN & STANLEY.

A C K N O W L E D G E M E N T S

I am greatly indebted to Professor K. Singh of the Chemistry Department, Ahmadu Bello University, Zaria, whose knowledge and professional handling of the project material, brought inspiration not only to this report but to me. His guidance and thoughtful comments have been most helpful to me. I wish to acknowledge the contributions of my lecturers especially Professor K. Singh, Dr. H. T. Bozimo (Head of Chemistry Department), Dr. J. Y. Olayemi, Dr. S. A. Thomas, Dr. E. G. Kolawole and Dr. M. S. Kazmi.

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A B S T R A C T

Petroleum contains a high percentage of hydrocarbon in addition to containing measurable quantities of metals. The metallic constituents may be indigenous to the crude oils as oil-soluble metallo-organic compounds, as a colloid, or as a filterable suspension. Metals may be introduced into the finished petroleum products extraneously in processing or during service. In certain cases the presence of metals in oils can cause the finished products to have undesirable properties such as corrosion of refinery equipment, reduction of activity of cracking catalysts (and whose replacement is expensive) equipment deterioration and premature failures in engines (resulting from excessive wear, bearing failure and radiation leaks). Moreover, metals lost to the environment as air pollutants as a result of fuel combustion and other processes through which metals are released into the environment, pose a direct health hazard. In Nigeria today, with the developing economy, the number of vehicles are on the increase,. Thus the threat posed by environmental pollution cannot be overlooked as some of these metals if inhaled or ingested can cause physiological problems.

In other cases the presence of controlled amount of added metal compounds, can bestow beneficial properties on lubricating oils. These lubricant additives resist oxidation, reduce wear, inhibit corrosion^ improve lubrication and combustion characteristics.

In view of the beneficial and ill-effects of having metals in lubricating oils, the present research project is intended to determine the metal content in Agip (SAE 20W-30) AP Super V (SAE 20W-50HD), Castrol GTX (SAE 2W-50) Mobil (SAE 40), National (SAE 30/40), Texaco (SAE 40) Total (SAE 40) Total SAE 30/40) and Unipetrol (SAE 20W-30), engine oils by atomic-absorption spectrometry using ashing procedures in order to monitor the level of metal contents in the oils.

The oil samples have been decomposed by the wet-oxidation procedure which involves decomposing the oil samples with concentrated sulphuric acid. The mixture of the sample and the acid is first charred with the aid of an infrared lamp, followed by ignition of the dry carbonaceous residue by means of a bunsen burner. Complete oxidation of carbon is accomplished in a muffle furnace, set at 600 C to give the residual ash necessary for subsequent elemental analysis.

The atomic-absorption spectrometric technique and flame photometry have been chosen to analyse the ashed samples of the oils for metals which are present in trace amounts.

The A.S.Sc technique has been used to determine calcium, cobalt, copper, iron, lead, magnesium, manganese, nickel and zinc in the oils whereas flame photometric measurement was used to obtain the experimental data for potassium and sodium.

The concentration range for the individual metallic element is as follows:-

Calcium	(14.44 - 29,66mg kg <sup>-1</sup> )
Cobalt	( 0.18 - 0,44mg kg <sup>-1</sup> )
Copper	( 0.78 - 14.06mg kg <sup>-1</sup> )
Iron	(1.85 - 16.58mg kg <sup>-1</sup> )
Lead	( 0.70 - 2.43mg kg <sup>-1</sup> )
Magnesium	( 9.50 - 31.03mg kg <sup>-1</sup> )
Manganese	( 0.28 - 2.58mg kg <sup>-1</sup> )
Nickel	( 1.61 - 2.30mg kg <sup>-1</sup> )
Potassium	( 0.40 - 3.48mg kg <sup>-1</sup> )
Sodium	( 3.40 - 15o91mg kg <sup>-1</sup> )
Zinc	(16.50 - 18.00mg kg <sup>-1</sup> )

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## CHAPTER 1

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

#### 1.1 OCCURRENCE AND COMPOSITION OF PETROLEUM

Petroleum has been discovered since the dawn of our modern civilization. Large reservoirs of petroleum crude oils have been discovered in Abu Dhabi, Britain, Gabon, Iraq, Iran, Mexico, Nigeria, Norway, Pennsylvania, Russia, Saudi Arabia, Venezuela, etc. Petroleum provides an important source of products such as gasoline, lubricating oils, vaseline and paraffin wax, textiles and chemicals. Petroleum products supply about 43% of the nation's energy requirements. Though large quantities of petroleum have been (and are being) recovered and consumed, its basic science is still developing, specifically the role of the metals in petroleum oils.

In addition to consisting a high percentage of hydrocarbon, petroleum contains measurable quantities of metals. Shirey (1) was able to determine thirteen metallic elements in the ashes of seven different oils. This and other early studies which have revealed the presence of metals such as vanadium, nickel, aluminium, sodium, cobalt, calcium, manganese, barium, silicon, iron, lead, molybdenum, zinc, potassium, magnesium, tin, beryllium, etc. in

petroleum oils, have generated interest in trace metal analysis.

### 1.2 SOURCES OF METALS IN PETROLEUM OILS

The metals may be indigenous to crude oils as inorganic particulate matter, as oil-soluble metallo-organic compounds, as a colloid, or as a filterable suspension. They may be introduced extraneously or through interaction of the oil components with the metal of transportation, and storage facilities.

### 1.3 EFFECTS OF PRESENCE OF METALS IN CRUDE OILS AND FINISHED PRODUCTS

The importance of trace metals in petroleum and its products cannot be underscored. In certain cases the presence of metals in oils can cause finished products to have undesirable properties such as corrosion of refinery equipment, reduction of activity of cracking catalysts (whose replacement is expensive), equipment deterioration and premature failures in engines. For example, compounds containing acid forming elements may cause corrosion of equipment; specifically vanadium compounds cause pitting in equipment; high temperature power generators such as gas turbine are susceptible to vanadium corrosion (2, 3). Also the need to control the metal content (copper, iron, nickel, vanadium) is important because some of these metallic elements, (especially nickel and vanadium which are indigenous to crude oils),

can poison solid cracking catalyst thus reducing gasoline production. The task of regenerating the catalyst or even replacing them, is an expensive exercise. Furthermore, inorganic deposition products from lubricating oils can give rise to engine failure; as the trace metal content increases such problems as excessive wear, bearing failure and radiation leaks, and lubricant breakdown (which is associated with trace metal if present in high enough concentration) in crank case oils, become pronounced (4, 5, 6). Table 1.1 lists some trouble areas and corresponding metal to which their increase in oil can be related.

TABLE 1.1\*

ELEMENT	AIRCRAFT	RAILROAD DIESEL ENGINE
Aluminium	Lubricating pump	Bearings
Boron		Water leaks
Cadmium		Bearings
Chromium	Chromium plated parts	Bearings
Copper	Bearings	Bearings
Iron	Excess wear	Various-Parts-excess wear
Lead	Bearings	Bearings
Magnesium	Gear box housing	
Nickel	7ppm	Alloy constituents
Silicon	Filter failure	airborne dirt filter failure 8ppm
Sodium	Salt water leak	
Tin	15ppm	Bearings
Zinc		Absence (a) (10ppm)
Oil Additives		Depletion

(a) The zinc additives used in some oils corrode silver bearings.

\* From Reference 4.

#### 1.4 PHYSIOLOGICAL EFFECTS OF METALS IN OILS

The possibility of some potentially "toxic" metals accumulating in our environment as a result of fuel combustion and other processes through which metals are released from their natural sources into the environment is a case of immediate concern. No metal is degradable. These metals if inhaled or ingested, pose a direct health hazard. The magnitude of this environmental pollution is compounded in Nigeria now, as the number of vehicles are on the increase, with the developing economy. Disposal of used lubricants on roads or on packing lots continues to be a wide practice.

Some recent study as reviewed by Smith et al (7), shows that some metals found in crude oils, refinery products and finished petroleum products are capable of causing some physiological problems in human, animals and plants, if certain concentrations which normally could have been tolerated, are exceeded. Table 1.2 lists some of the known physiological effects of metals in petroleum and petroleum products.



### 1.5 BENEFICIAL EFFECTS OF METALS IN OILS

Though the presence of trace metals in petroleum products can cause them to have undesirable properties, and in some cases give rise to physiological problems especially when they are present in high enough concentrations, in certain cases, the presence of controlled amount of specific chemical compounds including specially developed metal salts, can bestow beneficial characteristics on the finished petroleum products. These lubricating oil additives are sold as packages by a few firms and are designed for an individual consumer. The packages are generally complex mixtures which serve multifunctional purposes such as resisting oxidation, reducing wear, inhibiting corrosion, improving lubricating and combustion characteristics of oils, etc. Compound types include polyalkyl methacrylates, styrene-polymers, aromatic amines, complex metallo-organics, sulphonates naphthenates, disulphides, fatty acids and silicone polymers. Lubricating oils may contain mixtures of the above components at concentrations ranging between parts per million and 20 weight percent (8).

Smith et al (9) also reviewed the types of metal containing additives now in use. Table 1.3 lists some of the lubricant additives and their functions.

TABLE 1.3  
LUBRICANT ADDITIVES<sup>N</sup>

METAL	REPRESENTATIVE COMPOUNDS	PURPOSE
Antimony	Antimony dialkyl dithiocarbomates.	Antiwear, extreme pressure and antioxidant additive in conventional and low-ash-type automotive crank case oils, Industrial and automotive gear oils, greases (amount 1-3%).
Barium	Barium diorgano dithiophosphates Ba. Petroleum Sulphonates Ba. Phenolates Ba. Phosphates or dithiophosphates.	Corrosion inhibitors, detergents, rust inhibitor, automatic transmission fluids, greases.
Boron	Borax, Boric acid esters	Antiwear agents, antioxidant, deodorant cutting oils, greases brake fluid.
Cadmium	Cadmium dithiophosphates.	Steam turbine oils.
Chromium	Chromium Salts	Grease additive.
Lead	Lead naphthenates.	Extreme pressure additive, greases, gear oils.
Mercury	Organic mercury.	Bactericides e.g. cutting oil emulsions.
Molybdenum	MeS <sub>2</sub> Mo dibutyl dithiocarbamate and phosphate.	Grease, extreme pressure additives.
Nickel	Cyclopentadienyl nickel complexes.	Antiwear agents, minimizes carbon deposit, improve lubrication and combustion.
Selenium	Selenides	Oxidation and bearing corrosion inhibitor.

(CONTD.)

(TABLE 1.3 CONTD.)

METAL	REPRESENTATIVE COMPOUNDS	PURPOSE
Tin	Organotin Compound.	Antiscuffing additive metal deactivators.
Zinc	Zinc diorgano dithiophosphate Zinc dithiocarbamate Zinc phenolate.	Antioxidant, corrosion inhibitors, antiwear additives, detergent, extreme pressure additive in crank case oils, hypoid gear lubricant, greases, aircraft piston-engine oils, turbine oil, automatic transmission fluids, Railroad diesel engine oils, differential and wet brake lubricants.

N from Reference 8.

#### 1.6 SCOPE OF THE PRESENT WORK

In view of the aforementioned effects of trace metals in petroleum and finished petroleum products, the present study is intended to determine the metal contents in A.P. Super V, Total (Two-stroke V), National (X-100 motor oil), Mobil (Premium motor oil), Texaco, Agip, Unipetrol and Castrol GTX, engine oils using wet-oxidation technique for the preparation of the sample solutions, and the atomic-absorption spectrometric technique for the determination of calcium, cobalt, copper, iron, lead, magnesium, manganese, nickel and zinc in the oils. Flame photometric measurement is utilized to determine potassium and sodium in the oils.

## CHAPTER 2

DETERMINATION OF  
METALS IN  
LUBRICATING OILS2.1 REVIEW OF ANALYTICAL TECHNIQUES USED  
FOR ANALYSIS OF OILS

The determination of trace metals in lubricating oils is of vital importance. The results of oil analyses can be used to monitor the metal content in the oil and hence some measure of control can be brought to bear to maintain product quality. The analysis of lubricating oils could also be used to diagnose impending trouble in engine operations. In addition the control of potentially "toxic" metals will lead to a cleaner environment.

Against this background, several qualitative analytical techniques for the determination of individual metals in lubricating oils have been developed. Anderson and Hughes (10), Russel (11), and Dyroff et al (12), have described spectrographic emission methods for a number of elements in various petroleum fractions. Wrightson (13), Sandell (14) and Reay (15) describe the colorimetric procedures for vanadium, nickel copper and iron in crudes and petroleum distillates. The method is based on the

reaction of aliquots of the solubilized ash with reagents more or less specific for the elements being determined. Also Karchmer et al (16) described spectroscopic and colorimetric procedures for vanadium, nickel iron, titanium and chromium, in petroleum fractions. Milner et al (17) describe the colorimetric procedure for determining iron, nickel and vanadium in crudes and other petroleum oils. They also described the polarographic procedure for the determination of copper after isolation from other metals by a microelectrode position. The sensitivity of the determination under the conditions selected is about 1 $\mu$ g (one microgram).

Smith et al (18) discussed X-ray fluorescence and Atomic-Absorption Spectrometric methods for iron, nickel, copper and vanadium in feedstocks using a standard addition technique.

Conrad and Johnson (19) in 1950 were the first to apply Flame Emission method to oil analysis for the elements barium, calcium, lithium and sodium. In his book, Milner (20) reviewed applications for the analysis of potassium and sodium with regard to sodium being of interest mainly in residual fuel oils. Buell (21) reviewed the earlier applications of Flame Emission in the petroleum industry. Other methods in use include Spark Source Mass Spectroscopy, Neutron Activation Analysis, Atomic-Absorption Spectrometry, etc.

## 2.2 APPLICATIONS OF ATOMIC-ABSORPTION SPECTROMETRIC TECHNIQUE IN LUBRICATING OILS

Although the atomic-absorption spectrometric method was introduced as an analytical technique as far back as 1955, the first petroleum industry application was not reported until 1962-1963. In the period 1964-1967, other applications for lubricating oils analysis appear. The first atomic-absorption method for lubricating oil analysis was reported by Sprague and Slavin (22) in 1963. In the period 1964-1967 other application for lubricating oil analysis appeared (23, 24, 25). Slavin and Slavin (26) described a fully automated atomic-absorption procedure applied to aircraft lubricating oils.

Lush (27) discussed atomic-absorption methods for lubricating oils in a chapter dealing with the application of atomic absorption technique for trace element analysis in the petroleum industry. Lush also reviewed these applications for various barium, magnesium, calcium and zinc additive-types. He cited difficulty in the use of NBS oil-soluble standard materials because of solubilization and stability problems. He further stated that there were no interferences caused by the various additive types but showed that "there is no significant deviation from the curves by any additive-type other than through experimental error."

Kashiki et al (28) used the addition of iodine to level differences in atomic-absorption response for the different compounds containing barium, calcium, copper, lead and zinc. Although the procedure worked well with lead, it did not level differences found for zinc (29) nor did the addition of dithizone (to complex zinc) even though colour developed indicating the formation of a complex.

Holdings et al (30, 31, 32), and Guttenberge and Marold (33) used a mixed solvent system to analyse for barium, calcium and magnesium, and barium, calcium and zinc respectively in order to use inorganic compounds as standards.

Zsuzsa Wittmann (34) and Hon et al (35) described a mixed solvent system that enables aqueous inorganic standards to be used for the direct determination of both metal additives and wear metals in lubricating oils. Barium, calcium, copper, iron, and zinc were determined.

Of recent Palmer and Rush (36) developed a method which utilizes a mixture of acids (HCl 35.4% m/m AR) and a liquid anion exchanger (Aliquat 336) to analyse for lead in used engine oils. "The method is satisfactory for used engine oils having metallic additives containing barium, calcium, zinc, phosphorus, etc." The method is quantitative in the range (0.1-2.5% m/m).

From these and other applications it can be seen

that despite alternative techniques, atomic-absorption spectrometry is already established as a powerful, viable analytical technique for trace metal analysis within the petroleum industry. This popularity is primarily the result of the ease of applicability and high sensitivity of the technique for most metallic elements even at parts per billion levels. The a.a.s. technique is specific, with a few interferences.

As earlier mentioned, both atomic-absorption spectrometric technique and Flame photometric method have been chosen to analyse for the metals which are present in trace amounts in the engine oils. The flame emission method has been applied to the analysis of biological fluids, vegetable matter, cement, glasses, natural waters, soils, petroleum products. The most applications are for the determination of sodium, potassium and calcium (37, 38). The intense emission lines given by sodium and potassium in a flame enable very low concentrations to be determined by flame photometers. The flame photometric method has a very good sensitivity for some elements, and is rapid, simple and inexpensive.

### 2.3 PRINCIPLES OF ATOMIC-ABSORPTION SPECTROMETRY

Atomic-absorption spectra are formed by the absorption of radiation of certain wavelengths by atoms whose electrons are in the ground state. On absorbing this energy the atoms become excited. The extent of



absorption is dependent on the number of atoms in the ground state in the path of the radiation beam at any one time and can be used as a quantitative method for determining this number. Since atomic-absorption is based on absorption of radiation by ground state atoms, a source of radiation is required. Although a continuum light source can be used, a monochromatic light source such as hollow-cathode lamp provides a better sensitivity (40).

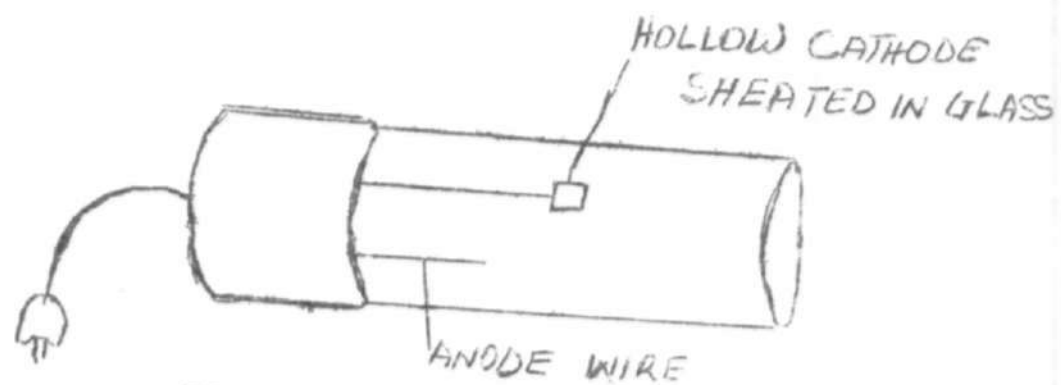
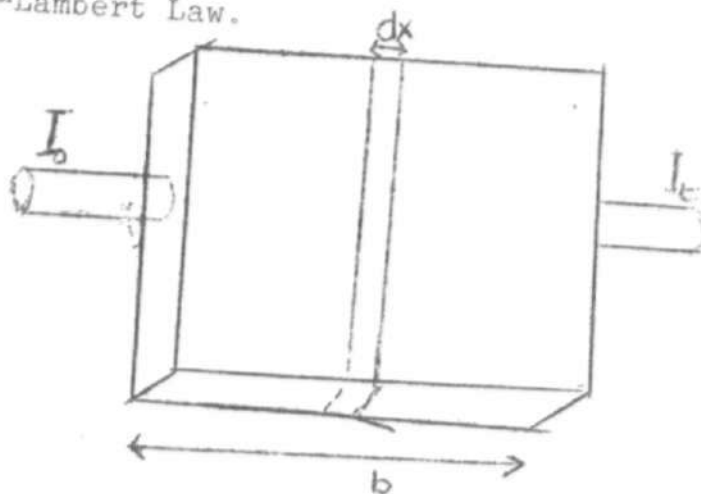


FIGURE 2.1. HOLLOW-CATHODE LAMP<sup>N</sup>  
<sup>N</sup> from Reference 40.

### 2.3.1 Relationship Between Absorbance and Concentration

Absorption of monochromatic radiation is governed by Beer-Lambert Law.



The degree of absorption of monochromatic light passing through a solution is related to the number of molecules or ions in the path. It is often expressed as the fraction of light transmitted ( $I_t/I_o$ ) and is logarithmically related to both the solution thickness (b) (Lambert's Law) and the concentration of solute (c) in solution (Beer's Law). It is usual to combine these two relations to form the Beer-Lambert Law whereby:

$$\frac{I_t}{I_o} = e^{-Kct}, \text{ where}$$

$I_o$  is the incident light

$I_t$  is the emergent light

$C$  is the concentration of the solute

$b$  is the solution thickness

$k$  is a constant.

Or alternatively

$$\log_e \frac{I_o}{I_t} = K.c.b. \text{ or } \log_{10} \frac{I_o}{I_t} = 0.4343 k.c.b. = \epsilon.c.b.$$

$$\text{i.e. } \log \frac{I_o}{I_t} = \epsilon'.c.b. = A.$$

where  $A$  is the absorbance and  $E$  is another constant called absorptivity. The above expression predicts a linear relationship between absorbance and concentration as long as the parameters  $E$  and  $b$  remain constant.

## 2.4 PRINCIPLES OF FLAME PHOTOMETRY

In flame photometry, thermal excitation is accomplished by spraying a solution of the sample into the flame of the burner. Some heat energy will be absorbed by a few of the atoms which then become excited. On returning to the ground state from high energy levels, the electrons lose the energy gained which is emitted as an electromagnetic radiation. The wavelength of the emitted radiation is governed by the energy change involved in the transition from the ground state to higher energy levels. For each element there are certain permitted shifts giving rise to a series of lines, each line being characteristic of the element. The intensity of any one line is governed principally by the flame temperature, other atomic species present in the flame at any one time instant. If the operation conditions are kept constant, the intensity of radiation will be a measure of this number. This is the basis of quantitative analysis in flame photometry.

### 2.4.1 Comparison of Atomic-Absorption With Flame Emission Spectroscopy

Flame emission and absorption are complementary techniques in that some elements can be detected at lower concentrations by emission measurements and some by absorption.

Atomic emission spectroscopy is based on the

intensity of radiation emitted by excited atoms whereas the unexcited atoms serve as the basis for atomic absorption measurements. The unexcited species predominate by a large margin at the temperature of the flame.

2. Because atomic-absorption methods are based on a larger population of particles it might be expected to be the more sensitive procedure. This apparent advantage is offset however, by the fact that an absorbance measurement involves a difference measurement ( $A = \log I_0 - \log I_t$ ). When the two numbers are nearly alike large relative errors in the difference result. As a consequence the two methods are often complementary in sensitivity.

3. In flame absorption spectroscopy the absolute number of unexcited species is much less dependent upon temperature than is the number of excited species which varies exponentially with temperature.

4. Also with the help of calibration curve, high precision and accuracy are obtainable. The task of making valid calibration curve is easier than in most analytical procedures because the absorption signal is considerably free of interferences.

5. Since most metals absorb at well defined wavelengths and over very narrow band widths absorption interference by atoms of other elements is rare.

6. Most elements emit radiation identical in wavelengths to that at which they absorb - this is important at

low wavelengths where emission intensities may be high. Unless this registered emission spectra is eliminated this can cause apparent change in an absorption signal which may be mistaken for inter-element interference. This spectral interference is more pronounced in emission spectroscopy than in atomic-absorption spectroscopy.

2.5 DETERMINATION OF CALCIUM, COBALT, COPPER, IRON, LEAD, MAGNESIUM, MANGANESE, NICKEL AND ZINC BY ATOMIC-ABSORPTION SPECTROMETRY

The essential components of atomic absorption spectrometer are diagrammed below.

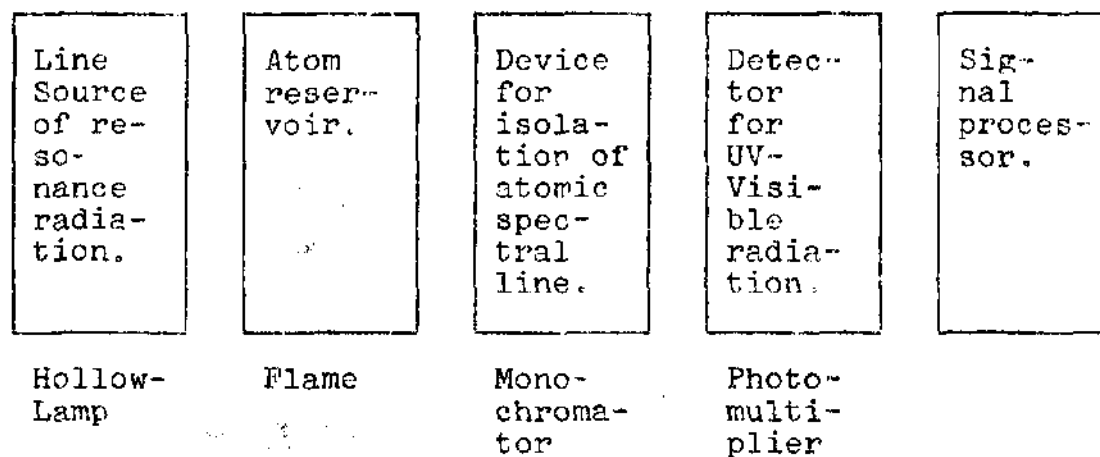


FIGURE 2.1.2: ESSENTIAL COMPONENTS OF ATOMIC-ABSORPTION SPECTROMETER.

Atomic-absorption technique is based on absorption of radiation by ground state atoms and thus there is need for a source of radiation. A hollow-cathode lamp provides a monochromatic light source.

The hollow-cathode lamp emits radiation

characteristic of the cathode material usually a single element (analyte). This beam consisting of resonance radiation is electronically pulsed. When the solution containing the element under study is aspirated into the flame of the spectrophotometer, the analyte atoms which predominate under these experimental conditions absorb radiation of specific wavelength from the hollow-cathode lamp, reducing the intensity of the incident beam. The monochromator isolates the desired resonance line and allows this to fall on the photomultiplier. An electrical signal is produced. The electronics of the unit are designed to respond selectively to the pulsed radiation source i.e. the hollow-cathode lamp. Signal processing occurs which results in the electronic output proportional to the absorption of the analyte atoms. A separate radiation source (the hollow-cathode lamp) for each individual metallic element was used in turn to obtain the experimental data.

#### 2.5.1 Experimental

##### 2.5.1.1 Apparatus

(i) Pye Unicam SP 1900 Atomic-Absorption Spectrophotometer, equipped with single slot burners for air-acetylene flame.

(ii) Hollow-cathode lamps for obtaining the experimental data.

(iii) Infrared lamp, 250 watts, with a variable transformer to regulate the heat intensity of the infrared lamp.

(iv) Muffle furnace.

(v) Bunsen burners.

(vi) Analytical balance.

(vii) Calibrated flasks - 50ml, 100ml, 250ml and 1 litre.

(viii) Pipettes.

(ix) Conical flasks.

#### 2.5.1.2 Reagents

Unless otherwise stated, all reagents used were of analytical reagent grade. Water was distilled.

(i) Concentrated sulphuric acid 98%  $\frac{m}{m}$  Analar grade.

(ii) 1.1 Nitric acid.

(iii) 1% Lanthanum ( $\frac{m}{V}$  in water).

(iv) Standard EDTA solution.

(v) Eriochrome Black T indicator - containing 0.2g of the dyestuff in 15.0ml of triethanolamine and 5.0ml of absolute alcohol.

(vi) Xylenol orange indicator - containing 0.5ml of xylenol orange in 100ml of distilled water.

(vii) Aqueous standard solutions of the metal salts prepared as follows:

(a) Calcium solution

0.63g  $\text{CaCO}_3$  of Anala R grade was

- dissolved in little nitric acid and diluted to 250ml with water.
- (b) Cobalt solution:  
2.47g  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  of Anala R grade was dissolved in 250ml water in a 250ml volumetric flask.
- (c) Iron Solution:  
1.75g  $\text{FeSO}_4 (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  was dissolved in little dilute sulphuric acid and diluted to 250ml with distilled water.
- (d) Copper Solution:  
0.98g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  Anala R grade was dissolved in 250ml of water.
- (e) Magnesium Solution:  
2.64g  $\text{Mg} (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was carefully weighed and dissolved in 250ml of water.
- (f) Manganese Solution:  
0.90g  $\text{Mn Cl}_2 \cdot 4\text{H}_2\text{O}$  was dissolved in 250ml of water.
- (g) Nickel Solution:  
The solution was prepared by dissolving 6.73g  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  AR grade in water and diluted to 1 litre.
- (h) Zinc Solution:  
1.138g  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  AR grade was dissolved in 250ml of distilled water.

The above solutions were standardized with standard



EDTA solution using Eriochrome Black T indicator and Xylenol Orange indicator where appropriate as detailed in Vogel (41).

#### 2.5.2 Samples Studied

The engine oil samples studied were obtained from filling stations in Zaria.

They included

- (i) Agip - HD Motor oil, SAE 20W-30
- (ii) A.P. Super V Visco-static  
Premium multigrade Engine Oil  
SAE 20W-50HD
- (iii) Castrol GTX Motor Oil SAE 20W-50
- (iv) Mobil Premium Motor Oil  
Heavy Duty SAE 40
- (v) National X-100 Motor oil  
SAE 30/40
- (vii) Texaco Motor Oil SAE 40
- (viii) Unipetrol  
Super Motor Oil, SAE 20W-30.

#### 2.5.3 Preparation of Sample Solutions Ashing Technique

The ashing of petroleum samples (which entails burning off of the oil leaving the metal as residual ash) is employed as a "short cut" method to get, the total mineral constituents and to provide ash for subsequent

elemental analysis. In employing this technique in sample preparation, possible losses of certain inorganic constituents (such as alkali, lead and zinc halides) through volatilization and mechanical entrainment have been reported (42, 43). Losses due to mechanical entrainment are caused by too rapid burning or the presence of moisture in the sample which causes surface turbulence. In order to overcome such losses, a good number of investigators have recommended methods of "fixing" the metals by presulphating the oil sample before decomposing it (44). This wet-ashing procedure not only minimizes losses due to volatility but provides some convenience, since excessive "sooting" during dry-ashing decomposing makes it difficult to keep the sample burning and increases the time required for the final ignition. Lynch (45) however opined that "the presulphating technique does not prevent the volatilization of boron, halogens, phosphorus and selenium. Nor will it ensure the retention of such metals as mercury, arsenic, antimony, germanium and perhaps lead, which are apt to be lost in the presence of halogen. Where these elements are to be determined non-ashing methods are utilized."

As earlier mentioned wet-ashing or wet-oxidation, involves decomposition of the oil sample with concentrated sulphuric acid without preliminary ignition.

#### 2.5.4 Procedure

25.0g of each oil sample was carefully weighed into a silica crucible to which was added 10ml of concentrated sulphuric acid. The mixture was placed on a hot plate and heated from top with the aid of an infrared lamp. By means of both the hot place and the transformer attached to the infrared lamp, the intensity of the heat supply was gradually increased until the evolution of sulphuric acid fumes ceased.

The dry carbonaceous residue was heated by means of a bunsen burner to decompose it. The crucible and its contents were transferred to a muffle furnace set at 600°C to complete the oxidation of carbon.

The residual ash, after cooling, was treated with 1:1 nitric acid. The solubilized ash was warmed on a water-bath for about ten minutes. The solution was then adjusted to volume in a 50-ml flask, any insoluble particle being removed by filtration.

#### 2.5.5 Calibration

For the preparation of reference solutions 1ml of each metal stock solution was pipetted and diluted ten times. 1ml, 2ml, 3ml, 4ml and 5ml of each diluted solution, containing 100ppm of the metal, were pipetted into five successive 100ml calibrated flasks and then diluted to volume with distilled water.

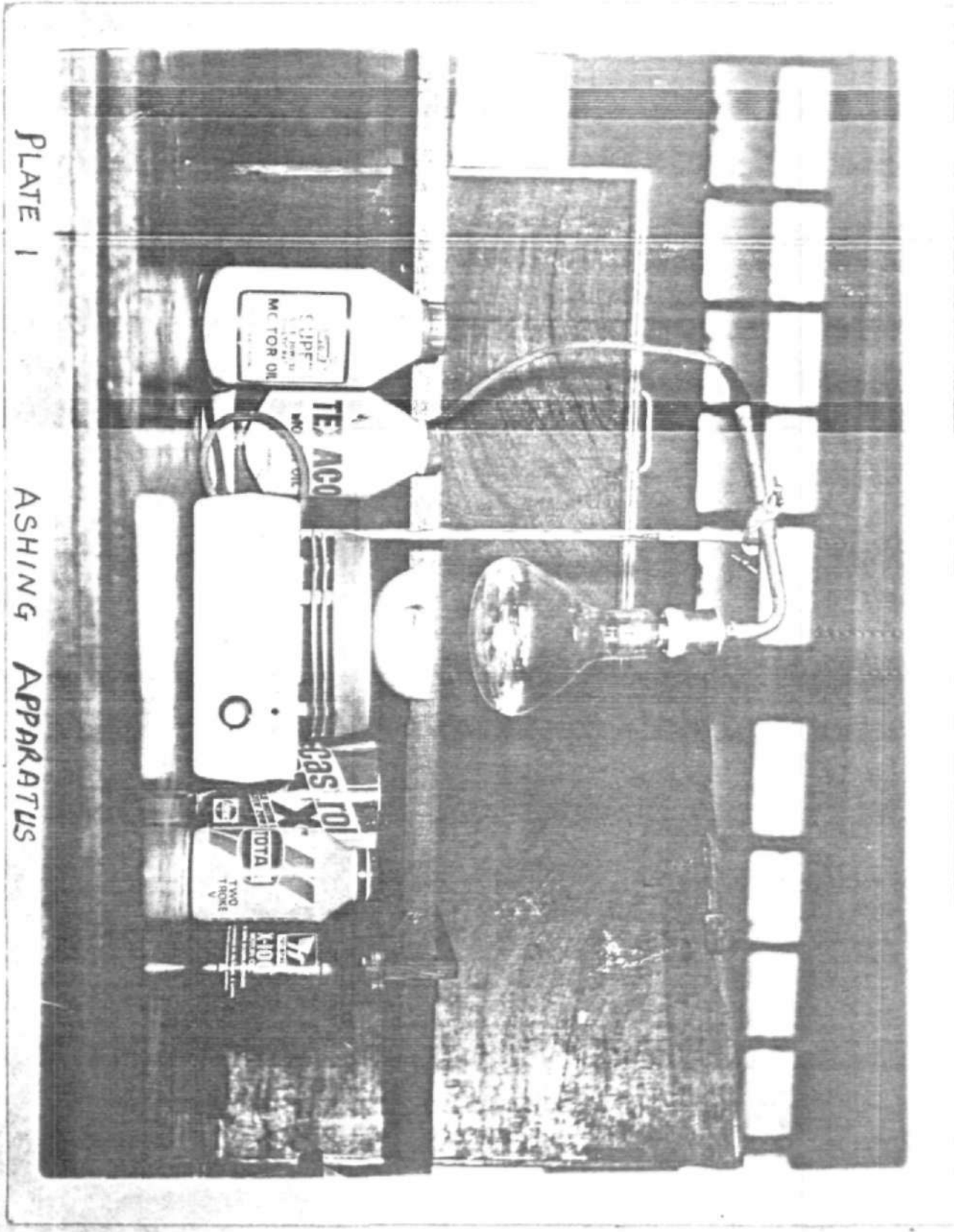


PLATE 1

ASHING APPARATUS

The reference solutions were aspirated into the flame of the atomic-absorption spectrophotometer in the order of increasing metal content and their absorbances were measured at the resonance line or wave-lengths quoted in Table 2.1. A calibration curve for each metal was prepared by plotting net absorbance on the ordinate against concentration of the metallic element under study on the abscissa.

Each calibration curve constructed from the reference solutions was used to determine the concentration of the metallic element in each test sample solution. Figures 2.1.3, 2.1.4, 2.1.5 give the calibration curves.

#### 2.5.6 Instrumental Operation and Measurement

The Pye Unicam SP 1900 atomic-absorption spectrophotometer was prepared for operation according to the instructions contained in the operator's manual. The respective elemental hollow-cathode lamps were placed in turn, in the lamp-housing receptacle. The power supply was switched on. The recommended optimum current for the lamp in use, was selected and an ample warm-up time was allowed so as to make the lamp attain stability.

The monochromator slit was adjusted and the elemental wavelength was set to the actual resonance line. The burner height and gas flow-rate were optimized. Table 2.1 lists the instrumental conditions for the air-acetylene flame.

TABLE 2.1

## INSTRUMENTAL CONDITIONS FOR USING AIR-ACETYLENE FLAME

	Ca	Co	Cu	Fe	Mg	Mn	Pb	Ni	Zn
Principal resonance line (nm)	422.67	240.72	324.75	248.33	285.21	279.48	217.0	232.0	213.86
Slit width	0.15-0.2	0.1-0.15	0.15-0.2	0.1-0.15	0.15-0.2	0.15	0.15-0.2	0.10	0.1-0.15
Flame	A	A	A	A	A	A	A	A	A
Air (litre min <sup>-1</sup> )	5	5	5	5	5	5	5	5	5
Acetylene (litre min <sup>-1</sup> )	0.9-0.1	0.8-1.0	0.8-1.0	0.8-1.0	0.9-1.1	0.8-1.0	0.8-1.0	0.8-1.1	0.8-1.1
Current (max) (mA)	10	15	5	15	4	12	6	15	10
Best precision (mA)	6-10	12-15	4-5	12-15	4	10-12	5-6	12-15	9-10
Best sensitivity	6-7	7-15	2-4	7-11	2-3	6-9	3-4	7-11	4-7

A = Air-acetylene.

To eliminate any inter-element effects upon the determination of calcium and magnesium 1% Lanthanum chloride solution was added to the sample in a ratio of 1.4.

The test solutions were aspirated into the air-acetylene flame of the spectrophotometer in turn and their absorbances measured. By careful reference to the calibration curves constructed from the standard solutions, the concentration of each metal in the test solutions was extrapolated.

## 2.6 DETERMINATION OF POTASSIUM AND SODIUM

Flame photometric methods have been applied to the analysis of biological fluids, vegetable matter, cement, glasses, natural water, soils, petroleum products. The most important applications are for the determination of sodium and potassium and calcium. The intense emission lines given by sodium and potassium in a flame enable very low concentrations to be determined by flame photometers (37, 38).

### 2.6.1 Experimental

#### 2.6.1.1 Apparatus

- (i) EEL Flame Photometer
- (ii) Infrared lamp, 250 watts, with a variable transformer to regulate the heat intensity of the infrared lamp.
- (iii) Muffle Furnace

- (iv) Bunsen burners
- (v) Analytical balance
- (vi) Calibrated flasks - 50ml, 100ml, 250ml, 500ml and 1 litre
- (vii) Pipettes.
- (viii) Conical flasks.

#### 2.6.1.2 Reagents

Unless otherwise stated, all reagents used were of analytical reagent grade.

Water was distilled.

(i) Concentrated sulphuric acid 98%  $\frac{m}{m}$  Anala R grade

(ii) 1.1 Nitric acid

(iii) 1% Caesium solution

(iv) Aqueous standard solution of sodium and potassium metal salt prepared as follows:

(a) Potassium Solution:

0.95g KCl was weighed (after having dried the salt at 110°C for three hours) this was dissolved in a little quantity of water in a 500ml flask and the solution diluted to volume with distilled water.

(b) Sodium Solution:

NaCl was dried at 110°C and 1.273g the salt was weighed and dissolved in 500ml of water.



### 2.6.1.3 Dilution Of Stock Solutions For Calibration Curves

For sodium metal solution, 1ml of the solution was diluted ten times. 1.0ml, 2.0ml, 3.0ml, 4.0ml and 5.0ml of this solution containing 100ppm of the metal, were pipetted into five successive 100ml calibrated flask and diluted to volume with distilled water. This was repeated for potassium stock solution. The absorbances of the solutions for each metal salt were determined using the EEL Flame Photometer after having been standardized with the highest concentration of the calibration solutions. The absorbances were plotted against concentration in parts per million to obtain the calibration curves for the respective metal ions.

### 2.6.2 Samples Analysed

The engine oil samples analysed included

- (i) Agip, HD Motor Oil SAE 20W-30
- (ii) AP Super V Visco-static, Premium multigrade Engine Oil SAE 20W-50HD
- (iii) Castrol GTX, Motor Oil SAE 20W-50
- (iv) National X-100 Motor Oil, SAE 30/40 Double grade
- (v) Mobil - Premium Motor oil Heavy Duty SAE 40
- (vi) Texaco - Motor Oil, SAE 40
- (vii) Total two stroke V Engine Oil SAE 30/40
- (viii) Unipetrol Super Motor oil SAE 20W-30.

#### 2.6.4 Preparation Of Sample Solutions

In order to get the total mineral constituents in engine oil sample, each sample was ignited after preliminary addition of concentrated sulphuric acid to get the residual ash. The aim of presulphating the oil sample before its decomposition was to fix the metals in the sample thereby minimizing losses due to volatility. Moreover the wet-ashing procedure provides some convenience since excessive "coking" during a dry-ashing decomposition makes it difficult to keep the sample burning and increases the time required for the final ignition.

#### 2.6.4 Procedure

25.0g of each engine oil sample was carefully weighed into a silica crucible to which was added 10ml of concentrated sulphuric acid. The mixture was placed on a hot-plate and heated from top with the aid of the infrared lamp. The intensity of the heat supply was gradually and cautiously increased by means of both the hot plate and the transformer attached to the infrared lamp, until the evolution of sulphuric acid ceased.

The dry carbonaceous residue was heated by means of a bunsen burner to decompose it. The crucible and its contents were transferred to a muffle furnace set at 600°C to complete the oxidation of carbon.

The residual ash was solubilized by treating it with 10ml of 1.1 nitric acid. The solubilized ash was warmed on a water-bath for about ten minutes. The solution was then adjusted to volume in a 50ml flask, any insoluble particle being removed by filtration.

#### 2.6.5 Instrumental Operation And Measurement

In flame photometry, thermal excitation is accomplished by spraying a solution of the sample into the flame of the burner of the flame photometer. The EEL flame photometer was standardized with 5ppm concentration of the standard solution after the flame and burner temperatures had been allowed to come to equilibrium. The flow-rate of the fuel and oxidant gas were carefully set at the beginning of, and maintained throughout the run to ensure maximum sensitivity and stability. The calibration solutions were run to obtain the experimental data for the calibration curve. This was followed by aspirating the test solutions into the flame of the burner. There was regular flushing of the nebulizer with distilled water and checking of the zero standard.

A calibration curve was constructed from the standard solutions and this was used to determine the concentration of the sample solutions. The calibration curves for sodium and potassium are given in figures 2.1.6 and 2.1.7.

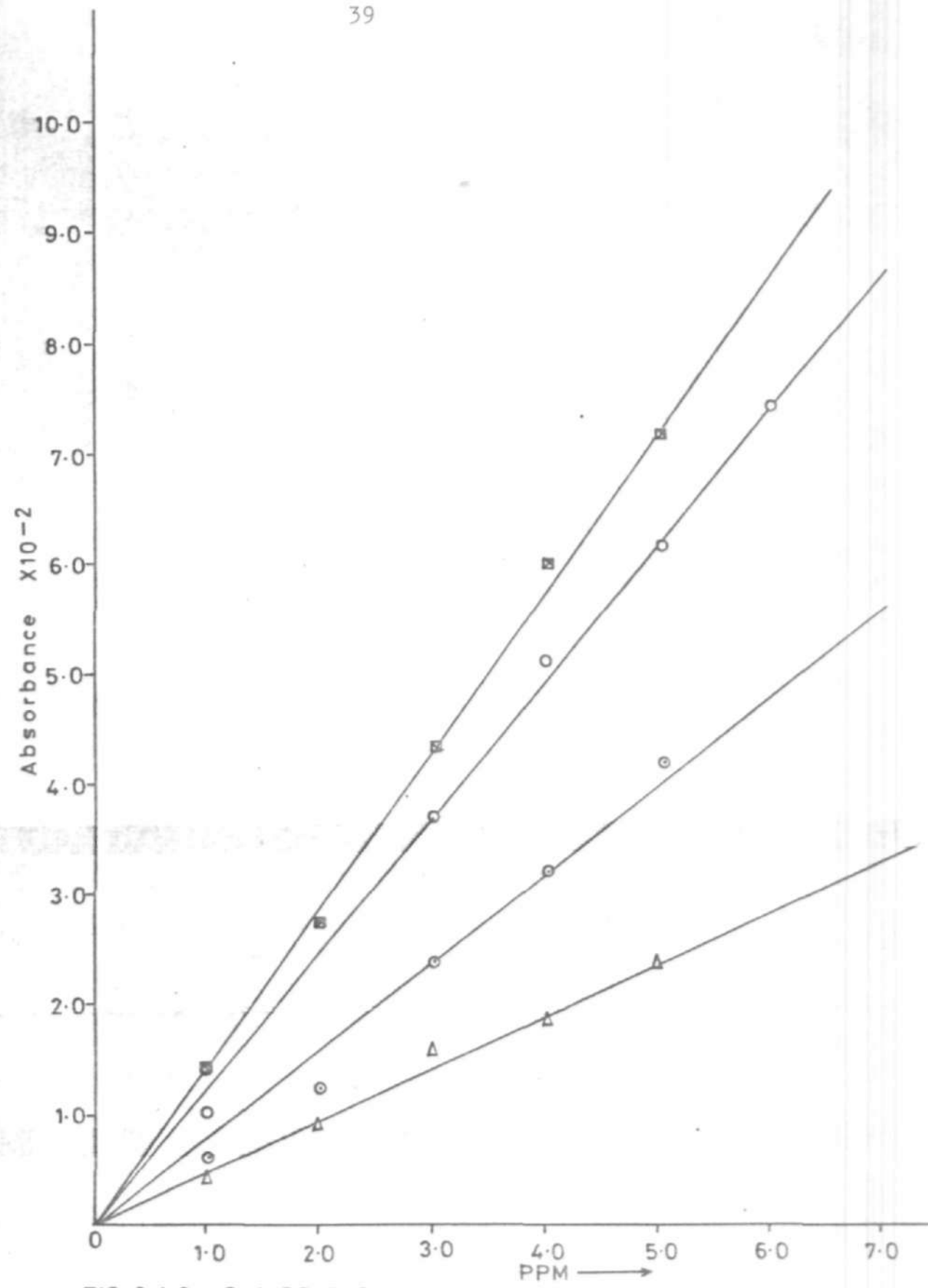


FIG. 2-1-3 CALIBRATION GRAPHS FOR COBALT, IRON LEAD AND NICKEL

□ COBALT    Δ IRON    ○ LEAD    ⊙ NICKEL

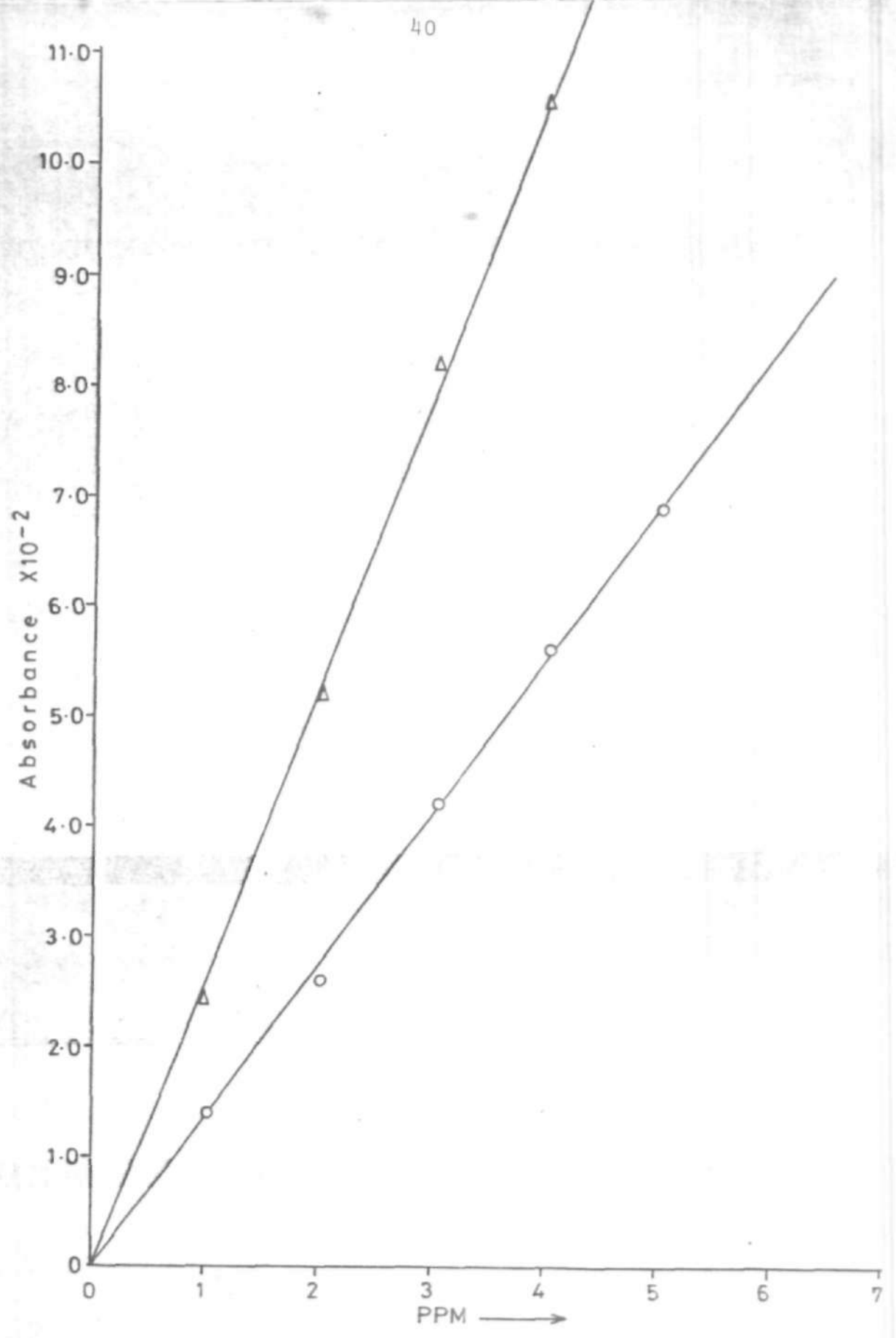


FIG. 2-1-4 CALIBRATION GRAPHS FOR MAGNESIUM & CALCIUM  
 $\Delta$  MANGANESE  $\circ$  CALCIUM

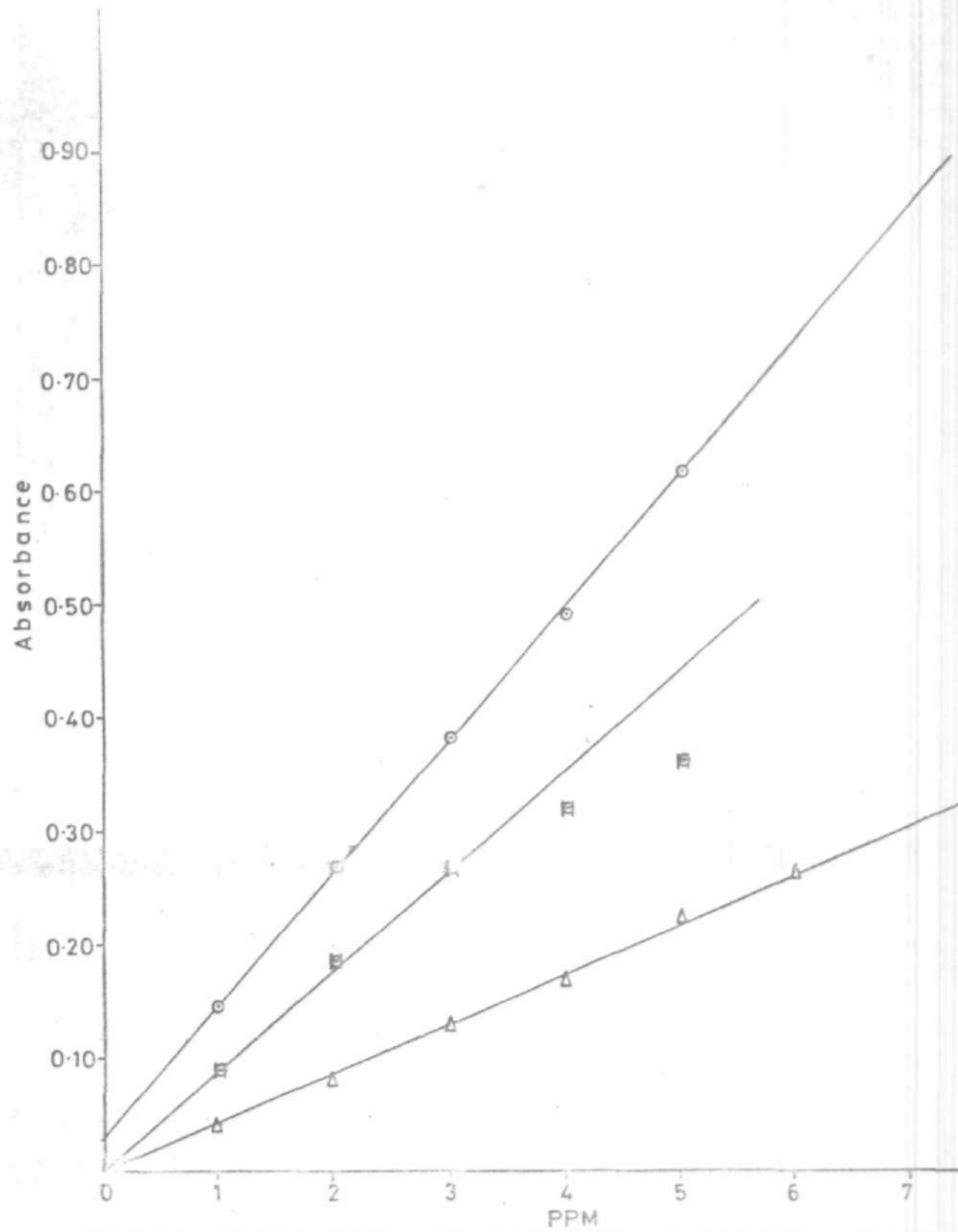


FIG. 2-1-5 CALIBRATION GRAPHS FOR MAGNESIUM, COPPER AND ZINC

○ MAGNESIUM      □ ZINC      △ COPPER

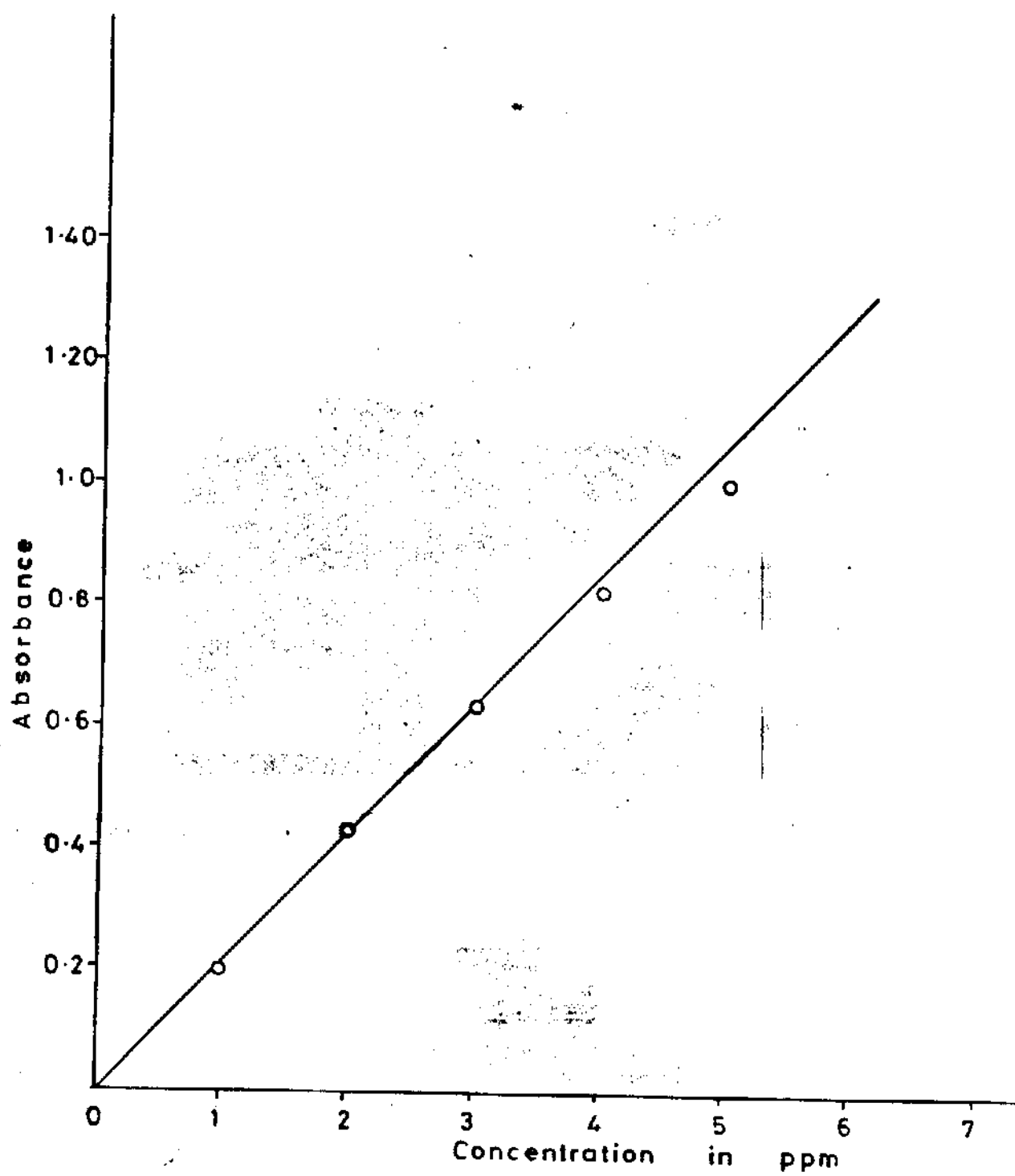


FIG. 2-1-6 CALIBRATION GRAPH FOR POTASSIUM

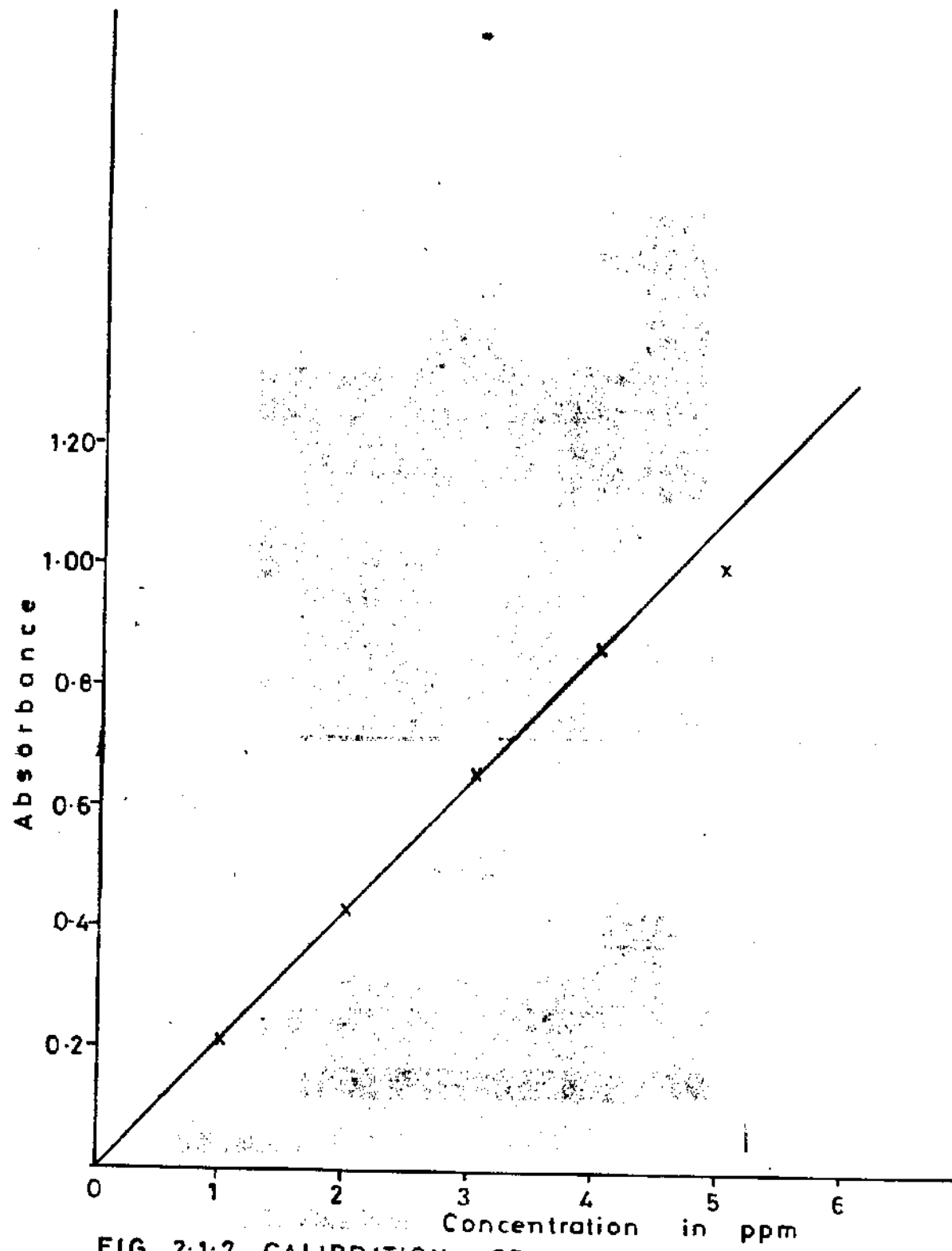


FIG. 2-1-7 CALIBRATION GRAPH FOR SODIUM



## CHAPTER 3

## 3.1

R E S U L T S

Atomic-absorption spectrometric technique has been utilized in the determination of calcium, cobalt, copper iron, lead, magnesium, manganese, nickel and zinc in the ashes of eight different engine oil samples. Potassium and sodium were determined with the aid of a flame photometer. The results of the analyses of the oil samples are given in Tables 3.1.1, 3.1.2, 3.1.3, 3.1.4.

TABLE 3.1.1

RESULTS OF ANALYSIS FOR COBALT,  
LEAD AND MANGANESE (in mg Kg<sup>-1</sup>)

SAMPLE		COBALT	LEAD	MANGANESE
AP super V, visco- static	a)	0.35	2.01	0.65
Premium multigrade	b)	0.25	1.70	0.70
SAE 20W - 50HD	c)	0.175	1.60	0.60
	d)	0.26	1.60	0.65
Average value		0.26	1.73	0.65

(CONTD.)

(TABLE 3.1.1 CONTD.)

SAMPLE		COBALT	LEAD	MANGANESE
Mobil premium motor oil	a)	0.25	1.60	0.40
Heavy duty SAE 40	b)	0.35	1.40	0.50
	c)	0.25	1.40	0.24
	d)	0.10	1.70	0.38
Average value		0.24	1.53	0.38
Total two stroke V	a)	0.175	0.60	0.24
Engine oil SAE 30/40	b)	0.10	0.60	0.24
	c)	0.25	0.90	0.40
	d)			0.24
Average value		0.175	0.70	0.28
National X-100 motor oil	a)	0.25	1.40	0.80
SAE 30/40 double grade	b)	0.18	1.70	0.70
	c)	0.18	0.60	0.80
	d)	0.24	0.90	0.80
Average value		0.21	1.15	0.78
Texaco motor oil	a)	0.45	2.10	0.50
SAE 40	b)	0.35	2.40	0.30
	c)	0.50	2.80	0.20
	d)	0.45	2.40	0.30
Average value		0.44	2.43	0.33

(CONTD.)

(TABLE 3.1.1 CONTD.)

SAMPLE		COBALT	LEAD	MANGANESE
Unipetrol super motor oil	a)	0.18	1.10	1.70
SAE 20W-30	b)	0.45	1.40	1.70
	c)	0.25	1.40	1.50
	d)	-	1.60	1.60
Average value		0.29	1.38	1.63
Agip HD motor oil	a)	0.35	1.40	2.50
SAE 20W-30	b)	0.35	1.70	2.60
	c)	0.16	1.10	2.70
Average value		0.27	1.48	2.58
Castrol GTX motor oil	a)	0.50	2.40	-
SAE 20W-50	b)	0.35	2.40	-
	c)	0.25	2.60	-
	d)	0.16	2.10	-
Average value		0.32	2.88	-

TABLE 3.1.2

RESULTS OF ANALYSIS FOR COPPER,  
IRON AND NICKEL (in mg Kg<sup>-1</sup>)

SAMPLE	COPPER	IRON	NICKEL
AP super V visco-static	a) 13.50	6.20	1.60
Premium multigrade engine oil	b) 14.80	6.90	1.64
SAE 20W-50HD	c) 13.76	7.50	1.62
	d) 14.20	8.00	1.56
Average value	14.06	7.15	1.61
Mobil premium motor oil	a) 9.70	10.40	2.00
Heavy duty SAE 40	b) 9.36	10.90	2.24
	c) 10.10	9.60	2.40
	d) -	10.60	1.92
Average value	9.72	10.38	2.14
Total two stroke V	a) 7.40	13.80	1.64
Engine oil SAE 30/40	b) 7.90	14.90	2.00
	c) 6.96	14.70	1.64
	d) -	14.20	1.60
Average value	7.42	14.40	1.72
National X-100 motor oil	a) 3.60	17.20	2.28
SAE 30/40 double grade	b) 4.20	16.80	2.00
	c) 3.60	16.80	2.68
	d) 3.90	15.50	1.64
Average value	3.83	16.58	2.15

(CONTD.)

(TABLE 3.1.2 CONTD.)

SAMPLE	COPPER	IRON	NICKEL
Texaco motor oil	a) 1.00	10.70	2.40
SAE 40	b) 1.00	12.10	2.28
	c) 0.90	10.40	2.00
	d) 1.00	10.80	2.00
Average value	0.98	12.40	2.00
Unipetrol	a) 2.40	12.40	2.00
Super motor oil	b) 2.40	13.60	2.28
SAE 20W-30	c) 2.30	16.30	2.58
	d) 1.90	16.40	2.28
Average value	2.25	14.68	2.29
Agrip HD motor oil	a) 1.90	1.60	0.80
SAE 20W-30	b) 1.90	1.80	0.80
	c) 1.89	2.08	1.00
	d) 1.50	1.92	0.80
Average value	1.79	1.85	0.85
Castrol GTX motor oil	a) 0.60	-	0.70
SAE 20W-50	b) 1.00	-	0.70
	c) -	-	0.66
	d) -	-	0.68
Average value	0.80	-	0.68

TABLE 3.1.3

RESULTS OF ANALYSIS FOR CALCIUM,  
MAGNESIUM AND ZINC (in mg Kg<sup>-1</sup>)

SAMPLE	CALCIUM	MAGNESIUM	ZINC
AP super V visco-static	a) 16.40	39.30	17.66
Premium multigrade engine oil	b) 13.60	31.60	17.76
SAE 20W-50HD	c) 14.36	31.50	17.72
	d) 13.40	31.70	17.70
Average value	14.44	31.03	17.71
Mobil premium motor oil	a) 29.40	30.60	17.60
Heavy duty SAE 40	b) 29.90	30.20	17.56
	c) 29.10	30.30	17.56
	d) 30.24	-	17.57
Average value	29.66	30.37	17.57
Total two stroke V Engine oil SAE 30/40	a) 29.20	12.60	13.40
	b) 27.20	12.50	11.90
	c) 28.60	13.55	11.30
	d) 28.10	-	10.90
Average value	28.28	12.88	11.87
National X-100 motor oil	a) 27.80	8.10	17.50
SAE 30/40 double grade	b) 27.00	11.66	17.60
	c) 28.40	10.55	17.62
	d) 27.50	7.50	17.58
Average value	27.67	9.45	17.58

(CONTD.)

(TABLE 3.1.3 CONTD.)

SAMPLE	CALCIUM	MAGNESIUM	ZINC
Texaco motor oil	a) 26.40	3.90	17.54
SAE 20W-30	b) 26.20	3.60	17.58
	c) 27.50	3.50	17.56
	d) 25.80	3.70	17.48
Average value	26.47	3.67	17.54
Unipetrol	a) 3.92	3.90	16.90
Super motor oil	b) 3.70	3.60	16.94
SAE 20W-30	c) 3.60	3.40	16.80
	d) -	3.80	-
Average value	3.74	3.10	16.26
Agrip HD motor oil	a) 0.72	3.10	16.20
SAE 20W-30	b) 0.72	3.30	16.30
	c) 0.72	2.90	16.28
	d) -	-	16.26
Average value	0.73	3.10	16.26
Castrol GTX	a) 0.43	0.34	16.60
Motor oil SAE 20W-50	b) 0.46	0.45	16.56
	c) 0.48	0.39	16.70
	d) 0.45	0.39	16.56
Average value	0.45	0.39	16.56

TABLE 3.1.4

RESULTS OF ANALYSIS FOR POTASSIUM  
AND SODIUM (in mg Kg<sup>-1</sup>)

SAMPLE	POTASSIUM	SODIUM
AP super visco-static	a) 2.00	4.38
Premium multigrade engine oil	b) 0.76	7.20
SAE 20W-50HD	c) 2.00	3.60
	d) 2.20	4.20
Average value	1.74	4.85
Mobil premium motor oil	a) 2.30	18.40
Heavy duty SAE 40	b) 2.20	16.50
	c) 1.50	15.00
	d) 4.80	13.75
Average value	2.70	15.91
Total two-stroke V. engine oil	a) 2.00	4.30
SAE 30/40	b) 1.90	4.90
	c) 2.10	4.38
	d) 3.30	4.00
Average value	2.33	4.39
National X-100 motor oil	a) 3.30	5.50
SAE 30/40 double grade	b) 3.40	6.10
	c) 2.20	6.80
	d) 1.60	5.20
Average value	2.65	5.90

(CONTD.)



(TABLE 3.1.4 CONTD.)

SAMPLE	POTASSIUM	SODIUM
Texaco motor oil	a) 2.40	7.25
SAE 20W-30	b) 3.90	6.40
	c) 4.00	5.64
	d) 3.60	6.50
Average value	3.48	6.45
Unipetrol super motor oil	a) 2.40	6.70
SAE 20W-30	b) 3.90	5.60
	c) 4.00	6.40
	d) -	-
Average value	3.43	6.23
Agip HD motor oil	a) 0.50	-
SAE 20W-30	b) 0.40	-
	c) 0.40	-
	d) 0.30	-
Average value	0.40	-
Castrol GTX motor oil	a) 1.15	3.25
SAE 20W-50	b) 1.20	3.10
	c) 1.00	2.80
	d) 1.30	3.00
Average value	1.16	3.04

### 3.2 DISCUSSION OF RESULTS

From the results of the analyses it is seen that the values of the individual metal content vary considerably. The result of analyses for zinc in the oils ranged from 11.87 to 17.71mg per kg of sample, whereas those of cobalt ranged from 0.18 to 0.44mg kg<sup>-1</sup>. Similarly manganese contents varied from 0.28 - 1.63mg kg<sup>-1</sup>.

The variation in the metal contents could be due to the differential requirement of the individual metal by the consumer oil companies, for the improvement of lubricant characteristics (or an indication of the extent of contamination). Lubricating oil additives are sold as packages by a few firms and are designed for an individual consumer.(46).

Aforementioned these packages of additives are generally complex mixtures which serve multifunctional purposes. Compound types include polyalkyl methacrylates, styrene polymers, aromatic amines, complex metallo-organics, sulphonates, naphthenates, disulphides, fatty acids and silicone polymers. Lubricating oils may contain mixtures of the above components at concentrations ranging from parts per million to 20 weight percent (47). Since the lubricating oil additives are designed for the individual consumer oil company, it follows therefore, that the actual value of each metal content in the oil cannot be got for purpose of trade secrecy.

From the Tables 3.1.1 - 3.1.4 it is evident that the results for even a set of determinations for a metallic element varied. When one considers the stages involved in the preparation of sample solutions possible errors through loss of the ash matter could result. In the process of ashing the sample, there could be losses through volatilization of the inorganic components during ignition. Loss of ash matter could also arise through mechanical entrainment either due to rapid heating or the presence of moisture in the sample giving rise to surface turbulence. This problem becomes compounded especially when one considers the open atmosphere in which the ashing technique was carried.

The atomic-absorption signals of the test solutions were steady except for unipetrol, Agip and Castrol GTX engine oil sample solutions where a different acetylene gas cylinder was used. The effect was much more pronounced in the analysis for calcium and magnesium. In event of the presence of fairly large particles and in case of incomplete vapourisation of the particles on passage through the flame such results would not be unexpected.

Since the metal content of the lubricating oil additives cannot be obtained for purpose of trade secrecy and moreover, since the earlier investigators on the analysis of petroleum oils have not disclosed the brand of lubricating oils which they have analysed, a comprehensive

comparison of the results of the present work with the results of other standard analytical techniques cannot be established. However a comparison of the results with results of three other different methods: direct determination of atomic-absorption spectrometry, atomic-absorption spectrometric determination after ashing and determination by chemical methods, show some good agreement (48). The results of the comparative determinations are given in Table 3.1.5 (in  $mg\ Kg^{-1}$ ).

TABLE 3.1.5\*

ELEMENT	SAMPLE	PRO- POSED ME- THOD	AAS ON AQUE- OUS SOL. AFTER ASHING	SAM- PLE NUM- BER	ASS USING ORG. MIXED SOL- VENT SYS- TEM	SAM- PLE NUM- BER	LITE- RA- TURE VALUE	SAM- PLE
Calcium	AP super V	14.44	14.0	(9)	14.0	(9)	14.10	(9)
	Mobil	29.66	28.0	(5)	27.50	(5)	27.0	(5)
	Total	28.28						
	National	27.67						
	Texaco	26.47						
Zinc	AP super V	17.76	-	(11)	16.60	(11)	16.50	(11)
	Mobil	17.57						
	National	17.60						
	Texaco	17.50						
	Unipetrol	16.88						
	Agip	16.28						
	Castrol	16.58						
Magnesium	National	9.45	8.70	(19)	8.70	(19)	8.60	(19)
	Texaco	3.68	2.60	(12)	2.50	(12)	2.50	(21)
	Unipetrol	3.57						
	Agip	3.10						

\*From Reference 48.

Appendices I, II & III show results of determinations of individual metals by AAS and Colorimetric methods.

### 3.3 SUMMARY AND CONCLUSION

Minerals occur in petroleum products in amounts ranging from a few parts per million to several tenths of a percent depending on the sources of the crude and the history of the specific sample. Recent studies have revealed that these metallic constituents may be present as oil-soluble metallo-organic compounds, as a colloid, as a filterable suspension or as coarse particles. These metals may be introduced into the petroleum products through interaction of the oil components with the metal of transportation, storage facilities or even in the process of refining.

In some cases the presence of metals in oils could be detrimental to the quality of the finished petroleum products; for instance, some metals may have ill-effects on engine parts. With the nation's growing economy with the attendant increase in number of vehicles on the roads, the problem becomes compounded with the increasing fear of the possible accumulation of "toxic" metals in the environment as air pollutants. Once released from their natural sources through fuel combustion, disposal of used lubricants and other processes through which metals become part of the environment, (no metal is degradable) if they are ingested or inhaled in grossly excessive quantity, they can be fatal.

In other cases the presence of controlled amounts of specific chemical compounds including added metal salts in

oils enhances beneficial properties on the products.

These lubricant additives reduce wear, resist oxidation, inhibit corrosion, etc.

In order to relate the effect of the individual metals on the petroleum products, it is necessary to have sensitive and reliable analytical techniques for determining individual metals with a view to monitoring the level of metal content in the products. Among such analytical techniques now in use for the analysis of oils include X-ray fluorescence, Neutron Activation Analysis, Colorimetry, Flame Emission Method, Atomic-Absorption Spectrometry, etc.

The present research work was intended to determine the metal contents in Agip (HD Motor Oil SAE 20W-30), AP Super V Visco-Static (Premium Multigrade Engine Oil SAE 20W-50HD), Castrol GTX (Motor Oil SAE 20W-30), National (X-100 Motor Oil, SAE 30/40 Double grade), Mobil (Premium Motor Oil, Heavy Duty SAE 40), Texaco (Motor Oil SAE 20W-30), Total (Two Stroke V Engine Oil SAE 30/40), Unipetrol (Super V Motor Oil SAE 20W-30) engine oils, by atomic-absorption spectrometry using ashing procedures.

The wet-ashing of petroleum (which involves decomposing the sample with concentrated sulphuric acid followed by complete oxidation of carbon in a muffle furnace), has long been used by the petroleum industry as a "short cut", method to obtain the total inorganic constituents and to

provide ash for subsequent elemental analysis. The mixture of the oil sample and concentrated sulphuric acid was charred with the aid of an infrared lamp followed by ignition of the dry carbonaceous residue by means of a bunsen burner. Complete oxidation of carbon was accomplished in a muffle furnace, pre-set at  $600^{\circ}\text{C}$  to give the residual ash required for the elemental analysis.

The wet-ashing technique not only minimizes losses of the inorganic components through volatilization but is more convenient since excessive coking often experienced during dry-ashing decomposition makes it difficult to keep the sample burning and increases the time required for final ignition.

The atomic absorption spectrometry has been used to determine calcium, cobalt, iron, copper, lead, magnesium, manganese, nickel and zinc in the ashes of the oils. Flame photometric measurement has been used to determine potassium and sodium metal contents respectively in the oils. The concentrations of the metals in the investigated engine oil samples were as follows:-



Calcium	(14.44 - 29.66mg Kg <sup>-1</sup> )
Cobalt	( 0.18 - 0.44 " " )
Copper	( 0.78 - 14.06 " " )
Iron	( 1.85 - 16.58 " " )
Lead	( 0.70 - 2.43 " " )
Magnesium	( 9.50 - 31.00 " " )
Manganese	( 0.28 - 2.58 " " )
Nickel	( 1.61 - 2.30 " " )
Zinc	(16.50 - 18.00 " " )
Potassium	( 0.40 - 3.48 " " )
Sodium	( 3.40 - 15.91 " " )

Atomic-absorption spectrometric technique is metal specific and responds only to compounds containing the analyte metal, thus yielding output of the simplest form.

Its ease of applicability and sensitivity for most metallic elements even at parts per billion levels renders it a viable technique for trace metal analysis.

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APPENDIX I

COMPARISON OF DIFFERENT METHODS TO DETERMINE WEAR METALS IN OIL

SAMPLES	Cu, ppm			Fe			Pb		
	DIRECT	ASHED	COLORI-METRIC	DIRECT	ASHED	COLORI-METRIC	DIRECT	ASHED	COLORI-METRIC
CR									
1 <sup>d,c</sup>	14.6	12.1	14.2	16.6	41.8	41.2	11.1	12	
2 <sup>b,c</sup>	15.5	14.3	16.4	20.6	28.5	29.1	12.3	13.9	
3 <sup>b</sup>	12.1	11.3	14.8	9.6	10.0	9.6	7.4	5.1	
4 <sup>b,c</sup>	11.6	10.8	9.2	24.7	59.3	(30.2) <sup>d</sup>	9.7	9.2	
5 <sup>b</sup>	9.6	8.8	8.8	3.4	3.9	4.4	2	3	
6 <sup>b</sup>	6.6	5.5	5.8	12.0	12.1	11.6	5	3	
7 <sup>b,c</sup>	1.7	2.1	2.4	10.8	11.7	12.2	3	3	
8 <sup>b,c</sup>	1.1	1.1	12	2.9	3.1	3.8	0.00	2	
9 <sup>b</sup>	7.6	7.5	9.0	14.9	15.8	16.8	98.0	96.4	
10 <sup>b</sup>	38.5	39.5	40.5	54.6	53.5	53.6	70.4	64.8	
11 <sup>f</sup>	7.3	6.8	(9.2) <sup>a</sup>	18.5	13.5	12.9	3	4	
12 <sup>h</sup>	21.2	21.0	22	28.3	28.0	30.4	10.0	10.5	
CS									
1	11.3	10.0	9 <sup>i</sup>	8.1	-	9.5	-	-	
2	12.7	11.0	11 <sup>i</sup>	9.2	-	7.5	14.3	15.4	
3	25.2	-	-	-	-	-	-	-	
4	36	35	-	-	-	-	-	-	

\*From Reference 29.

"Samples labelled "C.R." were measured at the Commonwealth Railways Laboratory, those labelled "CS" at the CSIRO Laboratory. Most of the latter were supplied by the Victorian Railways Laboratory.

<sup>b</sup>These oils when new were rated S.A.E. 40, with viscosities at 140°F of 50 to 80 centistokes, and had normal additive concentrations as follows: Ca 630ppm, Zn 8ppm, P 240ppm, S 340ppm.

<sup>c</sup>Heavy sludge deposit

<sup>d</sup>Interference from chromium

<sup>e</sup>Fuel dilution present

<sup>f</sup>This oil when new was rated as SAE 30, with a viscosity at 140°C of 34 centistokes and had normal additive concentrations as follows: Ca 1850ppm, Zn 600ppm, P 535ppm, S 550ppm.

## APPENDIX II\*\*

SUMMARY OF COLORIMETRIC PROCEDURE

COMPONENT	METHOD OR REAGENT	OPTIMUM CONCNS. IN FINAL SOLN. ppm	ABSORPTION PEAK OF COLOUR COMPLEX m/1
Iron	Thiocyanate	0.2 - 5.0	540
	O-Phenanthroline	0.4 - 8.0	500
Nickel	Dimethylglyoxime	0.1 - 1.50	525
Chromium	Diphenylcarbazide	0.02- 0.8	540
Vanadium	Hydrogen Peroxide	3 - 60	470
	Phosphotungstate	0.5 - 11	400
Titanium	Hydrogen Peroxide	3 - 30	420

\*\*REF 16, p.1738