CHEMICAL ANALYSIS OF SOME PROCESSED FOODS

BY

ODUOZA, FRIGIDIAN CHIKE
B.Sc, Biochemistry (University of Nigeria)

Thesis submitted in partial fulfillment of the
requirements for the degree of MASTER OF SCIENCE.

DEPARTMENT OF CHEMISTRY (ANALYTICAL CHEMISTRY)
FACULTY OF SCIENCE,
AHMADU BELLO UNIVERSITY,
SAMARU- ZARIA, NIGERIA.

JANUARY, 1981

D E C L A R A T I O N

"I hereby declare that all the work in this thesis is my work and that it has not been presented elsewhere as a requirement for a degree".

F. C. ODUOZA

20/2/87
DATE.

THESIS RECOMMENDATION

We hereby recommend that the thesis prepared by Mr. ODUOZA, F.C. titled Chemical Analysis of Some Processed Foods. be accepted in partial fulfilment of the requirements for the degree of M.Sc. Analytical Chemistry.

Internal Examiner

Date

External Examiner

Date.

D E D I C A T I O N

Dedicated to my parents, Mr. Peter O. Oduoza and Mrs. Martina B. Oduoza and also to my sister Chinyere Oduoza.

ACKNOWLEDGEMENT

I am grateful for the assistance and particularly for the encourangement given by my project supervisor, Dr. S.A. Thomas throughout the duration of my work. He was very kind and attended to my problems wherever and whenever consulted. I am also indebted to him for the critical review of my manuscript. Professor U. D. Gomwalk, the Head of Department of Chemistry and Dr. Kirpal Singh the Coordinator of analytical chemistry were also of immense help throughout the period of the course.

Grateful acknowledgement is made to my parents Mr. Peter O. Oduoza and Mrs. Beatrice M. Oduoza for financing this course and to my sister Chinyere for all the interest she showed in this work. My thanks is also due to my dear Nanlop L. Samuel for all her invaluable advice and encouragement during the rough period of my programme. She was nice to me.

The laboratory staff contributed in no small measure to the success of this work. Messers Smith, O.K. Abubakar and Yisa deserve a special thanks for their assistance in various ways. The Institute of Agricultural Research Library Staff were also very cooperative in supplying most of the literature and deserve my commendation.

To everybody else who contributed to the success of this work, I say well done. It is impossible to mention all the names.

Finally and above all God was very kind to me in eliminating all the obstacles encountered throughout the duration of the programme. I will praise him forever.

F. C. ODUOZA.

ABSTRACT

Analysis was performed on some processed foods namely Vegfru Tomato Paste (Factory Sample), Salsa Tomato Paste and Vegfru Tomato Paste (Shop Shelf Sample). Others were French Orange Pellorce and Nigerian Orange Juice, All the samples were canned. Two of the samples Salsa Tomato Paste and French Orange Pellorce were imported products while the rest were processed and canned in Nigeria. The samples were purchased from the shop shelves in Zaria except the Vegfru tomato paste (factory sample) which was obtained from the factory soon after processing.

They were analysed for Moisture, total solids, Ash, Fat, Sugar, Starch, Nitrogen, Protein, Crude fibre and Tannin, They were also analysed for inorganic elements which include Lead, Copper, Calcium, Magnesium, Sodium, Potassium, Phosphorous, Iron and Tin,

The imported samples were compared with the ones processed and canned in Nigeria for the above constituents. Their values did not differ significantly except in a few cases. However, Salsa tomato paste and the Nigerian Orange juice were relatively more contaminated with heavy metals compared to the other samples. The shop shelf sample of Vegfru tomato paste was also found to be more contaminated than the factory sample and in most cases the latter had higher nutritional values in terms

of proximate food composition.

The results al3o showed that pastes and orange products analysed were generally of similar qualities with other samples analysed and reported in the literature with the exception of the French orange pellorce which showed some appreciable deviations. Pre-digestion with Nitric acid (6%) up to 100 minutes proved a more efficient method for the determination of phosphorus compared to the other conventional methods employed.

Individual tins of each foodstuff were chosen randomly and it was found that in most cases they were fully representative of the whole foodstuff.

TABLE OF CONTENTS.

		PAGES.
Declaration		I
Thesis Recommendation		II
Dedication		III
Acknowledgement		IV
Abstract		VI
List of Tables..		VIII
Graphs		IX
Research Objectives		X
CHAPTER I - INTRODUCTION		
1.1	Introduction	1
1.2	Tomato Processing	3
1.3	Orange Processing	9
1.4	Limitations of Canning ..	13
1.5	Storage and the influence on proximate composition ..	17
1.6	Minerals in Canned Foods ..	21
CHAPTER II - MATERIALS AND METHODS.		25
2.1	Description of Samples ..	25
2.2	Sample Preparation ..	26
2.3	Moisture Determination ..	27
2.4	Total solids Determination ..	28
2.5	Determination of Ash ..	28
2.6	Determination of Nitrogen & Crude Protein	30
2.7	Determination of Crude Fat ..	32
2.8	Determination of Sugar ..	33
2.9	Determination of Starch ..	36
2.10	Determination of Crude Fibre	38
2.11	Determination of Tannin Content	40
2.12	Determination of Calcium ..	45
2.13	Determination of Copper ..	47

2.14 Determination of Magnesium. .. 48
2.15 Determination of Lead 50
2.16 Determination of Iron 51
2.17 Determination of Tin 52
2.18 Determination of Potassium .. 54
2.19 Determination of Sodium .. 55
2.20 Determination of Phosphorous .. 56

CHAPTER III. - RESULTS AND DISCUSSION.

3.1 Moisture Content
3.2 Total Solids Content 63
3.3 Ash Content 66
3.4 Liqid Content 70
3.5 Sugar Content 73
3.6 Starch Content 75
3.7 Nitrogen Content 76
3.8 Protein Content 77
3.9 Crude Fibre Content 78
3.10 Tannin Content 80
3.11 Lead Content 81
3.12 Copper Content 83
3.13 Calcium Content 84
3.14 Magnesium Content 85
3.15 Sodium Content 86
3.16 Potassium Content 88
3.17 Iron Content 89
3.18 Tin Content 91
3.19 Phosphorpus Content 94

CHAPTER IV. CONCLUSION AND SUGGESTIONS FOR FURTHER WORK 99

REFERENCES 104

LIST OF TABLES

Table Headings	Page.
1. Moisture determination	63
2. Determination of Total Solids	66
3. Ash Determination	68
4. Lipid determination	70
5. Sugar determination	73
6. Starch determination	75
7. Nitrogen determination	76
8. Protein determination	77
9. Crude Fibre determination	78
10. Tannin determination	80
11. Lead determination	81
12. Copper determination	82
13. Calcium determination	84
14. Magnesium determination	85
15. Sodium determination	86
16. Potassium determination	88
17. Phosphorous determination	95
18. Iron determination	89
19. Tin determination	91

G R A P H S.

Page.

1. Lead Calibration Curve.. 108
2. Copper Calibration Curve 109
3. Calcium Calibration Curve 110
4. Magnesium Calibration Curve 111
5. Sodium Calibration Curve .. .. .112
6. Potassium Calibration Curve 113
7. Phosphorous Calibration Curve 114
8. Iron Calibration Curve 115
9. Tin Calibration Curve 116
10. Starch Calibration Curve 117
11. Pre-digestion with Nitric acid - Comparative Curve 118
    for all samples .. ..
12. Pre-digestion with all acids - Comparative curve for
    all samples .. .. .119

Research Objective

Tomato pastes are used mainly in Nigeria for the preparation of stews and soups, while orange juices are often taken as light refreshments. Much of these products are imported while in recent years some have been processed and canned locally.

Analysis of these products in the Nigerian market have not been reported and as such it is not possible to ascertain whether locally canned products are comparable with imported ones.

In this work titled "Chemical Analysis of Some Processed Foods" some tomato pastes and orange products, imported and processed locally will be analysed to:-

i. determine the food value and content;
ii. determine the extent of contamination due to heavy metals;
iii. compare immediate factory products with shop shelves samples where possible;
iv. check whether any individual tin of each foodstuff chosen randomly is fully representative of the whole foodstuff;
v. investigate the mixed-acid and dry-ashing methods in the determination of phosphorous.

Products manufactured locally will be compared with the imported ones in terms of their major constituents, and appropriat

recommendations made to the authorities in charge of local manufacture and importation. The results of this analysis will be compared with those analyses recorded in the literature.

CHAPTER ONE

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

1.1. Introduction:

The ability to extend the period of availability of foods and food combinations in preserved forms that retain their nutritive value and palatability has improved man's health, added variety to his diet and reduced the time for food preparation. The technology of processing has greatly expanded the farm produce market and the increased need for processed foods has resulted from the rising standard of living, the desire for a more diversified diet the year round, an expanding urbanisation and an increase in population.

Food processing has many goals. Perishable foods are preserved in a stable form that can be stored and shipped to distant markets all year round. The basic preserving processes are canning, freezing, dehydration, salting, pickling and freez drying (Luh. and Woodroof 1975).

Food preservation is designed to prevent undesirable changes in food and food products. Such changes can be caused by the invasion and growth of micro-organism or by chemical, physical and biochemical reactions of the compounds present in the food itself. Examples of undesirable chemical changes include oxidative rancidity of fats and oils, loss of ascorbic acid and other vitamin through oxidative degradation

of pectin and discoloration. The flavour, colour, texture and appearance of the foods can also be affected by the methods and conditions of processing. (Luh and Woodroof, 1975).

Growth of undesirable micro-organisms in foods in addition to lowering the quality of the food can produce poisonous substances. Thus in any processing method both the growth of undesirable organisms and chemical, physical and biochemical reactions of the food itself must be considered.

Food manufacturers are realising the value of close control of the raw as well as the finished products. Many finished and raw food materials are being bought and paid for on the basis of their analyses. The standardisation of many of the food products now on the market has required the establishment of analytical control laboratories in the plant. The interest in the preparation and marketing of foods, retaining most of their original flavour, colour and nutritive value and in the development of new products has resulted in the need for food chemists with wider analytical training.

The division of the food industry may be made in various ways. One of the simplest is to divide the industry into the functions of raw material acquisition, manufacture and distribution. Under such a division the technologies of farming,

orchard management etc constitute raw material acquisition, manufacturing functions include the numerous unit operations and processes that may be considered to be the core of food technology. Distribution becomes involved in product form, weight and bulk, storage requirements and storage stability.

1.2. Tomato Processing:

Requirements of the canning industry for a variety of tomato relate to its appropriate size, skin toughness, wall thickness and cavity formation inside the fruit. The skin should be easily detachable on scalding. The common species that satisfy most of these requirements are Lycopersicon esculentum, Lycopersicon pimpinellifolium, Lycopersicon peruvianum, Lycopersicon glandulosum, Lycopersicon pissisi and Lycopersicon hirsitum.

Varieties should be chosen that are well adapted to the conditions under which the crop is to be grown and that are acceptable to the market for which they are intended. To select the best variety for any given purpose, season or locality, the past performance of the variety when grown in the region, the climatic characteristics of the area in which the crop will be grown and the qualities of the tomato desired should be considered. No one variety has been developed that has adaptability wide enough to produce the best yields of high quality tomatoes under all the conditions in which tomatoes are grown.

Harvesting, Storing and Transporting:

Great care must be observed in harvesting, transporting and storing for raw materials than for canning, because the former are not peeled. They should be transported to the plant without delay and utilised soon after arrival at the plant.

An important requisite to success in tomato products manufacture is the use of sound raw material (Luh and Woodroof 1975). The manufacturer must be particularly careful in the inspection of deliveries of tomatoes following heavy rains or during prolonged periods of damp weather. Rains cause splitting of the fruit, with subsequent rapid development of mold. Higher mold counts, worm and insect fragments are the most frequent cause for rejection or condemnation of tomato products.

The purchase of tomatoes on the basis of U.S. grades has been followed in some canneries. As defined by the Bureau of Agricultural Economics of the U.S.D.A; U.S. No.1 shall consist of tomatoes which are firm, ripe, well coloured and formed, free from molds and decay, damage caused by growth cracks, worm holes, cat faces, sun scald, and free from injury caused by freezing, mechanical or other causes. U.S. No.2 is defined as tomatoes which do not meet the requirements for the No.1 grade, but which are ripe and fairly well colored and which are free from serious damage from any cause. Culls are tomatoes which do not meet the requirements of No.1 and No.2 grades.

Washing:

The tomatoes should be thoroughly washed before sorting. Simple agitation in water is not satisfactory, because tomatoes often carry, in cracks and in the stem cavity, mold filaments which agitation does not dislodge and which appear later in the finished product.

The first requirement of a satisfactory tomato washer is water under heavy pressure driven against the tomatoes in sprays. Agitation during spraying is very essential.

Stemming:

The "Stem out" unit is used to remove the stems from tomatoes without hand labour operations. They are then sorted out carried on a broad and slowly moving belt before the sorters who remove unfit material and permit the sound fruit to pass over the end of the belt to the pulping machines. Some of the tomatoes removed by the sorters may be trimmed, and the sound portions of the fruit salvaged. The canner however, must not be too zealous in his attempt to salvage by trimming, or he may badly damage the quality of the finished product.

Pulping:

The washed, sorted and trimmed tomatoes are converted into pulp by a machine commonly known as a "cyclone" or pulper. The machine usually consists of a heavy monel, stainless steel in

form of a half cylinder which forms the lower half of the cylinder of the pulping machine. Heavy paddles revolve at a high speed within the cylinder and the tomatoes are broken by impact of the paddles or by being thrown against the walls of the pulper. The pulp and juice pass through the screen into a tank, and the skins, seeds and fibre pass out through an opening at the lower end of the pulper. The tomatoes enter the pulping cylinder through a hopper usually fed by a continuous conveyor and the mixture of pulp and juice is pumped to the concentration kettles or other equipment.

Concentrating the Pulp:

The raw pulp is evaporated to the desired consistency before canning. Pipes through which the pulp is conveyed should be of material that does not destroy the quality of the product. Stainless steel is preferred for pumps, pipelines and other such equipment. During concentration open kettles are used and are heated by rotating stainless steel coils. Such coils will under normal conditions reduce a charge of 500 gallon of pulp to one half its original volume in 35 to 45 minutes or less.

Vacuum pans are used to concentrate the tomato pulp. Their advantage is the reduction of the boiling point to 160°F or less making it possible to retain the colour and flavour of the tomatoes to a remarkable degree. In some cases double

effect or triple effect vaccum pans are used to increase output and to conserve steam. The first stage is designed to evaporate tomato pulp from 5% to 18% solids, and then the second stage evaporates it to 25% solids at a lower temperature. To prevent foaming and sticking of the pulping to the coils, some plants add a small amount of cotton-seed oil to the kettle, so that as the pulp rises during the filling of the kettle, the sides and coils are coated with oil. Silicone antifoaming agents in a concentration of a few parts per million will prevent foaming. Solids concentration monitored by a computer showed that although inflowing pulp varied in solids concentration, the product solids concentration was stable (Luh and Woodroof 1975), it is important to obtain a finished product of uniform composition and to stop the boiling process at the desired solid content. Most canners now determine the end point by use of a refractometer which is rapid, dependable and accurate. This can be achieved after a high speed centrifugation of a small sample in a specifically designed instrument for 20 minutes.

Finishing:

The finisher consists of a horizontal cylinder made of a fine sieve of stainless steel inside which are heavy paddles that revolve rapidly, causing the fine pulp to pass through the screen and the pieces of skin, seeds and fiber to pass out at

the end of the machine. The holes in the finisher screen are commonly 0.027 to 0.033 inch in diameter.

The process of heating the pulp at a specific temperature is known as blanching and is aimed at expelling air and gases, inactivation of enzymes and thus arresting changes in flavour. It is also aimed at softening the product so that more may be filled into the container. (Amos et al, 1962). Proper blanching by removing occluded gases reduces strain on the seams of cans during processing, particularly where the filled cans are not thermally exhausted.

Canning and Sterilising:

After the processing, the pulp is filled into metal containers which are conveyed by automatic runways through washers to the point of filling. Prior to filling they are cleaned by hot water steam or air blast. This mechanical method of filling ensures that the same quantity is maintained in all cans. Usually a vacuum of 12 to 15 inch Hg is kept in the can. Too high a vaccum in the larger can sizes will result in "paneling" or a drawing in of the sides of the can.

The filling is done at 170 - 185^{o}F and sealed hot. In sealing lids on metal cans, a double seam is created by interlocking the curl of the lid and flange of the can. Many closing machines are equipped to creat vacuum in the head space either

mechanically or by steam flow before lids are sealed. The sealed treatment in which foods are subjected after hermetic (air tight) sealing. During the process, micro-organisms which would cause spoilage are destroyed by heat. The temperature and time of processing vary with the nature of the product and the size of the containers. Acidic products like canned fruits with pH values between 4-5 are readily preserved at the temperature of boiling water using atmosperic steam or hot water cookers. Non acid products like tomato purees require higher temperature for sterilisation and are processed in steam tight pressure cookers - "retorts" or in continuous pressure cookers"- usually controlled by automatic devices. In general, the length of the process depends on the processing temperature; the higher the temperature the shorter the time required.

After the "process" containers are cooled quickly to prevent over cooking. This is done by conveying the containers from the cooker to a rotary cooler with a cold water spray.

1.3. Orange Juice Processing:

There are several varieties of oranges used for juice, the best known of them bearing such names as Homosassa, Parson Brown, Hamitin Jaffa and the most popular the Valencia (Potter 1968). These varieties differ in their growing season, resistance to frost and in their flavour, colour and acidity of the juice and in other respects.

The sweet orange (Citrus Sinensis) occupies a dominant position in the citrus industry, for no other, fruit is so universally liked and consumed. It is a native of China and is now cultivated in many tropical and subtropical regions where climatic and soil conditions are favourable.

Fruits to be used for juice production should be produced in the orchard, freshly picked, and should not consist of packing house culls that have stood too long in a packing shed. The latter fruit is apt to give juice of poor flavour and aroma. The fruit should also be well ripened. In most orange juice processing plants the oranges are delivered in bulk by truck and are stored in ventilated flat bottomed bins. Both practices result in some damage to the fruit particularly if it is allowed to stand in the bins several days before use. Best quality is obtained by using the fruit as soon as delivered and with as little rough handling as possible en route from the grover.

The anatomy of the orange is a most important consideration and based on this structure is the design of machines used to obtain the juice. The peel of an orange consists of an inner white spongy layer - the albedo. Beneath the albedo are the pulpy orange segments containing the juice and the pits. The different parts of the orange contain volatile flavour compounds - sugars, enzymes, acids, protein, fats, pigments and vitamins. The mixture of these ending up in the juice depends upon the

variety of orange, the growing condition, the degree of ripeness, and the method of extracting or squeezing the juice. (Potter, 1968). The flavour, colour, nutritional value and the storage stability of the juice depend upon this mixture of components in the juice.

Truckloads of oranges arriving at the processing plant pass through washing troughs and a sizing and grading room. A "soak" tank of water and detergent is used in the washing, then to a brush washer, where rapidly revolving brushes and sprays wash the oranges very vigorously and thoroughly. A strong antiseptic solution may be used in the soak tank preceeding the brush washing to reduce the numbers of micro-organisms. A damaged and moldy fruit is rejected. The whole fruit next goes to the line of citrus juice extractors. The oranges drop into individual cups and radial fingers come down on them causing the peel to be split. Then a cylindrical knife comes up and cuts a plug out of the bottom of the fruit. The juice is then squeezed through the hole from this plug. The plug and peel are pushed upward and ejected as waste. The machine is so designed that during the squeezing, oil from the peel runs down the outside of the fruit to be collected separately from the juice. The juice stream containing some pits and minor amount of pulp then goes to screens for their removal.

Juices differing in acidity and flavour may then be blended and sweetened by the addition of sugar. The juice at this point contains considerable air and oxygen. Oxygen will cause destruction of vitamin C, loss of colour and loss of flavour so the juice is next passed through a vaccum deaerator to remove air and oxygen. The juice is still perishable due to micro-organisms and to natural enzymes (Potter, 1968) it is therefor passed through a pasteurizer and is then ready for concentration.

Natural orange juice contains about 10.5% solids and this value could be increased by subjecting the juice to a low temperature vaccum evaporation. The cooled concentrated juice slush is then filled into cans and sealed. The cans are filled, and just before sealing the air in the head space is swept out with steam or inert gas. It is sealed in the usual double-seaming operation. The sealed cans are flash heated quickly in a pasteuriser, where they are vigorously rotated or agitated and are thus heated extremely rapidly. They are heated to about 195°F and are then rapidly cooled under sprays of cold water with vigorous agitation. The purpose of heating the juice in the can to about 195°F or in the flash pasteuriser to 190 to 240°F is to inactivate pectic enzymes particularly the enzymes responsible for curdling of the juice after canning (Cruess, 1958).

It is perfectly feasible to preserve orange juice by pasteurisation to 150°F, but juice heated to such temperature would show curdling (Coarse granulation) after canning and standing a few weeks. The purpose of sweeping air out of the head space of the can is to remove exygen that would later damage the flavour. In California enamel lined cans ("Citrus enamel") are used, in order to protect the flacour. In Florida plain tin cans are generally used as they appear to provide adequate protection for the Florida juice.

Orange juice in cans held at room temperature deteriorates rather rapidly in flavour and aroma. Therefore it is now customary to store canned juice in cold storage until it is to be shipped to the retail trade. It retains the flavour for several months with very little deterioration at 30 to 40°F. Because of the perishability of the flavour of canned citrus juices, the retailer should be supplied frequently with small deliveries of juice rather than infrequently with larger deliveries.

1.4. Limitations of Canning

Canning is a new preservation method for modern times. It was invented in France in the beginning of the nineteenth century but made its triumphant break through in the past hundred years (Cruess, 1958). There are few foods which are not generally canned in one kind of pack or another, cereals being the

chief exception. But canning had its precursors in such procedures as the cooking of jams, the embedding of meats in fat, and boiling in general, sometimes with the addition of vinegar.

Corrosion is responsible for a number of defects in canned fruits, and for a few in canned products of a non acid nature (Amos et al 1962). Its action takes several different forms, such as etching of the surface of the plate, internal rusting of the cans, dissolution of tin, discoloration of the contents and production of hydrogen gas. The last of these is the most important and has been the subject of extensive researches. The tin plates used for cans consist of sheets of mild steel coated with a layer of almost pure tin the thickness of which is about 0.0001 inch. Minor constitutents of the steel are carbon, manganese, phosphorous, sulphur, copper, silicon, nickel, chromium and a few other substances in minute quantities (Amos et al 1962). These are of considerable importance in connection with the rate of corrosion of steel in dilute acid or fruit juice, and the physical microstructure which is determined by the method of heating and annealing the steel.

When dilute acid comes in contact with tin plate two corrosion systems develop:

(a) an electrochemical couple between the tin and iron of the tin plate and

(b) corrosion within the steel base itself, some points acting as cathodes and others as anodes.

Tin occupies a higher position in the electrochemical series than iron, consequently might be expected to form the cathode, the iron being dissolved. In the presence of fruit acids - citric, malic and tartaric acids, a reversal of potential however occurs (Amos et al 1962) the tin going into solution and the iron being left relatively free from attack. The reversal is of great practical importance, as otherwise the exposed areas of steel in the seams, and on the heavily tooled parts of these ends, would be open to severe localised attack with rapid production of hydrogen and risk of perforation of the metal. In lacquered cans the metal exposed to the action of fruit acids is mainly iron (for at certain points the tin coating is almost invariably fractured) and consequently the composition of the steel base plate is of prime importance. Corrosion is less severe in cans made from plate which has a low phosphorous content and a high copper content. In plain cans, where the anode is extended to include a large area of tin, the dissolution of iron in the seams and on the heavily stamped portions of the can is greatly reduced. This consequently lessens the rate of formation of hydrogen and retards the rate of perforation. Tin, when dissolved in the contents of the cans, acts as an inhibitor of the corrosion of the steel base.

Oxgen hastens the rate of corrosion of tin but does not produce such a marked effect on the steel base plate. Corrosion of the tin-iron couple proceeds more rapidly at higher acidities. Hydrogen swells are very seldom in canned vegetables, but the presence of small amounts of hydrogen in the headspace can often be detected by analysis (Amos et al 1962).

When the ends of cans dome outwards as a result of hydrogen formed through corrosion of the container they are known as "hydrogen swells". The contents of such cans are satisfactory for human consumption, but the blown appearance of the ends makes them unmarketable. As the formation of hydrogen is due to the interaction of the metal of the container with the solid and liquid contents, three methods of preventing or retarding this action may be studied:-

(a) the container may be made less corrodible

(b) an effective barrier of lacquer may be interposed between the metal of the can and the acid contents.

(c) the contents may be made less corrosive.

While tin cannot be regarded as a metal which exercises a serious physiological effect when taken in small quantities every effort should be made to prevent contamination of canned foods by tin from the containers. The whole matter has been the subject of reconsideration by the foods standard committee

who proposed that a concentration of 250ppm should be recognised as the limiting concentration of tin above which the product may become "potentially injurious to health" (Amos et al 1962). The recognised limit in the U.S.A. is 300ppm. The tin contents of fruits and vegitables packed in lacquered cans and stored at normal temperatures seldom exceed 40mg per kg even after long storage, post lacquered cans show very much lower figures. Fruits in plain cans do not often contain more than 100mg of tin per kg and the same applied to most vegetables. The tin dissolved by the action of the fruit or vegetable acids is not distributed evenly throughout the content of the can, but is concentrated more in the solid than in the liquid portions (Amos et al 1962). A more recent work by Dicknson and Raven has shown that modern cans are less likely to give rise to high tin contents.

1.5. Storage and the influence on proximate composition

The permanent seal of the container protects the food from changes in moisture content during storage. The quantities of the proximate food components - total solids, ash, fat, protein, crude fibre, and carbohydrates as measured by accepted methods of analysis would not be expected to change during the storage of canned fruits and vegetables (Harris and Von Loesecke, 1971). As a consequence the influence of storage on proximate

composition has not been extensively investigated. In the more acid fruits, hydrolysis of sucrose and other disaccharides producing monosaccharides accompanied storage. Such changes should not alter the nutritive value of the product. The influence of storage on the amount and quantity of proteins in canned fruits and vegetables has received little attention. Non enzymatic browning reactions, which involve organic acids, cabohydratcc ; and amino acids varies with conditions. It appears that changes of nutritional significance taking place during storage of canned fruits and vegetables primarily affect the minor components - the vitamins.

A review of the literature yielded only a few publications showing the specific influence of storage under commercial conditions of merchandising on the chemical composition of frosen foods. A rather extensive investigation of the temperature to which frozen foods are subjected during commercial storage and marketing was made by the Western Utilisation Research branch of the United States Department of Agriculture. Changes in composition occuring during storage vary from product to product as well as with the type of packaging. The effects of storage for even short times at unfavourable temperatures are cumulative (Harris and Von Loesecke 1971). The extent of dehydration should be influenced by time in storage, temperature,

humidity in storage area, as well as by the type of packaging material. Although the data on changes in concentration of total solids or other proximate components during storage are scanty, there is no reason to believe such changes would influence nutritive values. The mineral content should not be altered by storage (Harris and Von Loesecke 1971). Except under very unusual conditions no appreciable changes occur in the mineral content of grain and its products during storage. It has been shown by Moxon and Rhian (1963) however that grain grown on seleniferous soils may lose as much as 73% of its original selenium content during storage. The loss appears to be in the form of volatile selenium compounds present and on the temperature of the grain. It is possible for the percentage of total mineral matter in grain or its products as measured by the ash content, to increase because of the loss of other constitutents.

The period during which processed foods will retain acceptable quality is important to all who manufacture, transport, store or use them. Canned, dried, frozen or preserved foods are normally held from a few weeks to a year or more before being consumed. Factors which determine the storage life of processed foods include the type of product, method of processing manner of packaging and the temperature and humidity of storage.

Each item has a certain storage potential. This may be used up quickly by inadequate packaging, high temperature or adverse levels of humidity or it may be extended over long periods by selection of conditions which will protect the quality of both product and container (Luh and Woodroof 1975).

The rapid expansion and diversification of food storage in the decade after 1940 revealed that many of the relationships between products and storage conditions had not been sufficiently defined. Characteristics of stored foods on which more information was needed included colours, flavours, textures, aroma, vitamin content, moisture content, staleness, rancidity and overall acceptability. Additional data were also needed on the resistance of metal containers to corrosion, delamination, discoloration and loss of vaccum. In order to obtain such information a program of research on storage of representative processed foods was initiated at the Georgia Experiment Station in 1945. Projects included the storage of confections of many kinds, canned or cured, canned vegetables, preserved fruits and other types of commercial items. The studies showed a direct relationship between the stability of products and containers and storage temperatures and humidities.

1.6. Mineral in Canned Foods.

Although mineral matter is seldom gained or lost in storage, the availability of the element phosporous, nutritionally important to animals and man appears to increase in storage (Harris and Von Loesecke 1971). This is as a result of the action of the enzyme phytase on phytin to yield phosporous compounds.

The minerals which are present in fairly large quantities are:

(i) The base forming elements: Calcium, magnesum, sodium and potassium and

(ii) the acid forming elements: phosphorous, chlorine and sulphur (Luh and Woodroof 1975).

The principal minerals present in microquantities are iron, copper, cobalt, manganese, zinc, iodine and molybdenum. There are indications that selenum and chromium also function in metabolic systems.

Minerals can be affected by chemical or physical treatments. Some may be oxidised to higher valencies by exposure to oxygen; however, there is convincing evidence that this affects their function. Blanching of vegetables may result in losses of water - soluble components including minerals, vitamins, amino acids and carbohydrates. High temperature,-short time blanches

are more conducive to retention of such nutrients. Calcium is generally absorbed by vegetables during blanching, the extent of the increase depending upon the kind of vegetable, the hardness of the blanching water and the length of blanching time (Luh and Woodroof 1975). Iron is often in the water soluble form and thus may be leached.

The term "Contaminants" refers to undesirable materials which have been added inadvertently before, during or after processing of food (Pearson 1976). Vegetables may be contaminated by agricultural sprays and trace elements may get incorporated into the food due to attack on the processing plant or container. Cumulative poisoning due to ingestion of food containing elements such as lead or arsenic over a long period is probably rare. In addition to the action on the body, however, a few elements tend to have a detrimental effect on the quality or nutritive value of the food, e.g. Copper causes off flavours in milk and dairy products and tends to destroy vitamin C in fruit products. Copper in high concentrations is very toxic to plants, so the danger of poisoning from this source is minimal. High concentrations of copper can be found in soils derived from copper containing minerals and in areas where Bordeau ($CuSO_4 + CuCO_3$) sprays have been

used for disease control over extended periods of time. Vegetables are intermediate in copper content among the conomic plants ranging from 2.5 to 5.5 ppm in potato tubers and from 15 to 25 ppm in tomato fruits (Reuther and Labanaukas 1966).

Lead is a physiologically nonessential element to plants and animals. The principal sources are the air - from industrial emissions, gasoline combustion (tetraethyl lead), and natural sources - soil, mineral dust, volcanic and marine acrosols, and smoke from wood and fossil fuels. Plants can take up lead by root and foliage absorption. The element is retained in the cellular membranes. Radish plants growing in 12,000ppm lead soil contained 550ppm on a dry weight basis in the roots and 130ppm in the tops, whereas the control plants contained only 0.8 to 2.3ppm load (Dedolph et al. 1970).

Near highly traveled highways in Southern California, Page et al (1971) found that unwashed ripe tomatoes contained as high as 6.0ppm lead and that washing reduced the amount to 1.5ppm. Thomas et al (1973) concluded that the increased load content of canned foods in comparison to fresh foods was the result of contamination during processing or due to the release of lead from the soldered seams of the can.

In general, plants contain low quantities of arsonic, the roots accumulating more than the tops. Arsenic is quite toxic to plants, so they will not grow well in soils high in this elements. Hence arsonic salts, as well as organic arsenates such as mono and disodium methyl arsenates, and dimethyl arsonic acids, are used as general herbicides. The concentration in vegetables varies from 0 to 10ppm, depending upon the arsonic content of the soil (Liebig 1966).

CHAPTER TWO

MATERIALS AND METHODS

2.1. Description of Samples:

There were a total of five samples namely, Salsa, Tomato Paste, Vegfru Tomato Paste (Shop Shelf Sample), Vegfru Tomato Paste (Factory Sample), Canned Nigerian Orange Juice and Canned French Orange Pellorce.

Canned Salsa Tomato Paste: This sample is coded "Salsa" and is processed in Italy by LITHOLIT-NOCERA. The net weight is 94.300 7grams measured on an Analytical balance. The can is described as 8z short with a dimension of 211x300. The average weight of the content is 76.1228grams. Salsa tomato is a dark red and semisolid paste. It costs 25k per tin in the market.

Canned Vegfru Tomato Paste (Shop shelf): The sample is coded "Vs" and is processed in Gombe, Bauchi State of Nigeria by vegetable and food processing factory Gombe. The net weight is 89.4601grams and the average weight of the content is 68.2215grams. The can is similar in dimension to that for Salsa. Vegfru tomato paste is a bright red semisolid paste and it costs 25k per tin in the market.

Canned Vegfru Tomato Paste (Factory Product): This sample is coded "Vf" and was obtained directly from the factory soon after processing and canning. The net weight is 89.7021g. The can is similar in dimension to that for the Salsa Paste. It is a bright red, semi-solid paste and costs ₦14 per carton of 144 tins in the factory.

Canned Nigerian Orange Juice: This product is prepared and packed by Moon Enterprises (Nig) Company Box 1335 Ibadan - Oyo State of Nigeria. It is coded "NOJ" and has a net content of 44cl. It is packed in a large container of dimension 300x407. This juice is a uniformly liquid greenish yellow sample which is much denser than water namely 1.05g per dm^3. It costs ₦2.50 per can.

Canned French Orange Pellorce: This sample is coded "FOP" and is the product of Massy Essonne of France. It is packed in a large container of dimension 401 x 411 and weighs one kilogramme approximately. The content is slightly viscous and an admixture of liquid and semi-solid particles. It costs ₦4.50 per container.

2.2. Sample Preparation

All the samples except the immediate factory product of Vegfru were obtained from shop shelves. In all cases five tins of each sample were mixed together to obtain a quantity sufficient

for all the required determinations. For each sample the various determinations were carried out at least thrice and six times at a maximum. The mean determination was taken and the standard deviation from the maan calculated.

All the samples were stored in refrigerators to achieve a constant sample composition and to reduce microbial activity.

To examine how representative any individual tin was, determinations were also made using single tins of the different samples.

2.3. Moisture Determination:

This is normally carried out on the basis of loss in weight of sample due to drying at a temperature of about 100°C (Pearson, 1976). In thermal drying there is a maintenance of a differential between the vapour pressure of the substance to be dried and that of the atmosphere of the drying chamber. In practice a comparison is necessary and a drying time is specified which will bring the material to constant weight whilst leaving minute traces of tightly bound water. In spite of the difficulties, the overall simplicity of gravimetric drying is a great advantage and under controlled conditions can give satisfactory results.

Procedure: A suitable container was dried in the oven cooled in a dessicator and weighed. A thin sample of about 5g was spread in the container and weighed rapidly then dreied in an air circulation oven at 100 ± 1C to constant weight in 24 hours. It was then cooled in a dessicator and weighed.

Calculation:

$$\text{Moisture (\%)} = \frac{\text{Loss in weight on drying(g)}}{\text{Initial sample weight}} \times \frac{100}{1}$$

2.4. Determination of Total Solids:

The residue remaining after using a direct heating vaccum oven for dehydration of a sample is termed total solids (Morris Jacobs, 1938).

The procedure is similar to that for moisture determination at 100°C as recorded by Pearson, 1976.

Calculation:

$$\text{Total Solids(\%)} = \frac{\text{Oven dry weight(g)}}{\text{Initial sample weight(g)}} \times \frac{100}{1}$$

2.5. Determination of Ash:

The ash of a foodstuff is the inorganic residue remaining after the organic matter has been burnt away (Pearson, 1976). The ash obtained is not exactly the same in composition as the mineral matter present in the original food as there may be losses due to volatilisation or some interaction between

constituents. The ash figure can be regarded as a general measure of quality and often is a useful criterion in identifying the food.

The following precautions are normally taken during ashing in a muffle furnace.

(1) The presence of blackened particles may indicate an incomplete combustion hence it is necessary to choose a suitable temperature for the ashing process.

(2) It is important for the temperature to rise slowly to prevent losses if the samples suddenly catch fire.

(3) Periodic checks of the muffle furnace pyrometer are recommended.

Procedure: The crucible was preheated in a muffle furnace at about 500°C, cooled in a dessicator and weighed. 1g of the sample was transferred to the crucible, weighed and dried at 105°c. The crucible with the dry sample was then placed in a cold muffle furnace. The temperature was allowed to rise to about 550°c and the crucible with sample was left for 24 hours. It was allowed to cool, transferred to a dessicator and weighed.

Calculation:

$$\text{Ash (\%)} = \frac{\text{Ash Weight (g)}}{\text{Oven dry weight}} \times \frac{100}{1}$$

2.6. Determination of Nitrogen and Crude Protein

The Kjeldahl method for determining total nitrogen involves first heating with concentrated Sulphuric acid in a long-necked digestion flask (Pearson, 1976). The reaction is accelerated by adding sodium or potassium sulphate to raise the boiling point and catalysts containing usually copper, mercury or selenium. The oxidation causes the nitrogen to be converted to ammonium sulphate. After making alkaline with concentrated sodium hydroxide solution, the ammonia is distilled into either excess of boric acid or standard acid and is estimated by titration. For most routine purposes the crude protein in the sample is then calculated by multiplying the total nitrogen by an empirical factor. It should be borne in mind that such a figure for proten often includes some non protein nitrogenous substances.

Materials:

1. Catalyst mixture (a) anhydrous sodium sulphate (160g)
   (b) copper sulphate (10g)
   (c) selenium oxide (3g)
2. Concentrated sulphuric acid (20ml)
3. ~~Granulated zinc~~
4. Boric acid (1% m/v)

5. Screened methyl red indicator
   (a) methyl red (66mg)
   (b) bromocrosol green (99mg) in 100ml of ethanol.
   (c) thymol blue (1/mg)
6. Sodium hydroxide (40% m/v)
7. Hydroehloric acid (N/70). (0.014M)

Procedure: 0.25g of sample was transferred to a 100ml Kjeldahl digestion flask. 1g of catalyst mixture and 6ml of concentrated sulphuric acid together with a few chips of pumice stone were added. It was carefully digested over an electric heater in the hood initially with low flame until frothing subsided and then at a higher temperature until contents were clear greenish. The digestion was continued for a further 60 minutes after which the flask was then cooled. 15ml of distilled water was added and contents were quantitatively transferred to a 50ml volumetric flask using distilled water torinse but leaving the pumice stones behind. The volume was then made up with distilled water.

10ml of the digest was transferred into the Markham semi-micro nitrogen still and 10ml of 40% sodium hydroxide solution was added to the digest with caution. The ammonia liberated was steam distilled into a 5ml Boric acid solution containing 4 drops

of mixed indicator in a conical flask. The indicator turned green and distillation was continued for 2 more minutes.

The distillate was removed and titrated with the standard Hcl (N/70) (0.014M), an end point being reached when the indicator changes from green through grey to definite pink. The amount of acid consumed was noted. A blank run was made and the burettle reading substracted from the volume of acid used initially.

Calculation:

$$N_2(\%) \text{ in the sample} = \frac{\text{Corrected titre (ml)} \times 14 \times 5 \times 100}{1000 \times 70 \times \text{Sample weight (g)}}$$

Crude Protein (%) = 6.25 x Nitrogen (%)

2.7. Determination of Crude Fat by Soxhlet Extraction technique

The lipid content of a biological material can be estimated by directly extracting the dry material exhaustively using a suitable lipid solvent eg. petroleum ether ($40^{o}c$ - $60^{o}c$), diethylether in a convenient continuous extractor such as soxhlet, Bolton or Bailey Walker type (Pearson, 1976). Direct extraction gives the proportion of free fat.

Procedure: 5g of the sample powder was taken into a thimble of knwon weight (W_1). The sample and thimble were weighed (W_2). The thimble with sample was placed inside a soxhlet extractor. 300ml of diethylether was poured into a 500ml round bottom ground joint flask, which was placed in electricaly connected

heating mantle. The mantle was switched on and the heat increased carefully and slowly until the solvent boiled. The condensed solvent vapour which was collected in the thimble dissolved the lipid in the sample. The extraction process was continued for 6 hours and the thimble with contents was removed, dried in an oven at 50^{o}c for 24 hours cooled in a dessicator and weighed (W_3).

Calculation:

$$\text{Lipid } (\%) = \frac{100\ (W2 - W2)}{W2 - W1}$$

Alternatively the 500ml round bottom flask was weighed empty then again after extraction, on evaporation of ether in a warm water bath and leaving in a vaccum oven at 40^{o}c for 30 minutes. If W = gram residue in ether extract then

$$\text{Crude fat}(\%) = \frac{W(g) \times .100}{\text{Sample weight}(g)}$$

2.8. Determination of Sugar

The non stoichiometric volumetric method of Lane and Eynon (1923) is often the most convenient method for determing reducing sugars. The volume of sugar solution required to reduce completely 10 or 25ml mixed Fehlings solution is determined using methylene blue as the redox indicator for assessing the end point. A minute excess of reducing sugar solution is

necessary for the reduction of the indicator itself (Pearson, 1976).

The sugar solution should be neutral and preferably clarified (Lead and Calcium salts should be removed with potasium oxalate). The concentration of the sugar solution should be such that the titration is 15-50ml (this can be achieved usually with 0.1-0.3g sugar present per 100ml for 10ml Fehlings solution and 0.25 - 0.8g for 25ml. The sugar solution is placed in a 50ml burette fitted with a pinch cork.

Materials:

(a) Fehlings' solution A and B
(b) Neutral Lead Acetate (10% m/v)
(c) Potassium oxalate (10% m/v)
(d) Methylene Blue (1%)
(e) Alumina Cream (Prepared by adding excess Ammonia in saturated alum solution).

Preparation of Sample: 12.5g of the sample was dissolved in water and 25ml of neutral lead acetate solution (10% m/v) was added. Some alumina cream was added and it was made up to 250ml in a volumetric flask. The mixture was shaken thoroughly and filtered. To 100ml of the filtrate was added 10ml of potassium oxalate (10%m/v), made to 500ml, shaken and filtered.

Preliminary Titration: 10ml of mixed Fehling's solution was pipetted into a 300ml conical flask and 15ml of the sugar solution was added from the burette. The solution was boiled on an asbestos covered gauze and further quantities of the sugar solution (1ml at a time) was added at 10-15 second interval to the boiling liquid until the blue colour was nearly discharged. 3 drops of aqueous methylene blue solution (1%) was added and titration was continued on the boiling liquid until the indicator was completely decolorised.

Accurate Titration: The titration was repeated adding before heating almost all of the sugar solution required to affect reduction of the copper. It was boiled gently for 2 minutes and 3-5 drops of the methylene blue indicator was added. The titration was completed within a total boiling time of 3 minutes. At the end point all the blue colour was discharged and the liquid was orange red. The proportion of the various sugars equivalent to 10ml of Fehling's solution are obtained from Munson and Walker table for calculating invert sugar (Pearson, 1976).

Calculation: Amount of sugar may be calculated by use of the formula

$$\frac{\text{Factor} \times 100}{\text{Titre}} = \text{mg of Sugar in 100ml.}$$

The factor was ascertained by reference to Invert sugar tables in which the factor for each litration from 15 to 50ml is given. The tables give the miligrams of sugar corresponding to each factor. If the reduction is complete on the addition of 15ml or less of solution the 100ml aliquot must be further diluted. If the reduction is not complete on the addition of 50ml, then more of the original sample must be taken for analysis.

2.9. Determination of Starch:

Starch is the major storage polysaccharide in plant materials and is widely distributed. Large and relatively constant amounts are present in roots, seeds and fruits but the concentrations in other parts of the plant especially the leaves are subject to diurnal variation falling to a minimum at night (Allen, 1974).

Starch can be determined by colorimetric measurement after forming the blue complex with iodine.

Reagents: (1) Standard solution (1ml = 1mg starch). This was prepared by dissolving 0.05g pure starch in 5ml of distilled water and adding 5ml of $HClO_4$(60% rapidly with stirring. This was allowed to stand for 20 minutes, transferred to 50ml volumetric flask and then diluted to volume.

(2) Perchloric acid (60%, W/V)

(3) Phenol red Indicator (0.1% solution in industrial spirit)

(4) N sodium Hydroxide

(5) Potassium Iodide (10% m/V)

(6) Potassium iodate (0.0125m)

(7) Acetic Acid (10% v/v)

Procedure: 0.25g of sample was weighed into a suitable test tube. 0.20g fine sand and 5ml distilled water were added and mixed thoroughly with a stirring rod. The tube was heated in a boiling water bath for 15 minutes to gel the starch. It was then cooled to 20° to 30°c and 5ml of perchloric acid (60%) was added while stirring. The tissue inside the tube was ground intermittently against the side of the tube with rod for 20 minutes. It was then transferred to a 100ml vlumetric flask and diluted to volume. It was mixed well and allowed to settle.

An appropriate aliquot of this sample mixture was transferred to a 50ml volumetric flask. A range of standards containing from 0.1mg to 2.5mg starch were transferred into 50ml volumetric flasks. From this point standards and sample were treated in the same way.

A few drops of indicator solution and sodium hydroxide were added until the solutions turned red. Acetic acid was added to destroy the colour followed by a further 2.5ml. 05ml Potassium iodide solution and 5.0ml Potassium iodate solution were added

with shaking and then diluted to volume.

The absorbance of each solutions was then measured at 680mm using water as a reference. The measurement was made in Unicam Sp 1805 ultraviolet spectrophotometer. A calibration curve of the standards was prepared and used to determine milligram starch in the sample aliquot. Blank determinations were also carried out in the same way.

Calculation: If C is mg starch obtained from the graph then

$$\text{Starch (\%)} = \frac{C(mg) \times \text{Solution(ml)}}{10 \times \text{aliquot(ml)} \times \text{Sample wt.}(g)}$$

2.10 Determination of Crude Fibre:

"Crude Fibre" is the organic residue which remains after the material has been treated under standardised conditions with light petroleum, boiling dilute sulphuric acid, boiling dilute sodium hydroxide solution dilute hydrochloric acid, alcohol and ether (Pearson, 1976).

The crude fibre consists largely of cellulose together with a little lignin. As the recovery of cellulose using the specified procedure seldom exceeds four fifths of that actually present, the crude fibre does not represent a measure of a specific group of substances. Also as the figure obtained tends to vary with the conditions employed it is important to adopt a standardised procedure in order to obtain consistent results. The method employed is that of Fertilisers and Feeding stuff

regulations (Pearson, 1976).

Reagents: (1) Diethyl ether

(2) Asbestos

(3) Sulphuric acid (1.25% v/v)

(4) Sodium hydroxide (1.25% v/v)

(5) Light petroleum (40-60°c)

(6) Alcohol - Industrial methylated spirit

(7) Hydrochloric acid (1% v/v)

Procedure: 3.0g of the sample was weighed, transferred to an extraction apparatus and extracted with light petroleum. The extracted sample was air dried and transferred to a dry 1000ml conical flask. 200ml of sulphuric acid (1.25%) was added to ordinary temperature and it was brought to boiling point. Asbestos was added and boiling continued for exactly 30 minutes maintaining a constant volume while rotating the flask every few minutes in order to mix contents and remove particles from the side. The acid mixture was then poured immediately into an already prepared Buchner funnel (Pearson, 1976) and subjected to suction. The suction was adjusted so that the filtration of the bulk of the 200ml was completed within 10 minutes.

The insoluble matter was washed with boiling water until the washings were free from acid. It was then washed into the

original flask by means of a wash bottle containing 200ml sodium hydroxide solution (1.25% v/v) and brought to boiling point. The flask was boiled for 30 minutes with the same precuations as before. It was allowed to stand for 1 minute and filtered immediately through a suitable filter paper. The insoluble material was transferred to the filter paper washed with boiling water, then with hydrochloric acid (1% v/v) and finally with boiling water until free from acid. It was then washed twice with alcohol and thrice with ether. The insoluble matter was transferred to a dried, weighed ashless filter paper and dried at 100°c to a constant weight. The paper and contents were then incinerated to an ash at a dull red heat and the ash was weighed.

Calculation:

$$\text{Crude Fibre}(\%) = \frac{\text{Loss of weight on Ignition}}{\text{Weight of Sample}} \times \frac{100}{1}$$

2.11. Determination of Tannin Content:

The modified Lowenthal's permomganate oxidation process (Pearson, 1976) was adopted.

This is based on the precipitation of tannine with gelatine in the presence of Kaolin and on the oxidation of tannins with acid permanganate. The method involves titration of the sample extract before and after the precipitation of the tannins with gelatine in the presence of Kaolin. The difference in the

titre values of the two titrations gives the tannin titre i.e. the amount of permanganate reduced by tannin. This differential approach is needed because substances other than tannins can also reduce the permanganate.

Reagents: (1) Indigo Carmine Solution: This was prepared by dissolving 1.5g indigo carmine in 1dm^3 water containing 50cm^3 concentrated sulphuric acid.

(2) Gelatine Solution: Was prepared by soaking 25g gelatine for 1 hour in saturated sodium chloride solution. The mixture was warmed until the gelatine dissolved. The solution was then cooled and made up to 1 dm^3 with saturated sodium chloride solution.

(3) Acid Sodium Chloride Solution: Was prepared by adding 25cm^3 concentrated sulphuric acid to 975cm^3 saturated sodium chloride solution.

(4) Kaolin (China Clay)

(5) Potassium Permanganate Solution (0.004m): Was, prepared by dissolving 0.632g of potassium permanganate crystals in 1 dm^3 of water.

(6) Sulphuric acid (98% m/m).

Methods: An accurately known weight of about 5g of each sample was boiled with 400cm^3 distilled water for 1 hour. The extract was filtered through cotton wool into a 500cm^3 volumetric flask, allowed to cool and made up to the mark with distilled water. The extract was labelled A.

40cm^3 of this extract was pipetted into 100cm^3 volumetric flask, 20cm^3 gelatine solution was added and the mixture made up to the mark with acid sodium chloride solution. The mixture was then poured into a conical flask containing 6g Kaolin and shaken for 15 minutes. This was filtered and the filtrate labelled B.

4cm^3 extract A = 10cm^3 extract B.

4cm^3 of extract A was pipetted into a large beaker, 10cm^3 of indigo solution was added and the mixture diluted to 300cm^3 with distilled water. This was titrated with 0.004m potassium permanganate solution from a burette. The colour changed from blue through green to yellow. The titre value was coded Xcm^3.

10cm^3 of extract B was pipetted into a large beaker, 10cm^3 indigo solution was added and the mixture diluted to 300cm^3 with distilled water. This was titrated with 0.004m Potassium permanganate solution as was extract A. The titre value was coded Ycm^3.

10cm^3 of the indigo solution was diluted to 300cm^3 with distilled water and titrated with the permanganate solution. This was taken as the blank for extract A.

4cm^3 acid sodium chloride solution was added to 10cm^3 indigo solution and diluted to 300cm^3. This was also titrated with the permanganate solution and taken as the blank for extract B.

The tannin titre was given as (X - blank for A) - (Y - blank for B).

Calculation:

1cm^3 0.2m Kmno4 = 0.0416g tannin (Pearson, 1976) so that 1cm^3 0.004m kmno4 = 0.000832g tannin. The amount of tannin = tannin titre x 0.000832g tannin.

$$\% \text{ age Tannin} = \frac{\text{Weight of Tannin}}{\text{wt of sample in 4cm}^3\text{extract}} \times \frac{100}{1}$$

Determination of Minerals

The minerals estimated were calcium, Magnesium, Copper, Lead, Tin, Iron, Sodium, Potassium and Phosporous. Calcium, Magnesium, Copper, Lead, Iron and Tin were determined by Atomic Absorption Spectrophotomety, Sodium and Potassium by Flame Photometry while phosphorous was determined by the Vanadomolybdate method.

Although it is possible with some readily soluble food materials to apply reagents directly to a solution of the food,

it is usually necessary to destroy the organic matter before mineral determination. Methods of combustion both wet and dry have been recommended by the AMC (1960a).

Technique and Principles of Atomic Absorption Spectrophometry

The use of flame absorption spectra instead of emission spectra was first proposed and developed by Walsh (1955). Atomic Absorption Sepctra are formed by the absorption of radiation of certain wavelengths by atoms whose electrons are in the ground state (Allen, 1974). 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 thus be used as a quantitative method of determining this number.

In practice a solution of the element is sprayed into a relatively cool flame in which the atoms tend to remain in the ground state. Radiation of a characteristic wavelength from a hollow cathode discharge lamp is passed through the flame and the decrease in intensity is measured using a monochromator and detector system. This decrease is related to the concentration of the element in solution.

One of the most important points in good atomic absorption practice is the need for correct treatment of the source lamps. They must be run at their specified currents.

The sensitivity of the ~~instrument~~ method is particularly high for some elements, notably magnesium, manganese and zinc owing to the very high proportion of atoms remaining in the ground state in the flame (Allen, 1974).

2.12. Calcium determination by Atomic Absorption Spectrophotometry

1. Wavelength of determination = 422.7nm.
2. Mode = A
3. Flame = Air-C_2H_2
4. Suitable ranges (ppm) = 0 to 40 parts per million.
5. Potential Interferences = Al, P, Si, S.
6. Control of Interferences = Addition of releasing agent ($LaCl_3$)

Reagents:

1. Calcium Standards:

Stock Solution - 1000ppm. This was prepared by diseolving 2.4973g dry Calcium Carbonate in about 200ml water containing 5ml concentrated Hydrochloric acid. It was heated to drive off carbondioxide cooled and made up to 1 litre. Working standards were prepared from the stock solution with concentration ranging from 0 to 100ppm and sufficient stock lanthanum chloride was added to the standards bringing the concentration of Lanthanum to 400ppm.

2. Lanthanum Chloride - 5000 parts per million obtained by dissolving 6.6837g $LaCl_3.7H_2O$ in water containing 1ml of 2m Hcl and diluted to 500ml.

3. Sulphuric acid (10%v/v).

Procedure for Sample digestion:

Mixed acid digestion was adopted involving the following reagents (Allen, 1974).

1. Perchloric acid (60% m/m)
2. Nitric acid (69% m/m)
3. Sulphuric acid (98% m/m)

Sample Preparation: 0.25g of air dried sample was weighed out into a 100ml Kjeldahl flask and 1ml Perchloric acid (60%), 5ml Nitric acid (69% and 0.5ml sulphuric acid (98%)were added. The flask was swirled gently and digested slowly at moderate heat increasing later. It was digested for ten to fifteen minutes after the appearance of white fumes. It was set aside to cool (the cold digest was colourless) and then poured into a 50ml volumetric flask and diluted to volume. Blank digestions were also carried out in this way. (It is necessary to point out that prolonged heating at the white fume stage will lead to drying out with low recoveries).

Determination: The wavelength of 422.7nm was selected and air and gas flows adjusted properly. The slit width and other settings as recommended for the instrument were employed. The hollow cathode lamp was given adequate time to stabilise. A calibration curve was then obtained from the standard range by setting the top standard to a suitable scale deflection and the oppm standard to zero deflection.

The sample solutions were carried out in the same way and subtracted were necessary.

Using the calibration curve it was possible to obtain concentration of calcium in the sample solution.

Calculation: If C = ppm Calcium obtained from the graph then

$$Ca(\%) = \frac{C(ppm) \times \text{Solution volume (ml)}}{10^4 \times \text{Sample wt.(g)}}$$

2.13. Copper determination by Atomic Absorption Spectrophotometry

1. Wavelength of determination = 324.8nm.
2. Mode = A
3. Flame = Air-C_2H_2
4. Suitable ranges = 0 to 5ppm
5. Potential Interferences = None significant.

Reagents:

1). Copper Standard: Stock solution = 100ppm. This was prepared by dissolving 0.3930g of $CuSo4.5H_2o$ in water and made up to

1 litre. Working standards were prepared from the stock solution with concentrations ranging from 0 to 1ppm and digest acids were added as appropriate to match the sample solutions.

Sample Preparation: The sample was prepared for determination as for calcium and the determination was carried out after adjusting to a wavelength of 324.8nm.

Calculation: If C = ppm Copper obtained from the graph then

$$C_u(\%) = \frac{\text{Copper(ppm)} \times \text{Solution Volume(ml)}}{\text{Sample weight}(g)}$$

The procedure for copper by Atomic Absorption is virtually free from interference and is straightforward provided the sample concentration is adequate. As little as $0.02 Mg ml^{-1}$ in solution can be detected with reproducibility up to 3%.

2.14. Magnesium determination by Atomic Absorption Spectrophotometry

1. Wavelength of determination = 285.2nm
2. Mode = A
3. Flame = Air-C_2H_2, Air Propane.
4. Suitable range = 0 to 3ppm.
5. Potential Interferences = C_a, $A1$, P, S_1.
6. Control of Interference = Addition of releasing agent ($Lacl_3$). Levels as low as 30 to 40 Mg magnesium can be determined.

Reagents:

1) Magnesium Standard:

Stock Solution - 100ppm Magnesium. This was obtained by dissolving 1.0136g of $MgSo4.7H_2O$ in water containing about 1ml $H2So4$ and diluted to 1 litre. Working standards were prepared from the stock solution with concentrations ranging from 0 to 5ppm. Sufficient $Lacl_3$ solution was added to the standards bringing the concentration of Lanthqnum to 400ppm. Digest acids were added to the standards as appropriate.

2). Lanthanum Chloride Solution, 5000ppm (Prepared as before)

3). Sulphuric acid (10% v/v).

Sample Preparation: The sample was prepared for determination as for Calcium and Copper and the determination was carried out after adjusting to a wavelength of 285.2nm.

Calculation: If C = ppm Magnesium obtained from the graph then

$$Mg(\%) = \frac{C(ppm) \times \text{Solution Volume (ml)}}{10^4 \times \text{Sample wt. (g)}}.$$

2.15. Lead determination by Atomic Absorption Spectrophotometry

1). Wavelength of determination = 283.3m

2). Mode = A

3). Flame = Air C_2H_2

4). Suitable ranges = 0 to 10ppm

5). Potential Interferences = None.

Reagents:

1). Lead Standard:

Stock solution - 100ppm lead. This was obtained by dissolving 0.1599g $Pb(No_3)_2$ in 20ml NHo_3 (1% $^V/v$) and diluting to 1 litre with water. Working standards were prepared from the stock solution with concentrations ranging from 0 to 10pp and digest acids were added as appropriate to match the sample conditions.

Sample preparation: 2 to 5g Sample was taken with 1 ml sulphuric acid (98%), 15ml Nitric acid (69%) and 2ml of perchloric acid (60%) in a 100ml Kjeldahl digestion flask. Digestion was carried out in a way similar to that of Calcium, Copper and Magnesium. The determination was carried out after adjusting to a wavelength of 283.3nm and adjusting air and acetylene flows.

Calculation: If C = ppm lead obtained from the graph then

$$Pb(\%) = \frac{C(ppm) \times \text{Solution Volume (ml)}}{10^4 \times \text{Sample wt.(g)}}$$

Precaution: All glassware were treated with hydrochloric acid to avoid contamination from glassware.

2.16. Iron determination by Atomic Absorption Spectrophotometry

Atomic absorption has been found to be a satisfactory technique for the determination of iron in biological material as shown by Allan (1959; 1961), David (1962) and (Stewart, 1974).

Wavelength of determination	= 248.3nm
Mode	= A
Flame	= Air-C_2H_2
Suitable ranges	= 0 - 20ppm
Potential Interferences	= Silicon
Control of Interferences	= Add Cacl2.

Reagents: (i) Iron Standards - Stock Solution (100ppm Fe). This was prepared by dissolving 0.1g clean intarnished Iron in about 10ml of warm H_2So_4 (10% V/v). It was allowed to cool and then dilute to 1 litre.

Working standards were prepared within a range of 0 to 4pp. Digest acids were included to match samples.

Sample Preparation: The sample was prepared for determination as for Calcium, Copper and magnesium and the determination was carried out after adjusting to a wavelength of 248.3nm.

Calculation: If C = ppm Fe obtained from the graph then

$$Fe(\%) = \frac{C(ppm) \times Solution\ Volume(ml)}{10^4 \times Sample\ wt(g)}$$

2.17 Tin Determination of Atomic Absorption Spectrophotometry

Wavelength of determination = 224.6nm

Flame = N_2o/C_2H_2

Suitable ranges = 0 to 300ppm

Potential Interferences = air-C_2H_2, Air- H_2

Reagents: (1) Tin Standards - Stock Solution (1000ppm)
This was prepared by dissolving 1.000g of tin metal in 200cm^3 of hydrochloric acid (35% $^m/_m$) and 5cm^3 Nitric acid (69% $^m/_m$). It was then diluted to 1 litre in a volumetric flask with oleionised water. Working standards were prepared with concentrations ranging from 0ppm to 300ppm.

Sample Preparation: The sample was prepared for determination as before and the determination was carried but after adjusting to a wavelength of 224.6nm.

Calculation: If C is ppm Tin obtained from the graph then

$$Sn\ (\%) = \frac{C(ppm) \times Solution\ Volume\ (ml)}{10^4 \times Sample\ wt.\ (g)}$$

Flame Photometric determination of Potassium and Sodium

Technique and Principles of Flame Photometry

When atoms of an element are heated in a flame, some of the heat energy is absorbed by a few of the atoms which become excited i.e. there is a transition by one or more electrons from the ground state to higher energy levels. On reverting to the ground state the electrons lose this energy which is emitted as electromagnetic radiation. The wavelength of the emitted radiation is governed by the energy change involved in the transition. If operating conditions are kept constant the intensity of radiation will be a measure of this number (Allen, 1974). This is the basis of quantitative flame photometry.

Much of the skill in achieving good results with flame instrument involves the correct use of the nebuliser-flame system. Solutions must be free of suspended matter to avoid blocking the nebuliser. This is a cause of instability and may be checked by spraying with standard solutions regularly. Dust from the surroundings and the fibres picked up from filter papers used during prior preparation of the sample solution are often troublesome.

2.18. Flame Photometric determination of Potassium

This is the most sensitive methods for potassium determination (Allen, 1974).

Filter used - Potassium filter or wavelength of 766nm

Flame - Air-C_2H_2

Suitable ranges - 0 - 100ppm

Potential Interferences - Calcium, Sodium, H_2So_4, Hcl.

Control of Interferences -- include interfering substances into standards.

Reagents: (1) Potassium Standards - Stock Solution (1000ppm). This was prepared by dissolving 1.9068g dry Kcl in water and made up to 1 litre.

Working Standards were obtained by diluting to produce a suitable range from 0 to 15 ppm. The appropriate amounts of digest acid were added to the standards to match sample solution.

Sample Preparation: The sample was prepared for determination as for calcium, copper and magnesium.

Determination: Potassium filter was selected and gas pressures and slit width adjusted. Other settings were as recommended for the instrument. A calibration curve from the standard range was obtained by setting the top standard to a suitable scale deflection and the 0ppm standard to zero. The sample solution was

aspirated into the flame under the same conditions as for standards. At the end of the run the atomiser and burner were flushed with water. The calibration curve was used to determine the concentration of Potassium in the sample solutions.

Blank determinations were also carried out in the same way.

Calculation:

If C = ppm K obtained from the graph then

$$K(\%) = \frac{C(ppm) \times \text{Solution Volume (ml)}}{10^4 \times \text{Sample weight (g)}}$$

Flame Photometric determination of Sodium

Filter used - Sodium filter or wavelength of 589nm.

Flame - Air - C_2H_2

Suitable ranges - 0 - 5ppm

Potential Interferences - Potassium Calcium, H_2So_4, Hcl.

Control of Interferences - Include interfering substances into standards.

Reagents: Sodium Standards - Stock Solution (100ppm) was prepared by dissolving 0.2542g dry Nacl in distilled water. The solution was made up to 1 litre.

Working standards were obtained by diluting to produce a suitable range from 0 to 8ppm. The appropriate amount of

digest acid were added to the standards to match sample solutions.

Sample Preparation: The sample was prepared in the same way as for potassium.

For the determination, sodium fitter was used after adjusting gas pressures, slit width and other settings as recommended for the instrument. The calibration curve was prepared from the standard range after seting the top standard to zero.

The sample solutions were aspirated into the flame under the same conditions as the standards and the calibration curve was used to determine the concentration of sodium in ppm in the sample solution.

Calculation: If C = ppm Na obtained from the graph then Na(%) =

$$\frac{C\ (ppm) \times \text{Solution Volume (ml)}}{10^4 \times \text{Sample wt.(g)}}$$

Determination of Phosphorus as Phosphate by Vanadomoly bdate Method (Pearson, D. 1976).

The operating conditions for the Vanadomolybdate method are less critical than those for molybdenum blue but the former, as normally used is less sensitive (Allen, 1974). The yellow molybdate colour has a broad absorption spectra but a wavelength under 440nm is recommended for the low concentration samples often encountered in ecological studies. A compromise

may sometimes be necessary since the interference effects of other ions, especially iron (111), falls off at higher wavelengths.

The use of the vanadomolybdate method for soil extracts and waters may be complicated by the yellow brown tint frequently present in these samples. If it is impractical to remove the colour initially then the simplest way to correct for the background is to subtract the absorption due to the sample with all the reagents added except for the one used for final colour development.

The determination of phosphorous is vulnerable to laboratory contamination, in particular from detergents and from silicates and arsenates in new glassware. A thorough washing with hydrochloric acid is recommended before use.

Procedure:

Special Reagents: Vanadate - molybdate composite reagents. This was prepared by dissolving 20g ammonium molybdate in 400ml warm water ($50^{o}c$) and cooled. 1.0g ammonium vanadate was dissolved in 300ml boiling distilled water, cooled, and 140ml concentrated Nitric acid was gradually added with stiring. Then the molybdate solution was gradually added to the acid vanadate solution with stirring and diluted to a litre with distilled water.

Standard Phosphate Solution: The Stock solution was prepared by dissolving 3.834g potassium dihydrogen phosphate (KH_2Po_4) per litre. 25ml of the stock solution was diluted to 250ml (1ml ≡ 0.2mg P_2O5)

Preparation of Standard graph

To a series of 100ml volumetric flasks were added 0, 2.5, 5, 10, 20, 30, 40 and 50ml of the standard phosphate solution (≡ 0 - 10mg P_2O5) and each diluted to 50-60 ml with water. A few drops of Ammonia solution (0.88) was added and made just acid with Nitric acid (1.2). 25ml of the vanadate-molybdate reagent was added, diluted to the mark and mixed. They were alloed to stand for 10 minutes and the absorbance in a 0.25cm cell was taken at 470nm in Unicam Sp 1805 ultraviolet spectrophotometer.

Estimation of Phosphorous without Predigestion

Sample Preparation: The sample was digested by the wet digestion method using 5mls nitric acid (69%), 1ml perchloric acid (60%), 0.5ml sulphuric acid (98%). An aliquot of the sample solution was transferred to a 100ml volumetric flask. It was neutralised by the drop wise addition of0.88 ammonia (the volume of solution at this stage was 50-60ml) and then proceeded as for the standard graph.

Calculation:

If C = mg P obtained from the graph then

$$P(\%) = \frac{C(mg) \times \text{Solution volume (ml)}}{10 \times \text{aliquot(ml)} \times \text{sample wt.}}$$

Predigestion with Nitric acid (69% m/m)

In this experiment an attempt was made to determine the effect of predigestion with Nitric acid on the concentration of phosporous estimated. Literature survey has shown the importance of Nitric acid as a suitable oxidising agent for the determination of many minerals. For samples rich in fats, such as certain animal materials the dehydrating properties of sulphuric acid may be a disadvantage and pre-treatment with nutric acid is then advisable (Allen, 1974). When permissible, nitric acid should be present during an oxidation by perchloric acid and definitely before evaporation to fumes. The effect of nitric acid is to moderate the reaction by oxidising the more reactive components at lower temperatures.(AMC - 1959). It is believed that Predigestion with Nitric acid will get rid of the fat in fat rich samples and thus render the minerals and phosphorous available for estimation (Allen, 1974). The attack on the organic matter passes smoothly and automatically from one predominantly by

nitric acid to one prodominantly by perchloric acid (AMC 1960).

Determination: The samples were prepared for determination as before but this time they were left to stand in Nitric acid (69%) for 20, 40, 60, 80, 100, 120, 140 and 160 minutes respectively before the subsequent addition of 1ml perchloric acid (60% $^{m}/_{m}$) and 0.5ml sulphuric acid (98% $^{m}/_{m}$).

The determinations were carried out for a minimum of two times. The optical density was measured at 470nm in Unicam S.P. 1805 ultraviolet spectrophotometer.

Pre-digestion with all three acids:

Method: 0.25g of air dried sample was weighed into a 100ml Kjeldahl flask and 5mls of Nitric acid (69%) 0.5ml sulphuric acid (98%) and 1ml perchloric acid (60%) were all added at the same time and allowed to stand for 20 minutes before further digestion at moderate heating. This was repeated for pre-digestion times of 40, 60, 80, 100, 140 and 160 minutes respectively after which optical density measurements were made as before.

Dry Ashing Procedure without Ash aid:

Method: For each sample, 0.25g of sample was taken in acid washed percelam basins and was ignited to about 550°c for 6 hours in a muffle furnace. The ash obtained was treated as before and the absorbance was measured in Unicam SP 1750

Ultraviolet Spectrophotometer,

Dry Ashing Procedure: This method was also employed in the determination of phosphorous in the various samples and the results obtained were compared with those of pre-digestion with acids.

This procedure involves complete combustion of all the organic matter followed by the dissolution of the mineral constituents using hydrochloric acid. The combustion is preferably carried out in a muffle furnace which allows greater control than is possible using gas burners. The various methods of wet and dry ashing have been compared by Adrian (1973) and methods of burning organic matter both wet and dry have also been recommended by the AMC (1960a and 1967b).

The method has many advocates and is attractive because large samples can readily be handled and reagents blanks are generally low so that it is advantageous for trace element work. Nevertheless many workers have reported low recoveries of specific elements (Pearson, 1976). The earlier work was reviewed by Middleton and Stuckey (1953) and other discussions include those of Piper (1950), Chapman and Pratt (1961) and Isaac and Jones (1972).

The variations from a simple dry ashing procedure that have been found necessary are generally occasioned either by

the amount or nature of the ash present in the material or by the nature of the metal under investigation (AMC, 1960).

Reagents: (1) Magnesium acetate (20% m/v)

(2) 5M Hcl

Method: For each sample 0.25g of sample was taken in acid washed porcelain basins. 1ml of distilled water and 2mls of Magnesium acelate (20%) were added. This was ignited to about 550^{o}_{c} for 6 hours in a muffle furnace. The ash obtained was cooled, boiled with 10ml of 5mHcl and washed into a 50ml volumetric flask. It was then diluted to the mark with distilled water. 25ml aliquot of the solution was pipetted into a 100ml volumetric flask, neutralised by dropwise addition of ammonia (S.G. 0.88), made acid with dilute nitric acid. 25ml of Vanadate - molybdate reagent was added. The solution was diluted to the mark and to stand for ten minutes. The absorbance was measured at 470nm in Unicam S.P. 1750 ultraviolet spectrophotometer.

CHAPTER THREE

RESULTS AND DISCUSSION

Table 1: Moisture Content

Sample	Moisture(%) (Bulking)	Moisture(%) (Single Tins)
Vs	73.98 ± 0.52	70.95 ± 1.20
Vf	71.59 ± 0.31	70.42 ± 1.0
Salsa	74.23 ± 0.20	*(Single tins not available)
FOP	27.38 ± 1.03	27.54 ± 0.65
NOJ	86,47 ± 2.38	86.83 ± 3.43

The moisture content of the various foods analysed is shown in Table 1 above. It is observed that NOJ has a higher value than FOP. The tomato pastes have moisture content values which are comparable. However sample Salsa has the highest value among the pastes while V_F has the lowest. Generally, NOJ has the highest moisture content while sample FOP contains the least moisture. The variation in moisture content amongst the samples analysed could be as a result of varying levels of sample concentration during processing. Secondly, the factory samples could be expected to be more concentrated than the Shop shelf samples since loss of some total solids by

volatilisation (Lutt and Woodroof, 1975) in the shop shelf samples could increase dilution.

The FOP sample has a very low moisture content compared to the NOJ. One would suspect that this sample was highly concentrated during processing and might have had a lot of additives to the natural juice as compared to Sample NOJ. A preliminary observation of the samples analysed shows that the tomato pastes were thicker and more viscous that the NOJ sample but were not as viscous as the FOP sample. This agrees with the values obtained in Table 1.

A literature survey shows that Canned Tomato Pastes should contain at most 75% moisture while canned orange juices should have moisture content within the range of 83.0 - 89.0% (Joslyn, 1970). These literature values are very much comparable to the values of the samples analysed. However, the FOP has a very low moisture content which could be as a result of concentration of the juice and the addition of additives during processing.

The moisture content of these samples obtained from bulking was compared to those of single tins. T - test analyses carried out for all the samples showed that the differences observed between the percentage moisture from

bulking and that from single tins were not statistically significant except in the case of Vs. Thus the moisture content observed in single tin of Vs analysed is not representative of the whole foodstuff.

The determination of moisture is one of the most important and most widely used analytical measurements in the processing and testing of food products. The moisture content is frequently an index of stability and quality and also a measure of yield and quantity of food solid (Joslyn, 1970). The storage life of a food and the processing and packaging conditions required are influenced by the partial pressure of an atmosphere in thermal and moisture equilibrium with the food. Advantage is taken of the possibilities of increasing storage stability by decreasing available water content in the preservation of foods and food products by drying and dehydration.

High moisture content values in processed foods will give rise to mould attack and loss of flavour (Pearson,1976). Thus sample NOJ will be expected to undergo spoilage in terms of mould attack and loss of flavour more easily than the other products.

Since the appearance, keeping quality and yield of tomato products (Lutt and Woodroof) are related to moisture contents,

the later must be known accurately in the evaluation of processing losses, estimating yields, and in determining whether or not the product meets the requirements of the pertinent standards of identity and quality and marketing restrictions.

Table 2:

Total Solids

Sample	% Total Solids (Bulking)	% Total Solids (Single Tins)
Vs	26.02 ± 0.52	29.05 ± 1.20
Vf	28.41 ± 0.31	29.58 ± 1.00
Salsa	25.77 ± 0.20	*
FOP	72.62 ± 1.03	72.46 ± 0.65
NOJ	13.53 ± 2.38	13.17 ± 3.43

* Single tins not available.

Table 2 gives a summary of percentage total solids in the analysed samples. Sample FOP has the highest percentage while NOJ has the least. V_F contains more total solids than the shop shelf sample. This could be as a result of higher concentration of the former compared to the later. Salsa has

the least total solid of the tomato pastes, probably because Salsa is less concentrated right from the factory. The value for FOP is very high and may possibly be accounted for by the presence of additives during processing. Another factor that would have boosted the total solids could be prolonged concentration during processing. This is normally aimed at dehydration. FOP has a high concentration of sugar and this could contribute to the high value of its total solids (Pearson, 1976).

Present standards require that tomato pastes contain at least 25 percent of total solids (Lutt and Woodroof, 1975). The values obtained in the analyses fall within this specification. Macdowell (1945) found that total solids in Orange juices range from 10 to 15%. The dry solids of tomato pastes contain about 9.5% ash, 13.8% protein, 50-65% total sugar (as Inverted sugar), 5.8 -13.4% total acidity (as citric acid) and 4.8% Potassium as Potassium oxide. (Dickinson, 1962). Similar figures were not available for the constitution of total solids in orange juices.

T - test analyses were carried out for all samples. The differences between the percentage total solids from bulking and that from single tins were not statistically different except in the case of Vs. The difference in the case of Vs

could be as a result of the different extents to which individual tins are affected by factors responsible for increasing the moisture (and hence reducing total solids) with storage in Vs compared to Vf.

Table 3:

Ash Content

Sample	% Ash (Bulking)	% Ash (Single Tins)
Vs	2.69 ± 0.41	2.75 ± 0.088
Vf	4.15 ± 0.12	5.04 ± 0.06
Salsa	2.30 ± 0.38	*
FOP	0.142 ± 0.013	0.106 ± 0.00
NOJ	0.380 ± 0.03	0.421 ± 0.12

* Single Tins not available.

Table 3, shows the ash content of the various items analysed. The factory sample of the Vegfru Paste has the highest ash value of the pastes while a higher value for ash was observed in NOJ compared to FOP. The orange juice have very low ash values compared to the tomato pastes. The Vs and Salsa samples have similar ash contents while Vf, the

factory paste has a relatively higher value. This might have something to do with its proper preservation in the factory. There is also a possibility of the presence of an adulterant.

A literature survey shows that citrus juices contain on the average, 0.4% of ash (Braverman, 1948). The values obtained in the analyses were slightly smaller than the suggested value. This might be as a result of losses due to volatilisation or because of some interaction between constituents. (Allen, 1974). The ash content of fresh vegetables varies from 4% to about 18% (Pearson, 1976). The smaller values obtained in Salsa and Vs samples could possibly be as a result of two factors. Since the values given are for fresh vegetables then losses during processing will affect the total ash content of the processed food. Secondly, during the process of ash determination there would have been obvious losses due to volatilisation and interaction between constituents. Of course this factor has a general effect on all samples since they were ashed under similar conditions.

T - test analysis was carried out to determine whether the ash value obtained from single tins were representative of the whole foodstuff. Statistically, different values were obtained in V_F, FOP and NOJ samples while the difference observed in Vs was not statistically significant at 95%

confidence limit.

The main use of the ash determination has been with regard to the determination of adulteration of certain foods. Thus the knowledge of the amount and composition of the ash of fruit jellies and marmalades is useful in determination of the percent of fruit used.

Ash values are also significant in the determination of metallic salts present as contaminants from corrodible surfaces with which the food comes in contact during processing and after packaging from insecticidal and other residues(Joslyn 1970).

Table 4: Lipid Content

Sample	% Lipid (Bulking)	% Lipid (Single Tins)
Vs	1.57 ± 0.38	1.56 ± 0.01
Vf	1.86 ± 0.39	1.89 ± 0.02
Salsa	1.83 ± 0.35	*
FOP	1.27 ± 0.21	1.64 ± 0.34
NOJ	1.56 ± 0.04	1.78 ± 0.04

* Single tins not available.

Table 4, summarises the values obtained for the lipid contents of the various items analysed. All the samples contained similar concentrations of lipid. Vf had the highest value of the tomato pastes while a higher value was observed in NOJ compared to FOP.

The imported salsa has a value quite close to Vf. The lower values obtained in samples Vs and Salsa compared to Vf might have been as a result of different processing conditions. Secondly it could have been as a result of depreciation in lipid value with exposure to varying temperature conditions. Another probable reason could be as a result of incomplete extraction of the fat.

In general the tomato pastes have higher lipid contents compared to the orange juices.

On moisture free basis the fat content of orange juices range from 0.2 to 1.6% while in tin tomatoes it ranges from 0.3 to 5.2% (Joslyn, 1970). The values obtained in the analyses were within the range of those recorded in literature. However, optimum concentration values are not generally obtained as a result of certain factors already investigated and reported elsewhere (Luh and Woodroof, 1975).

Factors which tend to accelerate oxidation of lipids include the presence of unsaturated fatty acids, exposure to high temperature, ultraviolet light, ionising radiations, contamination with peroxides, presence of copper or Iron and presence of lipoxidase enzymes, (Tuomy et al 1970). Thus the relatively low values recorded for the tomato pastes may have been as a result of oxidative changes.

It has not yet been definitely established whether fresh citrus juices naturally contain small amount of fatty constituents or whether these are introduced through seeds crushed during extraction. In comparing juices obtained from orange by different methods of extraction it was found that juices extracted with a burr reamer method (crushing both the seeds) contained 25% more lipid material than those squeezed out by an automatic juice extractor (Braverman, 1948). Thus the mode of extraction is another determinant of lipid concentration.

Bulking and single tin determinations for the pastes would suggest that each tin is representative while a t-test shows a significant difference for the corresponding values for the orange products at the 95% confidence limit.

Possibly each tin is affected to a different extent by lipid modifying agents.

Table 5

Sugar Content as Invert Suger

Sample	mg/100ml Sugar (Bulking)	% Sugar (Bulking)
Vs	111.5 ± 4.09	0.112 ± 0.004
Vf	113.7 ± 0.00	0.114 ± 0.00
Salsa	120.1 ± 2.65	0.120 ± 0.003
FOP	658.25± 11.66	0.658 ± 0.01
NOJ	82.00± 1.98	0.082 ± 0.002

Table 5 is a summary of the sugar content of the analysed sample. While FOP has a higher sugar content than NOJ, Salsa has the highest value of the tomato pastes. In general FOP has the highest value while NOJ contains the least sugar.

The difference in sugar concentration of FOP and NOJ is so large that one would not know the true sugar concentration of Orange juices. However, other reports elsewhere show that orange juices have a total sugar concentration ranging from 0 to 0.15%. (Braverman, 1949). Such literature values were not available for tomato pastes. The concentration of

reducing sugars in oranges range from 0 to 4.40% (Braverman, 1949). These values depended on the orange variety and the mode of extraction of the juice. However, the relatively high value of sugar (invert sugar) observed in FOP is suggestive of the addition of large quantity of sugar to the orange juice during processing. This sample was also observed to contain the largest value of total solids. Since the major part of total solids is sugar (Jacobs, 1938) there appears to be an exact relationship between the concentration of sugar and total solids observed in this sample.

According to the recommended standard by Codex alimentarius for various fruit juices (Pearson, 1976), the maximum added sugar to orange fruit juices should be 5g/100ml. Thus from the observed values the sugar concentrations, of FOP and NOJ do not exceed the limit. However, in considering the legal requirement for added sugar it should be borne in mind that although fruit naturally contains reducing sugars some may be produced by hydrolysis of sucrose during storage.

Potatoes and some other varieties of vegetables which have been stored at temperatures around $0^{o}c$ tend to be over-sweet due to conversion of starch to sugar, but storage at relatively higher temperature ($16^{o}c$) tends to produce a "mealy" food due to the production of starch from sugar (Pearson, 1976).

This factor could possibly be responsible for the observed difference in sugar concentration between Vs (shop shelf paste) and Vf (Factory paste) samples.

Table 6:

Starch Content

Sample	% Starch (Bulking)
Vs	1.04 ± 0.40
Vf	0.63 ± 0.27
Salsa	0.31 ± 0.10
FOP	0.15 ± 0.05
NOJ	0.17 ± 0.02

As shown in table 6, starch was found to be present in trace amounts in the tomato pastes and the orange juices. Amongst the pastes, sample Vs has the highest starch content while salsa has the lowest. The FOP and NOJ samples had almost equal amounts. Generally, the tomato juice have higher starch values than the orange juices.

Most mature fruits are almost free from starch, succulent vegetables have less than 1% of starch, while in leafy vegetables the starch content is usually below 0.2% (Joslyn, 1970). The observed values are in agreement with the literature values.

While the orange juices have little or no starch, the succulent vegetables, tomato pastes inclusive have less than 1% of starch. The relatively higher value observed in Vs may be as a result of storage under a high temperature condition. Storage at relatively higher temperatures ($16^{o}c$) tends to produce a "mealy" food due to the production of starch from sugar (Pearson, 1976). This factor may be responsible for the higher starch value recorded for Vs.

Table 7:

Nitrogen Content

Sample	% Nitrogen (Bulking)
Vs	0.493 ± 0.013
Vf	0.892 ± 0.012
Salsa	0.606 ± 0.042
POP	0.420 ± 0.027
NOJ	0.189 ± 0.000

Table 8: Protein Content

Sample	% Protein(Bulking)
Vs	3.08 ± 0.09
Vf	5.57 ± 0.08
Salsa	3.79 ± 0.27
FOP	2.63 ± 0.18
NOJ	1.18 ± 0.00

Table 7 and 8 summarise the Nitrogen and Protein Content of the analysed samples. Sample Vf has the highest concentration of Nitrogen and Protein of all the pastes while FOP has higher values than NOJ. Generally the tomato pastes have higher Nitrogen and Protein contents than the orange juices.

The proteins amount to about 1.04 to 2.05% in orange juices while Nitrogen is in the range of 0.060 to 0.180% (Pearson, 1976).. Fresh vegetables usually provide only 1 to 2% proteins. The composition and amount of protein in tomatoes depend on the variety, location grown and degree of ripening (Lutt, 1975).

The literature values deviate from the observed values. Higher protein and Nitogen contents were obtained for Vs, Vf and Salsa samples. However, the values for the orange products were similar to those in the literature. The higher values

of Nitrogen and Protein observed in FOP as compared to NOJ may be as a result of the variety, location grown and the extent of ripening of the oranges. The slight variation observed between Vs and Salsa samples could also be accounted for by the above reasons.

The high value of Vf compared to the Vs could possibly be as a result of depreciation in protein value with storage of the shop shelf sample of the tomato paste.

Petropavlovskiiand Troyan (1970), found that ripe red tomatoes contained more protoins than green ones and that storage of ripe tomatoes for 3 days resulted in decrease of proteins. Changes in proteins and amino acids occur in stored processed foods. Freeze dried mushrooms stored at 30°c for 9 months showed decreases in protein content (Lutt, 1975).

Table 9: Crude Fibre Content

Sample	% Crude Fibre (Bulking)
Vs	1.215 ± 0.36
Vf	1.385 ± 0.21
Salsa	1.435 ± 0.091
FOP	0.321 ± 0.01
NOJ	0.213 ± 0.002

The crude fibre content of the analysed sample is given in table 9. Salsa had the highest percentage crude fibre amongst the pastes while FOP contained a relatively higher value than NOJ. Generally the tomato pastes had higher crude fibre content than the orange juices. Values observed for Vf and Vs were very close.

The fibre content of fruits and fruit products varies from 0.1 to 6.8% being low for juicier large fruits. In vegetables it varies from 0.4% to 1.30% in succulent vegetables but in beans and other fibrous vegetables from 2 to 4.0%. The crude fibre content of many vegetables varies with maturity, thus in green peas it varies from 1.8% in young peas to 2.2% in medium quality, to 2.5% in mature large peas. Thus relatively higher values of crude fibre in the vegetable (tomato pastes) compared to the fruits as shown in table 9 could be attributed to the period of storage of the canned vegetables (Lutt, 1975). The state of maturity of the fruits and the vegetables would also have accounted for the crude fibre content of these analysed samples. The Salsa sample might have stored longest of the tomato pastes. This may also be responsible for the slightly higher value for FOP compared to NOJ.

Table 10 Tannin Content

Sample	% Tannin (Bulking)
Vs	0.104 ± 0.00
Vf	0.259 ± 0.07
Salsa	0.415 ± 0.14
FOP	0.001 ± 0.000
NOJ	0.099 ± 0.001

From Table 10, NOJ has a higher tannin content than FOP while Salsa has the highest percentage tannin of the tomato pastes. Generally the tomato pastes have higher values than the orange juices.

Nakamura (1961) investigated the effects of storage between -12 and -75°c on soluble tannin content of fruits and found soluble tannin content to decrease most effectvely at - 25°c and least at -12°c. The tannin content, depending on the variety was reduced from a value between 0.5 - 0.73% soluble tannin down to 0.05%. Thus the various conditions of storage of the analysed samples might possibly have affected the tannin yield.

No literature values have been recorded for tannin in orange juices and tomato pastes but these have been observed for related substances. The tannin content of apple juice varies with variety and growing conditions; it is usually 0.05% but may be over 0.2% particularly in the juice of cider apples. In pears the range lies between 0.1% (for desert pears) and 1.2% (for some perry pears). The tannin content of white table wines varies from 0.02 to 0.09%, of red dessert wines from 0.04 to 0.16%. These values are similar to those obtained in this work.

Table II: Lead Content

Sample	% Lead (Bulking)	PPm
V_S	$3.00 \times 10^{-3} \pm 0.00$	0.32
Vf	$2.30 \times 10^{-3} \pm 0.001$	0.31
$Sals_a$	$2.10 \times 10^{-3} \pm 0.001$	0.28
FOP	$1.84 \times 10^{-3} \pm 0.001$	0.25
NOJ	$1.65 \times 10^{-3} \pm 0.00$	0.23

Table 11 shows the lead content of the samples analysed. The values are very similar and show that lead is only present in trace amounts. Vs has the highest lead content amongst the tomato paste while FOP has a slightly higher value than NOJ.

Generally the pastes contain larger quantities of lead than the orange juices.

The specified limits in parts per million for loed are 2.0ppm for concentrated fruit juices, 3.0ppm for tomato paste with total solids between 15 and 25%, 5.0ppm for tomato paste with total solids greater than 25% (Pearson, 1976). The values lead in ppm present in the analysed samples were 0.32ppm for sample Vs, 0.31ppm for Vf, 0.28ppm for Salsa, 0.25ppm for FOP and 0.23ppm for NOJ. These concentrations are within the specified limits. According to the above specified limits, tomato pastes have higher levels of lead contamination compared to orange juices. This was in agreement with the observed values in this work.

Thomas et al (1973) pointed out that the increased lead content of canned foods in comparison to fresh foods was the result of contamination during processing or due to release of lead from the soldered seams of cans.

The standard graph for lead could be seen in the appendix.

...

Table 12:

Copper Content

Sample	% Copper (Bulking)	PPm
Vs	$4.70 \times 10^{-3} \pm 0.00$	0.53
Vf	$2.52 \times 10^{-3} \pm 0.00$	0.30
Salsa	$3.54 \times 10^{-3} \pm 0.00$	0.50
FOP	$0.446 \times 10^{-3} \pm 0.00$	0.25
NOJ	$0.395 \times 10^{-3} \pm 0.00$	0.17

The copper content of the samples analysed is listed in Table 12. Vs has the highest copper content of the pastes while a higher value was observed in FOP compared to NOJ. In general the pastes have higher copper content.

Vegetables are intermediate in copper content among the economic plants, ranging from 2.5 to 5.5ppm in potato tubers and from 15 to 25ppm in tomato fruits.(Reuther and Labanaukas, 1966). Citrus juices contain 0.3 to 0.9ppm of copper. The values obtained for tomato pastes in this analysis were significantly lower than the literature values.

Cupric ion in concentrations higher than the recommended values has an important bearing on the destruction of vitamin C

in juice (Braverman, 1949). The observed values in these analyses were not sufficient enough to give rise to such an effect.

The calibration curve for copper is shown in the appendix.

Table 13:

Calcium Content

Sample	% Calcium (Bulking)
Vs	$27.2 \times 10^{-3} \pm 0.003$
Vf	$24.3 \times 10^{-3} \pm 0.013$
Salsa	$105.0 \times 10^{-3} \pm 0.019$
FOP	$6.50 \times 10^{-3} \pm 0.002$
NOJ	$6.17 \times 10^{-3} \pm 0.003$

Table 13 summarises the calcium content of the analysed samples of the three pastes. Salsa has the highest Calcium content while the orange juices have similar values. Generally the tomato pastes have higher concentrations of calcium than the orange juices. Orange juices are known to contain calcium in the range of 6 to 9×10^{-3} % (Braverman, 1947) while Tomato pastes have calcium in the range of 20 to 28×10^{-3}. The values observed in this work for both the orange juices and tomato pastes are comparable with the literature except the concentration obtained for Salsa which is appreciably higher than

recommended values. Bear (1948) and Sims and Volk(1947) contend that calcium content of plants generally varies with the soils in which they are grown. Thus Salsa tomato might have been cultivated in a calcium rich soil which boosted its calcium concentration. This value could also be rationalised by the balanching of the paste during the manufacture process (Luh, 1975). The extent of increase in calcium content with blanching depends upon the kind of vegetable, the hardness of the blanching water and the length of blanching time.

The shading of calcium deficient plants caused a large loss in combined calcium and an increase in free calcium in tomato plants (Nightingale et al 1931).

The calibration curve for calcium is given in the appendix.

Table 14: Magnesium Content

Sample	% Magnesium (Bulking)
Vs	$87.21 \times 10^{-3} \pm 0.003$
Vf	$26.03 \times 10^{-3} \pm 0.00$
Salsa	$89.65 \times 10^{-3} \pm 0.002$
FOP	$8.73 \times 10^{-3} \pm 0.004$
NOJ	$13.72 \times 10^{-3} \pm 0.001$

Table 14 summarises the magnesium content of the analysed samples. Salsa has the highest value of the pastes while a higher value was recorded in NOJ than FOP.

Generally the tomato pastes have higher magnesium values than the orange juices.

Orange juices usually contain about 0.005% (5×10^{-3}%) of Magnesium (Braverman, 1947), while tomato pastes contain upwards of 11×10^{-3}% (Luh. et al 1975).

The values obtained in this work are on the high side of the literature values. The variations from sample to sample may be a reflection of the soil conditions in which the raw materials for the samples were cultivated.

The standard curve for magnesium is given in the appendix.

Table 15:

Sodium Content

Sample	% Sodium (Bulking)	%Sodium (Single Tin)
Vs	$166.1 \times 10^{-3} \pm 0.074$	$156.0 \times 10^{-2} \pm 0.63$
Vf	$79.6 \times 10^{-2} \pm 0.13$	$89.6 \times 10^{-2} \pm 0.13$
Salsa	$135,3 \times 10^{-2} \pm 0.055$	*
FOP	$0.70 \times 10^{-2} \pm 0.00$	$0.90 \times 10^{-2} \pm 0.00$
NOJ	$0.36 \times 10^{-2} \pm 0.00$	$0.38 \times 10^{-2} \pm 0.00$

* Single Tins not available.

Table 15 is a summary of the sodium content of the analysed samples. The paste Vs, has the highest value of the three pastes, while FOP has a higher value of sodium than NOJ. This mineral is in a relatively higher concentration in the samples than most other minerals. Relatively higher values were observed in the tomato pastes compared to the orange juices.

The sodium content of natural fruit juices range from 0.009% upwards while in tomato pastes a concentration of 3 to 5 x 10^{-3}% have been found (Lutt, 1975).

The sodium values observed in this work are on the higher side of the literature figures. This may be as a result of residual sodium chloride which was used in the storage and preservation of these products prior to processing. The desalting process during manufacture did not totally remove this preservative.

T-test analyses showed that sodium concentrations obtained with bulking were similar to those from single tins at the 95% confidence limit.

The calibration curve for sodium is shown in the appendix.

Table 16:

Potassium Content

Sample	% Potassium (Bulking)	% Potassium (Single Tins
Vs	$206.1 \times 10^{-2} \pm 0.14$	$198.1 \times 10^{-2} \pm 0.14$
Vf	$118,8 \times 10^{-2} \pm 0.00$	$126.8 \times 10^{-2} \pm 0.00$
Salsa	$240.1 \times 10^{-2} \pm 0.129$	*
FOP	$2.45 \times 10^{-2} \pm 0.01$	$2.68 \times 10^{-2} \pm 0.00$
NOJ	$8.76 \times 10^{-2} \pm 0.00$	$9.23 \times 10^{-2} \pm 0.00$

* Single Tins not available.

Table 16 shows the values for Potassium obtained in this work. Salsa has the highest Potassium content of the tomato pastes while NOJ has a higher value of Potassium than FOP. The orange juices have lower values of potassium compared to the tomato pastes. Potassium is in very high concentration in these samples compared to other minerals. The minimum concentration of potassium in orange juices is $8.9 \times 10^{-2}\%$ and about $28.8 \times 10^{-2}\%$ in raw tomatoes (Pearson, 1976), (Amos et al 1962). Except in the case of NOJ where the literature value is comparable to those analysed in this work, in all other cases the literature values were far lower than the observed values. Probably some potassium salts were also added to these samples

as preservatives prior to processing. There is also the probability that the various plants were grown under different soil conditions.

T-test analyses showed that potassium concentrations obtained with bulking were similar to those from single tins in the case of NOJ and FOP but different in Vs and Vf samples.

Standard curve for potassium is shown in the appendix.

Table 17: Iron Content

Sample	% Iron
Vs	$7.2 \times 10^{-2} \pm 0.01$
Vf	$6.0 \times 10^{-2} \pm 0.01$
Salsa	$12.5 \times 10^{-2} \pm 0.01$
FOP	$0.909 \times 10^{-2} \pm 0.003$
NOJ	14.05 ± 0.01.

Table 17 above summarises the iron content of the analysed samples: Sample NOJ has a relatively higher value than FOP. Salsa has the highest concentration of Iron compared to the Vs and Vf samples.

The concentration of iron in any of the above samples is as a result of two factors:-

(1) Concentration of iron naturally present in the food.

(2) The extent of contamination by the can which stores the food.

Therefore, the values obtained are representative of the total iron present in these samples.

The natural iron content of these food items are 0.43 x 10^{-3}% for raw tomatoes and 0.30 x 10^{-3}% for orange juices (Amos et al 1962). These values are far lower than those observed for the various samples analysed in this work. The differences were statistically significant. The excess iron found in these samples could probably be attributed to the effect of corrosion of these canned foods. Comparing the literature and observed values the probable level of corrosion is more than ten times in the tomato paste while it is about 10^3 in NOJ and ten times in FoP.

From the figures obtained for the factory and shop shelf samples of the Vegfru paste it could be reasonably inferred that corrosion with iron is probably enhanced with increased period of storage.

The imported tomato paste (Salsa) which was obtained from the shop shelf had a significant level of iron concentration and was even much higher than the locally made tomato pastes.

Sample FOP had a relatively low value. This could be as a result of the can quality. Probably the can is of a better quality compared to the other items.

The calibration curve for iron is given in the appendix.

Table 18:

Tin Content

Sample	% Tin	ppm
Vs	0.335 ± 0.201	18
Vf	0.217 ± 0.099	12.1
Salsa	0.495 ± 0.188	28
FOP	0.248 ± 0.097	14
NOJ	0.418 ± 0.154	26

The Tin content of the analysed samples is summarised in table 18.

Amongst the tomato pastes, the highest value was recorded for Salsa while NOJ had a lower tin content than FOP in the orange juices.

However, relatively higher values of tin were observed in all the samples compared to iron.

Sample Vs had a higher concentration of Tin compared to sample Vf which could be as a result of prolonged storage of the former. Probably samples NOJ, Salsa and Vs had relatively higher acidities than the rest of the samples since dissolution of tin into the food from the can is a function of PH.

Another factor that can contribute to the quantity of tin dissolved in the food is the can quality. A thorough preliminary observation of the cans showed that NOJ had a very poor can quality whose corrosion was very conspicuous. The can for sample FOP was shiny and attractive on the other hand.

Tin is a non nutritive non toxic element which is not known to produce harmful effects when present in quantities not exceeding 100ppm (Pearson, 1976). The food standards committee proposed that a concentration of 250ppm should be recognised as the limiting concentration of tin above which the product may become "potentially injurious to health". The recognised limit in the U.S.A. is 300ppm (Amos et al 1962). An amount of tin in beer of 0.02ppm may give rise to haze and a concentration above 0.1ppm may be objected to on aesthetic grounds (Pearson, 1976).

The concentrations of tin in ppm observed in the samples analysed in this work are very low compared to the recommended limits. However, it appears the effect of dissolved tin in food varies with different products as shown for beer. Specific recommended thresholds were not available in the literature for orange juices and tomato pastes.

Tin contents of fruits and vegetables packed in lacquered cans and stored at normal temperatures seldom exceed 0.004% even after long storage (Amos et al 1962). The results of this work show that an appreciable amount of tin was probably dissolved in all the samples.

According to Amos et al 1962, post lacquered cans show very much lower figures. Fruits in plain cans do not often contain more than 100mg of tin per kg (0.1%) and the same applies to most vegetables except asparagus (Amos et al 1967).

The tin dissolved by the action of the fruit or vegetable acids is not distributed evenly throughout the content of the can, but is concentrated more in the solid than in the liquid portions. More recent work by Dickinson and Raven (1962) has shown that modern cans are less likely to give rise to high tin contents.

TABLE 19 PHOSPHORUS CONTENT

Sample	% Phosphorus				
	Estimation without Predigestion	Predigestion with HNO_3 only	Predigestion with all acids	Estimation with Ashed Samples with Ash aid	without Ash aid
Vs	0.95± 0.22	1.41 ± 0.21	0.94 ± 0.02	0.71 ± 0.02	0.68 ± 0.18
Vf	0.75 ± 0.01	1.39 ± 0.02	0.78 ± 0.01	0.68 ± 0.01	0.65 ± 0.12
Salsa	1.10 ± 0.23	1.58 ± 0.18	0.96 ± 0.03	0.95 ± 0.01	0.94 ± 0.35
FOP	0.23 ± 0.01	0.36 ± 0.00	0.24 ± 0.01	0.35 ± 0.02	0.34 ± 0.21
NOJ	0.27 ± 0.01	0.44 ± 0.11	0.35 ± 0.01	0.41 ± 0.02	0.40 ± 0.18

Fig. II

Variation of absorbance with Conc. Nitric Acid Predigestion time

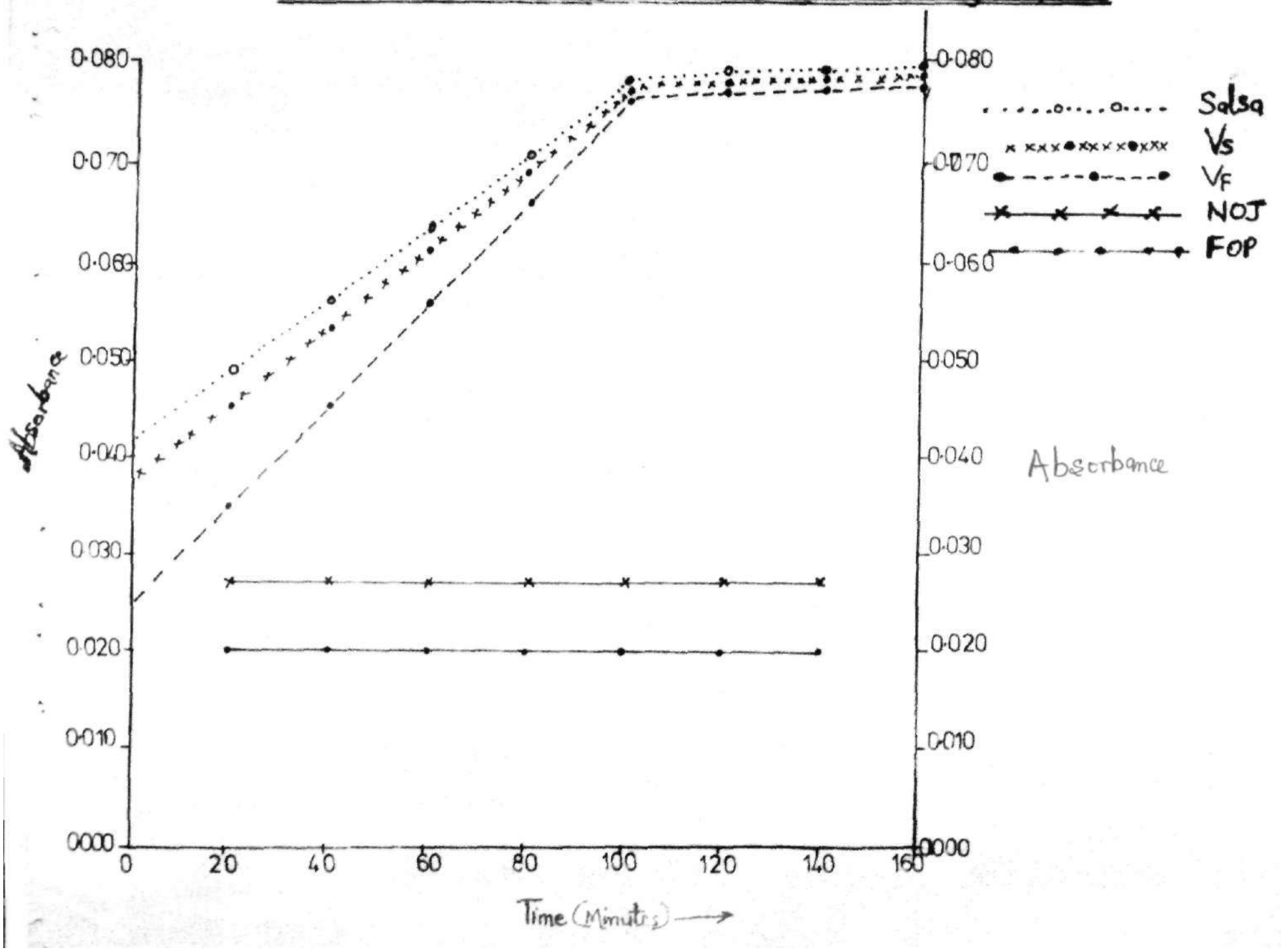


Fig. 1d

Variation of absorbance with Nitric, Perchloric and Sulphuric acids predigestion time

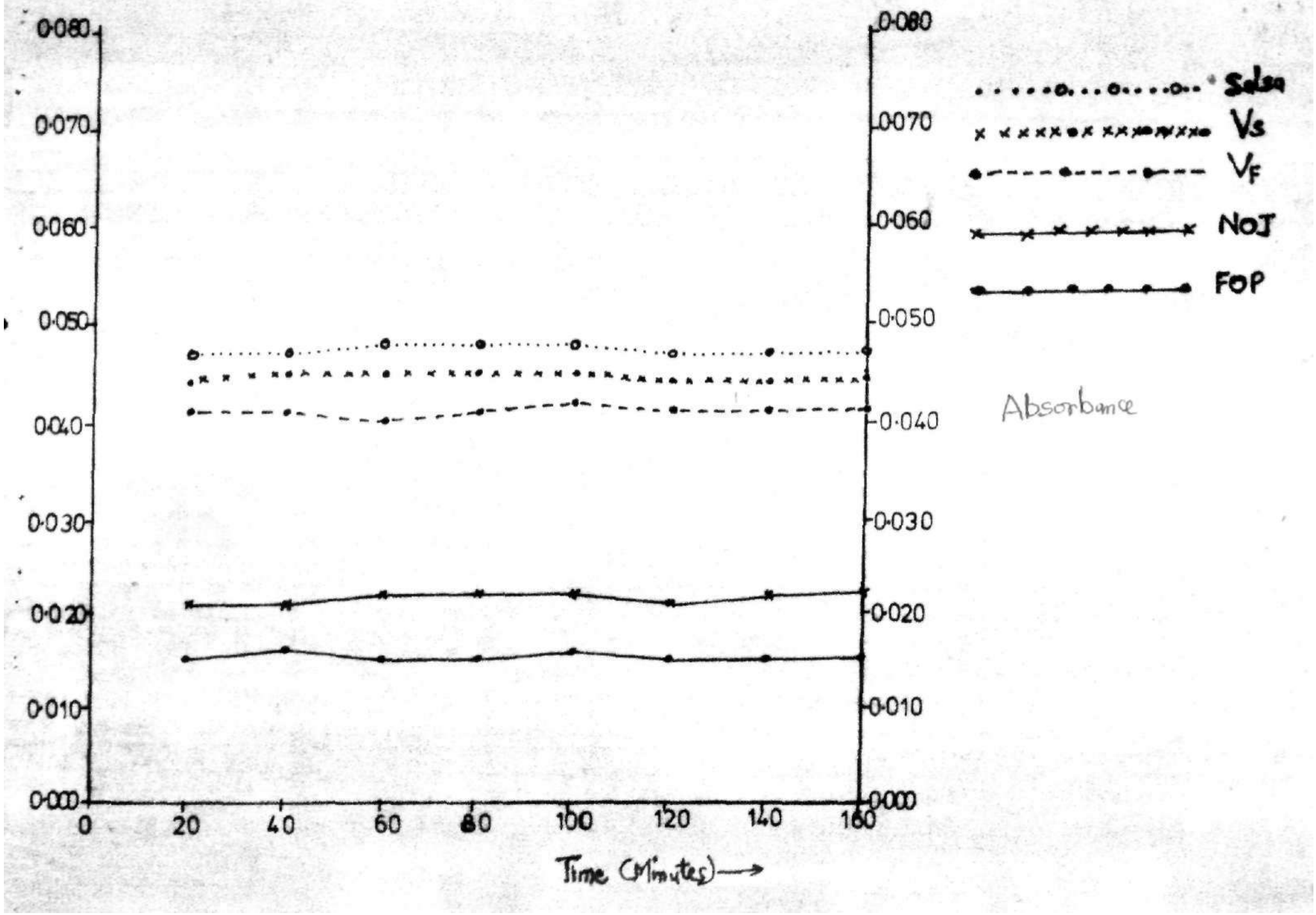


Table 19 gives a comprehensive summary of phosphorus determination carried but in five different ways.

In all the samples it was observed that the concentration of phosphorous obtained by predigestion with Nitric acid (69%) only (before the addition of perchloric acid (60%) and sulphuric acid (98%) was relatively higher than the values by the other methods of estimation. From figure 11, the amount of phosphorus determined increased initially with time of predigestion with concentrated Nitric acid and eventually levels up after about 100 minutes for the tomato pastes. For FOP and NOJ samples there was no significant variation of absorbance with nitric acid predigestion time. However, for these samples relatively higher values were obtained for nitric acid predigestion than with other methods. By the method of predigestion with Nitric acid only, Salsa had the highest value while FOP had the least. Generally the tomato pastes had a comparatively higher phosphorus values than the orange juices. The concentration of phosphorus observed in NOJ was slightly higher than FOP but their values were comparable.

In general values obtained by predigestion with all acids (fig.12) did not differ significantly from those without predigestion with all acids but were slightly higher than the latter in the case of NOJ, FOP and Vf samples. It does not

appear predigestion with all acids together is necessary for these samples and is not worth the time and effort. However, a significant improvement was achieved for NOJ.

As can be seen from Table 19, the use of ash aid (Magnesium acetate 20% $^{m}/_{V}$) did not lead to any significant improvement in the efficiency of the ashing procedure for these samples.

In all the methods employed, the pattern of phosphorous distribution among the various samples remained constant with Salsa having the highest value and POP with the least. It seemed that predigestion with nitric acid is the most efficient of these methods for the determination of phosphorous in the given samples.

Literature values show that natural orange juices contained about 0.032% (Braverman, 1947) while tomato pastes had 0.02% (Lutt, 1975). The values obtained in this work by all the methods of determination were much higher than the literature values, and could be as a result of introduction of more phosphorous during processing, and due to the action of the enzyme phytase on phytic acid liberating more phosphorous.

A wet digestion method for the determination of metals and phosphorous in biological materials that involves the use of

pressure has been described and comparisons made with the standard dry and wet ashing methods, and the sulphuric acid - hydrogen peroxide method (Adrian, 1973). The pressure method has the advantage of being able to digest many samples at the same time (to the extent that the cations sought and phosphorus can be extracted into dilute nitric acid) with very little equipment, small volumes of acid and with a low digestion temperature, with the precision of more laborious standard methods.

The relative merits of wet and dry oxidations have been exhaustively discussed (Gorsuch, 1959). In favour of the former are cited the low temperatures involved, the maintenance of liquid conditions, which reduce the chances of retention losses, the simple apparatus required and the speed of oxidation. On the debit side may be laid the large amounts of reagents added with the consequent risk of increased blank values, the difficulty of handling large samples and the greater amount of operators time required.

The advantages of dry-ashing methods are the lack of added reagents, the simplicity of operation and the ease with which large samples can be handled. Against this must be balanced the lack of knowledge of the interaction between

sample constituents, the trace elements and the material of the receptable, with the consequent risk of loss by volatilisation or retention; also the high temperature required for such reactions, the need for relatively expensive equipment and the length of time required to complete the oxidation.

CHAPTER FOUR

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

The results showed that samples analysed were of similar qualities with other samples analysed and reported in literature with a few exceptions in the case of canned French orange pellorce. The latter product had very high values of sugar and total solids which did not compare with those recorded in literature. It also had very low moisture content compared to reports elsewhere. Canned orange juices should have moisture content within the range of 83.0-89.0% (Joslyn, 1970). This value differed significantly with 27% observed for this product. Similarly, sample FOP recorded a total solids content of 72% as compared to 10-15% recorded elsewhere (Macdowell, 1945). The sugar content as invert sugar recorded for this product was 0.658% as different from 0 to 0.15% reported in literature (Braverman, 1949). It will be pertinent to conclude that a lot of sugar was added to the natural orange juice during processing. Thus in the presence of sugar and other additives there was a relative increase in the total solids content and consequently a corresponding decrease in the moisture content.

The canned Nigerian orgnge juice on the other hand had values comparable to those recorded in literature. However,

this particular juice was found to contain relatively higher concentrations of heavy metals, tin and iron compared to the French orange pellorce. However, the levels were not beyond permissible thresholds. The concentration of heavy metals in these canned foods could be attributed to the quality of the can, the nature of the processing plant, the length of storage and the acidity of the food (Amos et al 1962; Luh and Woodroof, 1975). The canned Nigerian orange juice had an iron concentration of 14% compared to 0.909 x 10^{-2}% found in the French orange pellorce.

It is thus essential that good quality cans be used in storing the Nigerian orange juice. In addition, efforts should be made at decreasing the storage duration. Alternatively canned food products should be preserved at suitable temperature to prolong storage and at the same time retaining flavour and other nutritional values. The processing plants should be regularly cleaned to avoid contamination by heavy metals.

The Italian canned Salsa tomato paste had most of the nutritional values comparable to the Nigerian Processed Vegfru tomato paste. It might be necessary to reduce the importation of tomato paste since the ones manufactured locally have the same quality as those imported.

The factory Vegfru paste had the highest Ash content of the samples analysed but this was not reflected in the mineral content. This seems to suggest that there is no exact relationship between Ash content and minerals values. The Salsa paste which had relatively lower values of ash ironically had the highest mineral concentration in most cases.

Analyses of individual tins were carried out several times for various constituents. Results showed that in most cases values obtained were representative of the whole food-stuff when compared to those obtained by bulking.

A further appraisal of the entire analyses showed that the tomato pastes had very high nutritional values compared to the orange juices. The nutritional values obtained in most cases were comparable to literature values. This probably ruled out the presence of additives during processing except in the case of French orange pellorce where there was evidence of sugar and a few other additives.

Predigestion with Nitric acid (69%) up to 100 minutes proved a very efficient method of determining phosphorous compared to the other conventional ashing methods. It is probable that pre-digestion with Nitric acid was essential

for destroying the relatively higher lipid, tannin, starch, crude fibre and protein of the tomato pastes. Even in the presence of ash aid (Magnesium acetate, 20%) the phosphorous estimated did not differ significantly from that without an ash aid. However, it would be necessary to mention that trial digestions should be carried out to ascertain the most suitable method of sample digestion. The relative merits of wet and dry oxidations have been exhaustively discussed (Gorsuch, 1959) and there are a host of citations in favour of wet oxidation especially involving the use of nitric acid (69%) and perchloric acid (60%).

The government should lay down legal requirements for the products processed in the country and also for those imported. It would be necessary to specify expiry dates on processed foods by food manufacturing companies to avoid the hazards of consuming foods which are contaminated due to prolonged storage. It would be necessary to improve the quality of cans used to avoid easy dissolution of the materials under acidic conditions.

As an extension of this work for future researchers it is suggested that further investigation be carried out on the effect of predigestion with acids on the estimation of other

minerals other than phosphorous. It is also suggested that detailed and systematic investigation be carried out on the contamination of canned foods by iron, lead and tin.

REFERENCES

1. Adrian, W.J. "Analyst" 89 pg. 213, (1975)

2. Allan, J.E. "Spectrochim" Act (1959) 10. Pg. 108.

3 Allan, J.E. "Spectrochim Acta" (1961) 17 Pg. 459.

4 Allen, S. E., Grimshaw, H: Parkinson, J.A.; and Quarmby C;
Chemical Analysis of Ecological Materials.
Blackwell Scientific Publications (1974).Ch. 1-VIII

5. Analytical Methods Committee - "Analyst (1960) 85 Pg. 629

6. Analytical Methods Committee - "Analyst (1967) 92 Pg. 320.

7. Analytical Methods Committee - "Analyst (1959) 84 Pg. 127.

8 Amos, A,J; Billington, A.E.; Burrell,J.R; Cutting,C.L;

9 Davis, J.G. Nickinson, D; Evans,G; Gane, R; Gerrard, F; Gooding,
E.G.B.; Ingrams, C.D; Paine. F.A; Slade F.H. Williams,C.T.
Food industries manual (1962) London. Chapter 1 -VII.

9 Bear, F. E. "Land (1948) 7 Pg. 378.

10 Bengtsson, B.L. "Journal of food technology" (1968) 4 Pg.141.

11 Bidwell, G.L. and Bopst, L.E. "Journal of the Association of
official Agricultural Chemist" (1971) vol.5, Pg. 58.

12 Braverman, J.B.S. Citrus Products (1949). Interscience Publishers
Inc. New York. Chapter 1 - 10.
Commercial Production of Tomatoes - "Farmers bulletin" (1952)
No.2045.

13 Crues, W.V. Commercial Fruit and Vegetable Products. (1958) Mcgraw Hill Book Company, Inc. New York. Chapter 1- 26

14 David, D.J. "Atomic Absorption Newsletter". Dec. 1962.

15 Dedolph. "Environmental Science Technology" 1970) 4

16 Dickinson and Raven, T.W. "Food Manufacture" (1962) 37 Pg.480

17 George, S and Maynard, A. Introduction to Food Science and Technology. Academic Press, New York, 1973.

18 Goldstein, J.L. and Swain, T. "Phytochemistry" (1963) 4 Pg.185

19 Gorsuch, T.T. "Analyst" (1959) 84 Pg. 135.

20 Harris, S.R. and Loesecke, H.V. Nutritional Evaluation of Food Processing. Avi Publishing Company (1971).Chapter 1-8.

21 Isaac, R.A. and Jones, J.B. (1972) "Comm in Soil Sci and Plant. Anal". 3 2261.

22 Jacobs, B. Morris. Chemical Analysis of Foods and Food Products. 3rd Edition. National Company Incorporated Toronto. 1938. Chapter 1 - 20

23 Joslyn, Maynard - Methods in Food Analysis 2nd Edition Academic Press London(1970). Chapters 1-22

24 Luh, S.B. and Woodroof Jasper. Commercial and Vegetable processing. Avi Publishing Company, 1975. Chapters 1-16

25 Lane, J.H. and Eynon L. "Journal of Society of Chemical Industry" 1923 42 32T.

Middleton and Stuckey (1953). Cited from Chemical Analysis of Ecological Materials by stewart E. Allen.

Mital, S.P. and Thomas, T.A. "Indian Council of Agric. Research New Delhi". 1923 Pg. 1.

Moxon A and Rhian H. "Proc S. Dakota Acad. Sci" 18, Pg.20

Nakamura, R. "Journal of Horticultural Association Japan" (1961) 30 Pg.73.

Nightingale. G.T. "Plant Physiology" (1931) 6 Pg.605

Page. A. Lead quantities in Plants Soils and Air near some major highways in Southern California, 1971.

Pearson, D. Chemical Analysis of Foods 7th Edition Edinburgh, 1976. Chapter 1-7

Petropavlovskii, E.I. and Troyan, Z.A. "Chemical Abstract" 73 Pg. 2746d. 1962.

Piper, C.S. (1950). Soil and Plant Analysis.

Potter, N. Food Science. Avi Publishing Company, 1968. Pg.245

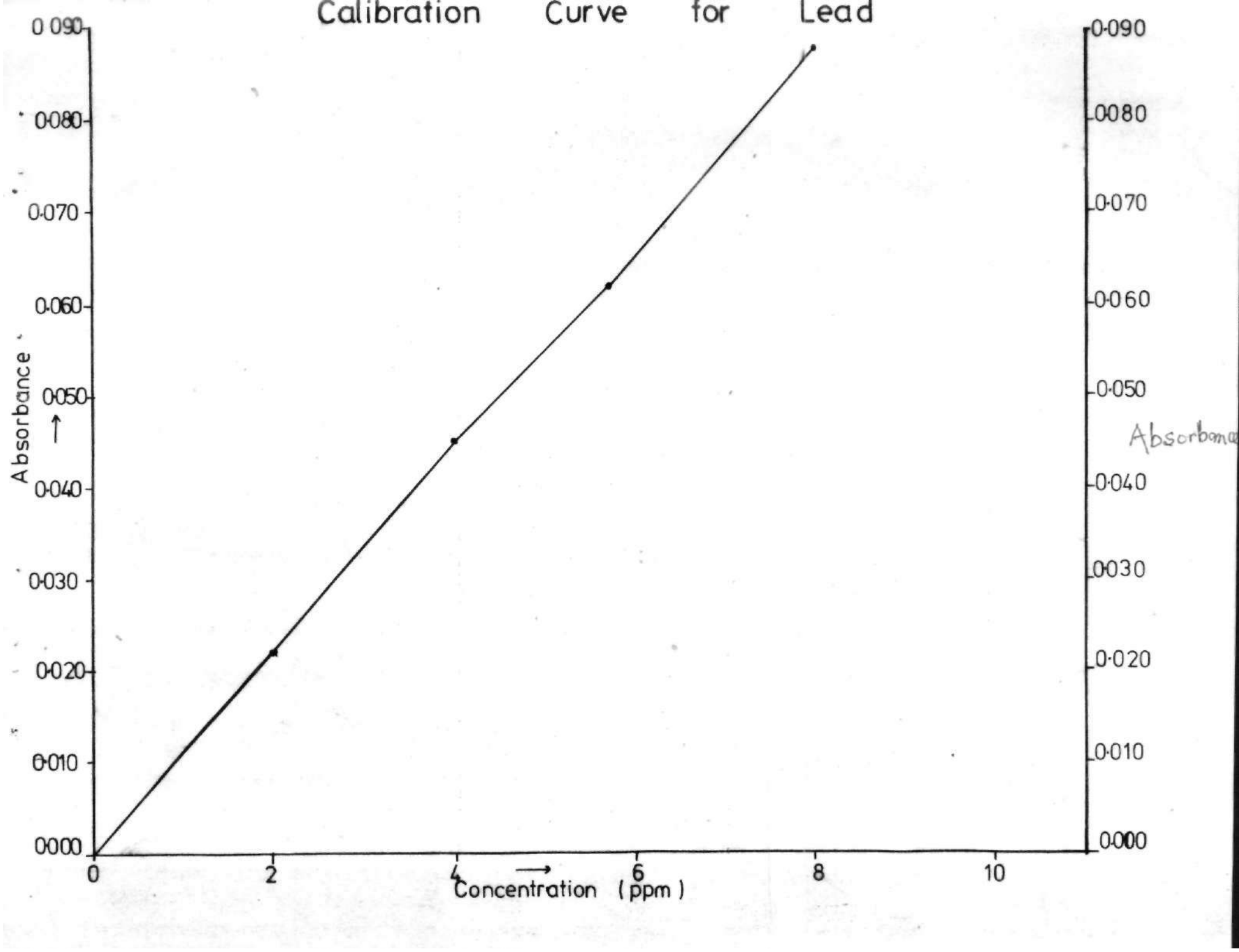
Pratt, P.F. and Chapman, H.D. (1961) Methods of Analysis for Soils, Plants and Water, University of California.

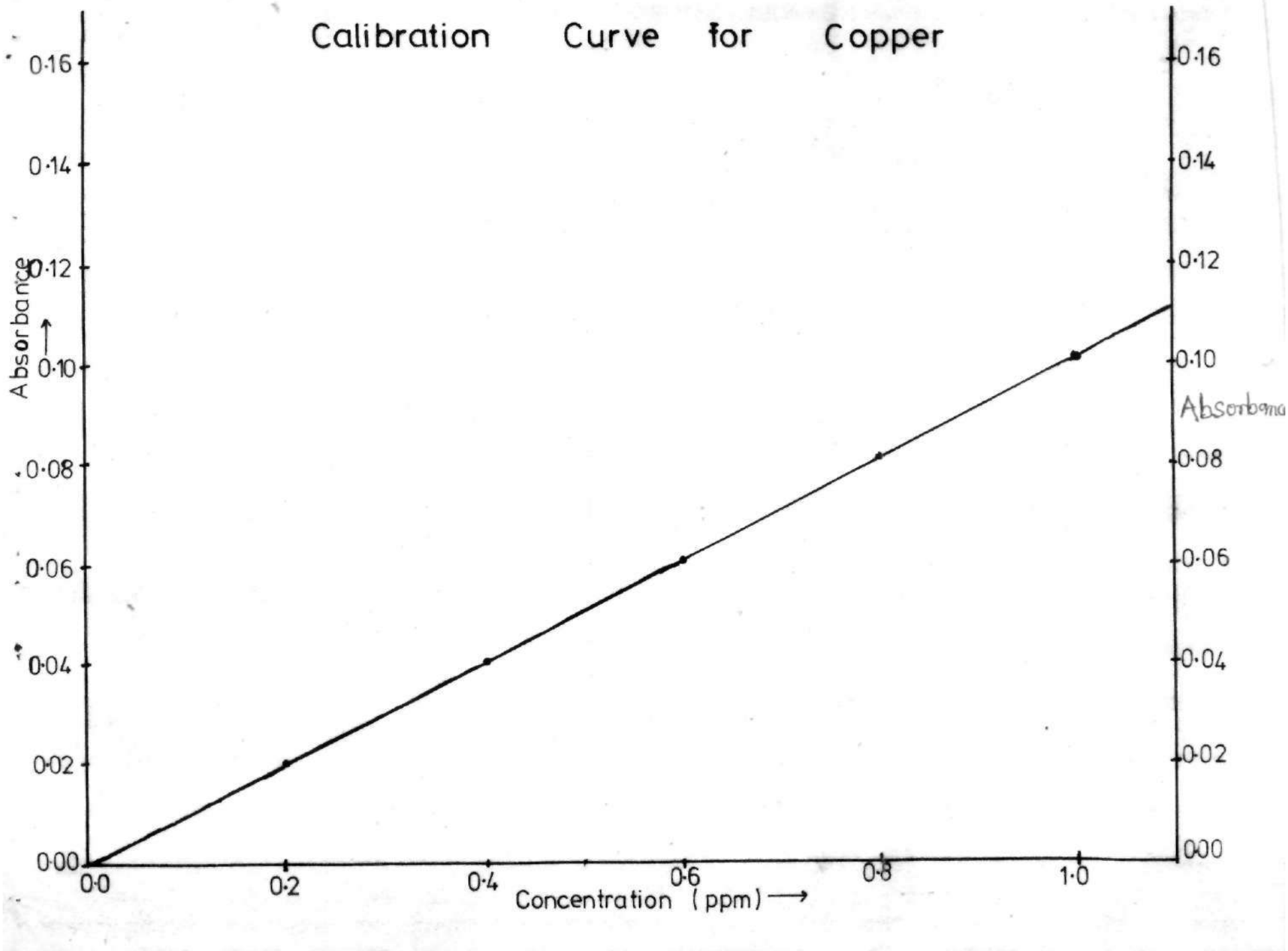
Reuther, W and Labanaukas. Copper in diagnostic criteria for plant and soils. 1966.

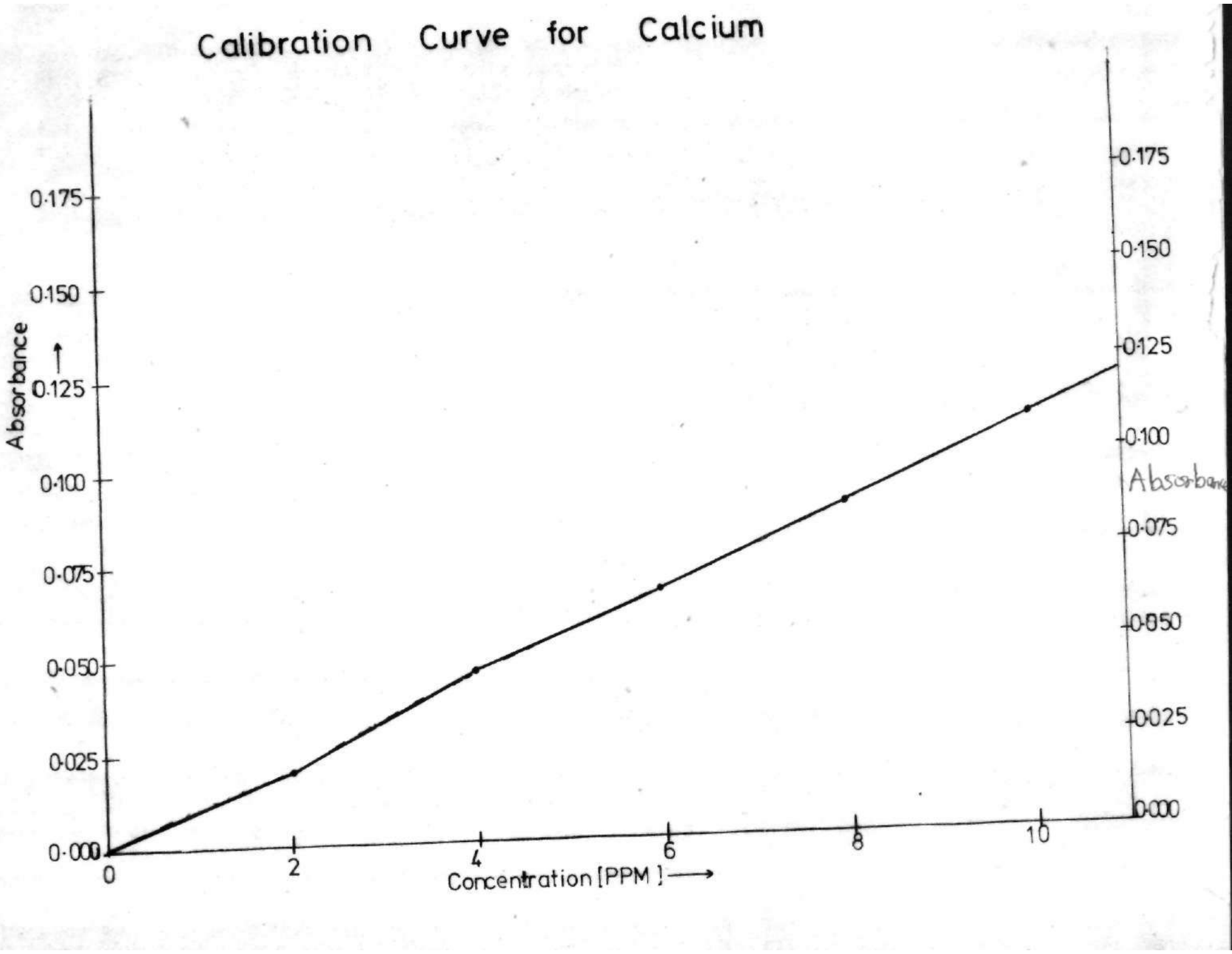
Rowe. B.C. and Bonney, V.B. "Journal of Assoc. of Agric. Chemists" (1965) 19 Pg. 620.

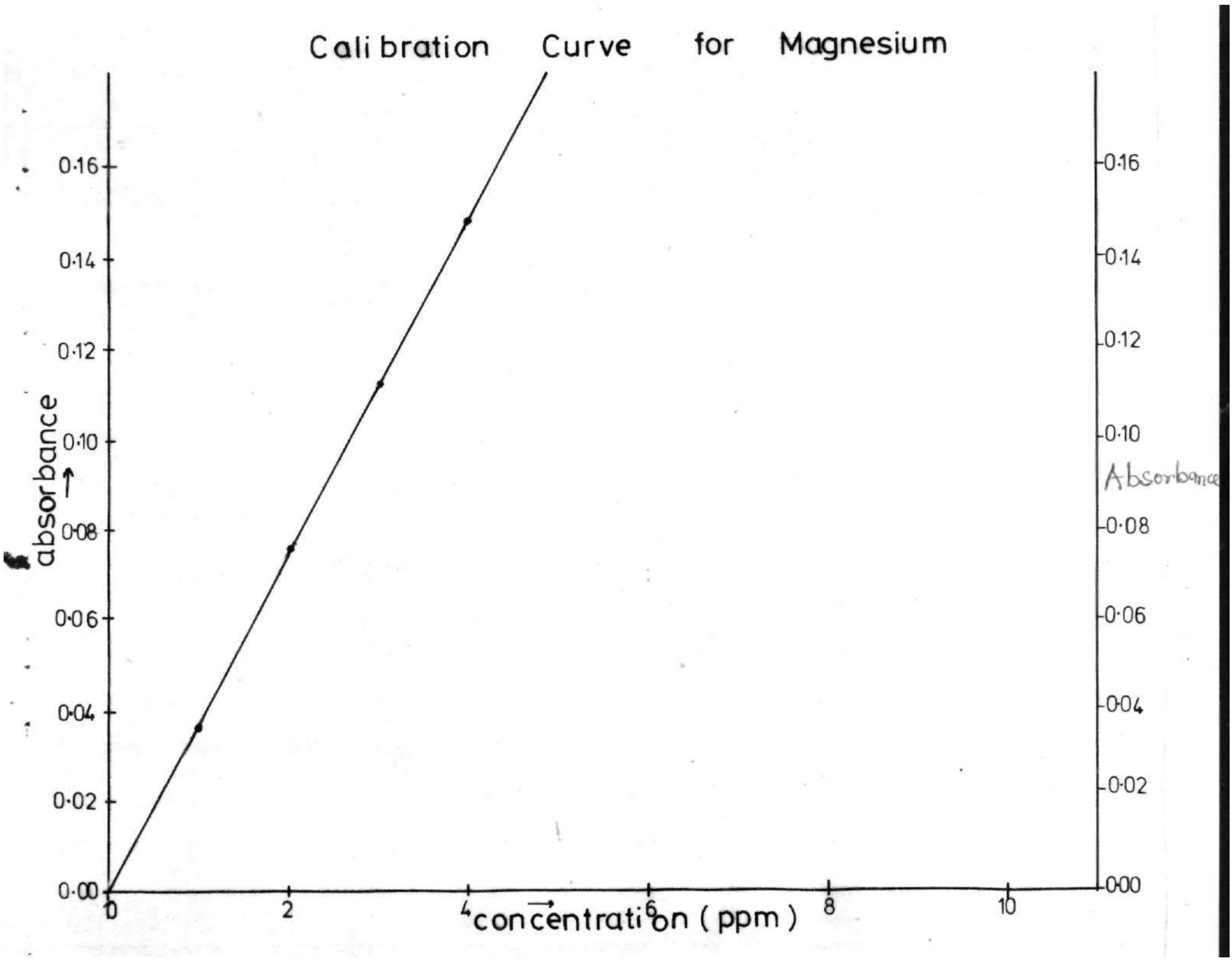
Sims, G. T. and Volk, G.M.niv. Agric. Expt. Sta. Bull.
No.438. (1967).

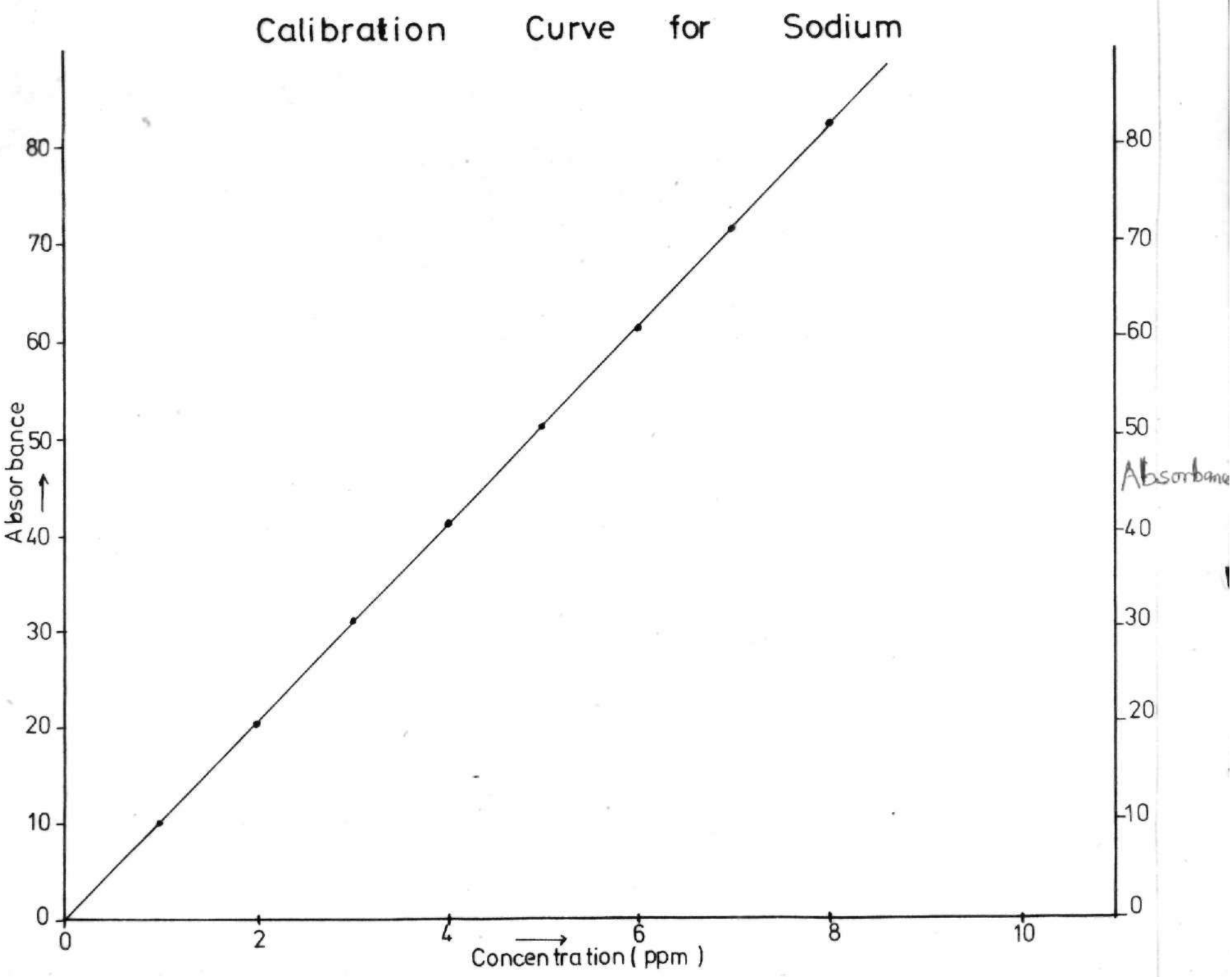
Thomas B and Rou;ham J. Jci. Food Agr. (1973) 24 Pg. 447.

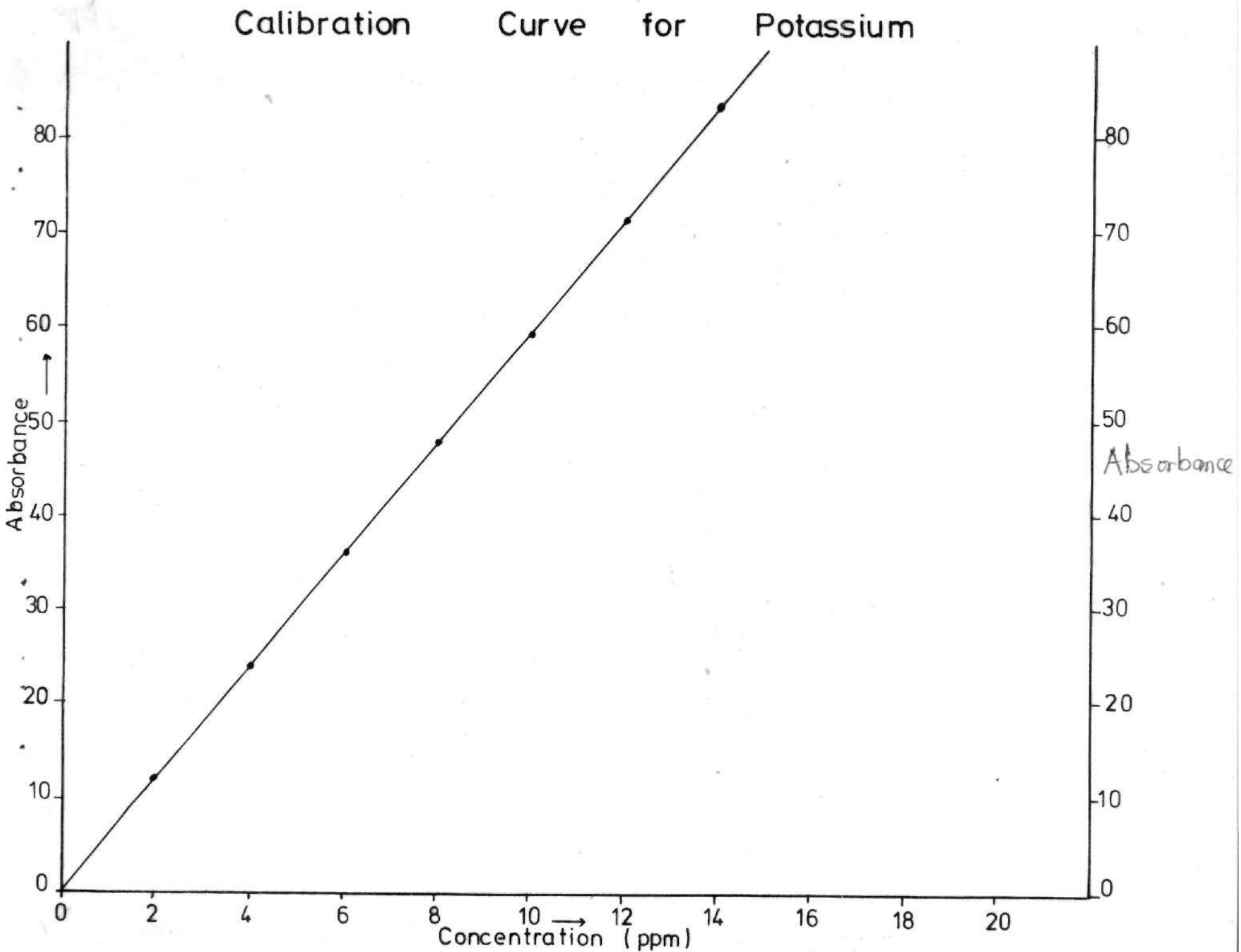

Calibration Curve for Lead
Absorbance
0·090
0·080
0·070
0·060
0·050
0·040
0·030
0·020
0·010
0·000
0
2
4
6
8
10
Concentration (ppm)

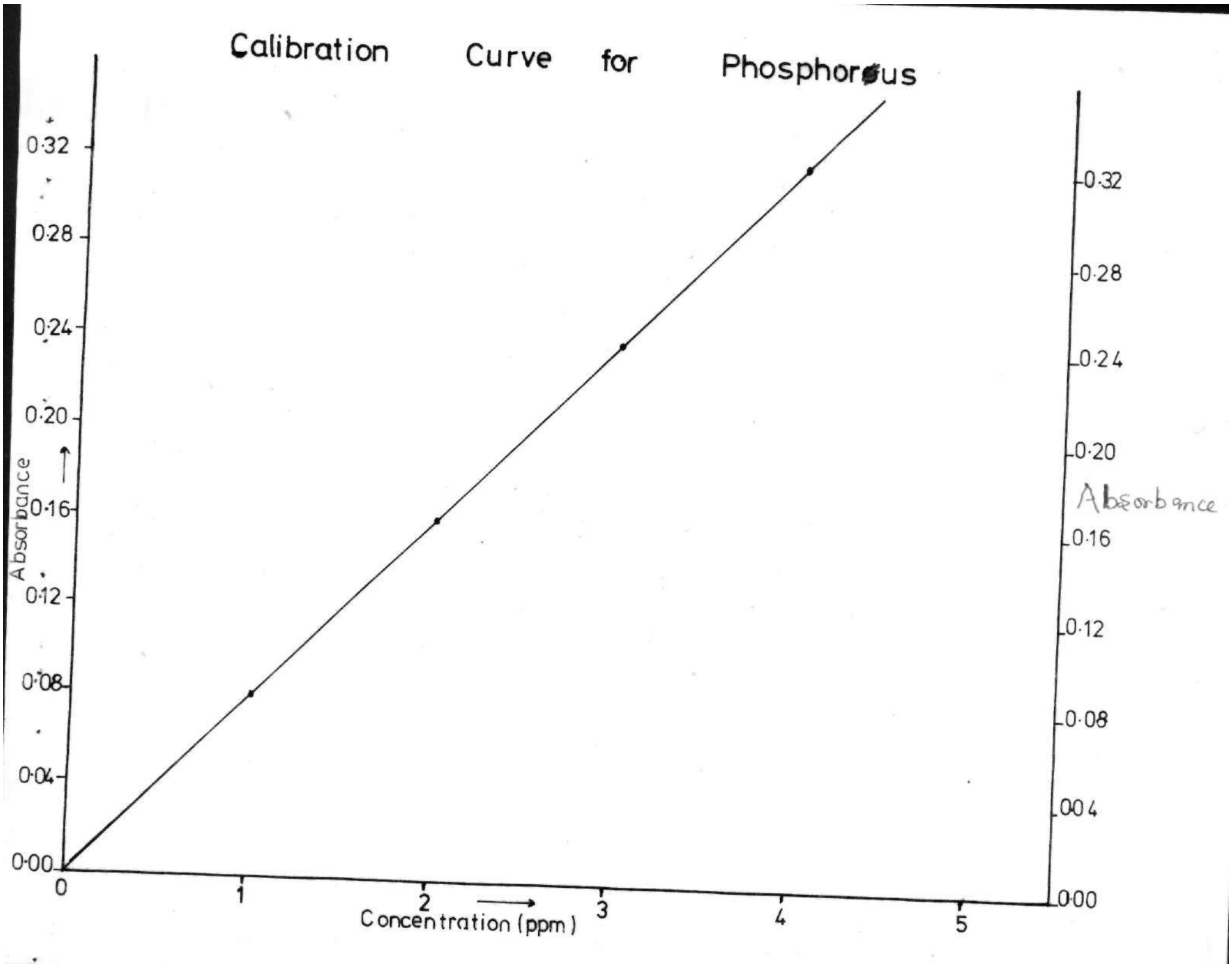

Calibration Curve for Copper
Absorbance
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0·00
0·0
0·2
0·4
0·6
0·8
1·0
Concentration (ppm)

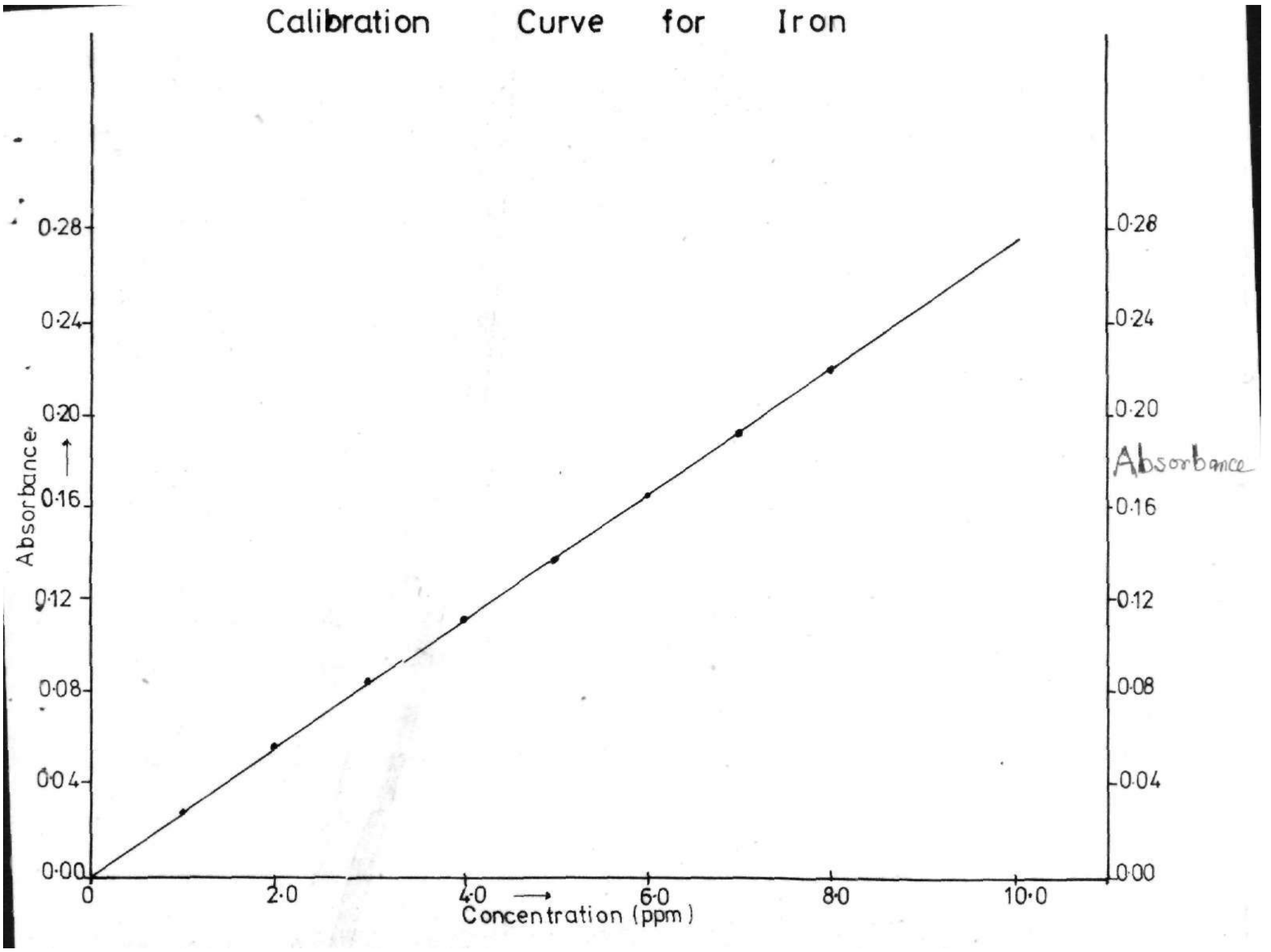

Calibration Curve for Calcium
Absorbance
0·175
0·150
0·125
0·100
0·075
0·050
0·025
0·000
0
2
4
6
8
10
Concentration [PPM] ⟶

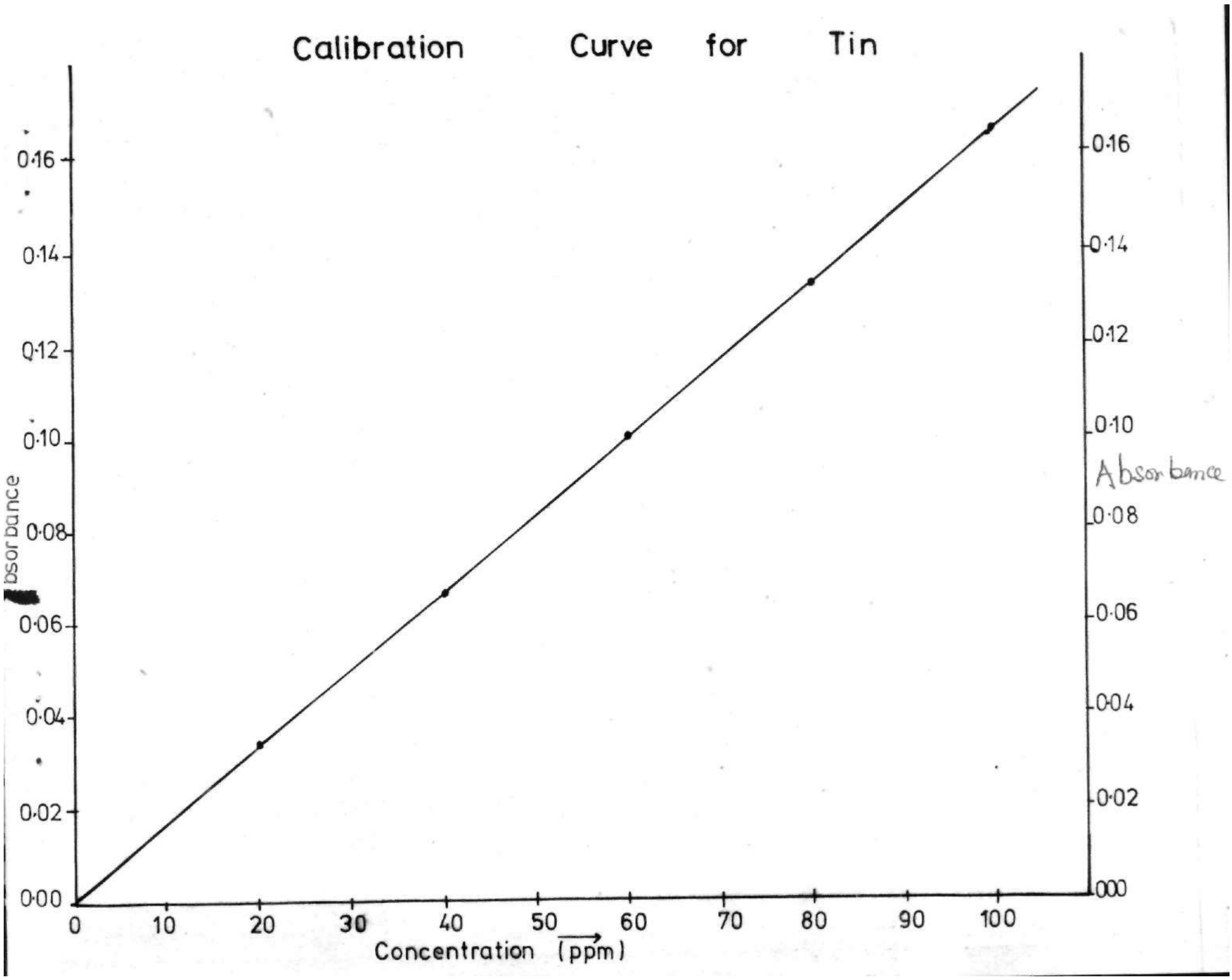

Calibration Curve for Magnesium
absorbance
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0·00
0
2
4
6
8
10
concentration (ppm)
Absorbance

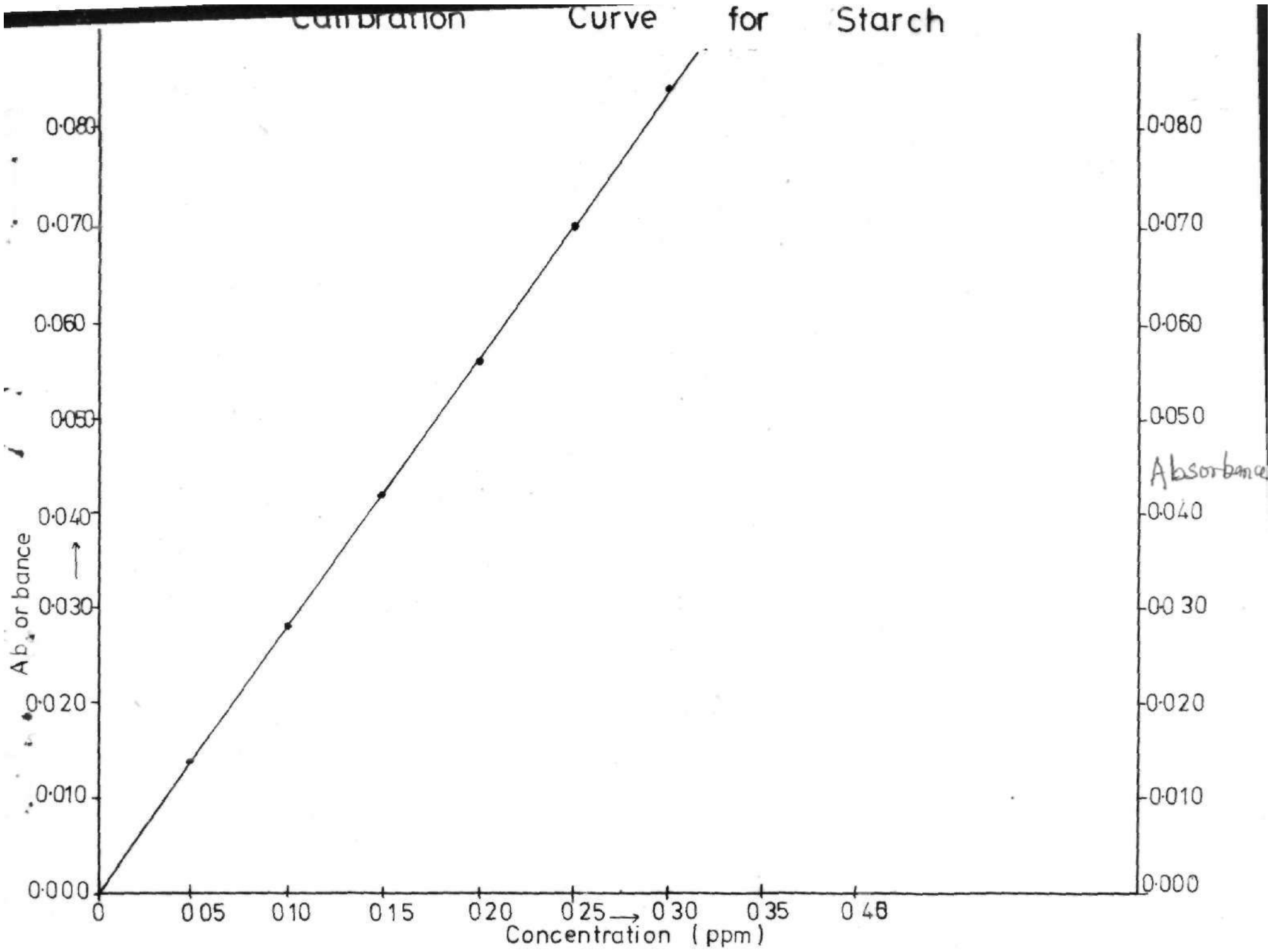

Calibration Curve for Sodium
Absorbance
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
Concentration (ppm)


Calibration Curve for Potassium
Absorbance
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10
12
14
16
18
20
Concentration (ppm)
Absorbance


Calibration Curve for Phosphorous
Absorbance
0·32
0·28
0·24
0·20
0·16
0·12
0·08
0·04
0·00
0
1
2
3
4
5
Concentration (ppm)


Calibration Curve for Iron
0·28
0·24
0·20
0·16
0·12
0·08
0·04
0·00
Absorbance
0
2·0
4·0
6·0
8·0
10·0
Concentration (ppm)


Calibration Curve for Tin
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0·00
Absorbance
0
10
20
30
40
50
60
70
80
90
100
Concentration (ppm)


Calibration Curve for Starch
0·080
0·070
0·060
0·050
0·040
0·030
0·020
0·010
0·000
Absorbance
0 005 010 015 020 025 030 035 040
Concentration (ppm)