PRELIMINARY CHEMICAL ANALYSIS OF SHEA BUTTER TREE (BUTYROSPERMUM PARKII) LATEX

BY

MOJEEP IDOWU ADAGEJE, (B.SC. (HONS.), LAGOS)

A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL,
AHMADU BELLO UNIVERSITY, IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

AHMADU BELLO UNIVERSITY, ZARIA

D E C L A R A T I O N

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.

Mojeed Idowu Adageje

April 1983.

D E D I C A T I O N

To the generation of Chemists whose memories were vague at the time of compilation of this work.

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

I wish to acknowledge with thanks the untiring efforts of my project Supervisor, Dr. E. G. Kolawole, whose suggestions, criticisms and ideas are among the major tools towards the successful accomplishment of this work.

My sincere gratitude also goes to Dr. Henry T. Bozimo, Head of Chemistry Department for providing the facilities in the Chemistry Department.

I thank all the members of staff and students of Chemistry Department whose cooperations have enabled me complete this work.

Finally, I am grateful to my Mother, my sisters and brothers whose financial and moral supports have made this course a reality.

A B S T R A C T

Shea Butter tree latex collected from two localities in Zaria, namely Shika and Bassawa have been investigated.

The results obtained from classical non-instrumental analysis of latex compares favourably well with what was obtained from infra-red and n.m.r. spectroscopic analysis.

A rough estimate of molecular mass of shea latex was determined by viscosity experiments.

Various components of shea latex and their percentage compositions have been determined.

Some physical properties of the shea latex for the purpose of characterization have also been investigated.

A general account and economic importance of the tree is given.

TABLE OF CONTENTS

		Page
Title page		Page
Declaration		ii
Dedication		iii
Aknowledgements		iv
Abstract		v
List of Tables		x
List of Figures		xi
CHAPTER 1: INTRODUCTION		1
	1.2 Shea butter tree (general account)	1
	1.2 Economic importance	3
	1.21 The fruit	3
	1.22 The stem	4
	1.23 The latex	4
	1.3 Account of previous work done	5
	1.4 Scope of this research work	7
	1.5 Analytical techniques used and their theory	8
	1.51 Classical non-instrumental technique	8
	1.52 Viscosity determination	8
	1.53 Infrared spectroscopy	9
	1.54 Nuclear magnetic resonance	9
	1.55 Chromatographic techniqe	10
	1.56 Flame photometer	

			Page
	1.57	Atomic absorption spectrophotometer	11
CHAPTER 2:	EXPERIMENTAL		13
	2.1	Sampling and sample pretreatment ..	13
	2.2	Extraction	14
	2.3	Preliminary chemical analysis	15
	2.31	Burning	15
	2.32	Pyrolysis	16
	2.33	Boiling with 80% sulphuric acid	16
	2.4	Elemental analysis	16
	2.41	Nitrogen	16
	2.42	Halogens	16
	2.43	Sulphur	17
	2.44	Beilstein test	17
	2.45	Soda-lime test	17
	2.46	Weber Test	17
	2.5	Functional group analysis	18
	2.51	Acid and basic functional group test	18
	2.52	Carbonyl test	19
	2.53	Amide test	19
	2.54	Amine test	19
	2.55	Alcohol test	19
	2.56	Phenol test	19
	2.57	Carboxylic acid test	20
	2.6	Some physical properties determination of the shea tree latex	20
	2.61	pH determination	20
	2.62	Specific gravity	20
	2.63	Viscosity	21

			Page
2.7	Trace metal analysis		23
2.71	Qualitative analysis		23
2.72	Quantitative analysis		24
2.73	Sodium		24
2.74	Potassium		24
2.75	Magnesium		24
2.76	Calcium		25
2.77	Lead		25
2.78	Zinc		25
2.79	Nickel		34
2.8	Quantitative analysis		34
2.81	Percentage dry weight of latex ..		34
2.82	Percentage acetone extract		35
2.83	Percentage ash composition		35
2.84	Percentage rubber-like material ..		36
2.9	Chromatographic separation of extracted solid latex		36
2.91	Thin-layer chromatography preparation of adsorbent		36
2.92	Preparative thin-layer chromatography		37
2.93	Column chromatography		37
2.10	Infra-red spectroscopy		39
2.11	Nuclear magnetic resonance spectroscopy		39
CHAPTER 3:	RESULTS AND DISCUSSION		41
3.1	Sampling		41
3.2	Solubility of latex		42
3.3	Quantitative extraction		42
3.4	Preliminary chemical examination of shea latex		43
3.5	Qualitative analysis (elemental analysis)		44

			Page
	3.6	Qualitative analysis (functional group)	45
	3.7	Physical properties	46
	3.8	Quantitative analysis (trace metal) ..	47
	3.9	Quantitative analysis (percentage composition of different components of shea latex)	48
	3.10	Percentage total solid	50
	3.11	Weber Test	51
	3.12	Chromatographic separation (pilot T.L.C.)	53
	3.13	Infrared spectroscopy	54
	3.14	Nuclear magnetic resonance	55
CHAPTER 4:	CONCLUSION SUMMARY		62
	4.1	Conclusion	62
	4.2	Summary	64
	4.3	Suggestions for further work	65
REFERENCES:	.. ..		66

L I S T O F T A B L E S

			Page
Table	3.1	Percentage solvent extracts from shea latex	42
"	3.2	Elemental analysis	44
"	3.3	Functional groups analysis of shea tree latex	45
"	3.4	Physical properties of shea latex	46
"	3.5	Trace metal contents of the ash of shea latex	47
"	3.6	Percentage composition of different components of shea latex	48
"	3.7	Percentage total solid of shea latex	50
"	3.8	Different R.f values obtained with different solvent mixtures	52
"	3.9	Infra-red absorption peaks for shea latex	53
"	3.10	N.M.R. spectra signals and peak's assignment.	55b

LIST OF FIGURES

			Page
Figure	1	Graph of reduced viscosity against concentration	22
"	2	Graph of percentage T versus concentration (44) potassium	26
"	3	Calibration curve for lead	27
"	4	Calibration curve for nickel	28
"	5	Calibration curve for zinc	29
"	6	Calibration curve for cobalt	30
"	7	Calibration curve for calcium	31
"	8	Calibration curve for copper	32
"	9	Calibration curve for magnesium	33
"	10	I.R. spectra of solid latex in carbon tetrachloride	57
"	11	I.R. spectra of solid latex in Nujol after extraction	58
"	12	N.M.R. chart of solid latex	59
"	13	N.M.R. chart of solid latex eluted from Band B of Thin-layer plate with benzene: petether	60
"	14	N.M.R. chart of solid latex eluted from Band A of Thin-layer plates with benzene: pet ether	61

Chapter 1

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

1.1 SHEA BUTTER TREE

Shea butter tree, Butyrospermum parkii (1) is a medium sized tree of the drier parts of Central Africa, occurring naturally on the lateritic slopes of the Savannah zone of the hinter-land of West Africa, throughout the equatorial region of Africa where rainfall is not too high and parts of the southern Sudan.

The tree grows to a height of 9-12 meters and has a thick trunk, branching into a number of spreading branches which form a denser crown. The tree has a rough grey bark, which is in the form of almost square, very thick, rectangular scales due to the fact that fissures occur on the back both vertically and horizontally. The stem produces a milky latex when cut. Leaves are crowded together at the end of the stout younger branches. They are reddish in colour when young, simple and slightly pointed, more or less oblong in shape and from five to ten inches (25 cm) long and 2-4 inches (5-10cm) broad. The leaves are carried on petioles up to four inches (20cm) in length, and the leaves are deciduous. The lamina is supplied by a large number of lateral veins,

running parallel to each other and almost at right angles to the Midrib. The sweet scented white flowers are carried in dense groups in the axils of the leaves and possess two rows of sepals in each whorl. The Outer sepals are reddish brown in colour, and the inner sepals have a greenish tinge. The light petals are fused at the base and the segments have dentate margins. The flowers have light stamens, with long medifixed anthers carried on bent filaments, and alternating with these are eight petalloid, staminoid smaller than the petals and with toothed margins. The superior ovary has between eight and ten locules, each locules containing a single ascending ovules and is surmounted by a simple style which persists in the fruits. The fruit requires from four to six months to mature and when ripe takes the form of a rather hard berry, with a thin brown wrinkled skin enclosing a single seed embedded in a sweet pulp. The fruit is roughly egg-shaped, and about two inches (5cm) long. The single seed measuring about $1\frac{1}{2}$ inches (4cm) in length, oval in shape and with a shinning brown testa. The seed contains no endos perm.

Different varieties of the plant are known to occur throughout Africa, some having long fruits and others with more rounded fruits. The trees of the southern Sudan have been identified as the Butyrospermum parkii, variety niloticum and family sapotaceae (1).

1.2 ECONOMIC IMPORTANCE OF DIFFERENT PARTS OF THE TREE:

Almost all the parts of the tree find its use in different areas. Their uses vary, however, from locality to locality. In Nigeria, here, the most useful part of the tree is its fruit. A general account of the usefulness of different parts of the tree is as follows.

1.21 The Fruit

The fruits of Butyrospermum parkii are called sheanuts. In Hausa it is known as 'kadanya', in Yoruba - 'eso ori'.

In Nigeria sheanuts are found mostly in the Sudan Savannah belt. Its occurrence being very sparse in Sahel Savannah belt.

The sheanut is an edible fruit and in most places the succulent mesocarp of the fruit is chewed to expose the nut, which forms a hard endocarp. The nut houses the most useful part of the fruit, namely, the shea butter. The shea nut butter has different uses in different localities. In the northern States, and other parts of Nigeria, shea nut butter is used especially in rural areas for lighting using a wick rolled out of cotton and may also be used as a cooking medium as a substitute of palm oil and groundnut oil.

In other places it is used for making Darnish patries and soap. It has some medicinal activity and could be used as medicinal rub or pain remedy, as an antibiotics against boil as well as pomade. Shea nut

cake contains toxic saponin and is palatable. It has therefore no value as animal feed and usually wasted.

Shea nut did not attract much attention from the Northern States Marketing Board. (2) earlier probably due to availability of other vegetable oils at cheaper prices. With recent increases in world prices and higher demands for vegetable oils in the world market, sheanuts became a scheduled commodity of the Northern States Marketing Board in 1969, and the Board purchased about 3,400 tons for export. Shea butter is prepared locally by boiling the kernels and the fats skimmed from the surface of the hot water. It takes the form of a tallow-like substance. Considerable quantities (1) of seeds are imported annually from West Africa to various parts of Europe, where the oil is extracted and used in the manufacture of candles and soaps. The refined oil is used as an edible oil and in the preparation of a butter substitutes.

1.22 The stem

The stem of the tree is rough and very hard. In Africa the wood obtained from the tree finds uses in the carving of bowls, mortars, boats. Also it is used in rough furniture industry, in building. The latex found in the parenchyma cells of the stem may be responsible for the hardness of the wood.

1.23 The latex

This is the milky liquid or sap normally obtained

when a cut is made on the stem. They are produced from the parenchyma (1) cells of the stem. It is sticky in nature and solidifies on long exposure to atmosphere.

The latex can be found in other parts of the plant such as the leaves. The unsaponifiable portion of the shea butter has been associated with the presence of latex (3) in the seeds. The latex is used locally as gum (3).

1.3 ACCOUNT OF PREVIOUS WORK DONE

Analysis of shea butter tree latex has not attracted much research attention. Most documented work on Butyrospermum parkii has been mainly on the analysis of the shea butter obtained from the nut partly because of its economic importance. Qureshi and Ajulo (2) studied the quality of shea butter and its suitability as edible fat. Shea butter rich in unsaponifiable matter has very poor quality as a vegetable fat. The presence of this unsaponifiable matter has been associated with the presence of latex bearing cells in the seeds (4).

Bauer and Umback (5) investigated the constituents of the unsaponifiable portion of the shea fats. They noted that its composition agrees quite satisfactorily with the formular $(C_5 H_8)x$. It was included in their report that shea tree also yield a kind of rubber (karite rubber) which shows many properties of ordinary rubber.

A lot of species of plants that belong to the family Sapotaceae have been known (6) to contain gutta percha. Gutta-percha has the same chemical composition as rubber but different chemical structure.

Emile Andre (3) reported that latex found as unsaponifiable constituents of the fat contains a carbide of hydrogen of the family of India rubber and gutta-percha karitene. It is composite strongly non-saturated. Its formula was reported as C_{32} H_{56} and an iodine number raised by the presence of five ethylenic bonds in its molecules.

Some of the reports published on the research on shea butter has provided some clue for the analysis of latex obtained from the tree. Pradain (7) gave the constituents of the sheafat as a mixture of fatty acids stearic acid and oleic acid, 5% palmitic acid, and 5% linoleic acid phytosterols and latex karitene, and resins, B amyrins and its isomers, basseol and parkeol.

Emile Andre (3) gave a botanical, geographical and historical discussion of Butyrospermum parkii tree along with the following constitution of the fats obtained from the tree. d60 0.903, viscosity (centipoises at 60°C) 35.57, M.P. 32°, or 1.4580 α_D 2° 34min, acid no 1.5, saponification no 1.82, iodine no 53-54 and percentage unsaponifiable 5.7. Karite oil is known to contain about 5-10% of a gutta-percha like latex (1) which can be seperated into two fractions (1) resin alcohol. Cinnamates and (2) polymerized terpenoid

hydro carbon of the Indian rubber family, called karitene or illipene. The ester fraction can be subfractionated into seven components.

1.4 SCOPE OF THIS RESEARCH PROJECT

The Author's interest in the analysis of shea butter tree latex stems out from the various local uses of the latex as well as the characteristic properties of the wood obtained from the shea butter tree. Some of the local uses of the latex have been mentioned under the economic importance of the tree. It is therefore the Author's interest to carryout a general preliminary chemical investigation of the components of the latex that are responsbile for these properties.

For instance, to find out whether the hardness and toughness of the wood is attributable to coagulation of the latex thereby cementing the fibres in the tree together. The wood is also known to be termite proof (1). It is also the author's main pre-occupation to find out the component of the latex that is responsible for this property.

However, this investigation is of preliminary nature and it sought to provide general chemical nature of the latex so that other workers would have a basis for further analysis. From the physical appearance of the latex, it is assumed that it is probably a macro molecule. Its viscous nature suggests that it could be a rubber-like latex, and the technique employed for the

analysis is that commonly followed for the analysis of rubber-like materials.

1.5 ANALYTICAL TECHNIQUES USED AND THEIR THEORY

1.51 Classical non-instrumental technique

Characterization of latex sample was made by some of the properties it possesses as a whole, chemical identification by classical method of one or more functional groups or atoms forming part of a unit.

These are based on the conventional chemical properties of these chemical units or functional groups.

A preliminary examination, usually on a small piece of the sample was done, this include, burning test, appearance and pyrolysis test.

Elemental analysis was accomplished by the popular Lassaignets test or sodium fusion test.

1.52 Viscosity determination

Viscosity is a hydrodynamic property of a macro molecule and is dependent on the molecular mass. The most directly related to the nature of individual solute molecule is the intrinsic viscosity which is obtained by extrapolation of the graph of reduced viscosity against concentration to infinite dilution.

It represents the fractional change in the viscosity of a solution per unit concentration of polymer or macro

molecule at infinite dilution.

This expression relates intrinsic viscosity with molecular mass

$$[\eta] = KM^{c}{}^{15}$$

where k and c are empirical constant which depend on the solvent, the solute and temperature. $[\eta]$ is the intrinsic viscosity and M is the molecular mass.

Viscosity determination was employed to obtain a rough estimate of molecular mass of the latex. Other techniques that can be used for molecular mass determination of macromolecule include light scattering (16) and osmometry.

1.53 Infra-red spectroscopy

The presence of functional groups determined by classical analysis was confirmed by infra-red spectroscopy. This technique is based on the determination of vibration between two atoms in a molecule giving rise to a vibrational spectra. This vibrational spectra occur by two different mechanisms. Firstly quanta of infra-red radiation can excite atoms to vibrate directly - the absorption of infra-red radiation gives rise to the infra-red spectrum (9).

1.54 Nuclear Magnetic Resonance

N.M.R. studies reveal the number of protons in the latex and from the position and integration of

the signal a structure can be suggested for the latex.

The n.m.r. is based on the principle of absorption of energy when protons jump from low spin to high spin level (9).

1.55 Chromatographic technique

To separate a mixture, a column such as burette may be used. It is packed with an active solid such as alumina. The stationary phase covered with a solvent such as hexane - the mobile phase. A small sample of the mixture applied to the top of the column forms a band of adsorbed materials. When solvent is allowed to flow through the column, it carries with it the components of the mixture. The rate of movement of a given component depends on how much it is retarded by adsorption on the column packing. Thus a weakly adsorbed substance travels more rapidly than a strongly adsorbed one. It can be seen that if the differences in adsorption are sufficiently great there will be complete separation. This is referred to as complete development.

This description is an example of liquid-solid chromatography. Separation is caused by differences in the adsorption forces between the various components of the mixture and the stationary phase. These forces may be either Van der Waals forces, as in the case of alumina, or electrostatic forces, as in the separation of ions, by ion-exchange chromatography, where the stationary phase is an ion exchange material or a column

packing of a suitable porous nature may be used to separate solutes according to their molecular size - as in gel chromatography. Thin-layer chromatography is a special example of adsorption chromatography where the adsorbent is spread out as thin film on a glass plate instead of being packed in a cylindrical column.

1.56 Flame photometer

Flame photometry is concerned with the emission of characteristic radiation in flames by individual elements and the correlation of the emission intensity with the concentration of these elements (10). The instruments are of two types: photometer and flame spectrophotometer. Flame photometer makes use of filters and the intensity of the filtered radiation of the flame is measured with a photoelectric detector.

1.57 Atomic Absorption Spectrophotometer

When a solution containing a considerable quantity of metal is aspirated into a flame, the sample is converted to the gaseous form. Some of the atoms will absorb radiation and become excited. If the energy absorbed is sufficiently high, the excited atoms will emit the characteristic radiation of that metal. But the vast majority of the atoms will remain in the ground state.

When a light mono chromatic wavelength, usually from a hollow cathode discharge lamp, is passed through the flame containing atoms of the element part of the light will be absorbed, the intensity of absorption is

a function of concentration of the atoms in the flame. In this technique, it is the light absorbed that is responsible for the analytical determination (10).

Chapter 2

EXPERIMENTAL

2.1 SAMPLING AND SAMPLE PRE-TREATMENT

Latex samples in Zaria locality were collected from two places: Basawa and Shika. The method of sampling involves making a triangular cutting on the trunk of the tree, by means of a cutlass. A nail is stuck to the apex of the triangular incision. The neck of the conical flask is tied to the nail. Fresh latex samples were guided to the mouth of the flask by means of a thin aluminium foil. The volume of latex obtained vary from tree to tree and this depends on many factors such as the time latex was collected. Latex flow rate is known to be high during wet season as there is a lot of water absorption from the soil. Age of the tree also affects latex production. Young trees are found to produce more latex than old trees. Lastly, frequency of tapping affects the volume of latex obtained from the tree.

The latex if properly tapped is a milky white adhesive, viscous liquid.

The latex samples were pre-treated by the addition

of formic acid previously tested and found to be the most suitable coagulant. The solution of latex and formic acid was kept in the refrigerator overnight so as to coagulate it. The coagulated latex was washed several times with distilled water and filtered through a sintered funnel with the aid of a suction pump. The coagulated latex in form of a white cake was dried in a vacuum oven at room temperature for 24 hours. The latex were preserved in this form in a dessicator for further analysis.

2.2 EXTRACTION

It is necessary to extract polymeric sample prior to chemical analysis. This is because some extracts in the sample might interfere with the results obtained from chemical analysis. Such extraction to be of value must be quantitative, in the sense that it must be complete. For example incomplete extraction of rosin from a neoprene rubber sample will result in a positive result if the Weber test for natural rubber is tried (21). All solvents commonly employed for extraction will usually extract all extractable materials, where they fail is in extracting some polymers as well as non-polymeric materials.

Method

The solubility of the coagulated latex was tested with the following solvents, chloroform, ether, benzene ethanol, dichloromethane, carbon tetrachloride, pet ether,

acetone, and methanol. The latex was found to be soluble in chloroform and dichloro methane, slightly soluble in benzene and completely insoluble in ether, ethanol, pet ether, acetone and methanol.

The following solvents were used for the extraction. Acetone, ethanol, ether and isopropyl alcohol.

1g of the dry coagulated latex was weighed in each case in a paper thimble. 50ml of the solvent was taken in 100ml round bottom flask already seated in a mantle.

The extraction was allowed to proceed for a period of ten hours (11) after which the pure solvent was recovered from distillation. The extract was weighed and the percentage extract with different solvents was calculated.

2.3 PRELIMINARY CHEMICAL ANALYSIS

A small piece of dry latex sample was used for the preliminary analysis which includes the following.

2.31 Burning

Small piece of dry latex about 0.02gm was taken with a spatula and heated on a bunsen flame. A sooty flame was produced. The odour was distinctive and is characteristic of a burning rubber. The flame produced was self-extinguishing.

2.32 Pyrolysis

About 0.02gm of dry latex sample was subjected to pyrolysis in a dry test tube for a prolonged period of time. A dark coloured liquid condensed at the cold part of the test tube.

2.33 Boiling with 80% sulphuric acid

About 0.02gm of dry latex sample was taken in a clean dry test tube, the test tube was covered with sufficient volume of 80% sulphuric acid. The test tube with its content was heated until the liquid started to boil. The dry latex decomposed after prolonged heating.

2.4 ELEMENTAL ANALYSIS

Lassaigne's test (sodium fusion) was the basis for the elemental analysis. The sodium fusion extract was divided into four parts and tested for the elements as follows.

2.41 Nitrogen

Small quantity of the extract was boiled in a test tube with freshly prepared ferrous sulphate. The solution was acidified with dilute hydrochloric acid and few drops of ferric chloride was added.

2.42 Halogens

Few ml of the extract was acidified with dilute nitric acid. Silver nitrate solution was added. Ammonia

solution was added in order to distinguish the test for the three halogens, namely, chlorine, bromine and iodine.

2.43 Sulphur

To a few mls of the sodium fusion extract one drop of freshly prepared solution of sodium nitroprusside was added.

2.44 Beilstein Test

This is an alternative test for the presence of nitrogen. A piece of copper wire was cleaned and heated to redness in a bunsen flame. The red hot wire was pushed into the sample briefly and returned to the flame. A bluish green colour was imparted to the flame.

2.45 Soda-Lime Test

This is also an alternative test for confirming the presence of nitrogen. Small amount of dry latex sample was fused with soda-lime to a depth of about 2.5cm. The fume given off was tested with a moistened litmus paper. This test did not give a positive result for the presence of nitrogen.

All these tests were tried with the solid latex after extraction with acetone and the acetone extract.

2.46 Weber Test (11)

0.05gm of dry latex sample was placed in a clean dry test-tube. 5ml of bromine solution (10% v/v in carbon tetrachloride) was added. The mixture was placed in a water-bath and the temperature raised slowly to the

boiling point. The heating was continued until not more than a trace of bromine remained. 5-6ml of phenol solution (10% v/v in carbon tetrachloride and heating continued for another 10-15 minutes. A bluish black precipitate was formed.

2.5. FUNCTIONAL GROUP ANALYSIS

The acetone extracted dry latex and the extract were analysed for the various functional groups present. The methods employed were the conventional organic reactions used for various functional groups. Owing to the polymeric nature of the latex sample, a careful approach as undertaken on the characteristic result for the different functional groups may not be very clear. The different functional group tests were as follows.

2.5.1 Acid and Basic Functional Group Test

Few ml of the extract was taken in a clean test tube. Dilute sodium hydroxide were added. Few drops of dilute hydrochloric acid were added.

To another few ml of the extract in a test tube were added a few drops of dilute hydrochloric acid. The solution was thoroughly shaken and few ml of sodium hydroxide were added.

These tests were repeated with 0.05g of the acetone extracted rubber-like material.

2.52 Carbonyl Test

2 ml of extract was taken in a test tube. Few ml of 2,4-dinitrophenyl hydrazine was added. The test was repeated using Schiffs reagent.

0.5g of the dry acetone extracted solid latex was dissolved in a few ml of chloroform. Two drops of 2,4-dinitrophenyl hydrazine was added. The test was repeated with Schiff's reagent.

2.53 Amide Test

2 ml of the solution of extract in chloroform was taken in a dry test tube. Two drops of NaOH and diluted HCl was added. The mixture was heated.

2.54 Amine Test

5ml of HCl was added to 5ml of solution of extract in a test tube. This test was repeated with 0.5g of acetone extracted solid.

2.55 Alcohol

To a concentrated solution of latex in benzene, small pieces of dry sodium was added and shaken vigorously. A glowing splint was placed close to the mouth of the test tube to test if any hydrogen gas is evolved.

2.56 Phenol

5ml of acetone extract solution in chloroform was taken in a test tube. 2ml of sodium hydrogen carbonate was added and is shaken vigorously. Again 5ml of acetone

extract solution in chloroform was taken in a clean dry test tube one drop of ferric chloride solution was added. This test was repeated with about 0.05g of the solid latex.

2.57 Carboxylic acid

About 5ml of the acetone extract was tested for carboxylic acid by shaking with few drops of sodium hydrogen carbonate solution.

Also to about 0.05g of the extracted solid is added sodium hydrogen carbonate solution.

2.6 SOME PHYSICAL PROPERTIES DETERMINATION OF THE SHEA TREE LATEX

2.61 pH

The pH of the raw, freshly collected latex sample was determined with the aid of pH meter.

The raw latex was taken in a 50ml beaker and diluted with deionised distilled water. The pH meter cell was standardised with buffer solutions of pH 4 and 9 before the pH of the latex was determined. The experiments was repeated with different latex samples.

2.62 Specific Gravity

$50cm^3$ specific gravity bottle was used for the determination of the specific gravity. The weight of the empty dry bottle was obtained. The bottle is filled with raw latex. The weight of the bottle

completely filled with latex was determined. The difference between the two groups gave the weight of 50ml of latex. The specific gravity is defined as

$$\text{Sp. gravity} = \frac{\text{weight in gm}}{\text{volume in cm}^3}$$

2.63 Viscosity

Determination of viscosity of pure solvent (chloroform). Redistilled chloroform was filtered through sintered funnel with suction pump to remove dust particles. 15ml of chloroform was pipetted into the viscometer which has been immersed in a water bath maintained at 27°C.

The solvent was allowed to equilibrate for fifteen minutes at 27°C.

The efflux time of the solvent was determined repeatedly until constant values were obtained.

Determination of intrinsic viscosity of the solution of dry latex in chloroform

1g of dry latex was dissolved in 100ml of chloroform. The solution was filtered with sintered funnel using suction pump.

5cm^3 of this solution was pipetted into the viscometer. The viscosity reading for this solution was obtained. This operation was repeated for subsequent dilutions.

The intrinsic viscosity was obtained from the graph

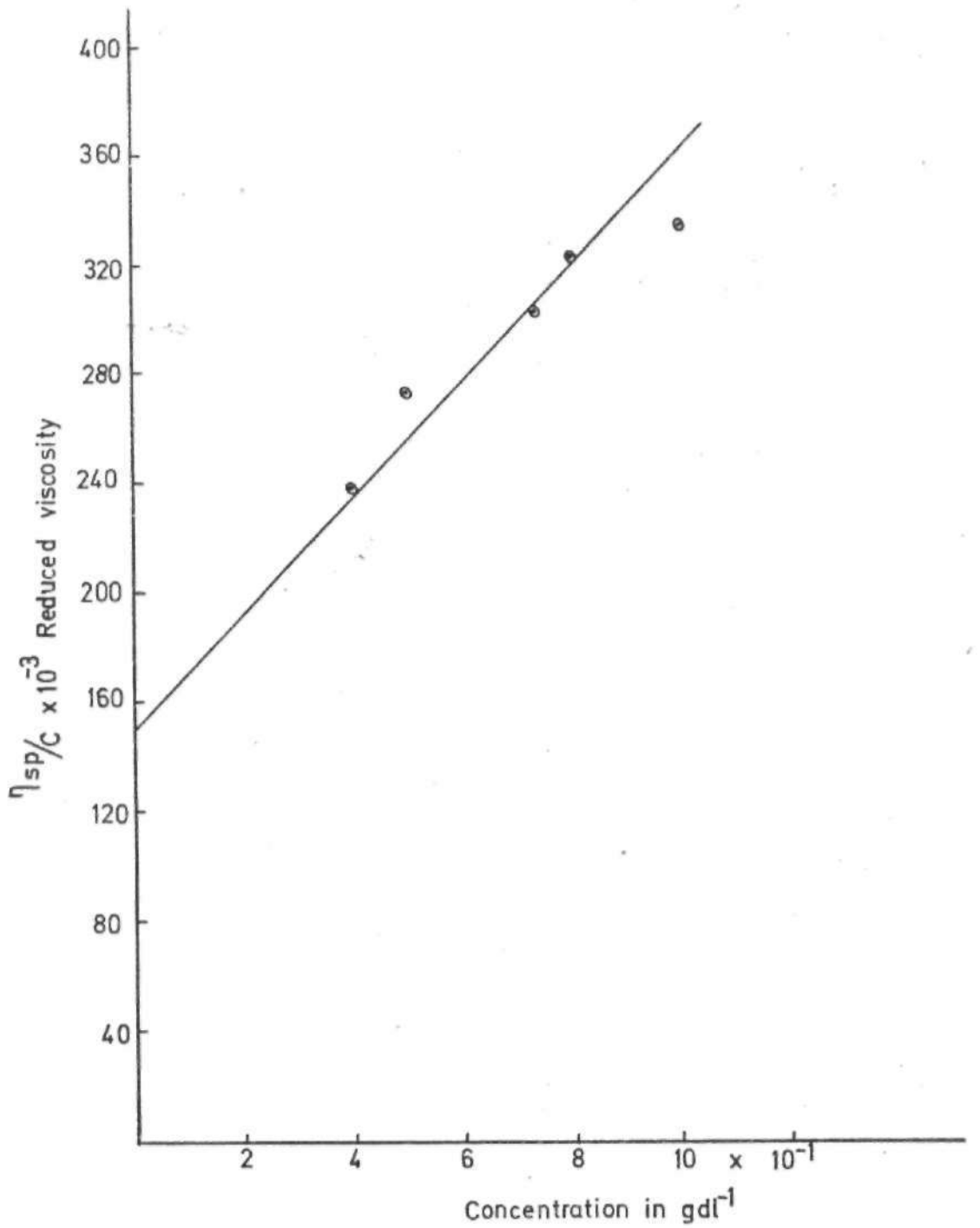


Fig. 1. Graph of reduced viscosity against concentration

of reduced viscosity versus concentration. Reduced viscosity is obtained by dividing specific viscosity by the concentration.

Specific viscosity is given by the expression

$$\frac{\eta}{\eta_o} - 1 \quad (12)$$

The ratio of efflux time of the solution to the efflux time of pure solvent gives the relative viscosity.

2.7 TRACE METAL ANALYSIS

Detection of the metals in ash of shea butter latex was made by atomic absorption spectrophotometer and flame photometer. Sodium, potassium and magnessium were detected by flame photometer, while the remaining metals were detected by the atomic absorption spectrophotometer.

2.71 Qualitative Analysis

The solution for qualitative analysis was prepared by digesting the ash obtained from burnt latex with concentrated nitric acid (1:1) and concentrated hydrochloric acid. The water extract was filtered and made up to the mark with distilled deionised water.

Qualitative identification was done by taking about 10ml of the water extract in a sample holder and aspirating it into the A.A.S. and Flame photometer as the case required.

2.72 Quantitative Analysis

The extent to which different metals were present in the ash was determined. A standard solution for each metal was prepared from the solution of their salts. A calibration curve was obtained with dilution of the stock solution for each metal as follows.

2.73 Sodium

A stock solution of 1000ppm of sodium ion was prepared by dissolving 2.5435g of sodium chloride in distilled deionised water. The solution was transferred to a 1 litre flask and made up to the mark. Solutions with concentration range of 1-5ppm was obtained from the stock solution by dilution.

2.74 Potassium

A stock solution of 1000ppm was prepared by dissolving 1.9066g of potassium chloride in 1 litre of distilled deionised water. This stock solution was used to obtain solutions of concentration range between 2-10ppm range by dilution. The potassium ion concentration in the ash was obtained from the calibration curve.

2.75 Magnesium

A 1000ppm stock solution of magnesium was prepared by dissolving 10.1357g of magnesium sulphate heptahydrate in distilled deionised water and the volume made up to 1 litre.

The solution was standardised with 0.1M EDTA

solution.

Solutions of concentration range of 1-10ppm was obtained by dilution of the stock solution. A calibration curve was prepared with these solutions.

2.76 Calcium

A 1000ppm stock solution of calcium was prepared by dissolving 2.5g. ofcalcium carbonate in 1 litre of distilled deionised water. This solution was standardised with 0.1M EDTA solution. The standard solution was used to prepare solutions with concentration 2-10ppm. These solutions was used to prepare a calibration curve for calcium. The concentration of calcium in the ash was determined from the calibration curve.

2.77 Lead

1.5898g of $Pb(NO_3)_2$ was estimated, by standardisation, to contain 0.9946g dl^{-1} of lead. A stock solution of 1.5898g of $Pb(NO_3)_2$ was obtained in 1 litre of distilled water. This solution was used to obtain 1-5ppm Pb ion solution. A calibration curve was obtained with this solutions.

2.78 Zinc

7.189g of zinc sulphate heptahydrate was estimated to contain 6.747g of zinc in 1 litre of solution. A calibration curve of zinc was obtained from a solution range of 1-5ppm.

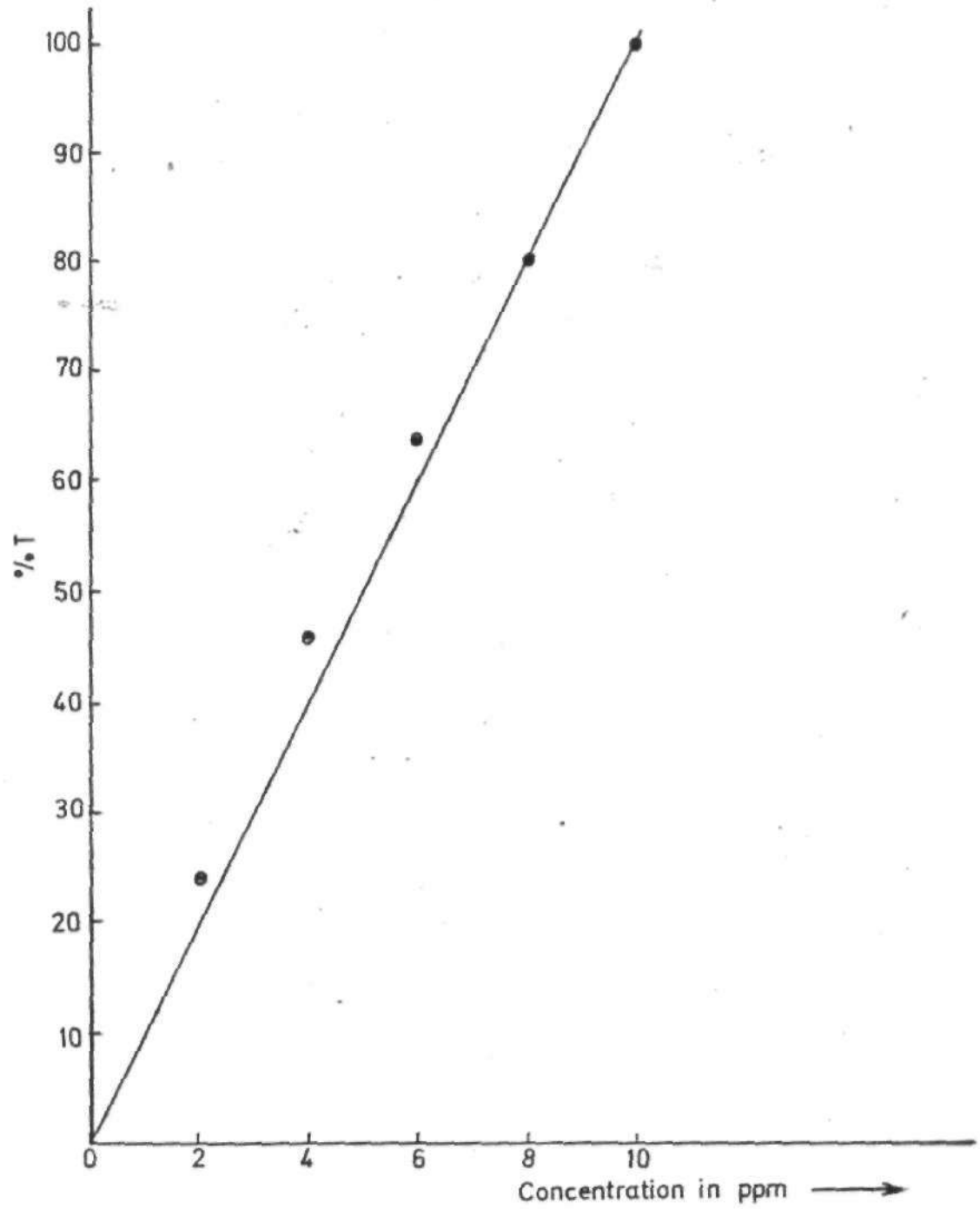
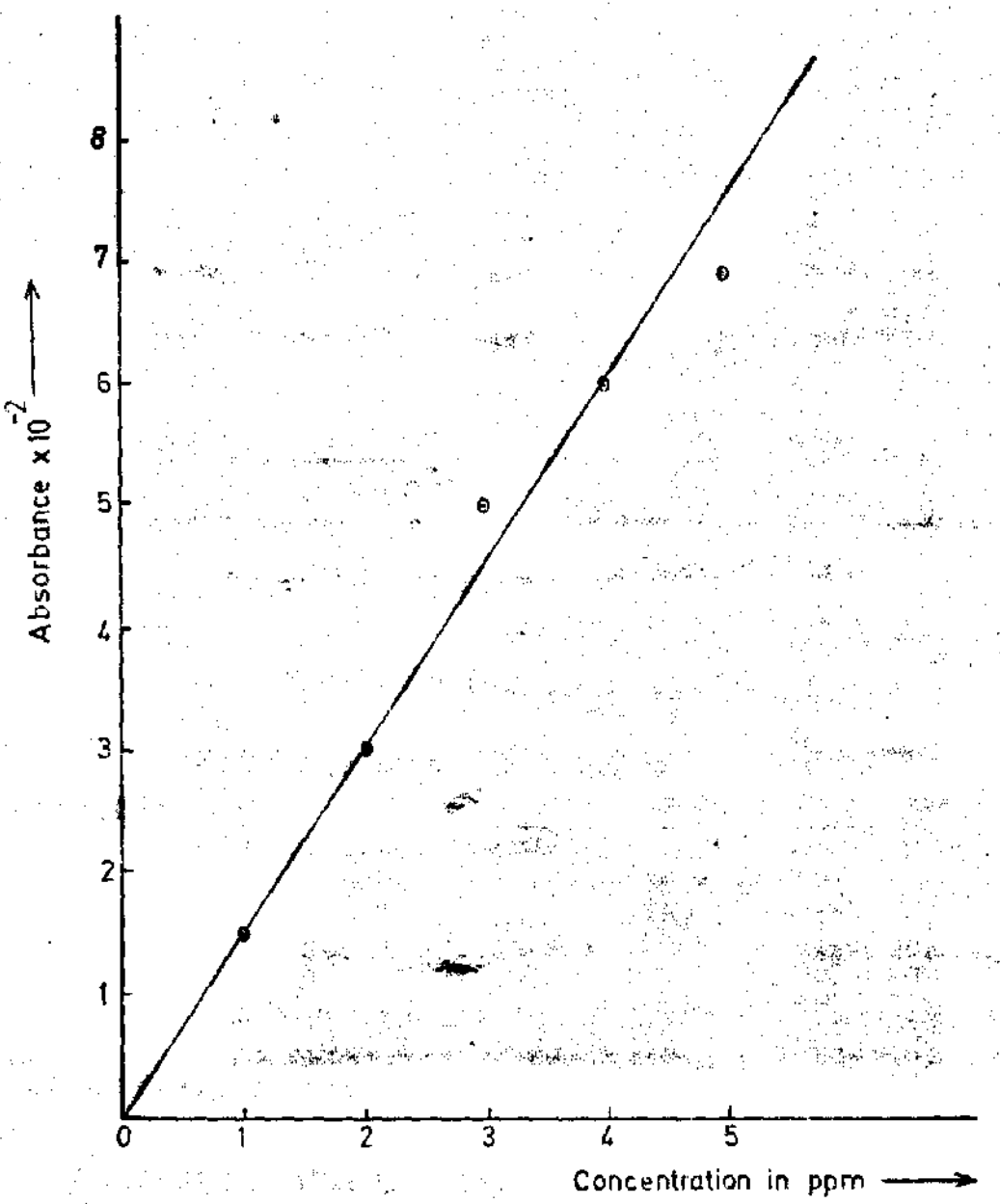


Fig. 2. Graph of %T versus concentration (ppm)(potassium)



Fig, 3. Calibration curve for lead.

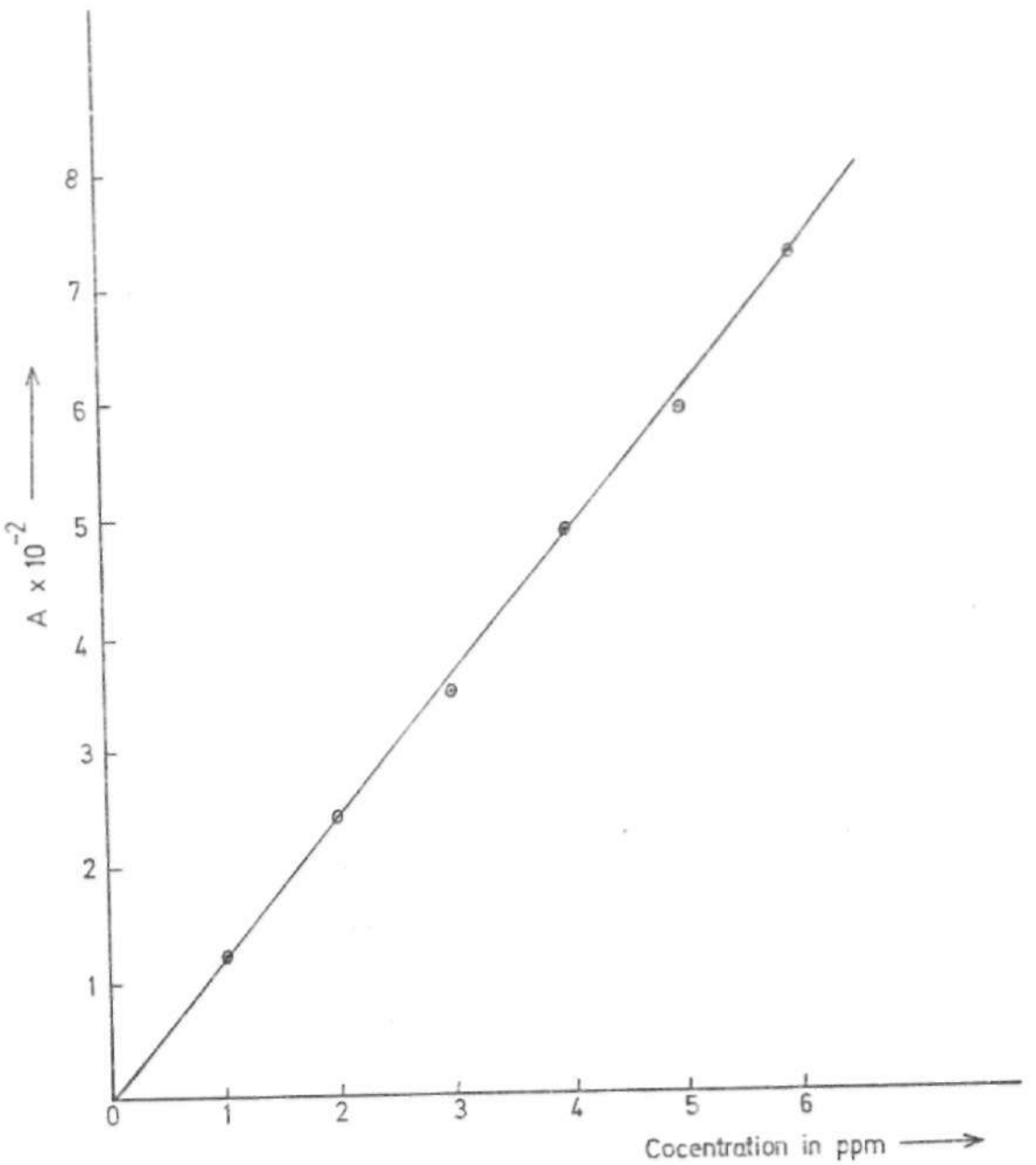


Fig. 4. Calibration curve for nickel.

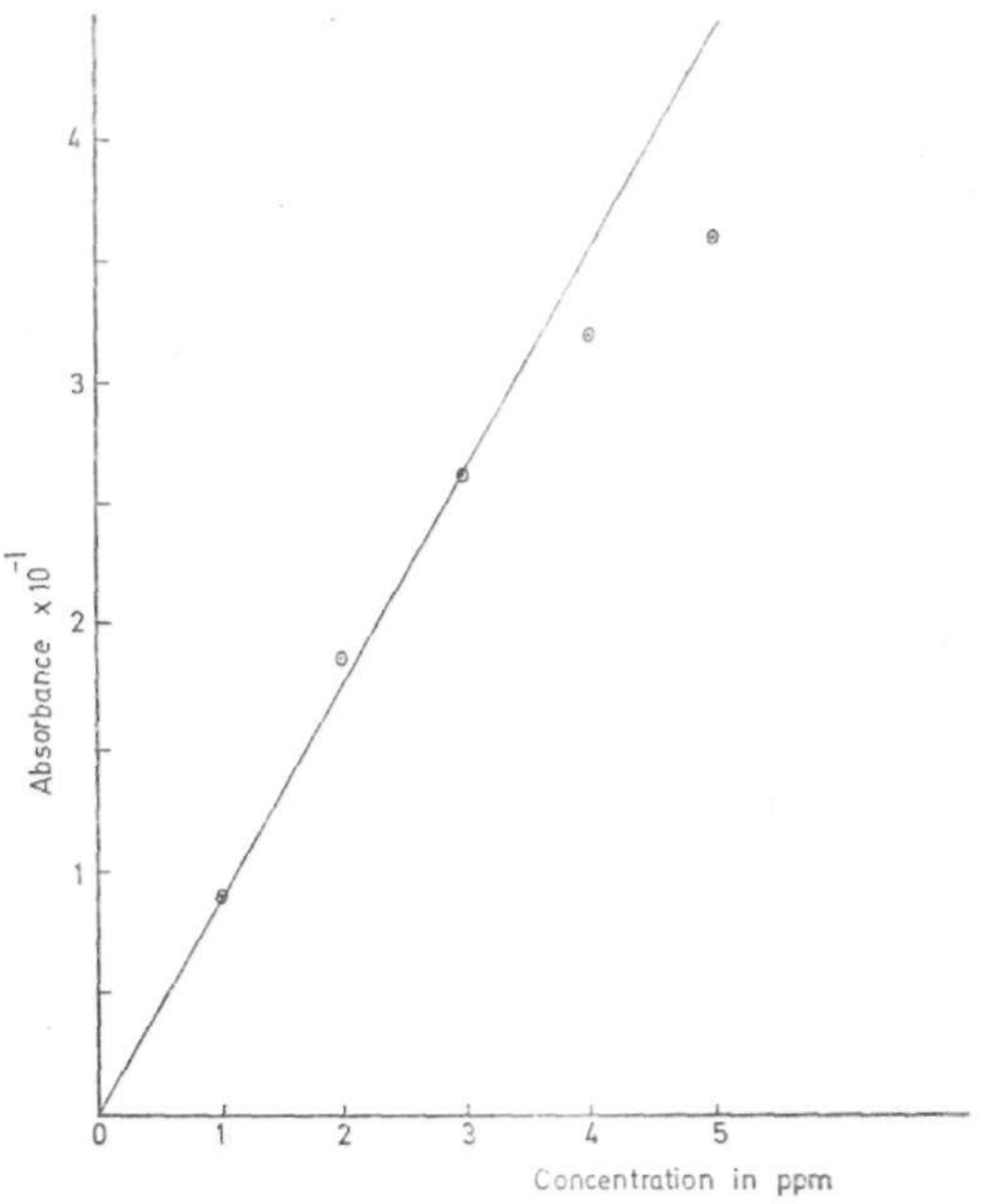


Fig. 5. Calibration curve for zinc.

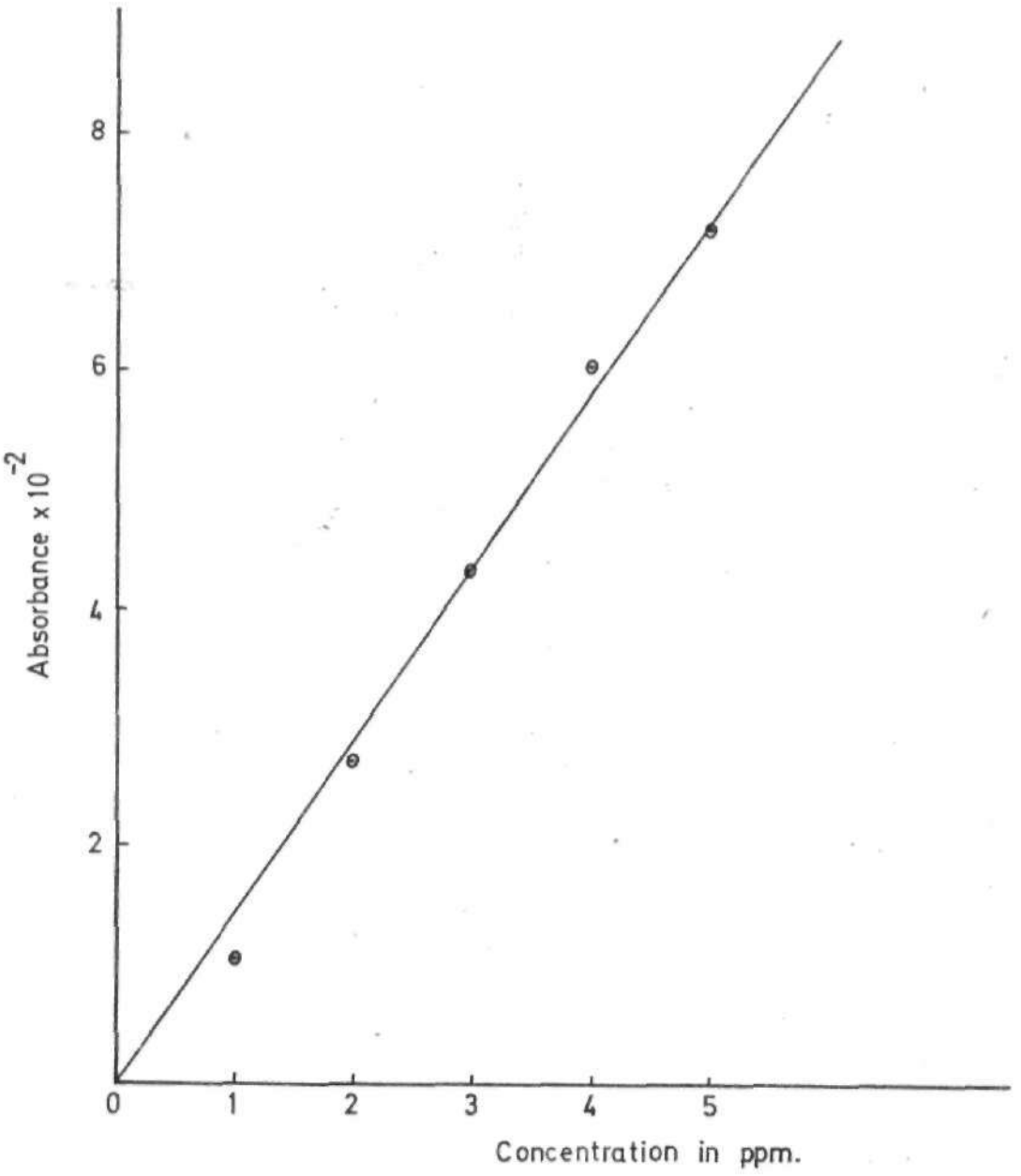


Fig. 6. Calibration curve for cobalt.

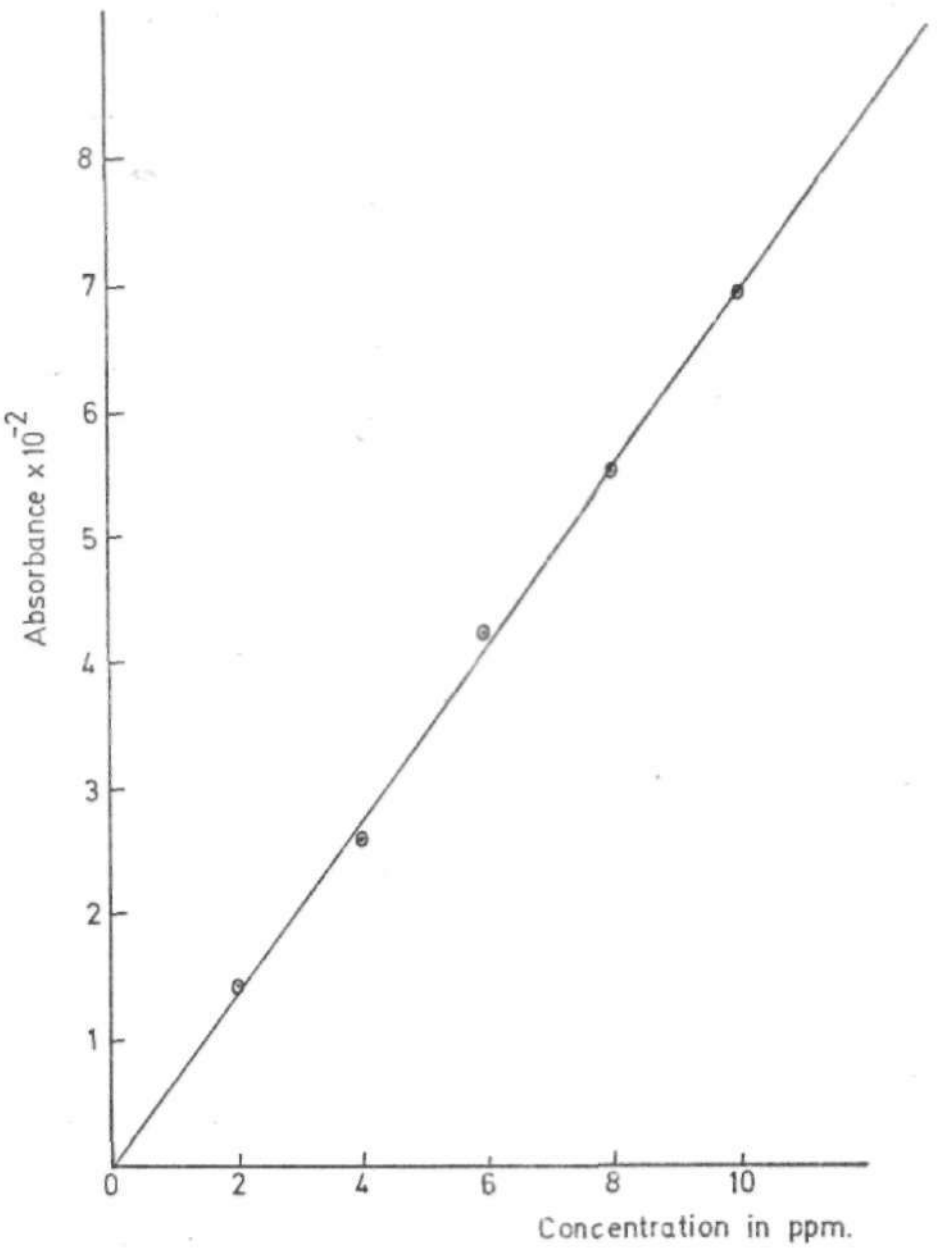


Fig. 7. Calibration curve for calcium.

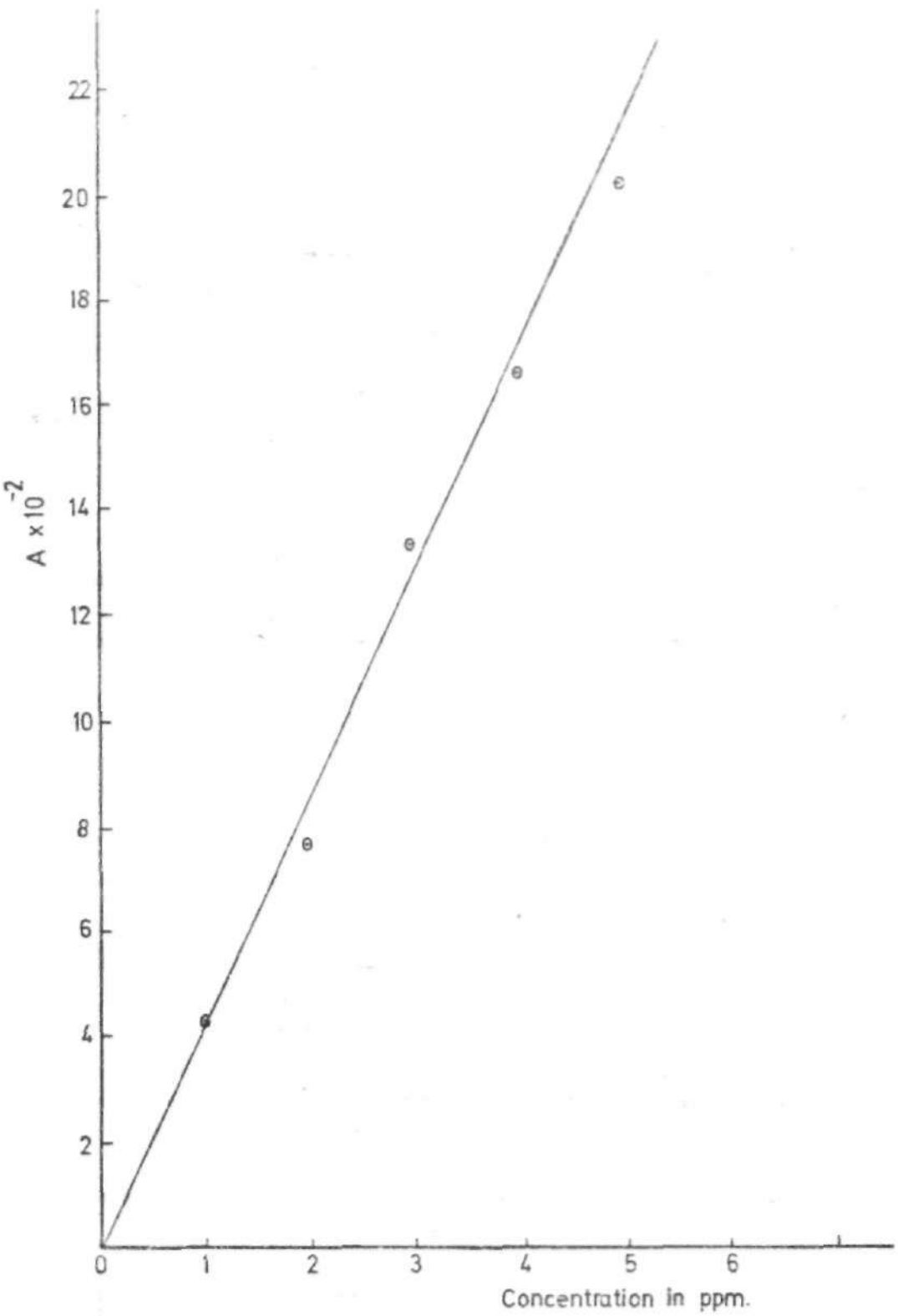


Fig. 8. Calibration curve for copper.

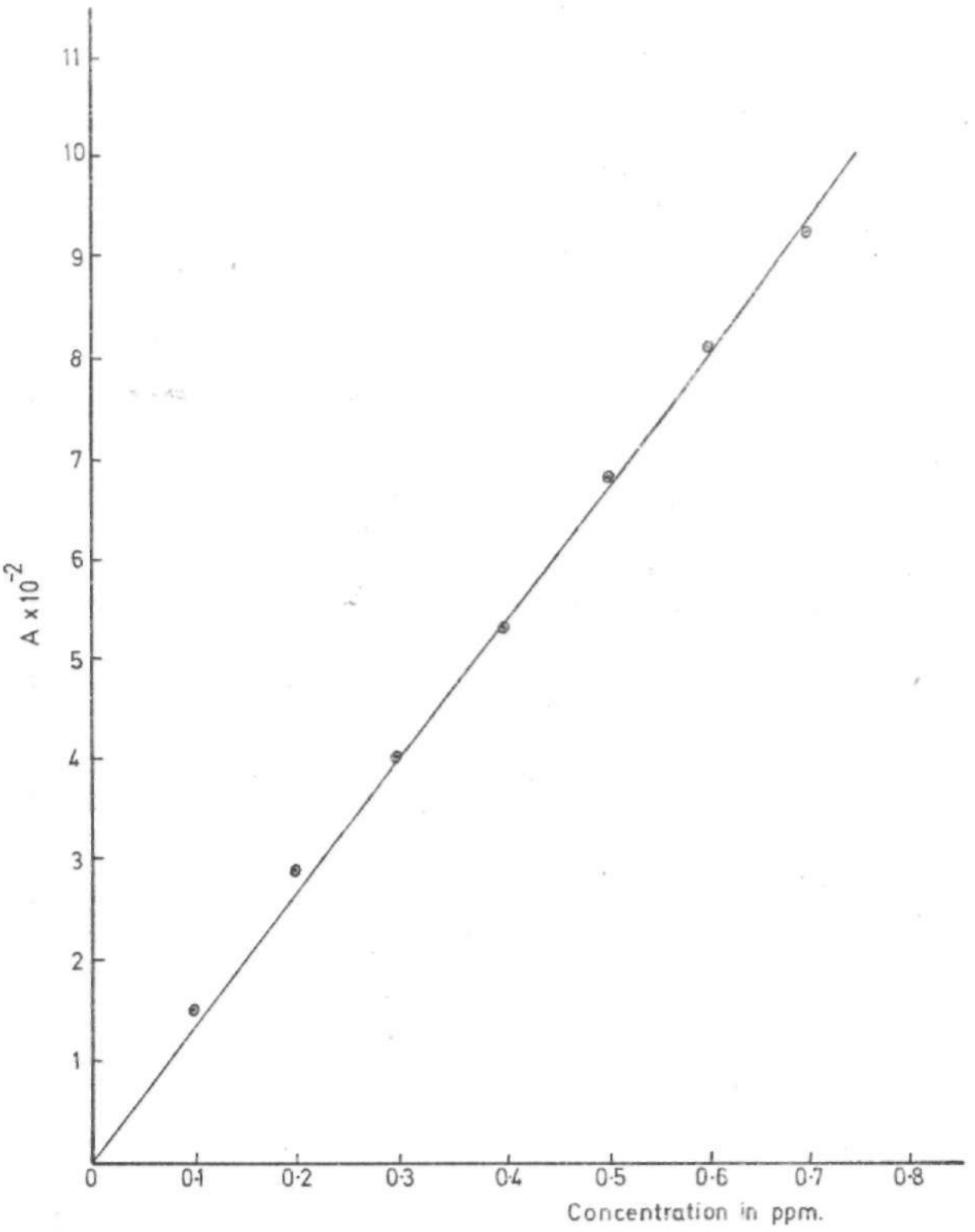


Fig. 9. Calibration curve for magnesium.

2.79 Nickel

A stock solution of Nickel ion was prepared by dissolving 4.049g Nickel chloride in 1 litre of distilled water. The solution after standardization was estimated to contain 4.041g of Nickel chloride. The concentration of Nickel in the solution was found to be 0.998g dm^{-3}. Appropriate dilutions was made to obtain solutions of 1-6ppm. A calibration curve was prepared from these solutions.

2.8 QUANTITATIVE ANALYSIS

2.81 Percentage Dry Weight of Latex

Two methods were employed for the determination of percentage Total Solid content in shea latex. The first method (A) was the evaporating dish method and the second method (B) was the sintered crucible method.

Method (A): 2g of replicate samples of latex was weighed in an evaporating dish and kept in a vacuum oven maintained at room temperature. Until constant weights were obtained.

Method (B): 2g of replicate latex samples was weighed in a beaker. An excess volume of formic acid was added. The solution was kept in the refrigetor for 24 hours. The coagulated latex was washed through a sintered crucible several times with distiled water. The coagulated latex cake was dried in a vacuum oven

at room temperature until constant weights were obtained.

The results of the two methods were taken for comparison.

2.82 Percentage Acetone Extract

1g of dry latex was weighed in a thimble and transferred to the soxhlet extractor. The extractor was connected to a 100ml round bottom flask already seated in a heating mantle. The whole set up was connected to a condenser. The extraction was allowed to proceed for a period of 10 hours after which the weight of dried extracted latex sample was determined. The weight of original latex sample before extraction minus the weight of the extracted latex was the weight of acetone extract. From this result, the percentage acetone extract was determined.

2.83 Percentage Ash Composition

Percentage ash content of the latex was obtained by burning the latex to ash. 4g of raw latex was weighed in a crucible. The sample was first heated on a Bunsen flame to eliminate all the organic components. The residue was transferred to a Muffle furnace maintained at 600°C for 48 hours.

The weight of the ash and the crucible was determined.

2.84 Percentage rubber-like material

The solid residue and other impurities constitute the remaining constituent of the latex. The percentage of this was obtained by finding the difference between the sum of moisture content, acetone extract and ash content and 100.

2.9 CHROMATOGRAPHIC SEPARATION OF EXTRACTED SOLID LATEX

2.91 Thin-Layer Chromatography - Preparation of the Adsorbent

A slurry of the absorbent silica-gel 254 + 366 was prepared by mixing 112g of the powder with 250cm^3 of distilled water. The slurry was thoroughly shaken intermittently with addition of the powder.

Coating of T.L.C. Plates: Glass plates 20 x 20cm and 20 x 5cm for preparative T.L.C. and pilot t.l.c. respectively were arranged tightly on the spreader. A layer of 0.25cm thickness was spread with the aid of the spreader. The coated plates were dried in the oven at 100^{o}C for more than 6 hours before use.

Choice of Solvent: Different solvent mixtures were prepared. The choice of solvent was based on their polarity. The solvent mixture was placed in the chromatographic tank.

Spotting of the Sample: Latex samples were dissolved in chloroform. The solution of latex were spotted on the chromatographic plate with micro pipette. The

spots were made on the plate with an interval of 2.5cm between each spots, a 3cm margin was left on both sides of the plate and from the origin.

The spoted plate was transferred to the chromatographic tank with the solvent mixture for development for 1 hour.

The developed plate was removed and dried. The spots were located with the aid of ultra-violet lamp.

2.92 Preparative Thin Layer Chromatography

20 x 20cm plates were used for the preparative T.L.C. The solution of solid sample was applied by streaking along a line 3cm from the lower edge of the plate and with 2cm margin from both sides. The streaked plate was allowed to dry by blowing air on it. The plate was transferred into the chromatographic tank for development. The plate was removed after one hour of development and dried. The different bands were located with the aid of an ultra-violet lamp. The two bands were scraped separately and eluted with chloroform. The yield obtained from this experiment was too low. This necessitated the use of column chromatography.

2.93 Column Chromatography

A column of 10 x 0.5cm was used for the separation. The column was packed with silica gel already ~~dissolved~~ suspended in carbon tetrachloride. Packing was accompanied by gentle taping to ensure homogeneous settling of the

packing material. Carbon tetrachloride was run through the packed adsorbent to ensure complete equilibration. A concentrated solution of the dry solid latex sample was loaded on the packed column as evenly as possible with the aid of a micro pipette. The latex solution was allowed to adsorb on the column top.

The adsorbed solution was seperated with the following solvent ratio 1:6:10 of benzene:acetic acid and pet ether. Two bands were located with U.V. lamp. The bands were marked on the glass. The glass was cut to isolate the two bands. The silica gel from each band was eluted with carbon tetrachloride. The eluent was concentrated by evaporation of the solvent. The yield obtained was still negligible.

The experiment was repeated with a bigger column. This time a column of 30 x 3cm was used. The column was packed as stated above and the solution of latex in chloroform was loaded on the column.

The adsorbed latex was eluted by simple elution method by allowing to run through the column a solvent mixture of ethyl acetate:cylohexane 1:40. Each fraction that eluted was collected separately until complete elution was ensured. The collected latex fractions were concentrated by evaporation and preserved for further analysis with I.R. and N.M.R.

2.10 INFRA RED SPECTROSCOPY

The purified solid sample was used for infra red spectroscopy. The media used were Nujol and carbon tetrachloride.

A homogeneous mixture of latex and nujol was obtained by mixing in a motar with a pestle. A smear of the mixture was made on a sodium chloride plate and mounted on the infra-red spectrophotometer (700 Perkin Elmer model). A blank run was made with nujol alone for the purpose of comparison. The spectra obtained are found on page 57.

As an alternative, dry latex samples were dissolved in carbon tetrachloride. A film of the solution was smeared on the sodium chloride cells and mounted on the infra-red spectrophotometer. The experiment was repeated with pure carbon tetrachloride alone for comparison. Since carbon tetrachloride does not absorb in the infra-red region there should not be any absorption due to the carbon tetrachloride.

Attempt to get potassium bromide press disc with the dry latex sample failed as it was impossible to grind the latex sample with the potassium bromide to give a homogeneous mixture.

2.11 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The N.M.R. instrument varian T-60 type was used. A dilute solution of dry latex was prepared in carbon

tetrachloride and tetramethyl silane was added. The solution was transferred to the sample container. The sample container was placed in the magnetic field to obtain the N.M.R. spectrum.

Chapter 3

RESULTS AND DISCUSSION

3.1 SAMPLING

In order to ensure that the latex collected was a good representative of all the latices, random collection of latex was made from various spots in both Shika and Basawa. The different latices were mixed together for analysis. The latex is adhesive milky white liquid if proper method of collection is adopted. The colour becomes pinkish white as a result of the exudates from the bark if the latex is carelessly tapped.

Formic acid was found to be most suitable coagulant and concentrated ammonia solution as most suitable anticoagulant. After coagulation of the latex, the resulting cake had to be washed several times with distilled water to eliminate all the formic acid which might affect the results of analysis. From the results obtained for the percentage total solids with coagulating method, loss of sample during washing and filtering lowered the percentage total solid. It is therefore recommended that sintered funnel be used for filtering to avoid excessive loss of sample.

Since concentrated ammonia was found to be most suitable anticoagulant, latex sample could be preserved in concentrated ammonia. The ammonia could be removed by bubbling stream of nitrogen gas to the latex solution.

Coagulation can also be achieved by several other methods. These include heating, addition of concentrated sulphuric acid, exposure to air, but coagulation with formic acid was much prefered as it did not affect the nature of the latex.

3.2 SOLUBILITY OF SOLID LATEX

The solidified latex obtained after coagulation was found to be generally soluble in non-polar solvents such as carbon tetrachloride, dichloro methane and insoluble in polar solvents such as acetone, petether and ether. Long chain hydrocarbon macromolecules have been found to possess this property (11). For example natural rubber is known to be soluble in pentachloroethane and tetrachloroethane.

3.3 QUANTITATIVE EXTRACTION

Table 3.1

Percentage solvent extracts obtained from solidified latex

Solvent	Percentage extract
Acetone	67.75
Diethylether	98.71
Propanol	69.82
Ethanol	62.42

The solvents above were used for extraction. It had been previously ascertained that the latex was not soluble in the solvents. It was necessary that the solvent to be used for extraction should only be capable of dissolving the extract of the material so that the result obtained will only be due to the extract.

From the result, therefore, all the solvents used gave almost the same percentage extract except diethyether with abnormally high percentage extract. This strongly suggests that the latex material was soluble in diethylether and dissolved slowly during extraction. The implication of this was that acetone, propanol and ethanol were ideal for the extraction of shea latex, while diethylether was not suitable for extraction of shea latex.

3.4 PRELIMINARY CHEMICAL EXAMINATION OF SHEA LATEX

Appearance:	Milky white solid.
Burning Test:	Smoky flame, repulsive odour, flame was self extinguishing burned with soothy flame.
Pyrolysis Test:	Solidified latex decompose with heat. A brown coloured liquied condensed at the cold part of the test tube.
Reaction with 80% H_2 SO_4:	The dry solidified latex decomposed on heating with 80% sulphuric acid.

The above preliminary test gave results that were close to a rubber-like material. The burning test gave result that was similar to natural rubber and macro molecules, judging from the sooty flame and the odour.

Pyrolysis of the coagulated latex gave a neutral brown liquid like natural rubber (11).

Decomposition with 80% sulphuric acid gave result that was true of long chain macro molecules with double bond.

3.5 QUALITATIVE ANALYSIS (ELEMENTAL ANALYSIS)

Table 3.2

Results of elemental analysis

Elements	Acetone extract	Solid latex
Nitrogen	-	+
Sulphur	-	-
Chlorine	+	+
Bromine	-	-
Iodine	-	-
Fluorine	-	-

The results obtained for elements in shea latex are shown above. Only nitrogen and chlorine were present in the solid latex. The extract had chlorine alone. The presence of protein in a rubber-like material obtained from most trees is enough (6) to give positive

Lassaigne's test for nitrogen. The presence of chlorine could be due to the fact that natural latex contains some chloride salts such as sodium chloride and potassium chloride.

3.6 QUALITATIVE ANALYSIS (FUNCTIONAL GROUP ANALYSIS)

Table 3.3

Functional groups analysis of shea tree latex

Functional groups		Extract	Solid
Alcohol	(-OH)	-	-
Acid	(-COOH)	-	-
Amine	($R-NH_2$)	-	-
Carbonyl	(-C=O)	-	-
Amide	(R-NHCO)	-	+
Phenol	(Ar-OH)	-	-
Double Bond (Unsaturation)	(C=C)	-	+

From the result shown in Table 3.3 above, all the functional group tests were negative except the test for amide with solid latex and the test for carbon-carbon double bond. This strongly suggests that the latex is an unsaturated hydrocarbon macromolecule, as they are usually associated with absence of any significant functional group (11). The smoky nature of the flame is an indication of the presence of aromatic compound. However, test for aromaticity gave a negative result. it is known that long chain hydrocarbon macro molecule

burn with smoky flame (14).

3.7 PHYSICAL PROPERTIES

Table 3.4

Physical properties of shea latex

pH	= 5.6
Specific gravity	= 1.072g/cm^3
Intrinsic viscosity	= 0.150
Molecular mass	= 45,827

Table 3.6 above shows the result of some of the physical properties of shea latex. It was found that the raw latex was slightly acidic. Its specific gravity is slightly higher than that of gutta-percha and balata 0.92 and 0.95 repectively (11). The latex was characterized with a value for intrinsic viscosity. Staudinger (15) however, showed that rubber and rubber-like macromolecules exhibit abnormal viscosity phenomenon. This finding invalidates the reliability of viscosity parameters such as intrinsic viscosity and reduced viscosity. Hence, only a rough estimate of molecular weight could be made.

This abnormal viscosity phenomenon was due to dissociation of macromolecules. In concentrated solutions where the largest molecule are present the viscosity is high. Whereas, there comes a point in the dilution where the viscosity suddenly decreases because of the formation of smaller molecules. Since the raw latex is opaque, no result was obtained for optical rotation.

From the high molecular weight of the latex determined by the viscosity experiment, it can be concluded that shea latex is a macro molecule.

3.8 QUANTITATIVE ANALYSIS (TRACE METAL)

Table 3.5

Trace metal contents of the ash of shea latex

Metals	Concentration in ug ml^{-1}
Sodium	16.00
Potassium	3.85
Magnesium	31.00
Calcium	3.10
Copper	3.30
Cobalt	0.43
Lead	0.14
Nickel	0.25
Zinc	2.77

The compositions of the following metals, potasium, magnesium, sodium, zinc, lead, iron and copper in the ash of the latex in ug/ml of solution are shown in Table 3.7 above. The magnesium content of the latex was the highest, this is not unusual since magnesium uptake, an element necessary for photosynthetic activity in the leaves, is transported by the xylem vessls along with the water from the soil. Magnesium is also important for its role in the growth of plants.

Next to magnesium is sodium, sodium in plants is present in form of sodium chloride and it helps in osmo regulatory control of the plant cells. Potassium concentration comes next to sodium, but its concentration is unusually low. Potassium is another important element necessary for plant's growth. However, low potassium content in the areas where the trees are found may be responsible for this abnormality.

Calcium and copper have almost the same concentration. Presence of calcium in plant is normal because it is used as an impregnating agent and it helps to make the cell wall rigid. But the presence of copper lead and zinc serve no useful purpose to plants. They are usually associated with plants found in industrially polluted areas. Lead, nickel, cobalt and zinc are found in trace quantity because they are foreign to the plant and since the site the latex was collected is not industrialised the presence of these metals in trace quantities is justified.

3.9 QUANTITATIVE ANALYSIS

Table 3.6

Percentage composition of different components of shea latex

Component	Percentage composition
Moisture	57.48
Acetone extract	35.20
Ash	0.04
Rubber-like material	7.28

The different percentage compositions of the components of shea latex is shown in Table 3.8 above. It can be seen that for most of the samples collected moisture has the highest percentage constitution in most cases above fifty percent. The average moisture content was 57.48 ± 1.45%, it was found to depend on many factors such as age of the tree, time of tapping, etc.

Acetone extract, which was resinoid in nature is next to moisture in constitution.

Beadle and Stevens (21) argued that resinous [illegible] content of natural rubber and rubber-like molecule has a profound effect on its quality. In their work, a number of tables illustrated the effect caused by removal of resin. In general, this leads to lower quality. In this present investigation, the coagulated dry latex before extraction had rubber-like properties. It could be drawn and it was not brittle, but after [illegible] extraction, the latex became cripsy and brittle, it had lower tensile strength compared to the unextracted solidified latex.

It could be concluded on this note that due to the high acetone extracts in the latex, the shea latex was bound to have good quality. The acetone extract was also responsible for the adhesive nature of the latex. The acetone extract was transparent and brownish in colour. It solidified on cooling and it could be used as gum. Most of the properties of the wood obtained from the trunk of shea tree could be attributed to this resinous

material. These properties included, its hardness, termite proof and toughness.

One possible mechanism that can be advanced for these properties is that when the trunk is cut, the latex solidified with the aid of this resinous material and bind all the wood fibres together thus increasing the strength of the wood.

The resinous material can be considered as the primary component responsible for the ability of the solidified latex to recover from extension because the extracted solid latex is brittle and non-resilient.

The ash content of the latex was very low. The percentage rubber-like material of the latex was 7.28% This was very low compared to what was obtained from other latex bearing plants. This could be due to the fact that some of these materials were lost during extraction.

3.10 PERCENTAGE TOTAL SOLID

Table 3.7

Percentage total solid of shea latex

Percentage Total solid By Method A	Percentage Total solid by Method B
53.21	43.29
53.71	42.12
54.20	41.26
49.90	44.63
53.81	41.26

The table above shows a statistical comparison of two methods used for the determination of percentage total solid. Detailed description of the two methods was given under experimental. From the result, it was found that procedure B with 42.83 ± 4.2 average was superior to procedure A with total solid percent average 52.75 ± 5.6. The small percentage total solid obtained with procedure B was a clear indication that almost all the moisture in the latex had been completely removed. The statistical standard error of the mean for procedure B is less than that for procedure A. This signified a smaller deviation from the true mean as compared to the results with procedure.

However, statistical comparison of the two methods suggests that they are both statistically equivalent at 99% confident level and nine degree of freedom.

3.11 WEBER TEST

Weber test was carried out on the latex sample to confirm the presence of double bond or unsaturation. The test was positive for the latex. This reaction is also true for tubber-like macro molecules.

This reaction seem to have been named the Weber Colour Test by Kirchhoff (16) and it came to be of some importance in 1939. Stern (17) listed the colours which are obtained when the test is applied to different rubber-like materials. The Chemistry of the reaction was established (18). Although the actual nature of the

coloured compound has not been elucidated.

Bromination of rubber-like sample by substitution at the methylene group next to the carbon carrying the methyl group is essential to the performance of the test. Under normal conditions at room temperature the action of bromine on rubber-like material produces a mixed reqction involving some saturation of the double bond and some substitution, but the careful use of special reagents enables these reactions to be separated and it was shown that addition at the double bond does not lead to the reaction with phenol. Rubber or rather polyisoprene has been shown by Farmer (32) and his colleagues to possess exceptional reactivity in that the primary place of attack by most reagents is due to the ease with which a proton is displaced from the methylene group alpha to the double bond. This reactivity is not shared by other 1,5-dienes and must be ascribed to the activating influence of the methyl substituent where the sequence of double bonds is interrupted by one methylene group instead of two, the proximity of the double bonds suffic es to activate the methylene group. This linoleic acid substituted quite easily at the marked methylene group and bromination at room temperature preferentially leads to bromine substitution at this point.

3.12 CHROMATOGRAPHIC SEPARATION (PILOT T.L.C.)

Two distinct bands were located with u.v. lamp in the darkroom. The various Rf values for the two bands with different solvent ratios are as follows.

Table 3.8

Different Rf values obtained with different solvent mixtures

Solvent mixture ratio	Rf Band A	Rf Band B
Benzene:Pet ether (1:10)	0.25	0.30
Benzene:Pet ether:Acetic acid (1:10:5)	0.25	0.35
Ethylacetate:Cyclohexane (1:40)	0.45	0.5
Ethylacetate:Cyclohexane (1:30)	0.36	0.48
Benzene:Pet ether (1:20)	0.20	0.35

From the results above, it follows that ethyl acetate:cyclohexane (1:30) solvent mixture is the best for separation on chromatographic plate.

The solvent was able to separate the two bands distinctly. The pure dry latex was contained in Band B which had the higher Rf. value Benzene:pet ether mixture was a poor solvent as the Rf value obtained were small. This implied that the dissolved dry solid latex did not move appreciably from the origin. Addition of acetic acid did not improve the result as the Rf value did not increase considerably.

Thin layer chromatography was not an adequate method

for separation of shea latex on a preparative scale as the yield obtained was always too small. This necessitated the use of column chromatography. This improved the yield.

3.13 INFRA-RED SPECTROSCOPY

The position of the peaks in the I.R. spectra are shown below with both Nujol and carbon tetrachloride medium with their corresponding peak assignment.

Table 3.9

Infra-red absorption peaks for shea latex (13)

Nujol medium cm^{-1}	Carbon Tetrachloride cm^{-1}	Peak's assignment
3425 wk	3425 wk	*O-H or N-H stretching
3325 wk	3325 wk	OH or N-H stretching
- Masked by Nujol*	2925 str.	C-H stretching
1625	1625 str.	C=C stretching
1450	-	Nujol peak
1370	-	Nujol peak
1310 str	1310 str.	C=str.

*The occurrence of peak at 3425 and 3325 cm^{-1} could be due to OH or NH group, but since OH has been found to be absent by classical analysis, the only possibility is that the peak is due to NH group.

From Table 3.11 above, it is noted that the functional groups determined by classical analysis were found by infra-red spectroscopy. These are N-H, C-H and C=C bond stretching.

The I.R. was run with two media and it is observed that both media gave the same spectra unless where absorption of the Nujol's C-H stretching has masked the C-H stretching peak of the latex.

Apart from the presence of N-H functional group, the latex is purely a hydrocarbon with carbon-carbon double bond. The presence of N-H functional group could be due to the presence of protein in the latex. This result supports the claim that shea latex is an unsaturated hydrocarbon molecule.

3.14 NUCLEAR MAGNETIC RESONANCE

The table below is the peak assignment for the signal obtained with the latex at different stages of purity. The two bands seperated by thin layer chromatography were eluted for N.M.R. analysis.

Table 3.10

N.M.R. spectra signals and peak assignment

Raw latex (unpurified) Signal (o)	Peak assignment
0.65	CH_3-CH_3
1.50	C-CH_3
2.0	Co_2R or C-N
5.0	C=C-H
7.1	Aromatic proton
Purified latex band A Signal (o)	**Peak assignment solvent mixture benzene: pet ether 1:10**
0.9	CH_3-CH_3
1.3	CH_3-C
Purified latex band B Signal (o)	**Assignment (purified latex Band B with solvent mixture Benzene:pet ether (1:10)**
0.9	CH_3-CH_3
1.4	CH_3-C
2.4	R-CH_2-R

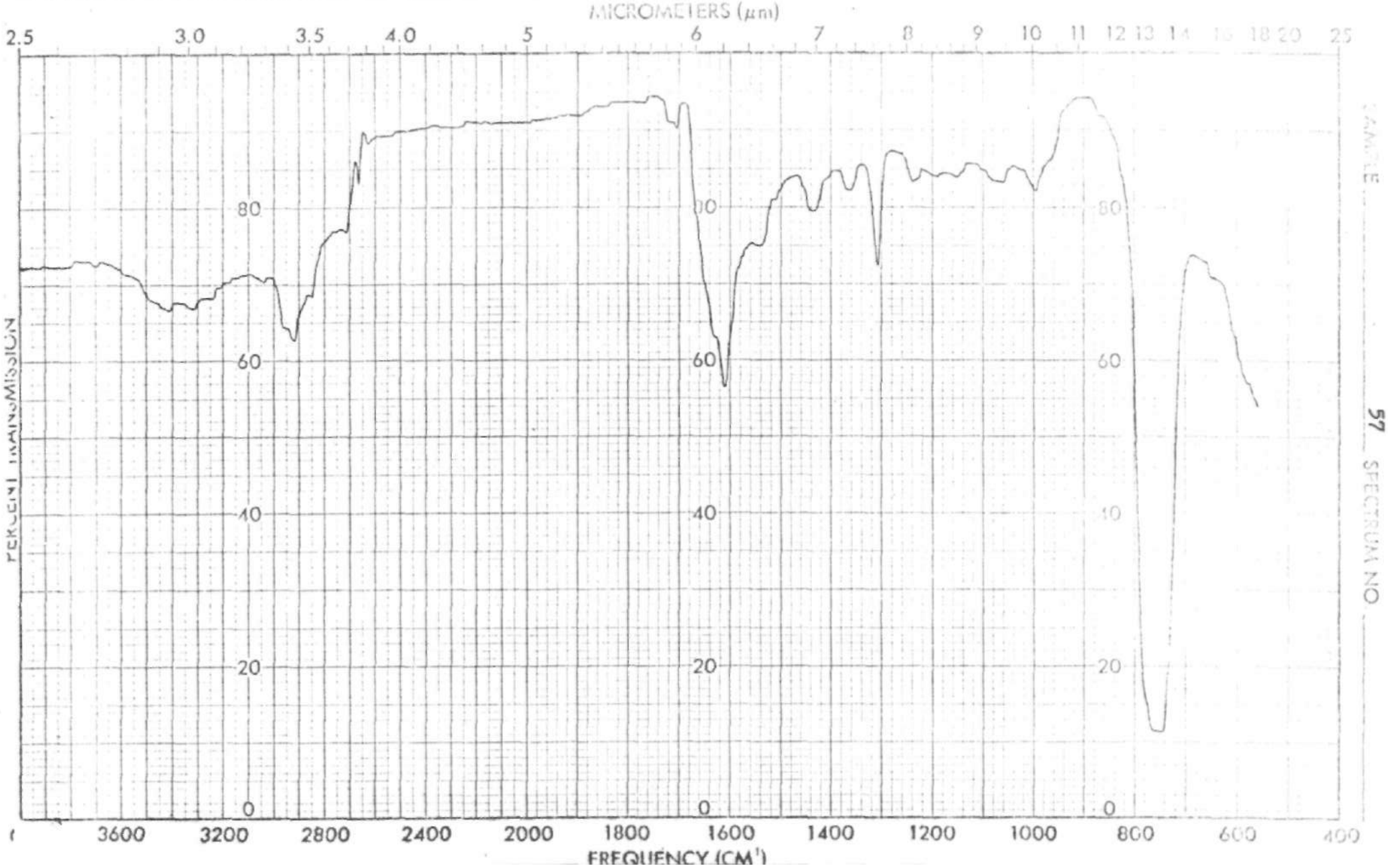
The major absorption signals as shown in Table 3.12 above are the two found between 1.4 and 2.2 delta. This is the signal for the hydrocarbon. The heights of the two absorption signals are almost the same. This implies that the two neighbouring protons are almost the same in number (13).

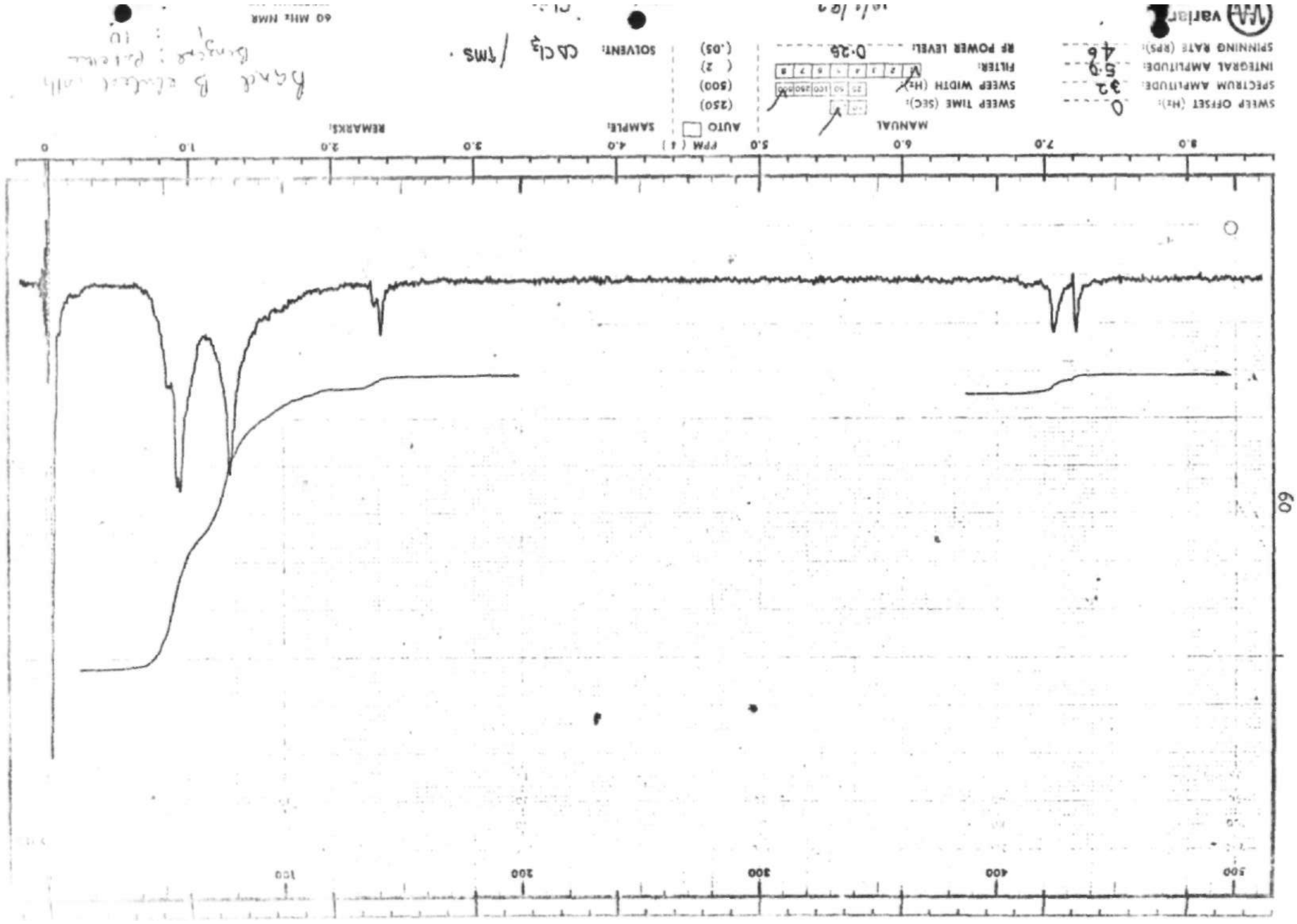
The presence of small signal at 5 and 7 (o) in the unpurified latex is due to the presence of impurities as these signals disappear with purified latex.

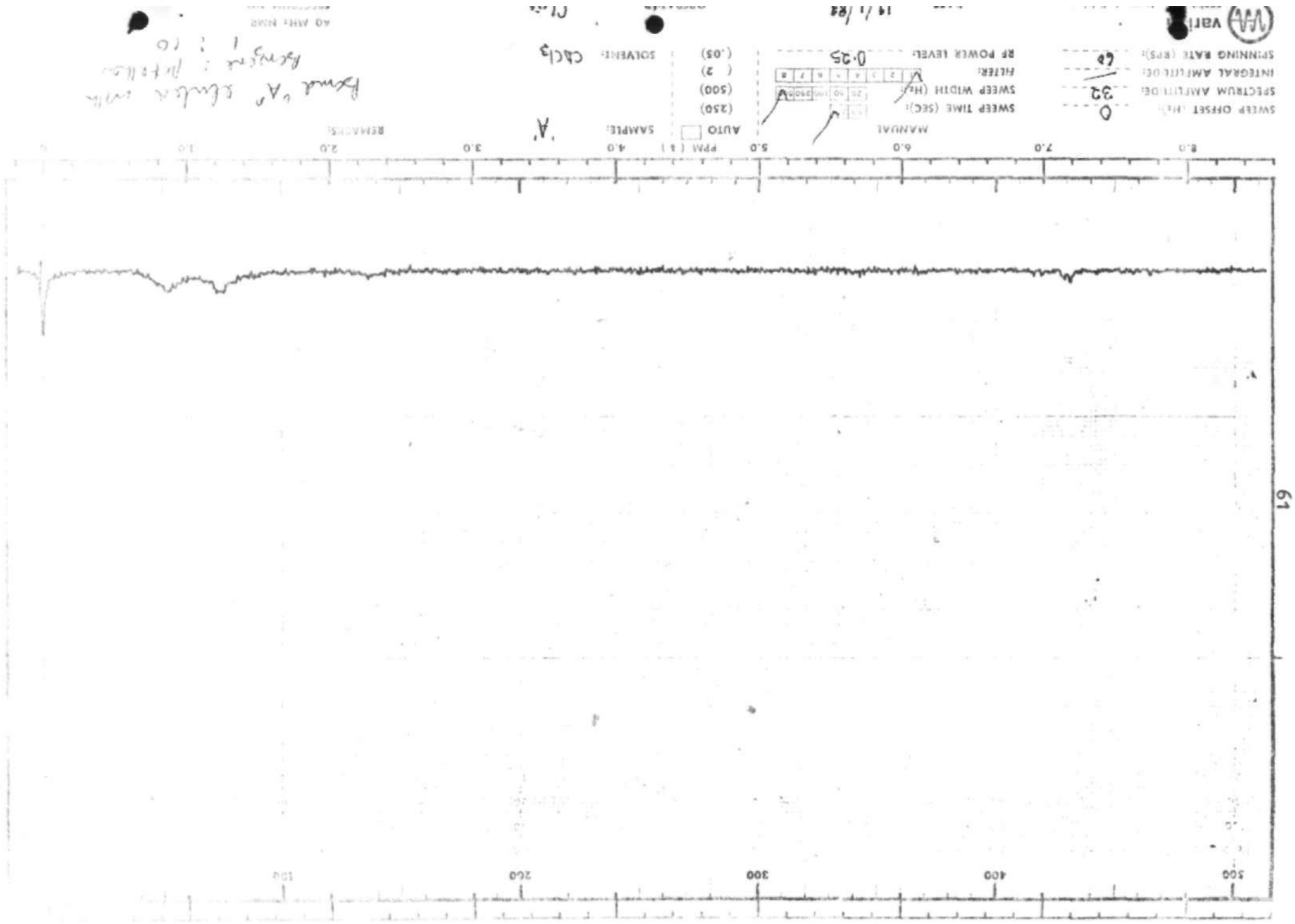
FHA:

REMARKS:

OPERATOR Adolph M.E. DATE 3/8/83




SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 32
INTEGRAL AMPLITUDE: 5.9
SPINNING RATE (RPS): 46
SWEEP TIME (SEC):
SWEEP WIDTH (Hz):
FILTER:
RF POWER LEVEL: 0.25
MANUAL
AUTO
(250)
(500)
(2)
(.05)
SOLVENT: CDCl3 /TMS
SAMPLE:
REMARKS:
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
60
100
200
300
400
500


SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 32
INTEGRAL AMPLITUDE: 64
SPINNING RATE (RPS):
SWEEP TIME (SEC):
SWEEP WIDTH (Hz):
FILTER:
RF POWER LEVEL: 0.25
MANUAL
AUTO
SAMPLE: 'A'
SOLVENT: CdCl3
(250)
(500)
(2)
(.03)
REMARKS:
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
500
400
300
200
100
61

Band B of the purified latex gave spectrum of pure hydrocarbon. The main signals are those of CH_3 and CH_2.

The spectrum of Band A has barely no significant signal, this implies that most of the latex has moved with the solvent front to form Band B. The two signals obtained are those of CH_3-CH_3 proton.

Chapter 4

CONCLUSION, SUMMARY AND SUGGESTIONS FOR FURTHER WORK

4.1 CONCLUSION

As the title of this research project suggests, the author's interest is to carry out a general preliminary investigation of the different chemical components of the shea latex obtained from Butyrospirmum parkii trees in Zaria locality.

A plant material of this nature always contain a complex mixture of all sorts, therefore this work would serve as a preparative tool for further research work.

The major components of the shea latex have been identified by means of classical analysis and instrumental techniques.

It could be concluded that shea latex is a mixture of a long chain hydrocarbon macro molecule, resinous extract which is responsible for most of the rubber-like properties shown by the latex, moisture and impurities.

The presence of unsaturation in the macromolecule was determined by chemical analysis, confirmed by Weber test and infra red spectroscopy.

From viscosity experiments, we have been able to arrive at a rough molecular weight of the shea latex which indicates that the solidified latex is a macro molecule.

It has also been found out in this research project the solvent mixture ratio for separation of the impurities in the shea latex and we have also worked out the various Rf values for the shea latex. The shea latex has been characterized, some of its physical properties have been determined, so that in future it can be easily distinguished from latex of other trees on the basis of some of its physical properties.

It is impossible to propose any structure for the solid component of shea latex from this preliminary analysis, this is because for an authentic structure to be suggested, these results ought to be combined with mass spectrometric measurement and micro analysis. Unfortunately due to the short period of time within which the project was undertaken, results from mass spectrometer could not be obtained.

However, combination of the results of I.R. and N.M.R. analysis of the solidified latex leads to the conclusion that the solidified latex belongs to the group of long chain unsaturated hydrocarbon macro molecule.

4.2 SUMMARY

Shea butter tree latex is mainly a mixture of long chain unsaturated hydrocarbon molecule and a resinous material. The molecular weight of shea tree latex is roughly 45,827.

The best solvent mixture for chromatographic separation has been worked out.

The resinous material has been noted to be probably responsible for the rubbery nature of shea latex and it is probably the component of shea latex that imparts many of the good qualities associated with the wood of shea tree in furniture, boat construction, mortar carving and to the fact that the wood is termite proof.

It is also known that shea latex is used locally as gum, this is probably due to the presence of this resinous extract.

Estimation of percentage metal contents was made by Flame Photometer and Atomic Absorption Spectrophotometer. Most of the metals are found in trace quantities.

Infra-red and N.M.R. Spectroscopic analysis gave results that are similar to classical non-instrumental analysis.

4.3 SUGGESTION FOR FURTHER WORK

The Author has attempted to provide a general preliminary analysis of the latex obtained from shea tree latex.

In the Author's report it is given that some of the properties of the latex and the wood of the tree can be attributed to a resinous acetone extract obtained from the latex. It is therefore necessary to further investigate the nature of this extract and provide a possible structure. This should be followed by an attempt to synthesise the compound in the laboratory such synthesised compound should be tested for quality, and an attempt to improve the quality be made if it comes out to be of poor quality.

Considering the Federal Government economic stabilization measures among which is the need to encourage the use of local raw materials for our local industries, it is further suggested that a research orientation toward obtaining the gum from shea latex in commercial quantity should be anticipated.

1. Lenlid, C., Introduction to Botany of tropical crops, 1976, 156, Longman, London.

2. Ghurbahi, A.H and Ajulo, E., 9th Annual report Nig. Stored product research Inst. Bulletin 1973, 55-62.

3. Andre, E. Inst. Recherche Huilles, Palme et Oleagineaux Paris, 1947, 2, 546-551.

4. Hoffet, G.L.; Spring, F.S., J. Chem. Soc. 1934 d, 1583 -85.

5. Bauer, K.H.; Umbach, G., 1932, 65B 859 - 62.

6. Dinsmore, R.P., Ind. Eng. Chem., 1926, 18, 1140-1145.

7. Kerslain, J. Ann Nutrition and aliment, 1949, 3, 459 - 69.

8. Barrow, G.M. "Physical Chemistry" 1973, 749, third edition, Tokyo.

9. Robert, S.S.; Clayton, G.B.; Terence, C.M.; "Spectrophotometric Identification of organic compounds" 1974, 163 third edition. New York.

10. Vogel, A.L. "A Textbook of Quantitative In-organic Analysis" 1971, 879, Third edition Longman London.

11. Wake, W.C.; The Analysis of rubber and Rubber-like polymers, 1969, 15, New edition, Maclaren, London.

12. Huggins, M.L., J. Amer. Chem. Soc., 1946, 64 2716.

13. Silverstein, R.M.: Bassler, C.G.; Morill, T.C., "Spectrometric Identification of organic compounds". 1947 73 - 83 Third edition, New York.

14. Olaiboye, S.O., "An Investigation into Acacia Sie berriana", M.Sc thesis submitted to Chemistry Department, Ahmadu Bello University, Zaria, 1981, 70.

15. Staudinger, Gummi Ztg, 1926, 40 1095.

16. Kirchoff, F.K, U. Gummi, 1960, 4, 190.

17. Stern, M.J., India Rubber J., 1906, 106 449 - 491.