A PRELIMINARY ANALYSIS Of SAMPLES OF 'KANWA' FOR SODIUM, POTASSIUM AND OTHER MATERIALS.

BY

E. J. EKANEM

THESES

Presented in Partial Fulfilment

For The Degree of

M.Sc. (Analytical Chemistry)

at

AHMADU BELLO UNIVERSITY,

ZARIA, NIGERIA.

JANUARY 1977

ACKNOWLEDGEMENTS

I am grateful to my teachers in the Chemistry Department for laying the foundation for this work and particularly to Dr. G.F.S. Harrison, who supervised all stages of it. My thanks are also due to Professor A.R. Mathieson, the Head of Chemistry Department, for arranging the facilities which sustained the work. My appreciation also go to the Soil Science Section of the Institute for Agricultural Research, Ahmadu Bello University, for permitting the use of certain equipments for this work, and Dr. F.R. Spalding.

DECLARATION

I wish to declare that this theses is wholly the result of my own investigations and that it has not been and is not being presented for any other degree.

.....
CANDIDATE

.....
SUPERVISOR

.....
Ag. HEAD OF DEPARTMENT

ABSTRACT

Forty three samples of Kanwa were analysed for **their** sodium and potassium content using flame photometry and atomic absorption spectroscopy. Both methods gave similar results; the samples showed about 30% of sodium and 0.1-4% of potassium; a few results were outside these ranges. The anions, carbonate, chloride and sulphate were detected in the samples; sulphide was not indicated in any sample. In the brightly coloured samples, sample nos. 5, 13, 28, 29, 38, and 40, manganese was detected and determined by the ammonium persulphate oxidation method. The proportion of manganese in these samples was of the order of 10 %.

CONTENTS

CHAPTERS		PAGES
	Acknowledgements	i
	Declaration	ii
	Abstract	iii
I	Introduction	1
	A. The Flame Methods	3
	B. Instrumentation	5
	C. Interferences	8
	D. Levels of Analysis	12
II	Materials and Methods	14
	Preparation of Samples	14
	Qualitative Analysis	14
	A. Solubility Properties of Samples	14
	B. Anion Analysis	14
	C. Flame Tests	15
	D. Qualitative Analysis for Transition Elements	15
	E. Detection of Transition Elements by Visible Spectrophotometry	24
	Quantitative Determinations	24
	A. Preparation of Samples Solutions	25
	B. Preparation of Standard Stock Solutions	25
	C. Determination of Sodium and Potassium by Flame Photometry	26
	D. Determination of Sodium and Potassium by Atomic Absorption Spectroscopy	29
	E. Colorimetric Determination of Manganese	30
	F. Determination of Manganese by Visible Spectrophotometry	34
III	Results	35
	Calculations	47

CONTENTS (CONTD)

CHAPTERS	PAGES
DISCUSSION	49
Conclusion	54
Appendix	55
References	58

I. INTRODUCTION

'Kanwa' is the Hausa name for natron, a dried lake salt which is largely hydrated sodium carborate (1). It is a product of the salt industry in many parts of Northern Africa (2), having a high sodium content but very little potassium (1). It is taken as a medicine for all sorts of minor ailments in Northern Nigeria (3). It is common practice in the areas of Hausa majority in Northern Nigeria to administer large quantities of 'kanwa', in the form of a porridge of guinea corn or millet, to nursing mothers as a medicine to increase the quantity and improve the quality of breast milk. This practice is continued daily for periods extending to six weeks and as much as 30g of the salt is consumed daily (1). Davidson and his co-workers (1) have associated the incidence of peripartum cardiac failure, a type of heart failure observed in nursing mothers, also in the areas of Hausa majority in Northern Nigeria, with this practice of taking 'kanwa'. They have, however, not given the sodium and potassium levels in the salt although they have explained the illness in terms of high sodium intake associated with the 'kanwa' diet. Although the analysis of 'kanwa' has not been reported in the literature, two varieties of it in Nigeria have been described - a variety containing about 20% of sodium carbonate with 27% of sodium sulphate and another containing about 88% of sodium sulphate. They both contain little or no potassium. All varieties marketed show much variation in composition, possibly due to adulteration (3).

The plan for this work then was to carry out an analytical survey of 'kanwa' samples with an aim to determine the proportions of sodium and potassium in them and also to qualitatively identify the anions present in the samples. It was planned to analyse the samples for these alkali elements by both flame photometric and atomic absorption methods ao that the results would mutually check one another. The presense of a nice pink colour in some of the samples suggested the presence, in them, of some transition elements. This suggestion was based on the general observation that transition elements exhibit colours in their condensed states. To attempt to detect the transition elements to which the observed colours would be ascribed it was also planned to perform selected chemical tests on those samples which had colour. It was then hoped that some colorimetric method would be employed to determine the colouring element.

THE FLAME METHODS

In practical flame photometry the substance to be analysed is introduced into a flame so that the element to be determined gets excited and emits a radiation of a characteristic frequency. The emission intensity is measured and related to the concentration of the emitting element in the analysis material. In atomic absorption spectroscopy the analysis material is also introduced into a flame in which it yields a population of free atoms of the element to be determined. The atoms are irradiated with radiant energy of a frequency which is characteristic of the element so that they get excited by absorbing part of the radiant energy. The diminution in the intensity of the radiation after it traverses the flame is measured and related to the concentration of the absorbing element in the analysed substance. The two methods are therefore similar in principle: the element to be determined is made to undergo a change in its electronic energy state and subsequently either emit radiant energy or absorb radiant energy supplied by an external source.

In both methods the analysis material, usually in a suitably diluted solution, is initially atomized to produce the element to be determined in an uncombined state. In flame photometry it is critical that the element atoms must initially be rendered in some excited electronic energy state; they then get de-excited and return to lower electronic energy state by emitting the characteristic frequency of the element. The flame serves the dual function of aiding the

atomization and exciting the analysed element to a high electronic energy state (4). In atomic absorption spectroscopy, on the other hand, the flame only aids the atomization of the sample and provides a medium for containing the ground state atomic population which is required. The excitation of the ground state atoms to higher electronic energy states and the attendant absorption of radiation are induced by the radiation from an external source (5). In either case the total intensity of radiation either emitted or absorbed usually varies as the number of particles of the element contributing to it. When thermal equilibrium is maintained in the flame the intensity, I, either emitted or absorbed from an externally supplied spectral line, shows the relationship

$$I = NAe^{-\Delta E/kT} .$$

where N = no. of particles of element either emitting or absorbing the radiation.

A = probability of transition from an initial to a final energy state.

ΔE = energy difference between the intial and final energy states.

K = Boltzmann constant

T = absolute temperature of the flame medium.

For a given chemical specie either emitting or absorbing radiation in a particular flame the term $Ae^{-\Delta E/kT}$ in the above equation remains constant. Then the intensity, I, depends only on the number, N, of the emitting or absorbing species when the introduction of the chemical specie into the flame is accomplished in a constant way; so the intensity

depends on the concentration of the element in the sample solution, everything else being equal. (4,6)

In practice the parameter measured is some function of the intensity: typically the emission from the flame (flame photometry) or the exciting radiation after it traverses the flame and recombines with a reference beam, is gathered onto a photosensitive device which generates a current of a magnitude corresponding to the emission or absorption intensity. This current is subsequently fed into a measuring device to incite a response which is directly proportional to the emission or absorption and to the concentration of the emitting or absorbing element in the sample. To permit the determination of unknown concentrations a calibration of the method is first performed by measuring the response for known concentrations of the element to be determined. A calibration curve is then prepared and used to deduce concentrations of the unknown solutions from their measurements.

INSTRUMENTATION

As shown in the flow diagram in Fig.1, similar components are involved in the design of equipments for both flame photometry and atomic absorption spectrophotometry.

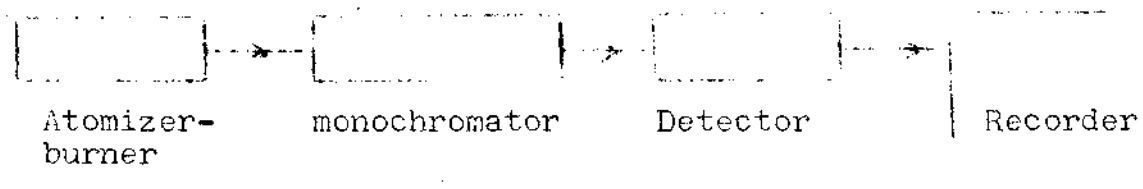


Fig. I

In the atomizer-burner unit some combustible gas is mixed with an oxidant gas and lighted to produce a flame above the burner (6, 7); the flow of the oxidant gas to the flame is utilized to aspirate the sample solution through the atomizer and carry the atomized particles sprayed into it to the flame (6, 7). Suitable provision in the design of the burner and apropriate control of the flow of the flame gases and of the sample solution through the atomizer and burner (4,6,7,8) are adopted to ensure stability of the flame. In flame photometry normal cooking gas, a propane-butane mixture, is dominantly employed as fuel gas and air/oxygen as oxidant; in atomic absorption spectroscopy acetylene is the usual fuel gas while air, oxygen or nitrous oxide are used as oxidants in various situations. (9,10)

Monochromators are employed for differentiating the radiation from the flame into narrow lines for measurements. A wide range of interference filters is currently available for monochromatic photometry and they are widely employed in combination with colour filters to eliminate background and other unwanted radiations in flame photometry. Interference filters produce a narrower spectral line width(11) and are prefered to coloured glass or gelatin filters which depend on absorption, reflection, or polarization effects(12). In flame photometers where the source has a large emitting surface and a very large fraction of its emission must be collected, filter monochromators are generally more efficient than dispersing elements which are prefered in systems, like

atomic absorption flames, as they can utilise light from a very small area of the source(4,6). So in atomic absorption spectrophotometers grating monochromators are employed and, by dispersion of the absorption line, they isolate the analytical spectral line, from others which lie close to it, for measurement. These other lines could originate from the source where a composite source, like a vapour discharge lamp, is employed.

In both flame methods the radiant line passed through the monochromator impinges on a detector and incites a response from it which varies as the intensity of the line. In flame photometry the detector is some kind of photocell (13) which changes the radiant intensity falling on it to some measurable form of energy, usually electrical energy. The detector in atomic absorption spectrophotometers is usually a photomultiplier (5) which permits very high amplification and makes the method specially suitable for determining trace concentrations of elements. In either case the response incited in the detector is displayed on the recorder. This could be a simple linear scale, measuring results like galvanometer deflections, in the flame photometer or a chart, scale or digital display in atomic absorption spectrophotometers.

In addition to the above components atomic absorption spectrophotometers contain a radiant source which contains the element to be analysed and emits the characteristic absorption frequency of the element. Hollow cathode lamps are dominantly employed as sources but for liquid and soft elements

like the alkali elements which possess high vapour pressures at comparatively low temperatures vapour discharge lamps are used (14). The best sources for these more volatile elements, however, are microwave discharge lamps which give increased sensitivity but they require a separate power supply (7, 14, 9,10). These sources are line sources with emissions which closely approximate the absorption lines of their respective elements. Their narrow band widths, about 0.001 nm at half height, places less demand on the monochromator for high resolving power (15).

Interferences

Literature account of interferences in flame photometry does not reflect agreement between the various reports. Sodium and potassium have been reported to mutually increase (16) their emissions in certain cases while in other reports they are reported (17) to mutually decrease their respective emissions. Excess sodium has been reported (18) to lead alternately to high and low results for potassium determination depending on the concentration of potassium while other reports (19) indicate that sodium does not affect the determination of potassium. The conflict in the literature reports has been attributed to wrong deductions arising from poor selection of wavelength for measurements and neglect of the background radiation (4). It is, however, believed that the conflict in the observations would be resolved if a sufficiently selective monochromator were used to select for measurement that narrow band containing the appropriate spectral line and by

measuring the line intensity above background level. The line intensity above background does not change significantly in the presenceof other cations eventhough there is a marked increase in background intensity (4).

Where an efficient monochromator has been utilized and suitable adjustment made to allow for background fluctuation, any correctly identified interference could arise from fluctuations in the pressures of both the fuel gas and oxidant. These fluctuations reduce the efficiency of the atomization process, lead to non-constant flame characteristics including its temperature and non-constant rate of introducing the atomized particles into the flame (4,6). The emission of a metal excited in a flame is, within certain limits, independent of the nature of the non-metal with which it is combined and of the other metals present in the same solution. In certain cases and above certain concentration limits, interferences in these emissions have been observed and attributed to variation in the normal emission of the flame i.e. background, a superposition of band spectra due to compounds present or formed in the flame over the line spectra of interest, and reactions occuring in the flame (6).

In the particular case of the alkali metals background correction is often not required because the highest sensitivity for these elements is obtained in very cool flames, in which other elements do not emit efficiently. Moreover, these elements exhibit an inherently high sensitivity compared to others; their spectra are simple and do not overlap one another. A type of cation interference reported

for these elements arise from their generally low ionization potentials, so that at higher flame temperatures a large proportion of any one of them may be in the ionic form. If at least two of them occur together in the same sample, mutual enhancement of their emissions may be observed (19). This is particularly true for cesium, rubidium, and potassium. The ionisation of an extraneous alkali element raises the concentration of electrons in the flame and reverses the ionization of the analysis element. This amounts to reversing the equilibrium

$$M \longrightarrow M^{+} + e^{-}$$

which has the effect of increasing the amount of the analysis element, M, in the flame. A correction for this type of interference is usually approximated by introducing a sufficiently large quantity of the interfering element into the analytical sample and reference so that maximum spectral enhancement is provided in both; then emission intensity does not vary with small changes in sample composition (4,20). The interference of chloride, which has also been reported for the alkali elements, may be reduced by suitably adjusting the flame to maintain optimum composition or temperature (7).

Interference effects encountered in atomic absorption methods and measures to correct them are similar to those relating to flame photometry. To prevent interferences associated with fluctuations in them the pressure of the flame gases, the efficiency of atomization and rate of flow of atomized particles to the flame are regulated by suitable

settings of the instruments. The flame always acts as a source as well as an absorber of resonance radiation; the emission of the analytical line by the flame constitutes an interference. With a photomultiplier detector, a modulated light source and a tuned amplifier can be used to minimise the effects of any unwanted emission or varying background from the flame. Nearly all instruments (7) provide this type of modulation either by supplying the lamp with pulsed current or by chopping the light beam with a rotary shutter, then the emission from the flame will not produce a response in the detector. A major chemical interference in atomic absorption, encountered particularly in analyses for alkaline earth element results from the formation of refractory compounds of the element to be determined: these could be the oxide of the element or some compound containing an oxyanion like silicate, phosphate, or sulphate. This type of interference is usually overcome by using a hotter flame for the determination, to enhance the breakdown of the stable compound into the element. Alternatively another element which is known to form a more stable oxide than the element analysed for is added to serve as a releasing agent. The releasing agent, M', normally introduced in excess of the analysed element, M, accepts the anion from the analysed element, thereby

$$M - Ox + M' \longrightarrow M' - Ox + M$$

releasing it to be determined. Strontium II and lanthanum III are commonly used as releasing agents. Another chemical interference, which characterises the determination of alkali

elements, arises from the ionization of the metal atoms in the flame and is allowed for by adding lanthanum III to act as ionization buffer (9,10).

Levels of Analysis

Flame photometry is intensively applied to the determination of the alkaline elements though the method has also been used to determine other elements (4,6). The method is sensitive enough for the ppm range of concentrations, given optimum efficiency of the atomizer system and photocell. With a more effective excitation method, the high amplification of the photomultiplier detector (13) and more effective ways of accounting for interference effects, atomic absorption methods are prefered for much lower concentrations of analysis elements. Atomic absorption spectroscopy is the method of choice for trace element analysis and generally where the concentration of the element of interest is minor. In this range of application the technique has measures for improving the sensitivity of the method: these include tuning the machine for higher sensitivity when concentrations are very low, a scale expansion device which permits a higher level of discrimination between similar concentrations and methods aimed at increasing the effective concentrations of the element of interest. To use atomic absorption spectrophotometry for determining major components, which is not the usual application, the sensitivity of the instrument has to be reduced. This is effected by selecting a spectral line which gives

the lowest sensitivity for the relevant element, reducing the pathlength by turning the burner head through 90° and by suitable dilution of the sample solution (9,10,15).

In addition to the above, other merrits of atomic absorption which commendits use for determining low concentrations of elements include the following:-
Since it deals with free atoms in the ground state it is a very sensitive method compared with the emission method in which the flame must raise the free atoms to an excited state after dissociating the molecules to release them; only the dissociation is required in the absorption method. A consequence of this difference is that while the absorption is independent of the flame temperature the emission depends critically on it (5). *Interference between the analytical spectral lines and background emission is more effectively controlled in atomic absorption methods and superposition of molecular band spectra over the atomic line spectra is of no significance since only the narrow absorption line of the modulated emission from the hollow cathode is measured by the instrument; any emission from the flame being without effect.

II. MATERIALS AND METHODS

Preparation of Samples

The samples were collected from different sources as listed in Appendix I. Each was visually observed with the aid of a hand lens to establish its properties as listed in Table I. The entire sample was ground fine with mortar and pestle, mixed thoroughly, and stored in a stoppered bottle. Sample specimens for qualitative analysis were taken from the ground bulk without further treatment. For quantitative analysis, however, the bulk of ground sample was coned and quartered to obtain a sample from which the specimen for analysis was weighed. The weights were taken on a mettler balance.

Qualitative Analysis (21,22)

A. Solubility Properties of Samples

To discover a suitable solvent for the samples the solubility behaviour of each was observed in water; dilute nitric acid (2M) was tried in cases where the solution in water was not clear. Results were observed as in Table II.

B. Anion Analysis

Classical methods of analysis were used to establish the presence in the samples of the anions $CO_3^{=}$, $S^{=}$, Cl^{-}, and $SO_4^{=}$. The reagents used were prepared to conform with specifications for normal qualitative anion analysis. Results were as listed in Table II.

C. Flame tests (22)

Flame tests were performed on the dry sample to establish the presence of sodium and potassium; this was to present the introduction of these elements in the solvent. Results were obtained as listed in Table II.

D. Qualitative Analysis for Transition Elements

The tests for transition elements were performed on only those samples which exhibited a colour: these included samples Nos.5, 13, 28, 29, 38, and 40. The following tests were performed for the respective elements using freshly prepared reagents and results were obtained as in Table II.

Titanium

(a) The most common method for detecting titanium is based on its reaction with hydrogen peroxide, which forms a complex with it giving a yellow to orange colour by which it is identified. This colour which is bleached by fluoride is also given by vanadium but the vanadium complex is not bleached by fluoride. The limit of detection is 2 ug of titanium in a limiting dilution of 1:25,000 (23,24).

Reagents: 3% hydrogen peroxide; 4M. $H_2 SO_4$

Procedure: A small amount of sample was dissolved in 4M sulphuric acid in a test tube; 1 ml of hydrogen peroxide (3%) was then added. The test was performed on a solution of titanium chloride as reference.

(b) In the Pavelka test, titanium produces a red-violet colour when mixed with alizarin and exposed to ammonia fumes.

The colour deppens on drying the mixture on fitter paper (25).

Reagents: An alcoholic solution of alizarin was made by dissolving 0.5 g of the reagent in a litre of rectified spirit; ammonia solution.

Procedure: A filter paper was treated with the alizarin reagent, a drop of the sample solution was then placed on the filter paper and exposed to ammonia fumes. Titanium chloride was tested as reference.

(c) Reagents: Thymol was dissolved to make a 2% solution in a 1:1 mixture of ethanol and acetic acid; 5 ml of conc. $H_2 SO_4$ was added in making 100 ml of the solution. Procedure: About 1 ml of the reagent solution was added to 1 ml of the sample solution in a test tube. The test was performed on a solution of titanium chloride as reference. A pale red colour indicated titanium (21).

(d) With aqueous chromotropic acid the detection limit is 0.1 ug at a dilution of 1:500,000.

Reagent: 5% aquoeous chromotropic acid

Procedure: A drop of the sample solution was placed with a drop of the reagent on a filter paper. Titanium chloride was used as reference; a red-brown colour developed.

(e) With morin the detection limit is 0.01 ug at a dilution of 1:500,000.

Reagent: A saturated solution of morin in methanol; 0.5 M HCl

Procedure: The sample powder was dissolved in 0.5 M HCl. One drop of the morin reagent was added onto a drop of the sample solution on a filter paper. The test was performed on titanium chloride solution as reference; a pale brown colour was formed.

Vanadium

(a) A vanadium solution acidified with sulphuric acid turns red-brown to blood red upon addition of hydrogen peroxide. Excess sulphuric acid or hydrogen peroxide causes the colour to become yellow-gold. Interference from ferric iron and peroxy complexes of titanium and chromium may be eliminated by the addition of phosphoric acid, an alkali fluoride, and extraction with ether. Then the aqueous phase is tested. The limit of detection is 2 ug at a dilution of 1:160,000 (24,25,26)

Procedure: To 1 ml of the sample solution in a test tube one drop of 6M sulphuric acid was added followed by a few drops of 1% hydrogen peroxide a few minutes later. Vanadium nitrate was tested as a reference; a red colour was produced (27).

(b) Detection through Reduction of Iron III by Vanadium IV

The reaction of ferrous iron with dimethylglyoxime is utilised in the equilibrium

$$Fe^{++} + V^{5+} \longrightarrow Fe^{3+} + V^{4+}$$

which goes right in an acid solution and to the left in

alkaline solution, to detect vanadium. Any oxidant or reductant that attacks iron interferes in this test, so cobalt, nickel, manganese, cerium, and copper should be removed by a sodium hydroxide separation. Interference by excess ferric ion is prevented by adding an alkali phosphate. The limit of detection is 1.0 ug at a dilution of 1:500,000.

Reagents: The sample solution for this test was obtained by adding 2M sodium hydroxide and filtering out any precipitate, the filtrate was neutralised by adding hydrochloric acid; concentrated hydrochloric acid; 1% aqueons ferric chloride solution; 1% ethanolic solution of dimethylglyoxime.

Procedure: In a micro test tube one drop of the sample solution was boiled with 3 drops of conc. HCl and reduced to half volume to reduce any vanadium present. The mixture was cooled, 3 drops of the 1% ferric chloride solution and 3 drops of the dimethylglyoxime solution and 1 drop of saturated disodium phosphate solution were added and the mixture made ammoniacal by adding 2 drops of conc. ammonia solution. A deep red colour was expected if vanadium was present; this was obtained when vanadium nitrate was tested as a reference. A strip of filter paper dipped in the solution indicated the red colour more obviously (24,27).

(c) Detection with 3, 3'- Dimethylnaphthidine (24,27,28,29)

Reagent: 1% solution of 3, 3'-dimethylnaphthidine in glacial acetic acid. Limit of detection is 0.1 ug at a dilution of 1:500,000. (28)

Procedure: 1 drop of the sample solution was rendered normal in sulphuric acid and treated with one drop of the reagent solution. Vanadium nitrate was tested as reference and the expected reddish violet colour was obtained. (24,28)

(d) Detection with α-benzoinoxime (23,26)

Reagent: A saturated solution of α-benzoinoxime in ethanol. Limit of detection is 1 ug at a dilution of 1:50,000.

Procedure: A drop of the sample solution was taken in a test tube followed by 2 drops of the reagent solution and 1 drop of 1.5M $H_2 SO_4$. Vanadium nitrate was tested as reference and the expected yellow colour developed. (24,27)

Cobalt (25)

Various colour producing reactions were used to test for cobalt. Cobalt chloride was used as reference in these tests.

(a) Detection with DMG

Reagents: 1% ethanolic solution of dimethylglyoxime.

Procedure: To 1 ml of the sample solution in a test tube a few drops of 6M $H_2 SO_4$ were added followed by a few drops of the reagent solution. A brown colour developed for cobalt chloride as expected when cobalt is present.

(b) Detection with Potassium Xanthate

Reagent: A 2% aqueous solution of potassium xanthate

Procedure: The reagent solution was slowly added to 1 ml of the aqueous sample solution. A green precipitate diagnostic of cobalt was obtained for cobalt chloride as reference.

(c) Detection with sodium bisulphite

Reagent: A 2% aqueous solution of sodium bisulphite

Procedure: To 1 ml of the sample solution in a test tube was added 0.5 ml of conc. ammonia and a few drops of the reagent solution. A yellow, orange, or red colour was expected for cobalt.

(d) Detection with Potassium nitrite

Procedure: To 1 ml of the sample solution in a test tube was added 0.5 ml of a 2M aqueous solution of potassium nitrite and a few drops of acetic acid. A yellow precipitate was expected if cobalt was present in the sample.

(e) Detection with Sodium Thiosulphate (27,30)

A neutral cobalt solution produces a blue colour with a concentrated solution of sodium thiosulphate. Limit of dection is 8 ug at a limiting dilution of 1:6,250.

Reagents: Solid sodium thiosulphate;

Procedure: Several centigrams of solid sodium thiosulphate was made into a paste with one drop of the neutral sample solution. For cobalt chloride solution an intense blue colour developed as expected if cobalt was present.

Manganese

(a) Detection by benzidine test (25,27)

Manganese and other oxidizing agents convert benzidine and its water soluble salts (27) into benzidine blue. In an alkaline medium the manganese is first precipitated as manganous hydroxide which by autoxidation in air forms some

hydrated manganese dioxide

$$2\ Mn(OH)_2 + O_2 \qquad 2\ MnO_2.H_2O$$

It is this dioxide which oxidizes benzidine to the benzidine blue. This reaction series has been employed in the form of a spot test on filter paper to detect manganese. To infer manganese from this test. interference by other oxidizing substances need be eliminated. Possible interferences arise from chromates, ferricyanides, cobalt, thallium III, silver, and cerium III salts. Limit of detection is 0.15 ug at a limiting dilution of 1:330,000.

Reagents: benzidine solution made by dissolving 0.05g of benzidine in 10 ml acetic acid, diluting to 100 ml and filtering. (27)

Procedure: One drop of the sample solution was added onto a drop of 0.05M sodium hydroxide on a filter paper. Then a drop of the benzidine solution was introduced. A blue colour after some time indicated manganese. Manganese chloride was tested as a reference.

Possible interference by cerium was checked by precipitating and filtering out any cerium as the fluoride. The sample solution was treated with acetic acid and warmed in a hot water bath with a little calcium fluoride. Then the excess calcium fluoride and any cerium fluoride formed was filtered out and the filtrate tested for manganese as above, The results were the same.

Sodium chloride solution was added to the sample solutions to precipitate out any silver and thalium which interfere in the benzidine test. No precipitate was produced.

(b) Detection with Potassium Chlorate

When the sample solution is shaken with potassium chlorate in a dispersion of ether in conc. HCl, a green colour in the ether layer indicates manganese (25).

Reagent: Solid potassium chlorate

Procedure: To 1 ml of the sample solution was added 2 ml. conc. HCl, 4 ml of ether saturated with HCl and a particle of potassium chlorate. The mixture was shaken to mix and allowed to settle. Manganese was indicated by a green colour in the ether layer when Manganese chloride was tested as a reference.

(c) Detection with Sodium Oxalate (25)

In an alkaline medium manganese treated successively with a few drops of sodium oxalate and a few drops of acetic acid forms a persistent rose colour.

Procedure: 1 ml of the aqueous sample solution was made alkaline by addition a few drops of 2M sodium hydroxide. To it were added a few drops of 2M sodium oxalate solution and a few drops of acetic acid. The pink colour was obtained for manganese chloride which was tested as a reference.

(d) Detection with 8-hydroxyquinoline

A useful field test for detecting manganese in minerals and rocks involves spotting the sample solution on filter paper which has been impregnated with 8-hydroxyquinoline.

When the test paper is exposed to ammonia fumes a brown stain indicates manganese (31).

Reagent: 2g of oxine was dissolved in 100 ml of 2M acetic acid; ammonia solution was added dropwise until a turbidity started to appear. The solution was rendered clear again by adding a little more acetic acid (21).

Procedure: A filter paper was impregnated with the reagent solution and allowed to dry. A drop of the aqueous sample solution was then added to the filter paper and exposed to ammonia fumes. A brown stain indicated manganese (31). Manganese chloride was tested as reference and distilled water as blank.

(e) Detection by Oxidation to Permanganate by Ammonium Persulfate

When heated with alkali persulphates in the presence of small amounts of soluble silver salts manganous salts, in faintly acid solution, get oxidized to permanganate and can be detected by the violet colour which results. The limit of detection is 0.1 ug at a dilution of 1:500,000. (27)

Procedure: A drop of the sample solution was mixed with a drop of conc. H_2SO_4 in a micro crucible. A drop of 0.1% silver nitrate solution was stirred in followed by a few milligrams of ammonium persulphate; the mixture was then heated gently. A red-violet colour was obtained when manganese was present.

(E) Detection of Transition Elements by visible Spectrophotometry.

In this method the visible absorption pattern of the sample was compared with that of authentic compounds of transition elements, performing measurements on the same instrument for both samples and standards.

Instrument: A unicam uv.-visible spectrophotometer SP 1700 with recorder and a digital display unit

Materials: Various concentrations of aqueous solutions of titanium chloride, vanadium nitrate, cobalt nitrate, nickel chloride, manganese chloride and chromium nitrate, suitably diluted solutions of the coloured samples.

Procedure: The visible spectra of the standard substances were recorded and their peak frequencies (Table III) noted. This was repeated for various concentrations of each compound to check on any shift in peak frequencies (Table III*). The visible spectra of all the coloured samples were also recorded for various concentrations of each sample and their absorption frequencies (Table IIIa) noted. The sample spectra were compared with the spectra of the standard compounds for any similarities.

Quantitative Determinations

Determinations of sodium and potassium were performed by both flame photometry and atomic absorption spectroscopy. Manganese was determined colorimetrically, measuring the colour both with a colorimeter and a spectrophotometer.

An attempt was also made, though unsuccessfully, to measure manganese in the samples spectrophotometrically without the prior development of colour.

A. Preparation of Sample Solutions

The same solution of each sample was employed to determine sodium and potassium by both flame photometry and atomic absorption spectroscopy.

Procedure: In each case a weight of the powdered solid sample required to give a concentration of 1g per litre of solution was weighed out. In some cases, where water alone gave a clear solution, the sample was shaken to dissolve in water in a volumetric flask and made up to mark with water. In other cases a clear solution was obtained by shaking the weighed sample with water and dilute hydrochloric acid in a volumetric flask and making up to mark with water. In some other cases (Table II) the sample was boiled with hydrogen fluoride to dissolve and made up to mark with water. A clear solution with a concentration of 1g per litre was obtained for each sample.

B. Preparation of Standard Stock Solutions

The same stock solutions were employed for flame photometry and atomic absorption spectroscopy.

Sodium Stock Solution. Analar sodium chloride was dried in the oven at 90°C for several hours and cooled in a dessicator. From this 0.6503g was weighed and dissolved in distilled water and made up to 250 ml in a volumetric flask. This

solution contained 1000 ppm of sodium.

Potassium Stock Solution: 0.4767g of **Analar** potassium chloride which had been dried and colled in the dessicator was dissolved in distilled water and made up to 250 ml in a volumetric flask. This solution contained 1000 ppm of potassium.

C. Determination of Sodium and Potassium by Flame Photometry.

Instrument: The flame photometer employed for analysis was a Gallenkamp, Mark II, **F** 500, having an interference filter system, a detector of selenium barrier layer cells and a direct reading meter as measuring apparatus; the combustive gas was air supplied at a constant pressure by a compressor, cooking gas, a propane butane mixture, was the combustible gas.

Materials: The stock solution of each sample containing 1g of sample per litre was suitably diluted to obtain the sample solution used for analysis. Each standard stock solution containing 1000 ppm was appropriately diluted to obtain a set of standard solutions containing 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 ppm of its element. The distilled water used for making solutions was used as blank (0.0 ppm) for both elements.

Procedure: To obtain a dilution factor of 100 a 0.2 ml volume of the stock solution of the sample was taken with a graduated pipette and made up to 20 ml with distilled water. For a two hundred fold dilution 0.1 ml of the stock

solution was made up to 20 ml. For some samples a three hundred fold dilution was similarly obtained before analysis. The flame photometer was connected to the gas and air supply and lighted at the burner. The appropriate controls were adjusted to provide optimum flow of air and gas and produce the recommended shape (Instrument Manual) of flame. Distilled water was aspirated to flush the instrument for some time before the analysis samples were introduced; then the flame should approximate the colourless bunsen flame. To calibrate the instrument for determining sodium the filter for sodium was selected; the sodium blank was first aspirated and the scale adjusted to read zero; then the most concentrated standard (this should be more concentrated than all the samples) solution was aspirated and the scale adjusted to read 100 (i.e. full scale reading). This procedure was repeated until zero reading was exactly obtained by simply presenting the blank and 100 reading by simply presenting the standard with highest concentration, without having to adjust the knobs. Then the standards with intervening concentrations were aspirated one at a time, and their readings were recorded. (Table IV) Distilled water was aspirated in between the standards to flush the instrument. The standards employed for the calibration were 0.0, 0.5, 1.0. 1.5, and 2.0 ppm in sodium and gave a calibration curve as in **Fig.** II. The diluted sample solutions were then aspirated, one at a time, and their scale readings recorded (**Table** IV(a). Frequent

zero and full scale checks were made during the measurements. For the determination of potassium the instrument was flushed with distilled water for about 1 hour; then the flame turned colourless and no sodium was indicated. The filter for potassium was inserted and the calibration performed as before using a blank and standard solutions 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 ppm in potassium (Table V), these gave the calibration curve in **Fig.** III. With frequent zero and full-scale checks as before the diluted sample solutions were measured in order for potassium. Results were recorded as in **Table** V(a). The sodium and potassium contents were derived as in Table IV(a) and Table V(A).

An Interference Check

To observe the extent to which sodium and potassium might mutually interfere in their determinations in the same sample solutions a calibration was repeated for sodium using a stock solution containing 1000 ppm sodium and 100 ppm potassium together. This solution was diluted to obtain standards having the concentrations of sodium and potassium shown:-

0.5	ppm	Na	+	0.05	ppm	K
1.0	"	"	+	0.10	"	"
1.5	"	"	+	0.15	"	"
2.0	"	"	+	0.20	"	K

Readings were obtained as in **Table** IV(b) which gave the calibration curve in **Fig** IV.

The effect of hydrochloric acid and hydrogen fluoride on the values obtained for the sodium standard solutions was investigated by adding 10 ml of each in making 200 ml of the standard solution. Readings were obtained as in Table IV(b).

D. Determination of Sodium and Potassium by Atomic Absorption Spectroscopy

Instrument: The determinations were performed on a Perkin Elmer atomic absorption spectrophotometer, model 306, measuring absorbances read out on a digital display and operated on an air-acetylene flame. This was a double beam instrument with the reference beam bypassing the flame rather than traversing a blank flame, the detector was a photomultiplier system.

Materials: The sodium and potassium stock solutions were appropriately diluted to obtain standard solutions with concentrations of 0.10, 0.20, 0.30, 0.40 ppm of sodium and 1.0, 2.0, 3.0, 4.0, and 5.0 ppm of potassium. In making the sodium standards 1 ml of 0.2% lithium chloride solution was added to make 50 ml of the diluted sodium solution. The lithium chloride solution was prepared by dissolving 0.2g of analar lithium chloride in distilled water and making up to 100 ml. The lithium so introduced in the standard sodium solution functioned as an ionization buffer to reduce ionization of the sodium. Each sample stock solution was suitably diluted to bring their concentrations within the range of the concentrations of the calibrating solutions.

Procedure: The instrument was adjusted for optimum flow of flame gases and test solutions, flushing initially with distilled water. The lamp for sodium was selected and the instrument set to obtain the appropriate absorption line. The calibration involved aspirating the blank solution and setting to obtain zero reading, then the most concentrated standard was aspirated and the instrument adjusted to get the appropriate absorbance. Intermediate concentrations were then measured and the readings (Table IV)used to construct a calibration curve (Fig V). Each sample solution was aspirated in turn and the readings (Table IV(a) used to deduce their concentrations (Table IV(a) from the calibration curve. Similarly potassium was determined by flushing the instrument, selecting the filter and adjusting to obtain a monochromatic spectral line for absorption. The calibration gave readings as in Table V which yielded the calibration curve in Fig VI. The readings for the sample solutions (Table V(a) were interpolated in the curve to obtain their concentrations (Table V(a)

E. Colorimetric Determination of Manganese

For manganese a number of coloured compounds and complexes have been made the bases of colorimetric analysis. The major method of determination, however, is as permanganate. In this method, manganese, in whatever form it occurs in the analytical sample is first oxidised to permanganate and the

colour intensity is measured colorimetrically. The most common oxidising agents used in the treatment to produce colour are persulphate and periodate, but bismuthate and lead dioxide are still used for certain types of samples. The absorption peaks are located at 526, 546, and 566 nm. Standard permanganate solutions are employed for calibration As much as five percent copper does not interfere but colours due to nickel and cobalt interfere regardless of the method of oxidation (32).

The Persulphate Oxidation Method

The permanganate colour produced by the persulphate method does not persist as long as that produced by periodate (31,32) but the colour is stable for, at least, twenty four hours if excess persulphate is present and organic matter is absent (31). Silver is used in this method to prevent the precipitation of manganese oxide. The concentration of silver can be kept so low that if caloride is present no visible precipitate is formed. Phosphoric acid prevents the precipitation of manganese dioxide and ensures smooth oxidation to permanganate; its concentration should be, at least, 0.1 M. Nitric acid should be present to about 0.3 M but no higher. Interference by chloride can be avoided by adding mercuric sulphate to form slightly dissociated complexes. Bromides and iodides do interfere even in small amounts. In thepresence of 2% sulphuric acid small amounts of titanium do not interfere (32) but with much

titanium persulphate oxidation of manganese is not complete and the periodate method is prefered. Reasonable amounts of organic matter are tolerated if the period of heating is increased and more persulphate added (31). The minimum detectable amount by this method is 5 ug of manganese.

Materials: A mercuric sulphate solution was prepared (31) by dissolving 75 g of analar mercuric sulphate in a mixture of 400 ml of conc. HNO_3 and 200 ml of water. To this were added 200 ml af 85% phosphoric acid and 0.035 g of silver nitrate. The mixture was cooled and diluted to one litre.

0.1 N potassium permanganate solution was prepared by dissoling 3.1606g of analar permanganate in water and making up to one litre in a volumetric flask. This solution was aged by heating for 3 hours near the boiling point and then filtering through a scintered glass crucible. It was then standardized against sodium oxalate (34); a 0.0998N solution was obtained.

The measurements were taken on a spectronic 20 colorimeter of Bausch and Lomb, Analytical Division and also on the unicam SP 1700 uv-visible spectrophotometer.

Procedure (31): 3.0 g of the powdered sample was dissolved in water, adding dilute nitric acid to obtain a clear solution and keeping the volume below 50 ml. 5ml of the mercuric sulphate solution was added and the mixture diluted to about 90 ml in a graduated conical flask. 1 g of analar ammonium persulphate, which had been exposed to moist air,

was added and the mixture brought to boil in about 3 minutes over a bunsen flame. The flask was then removed from the flame, allowed to stand for 1 minute, and then cooled under the tap. The mixture was transfered quantitatively into a 100 ml volumetric flask and made up to mark with distilled water. Photometric readings were then taken at 525 nm on both a spectronic 20 colorimeter and on the uv-visible spectrophotometer (Table VI). In either case the readings were taken against a blank solution obtained by treating pure distilled water as in the procedure. To calibrate the instrument a set of five graduated conical flask were charged with 50 ml of water and 5 ml of 85% phosphoric acid. To one conical flask in turn was added 0, 0.5, 1.0, 1.5, and 2.0 ml of the 0.0998N potassium permanganate solution from a graduated pipette. The mixture in each flask was diluted to about 75 ml and treated as in the above procedure for the samples. The photometric reading (Table VIa) obtained on the colorimeter were used to prepare the calibration curve (Fig. VII) which was used to derive the concentrations (Table VIa) of manganese in the samples by interpolation. Similarly readings obtained for these standards on the uv-visible spectrophotometer (Table VIa) gave the calibration curve (Fig. VIII) in which sample measurements were interpolated to obtain manganese concentrations (Table VI) in the samples.

F. Determination by Visible Spectrophotometry

To determine a coloured element quantitatively from its spectra the absorbance of a solution of the sample containing it is measured at a fixed wavelength which characterises the element and the concentration is deduced by calibrating the instrument used. The calibration requires a solution of a pure salt of the element determined: the absorbance is measured for solutions containing various concentrations of the salt; the values are used to prepare an absorbance versus concentration calibration curve.

Procedure: Solutions of various concentrations of analar manganese chloride were prepared in water. For each solution the wavelength of maximum absorption was found by scaning the spectrum on the uv-visible spectrophotometer. Then the absorbance of each solution was measured at this wavelength both on the spectrophotometer and on the spectronic 20 colorimeter. The above procedure was repeated for known concentrations of the coloured samples. Each absorbance was measured against a distilled water blank. The attempt here was to use the absorbance values of the standard manganese solutions to prepare a calibration curve from which the concentrations of the sample solutions could be deduced; the measurements did not reflect a satisfactory dependence of absorbance on concentration (Table VII).

III. Results

Table I: Results of Preliminary Observation

Sample No.	Appearance	Colour
1	Mixed range of large to micro crystals	white-orange bulk with black-grey stains
2	Cluster of small microcrystalline particles	Dirty white-grey
3	Crystalline particles of mixed grain sizes	Dirty white-grey
4	Crystalline sheets	Grey
5	Crystal aggregate	White containing rose pink stains
6	Microcrystalline sheets	White
7	Crystalline	Grey having orange patches
8	Crystal aggregate	White
9	Crystalline grains	White
10	Crystal agregate	White
11	Crystal agregate	Dirty white
12	Microcrystalline particle agregate	Grey
13	Microcrystalline	Mixed white and rose pink
14	Crystal agregate	White
15	Mixed crystalline and earthy mass	White mixed with grey-dark brown zones
16	Microcrystalline sheets	Grey
17	Microcrystalline Sheets with mixed grain sizes	Grey

Sample No	Appearance	Colour
18	Microcrystalline agregate	White containing grey stains
19	Crystal agregate	Grey
20	Microcrystalline agregate	Grey
21	Crystal agregate	Grey-black
22	Crystalline agregate showing layering	Grey-light brown
23	Crystalline crush	Grey
24	Amorphous-microdrystalline lump	white
25	Amorphous crush	Dirty white
26	Crystalline crush	Grey
27	Microcrystalline agregate with layering	Grey
28	Crystal agregate	Rose pink
29	Microcrystalline agregate	Rose pink with white patches
30	Crystalline lump	Brown
31	Lump of crystals	White
32	Agregate of transparent needle shaped crystals in earthy matter	Grey
33	Crystalline sheets rather like clay	Grey
34	Microcrystalline sheets	Grey-black
35	Crystal agregate	Dirty white-grey
36	Crystalline clayish sheets	Grey
37	Crystalline clayish sheets	Grey

Sample No	Appearance	Colour
38	Crystalline	Rose pink/white
39	Crystalline	White
40	Crystalline	Pink
41	Fractured transparent Sheets	Colourless
42	Agregate of Octagonal crystals	White
43	Microcrystalline sheets rather like shells	White

TABLE II

Results of Qualitative Analysis

Sample No	Solvent	Anions Indicated	Trans. Elements Indicated	Results of flames tests
1	water	$CO_3^{=}$; Cl^- ; $SO_4^{=}$		both sodium potassium were observed in all samples.
2	water	$CO_3^{=}$; Cl^- ; $SO_4^{=}$		
3	water	$CO_3^{=}$ and Cl^-		
4	water	$CO_3^{=}$ and Cl^-		
5	water	$CO_3^{=}$; Cl^- ; $SO_4^{=}$	Mn	
6	water	$CO_3^{=}$; Cl^-		
7	water	Cl^-; $SO_4^{=}$		
8	water	Cl^-; $SO_4^{=}$		
9	water	$CO_3^{=}$; Cl^-		
10	water	$CO_3^{=}$; Cl^-		
11	water	$CO_3^{=}$; Cl^- ; $SO_4^{=}$		
12	Water + acid	$CO_3^{=}$; Cl^-		

Table II (Contd)

Sample No	Solvent	Anions Indicated	Trans. Elements Indicated	Results of flames tests
13	water	$CO_3^=$; Cl^- ; $SO_4^=$	Mn	
14	water	$CO_3^=$; Cl^- ; $SO_4^=$		
15	water + acid	$CO_3^=$; Cl^-		
16	water + acid	$CO_3^=$; Cl^-		
17	water + acid	$CO_3^=$; Cl^- ; $SO_4^=$		
18	water	Cl^- only		
19	water + acid*	$CO_3^=$; Cl^-		
20	water + acid*	$CO_3^=$; Cl^- ; $SO_4^=$		
21	water + acid*	$CO_3^=$; Cl^-		
22	water + acid*	$CO_3^=$; Cl^- ; $SO_4^=$		
23	water + acid*	$CO_3^=$; Cl^-		
24	water + acid	$CO_3^=$; Cl^-		
25	water + acid	$CO_3^=$; Cl^-		
26	water + acid*	$CO_3^=$; Cl^-		
27	water + acid	$CO_3^=$; Cl^-		
28	water	$CO_3^=$; Cl^- ; $SO_4^=$	Mn	
29	water	$CO_3^=$; Cl^- ; $SO_4^=$	Mn	
30	water + acid	$CO_3^=$; Cl^-		
31	water	Cl^- only		
32	water + acid	$CO_3^=$; Cl^-		
33	water + acid*	$CO_3^=$; Cl^-		
34	water + acid*	$CO_3^=$; Cl^- ; $SO_4^=$		

TABLE II (CONTD)

Sample No	Solvent	Anions Indicated	Trans. elements indicated	Results of flames tests
35	water	$CO_3^=$; Cl^- ; $SO_4^=$		
36	water + acid*	$CO_3^=$; Cl^-		
37	water + acid*	$CO_3^=$; Cl^-		
38	water	Cl^- ; $SO_4^=$	Mn	
39	water	Cl^- ; $SO_4^=$		
40	water	$CO_3^=$; Cl^- ; $SO_4^=$	Mn	
41	water + acid*	$SO_4^=$ only		
42	water	$SO_4^=$ only		
43	water	Cl^- ; $SO_4^=$		

* Dil nitric acid could not effect complete solution in these cases.

NOTE:

The Pavelka test with alizarin was positive for sample nos. 13 and 40 but it was also positive for the blank solution.

TABLE III

Visible Absorption frequencies of reference Transition element.

Reference Element	Compound Used	Observed Peak Frequencies (nm)
Chromium	chromium nitrate	304 ; 470
Cobalt	cobalt nitrate	302 ; 491 ; 634
Nickel	nickel chloride	428
* Manganese	Manganese chloride	404 ; 804
Titanium	Titanium Chloride	380 ; 486 ; 520
Vanadium	Vanadium nitrate	472 ; 646

*Measurements on solutions of various concentrations indicated a negligibly small shift in absorption frequency.

TABLE III(a)

Visible absorption frequencies of Coloured Samples

Sample No.	Observed Peak Frequencies (nm)
5	404 ; 804
13	392 ; 800
28	404 ; 804
29	408 ; 804
38	404 ; 804
40	408 ; 808

TABLE IV

Calibrations for determining sodium by flame photometry and atomic absorption spectroscopy

Concentration of standard solution (ppm)	Flame Photo-meter readings	Atomic absorption spectrophotometer reading
0.00	0.0	0.00
0.10		0.10
0.20		0.20
0.30		0.30
0.40		0.40
0.50	26.0	
1.00	49.0	
1.50	74.5	
2.00	100.0	

Calibration curves were obtained as in fig II and fig V.

TABLE IV(a)

Determination of sodium - results for sample solutions

Sample No	Photo meter readings*	Correspon-ding concen-tration(ppm)	% in Sample by flame photometry	A.A.S, ** Readings/ Correspon-ding concen-tration(ppm)	% in sample by AAS
1	38.0	0.762	15.2	0.16	16.0
2.	70.5	1.413	28.3	0.27	27.0
3	70.0	1.404	28.1	0.27	27.0
4	71.0	1.422	28.4	0.28	28.0
5	80.5	1.611	32.2	0.31	31.0
6	77.5	1.550	31.0	0.29	29.0
7	79.0	1.584	31.7	0.29	29.0
8	78.0	1,562	31,2	0.31	31.0
9	80.0	1.605	32.1	0.33	33.0

TABLE IV(a) (CONTD)

Sample No	Photo meter readings*	Correspond ding concen-tration(ppm)	% in Sample by flame photometry	A.A.S. ** Readings/ Correspon-ding concen-tration(ppm)	% in Sample by AAS
10	86.0	1.722	34.4	0.34	34.0
11	70.0	1.404	28.1	0.27	27.0
12	70.5	1.413	28.3	0.27	27.0
13	79.0	1.584	31.7	0.31	31.0
14	74.0	1.484	44.5	0.17	42.5
15	55.0	1.105	22.1	0.20	20.0
16	25.0	0.504	10.1	0.08	8.0
17	71.0	1.422	28.4	0.28	28.0
18	40.5	0.816	16.3	0.16	16.0
19	54.0	1.085	21.7	0.22	22.0
20	50.0	1.002	20.0	0.18	18.0
21	69.5	1.395	27.9	0.27	27.0
22	85.0	1.703	34.1	0.34	34.0
23	46.0	0.922	18.4	0.18	18.0
24	79.0	1.584	31.7	0.30	30.0
25	75.0	1.501	30.0	0.30	30.0
26	40.0	0.800	16.0	0.15	15.0
27	70.0	1.403	28.1	0.26	26.0
28	80.0	1.602	32.0	0.32	32.0
29	85.0	1.702	34.0	0.33	33.0
30	70.5	1.413	28.3	0.27	27.0
31	92.5	1.855	37.1	0.35	35.0
32	75.0	1.501	30.0	0.30	30.0
33	21.5	0.435	8.7	0.06	6.0
34	68.5	1.372	27.4	0.26	26.0
35	79.0	1.584	31.7	0.31	31.0
36	41.5	0.830	16.6	0.16	16.0
37	31.0	0.623	12.5	0.10	10.0

TABLE IV(a) CONTD

Sample No	Photo meter readings*	Corresponding concentration(ppm)	% in Sample by flame photometry	A.A.S. ** Readings/ corresponding concentration(ppm)	% in Sample by AAS
38	73.0	1.462	29.2	0.31	31.0
39	80.0	1.605	32.1	0.31	31.0
40	80.0	1.605	32.1	0.32	32.0
41	2.5	0.050	1.0	0.08	0.8
42	83.0	1.663	33.3	0.32	32.0
43	76.5	1.533	30.7	0.32	32.0

* For the flame photometric measurements the dilution factor was 300 for sample No. 14 and 200 for all others.

** For atomic absorption measurements the dilution factor was 2,500 for sample No.14, 100 for sample No.41 and 1,000 for all other samples.

TABLE IV (b)

Interference check in flame photometric measurement for sodium

Concentration (ppm sodium)	Photometric readings	
	In presence of K*	In presence of HF
0.0	0.0	0.0
0.5	25.5	26.0
1.0	50.5	49.5
1.5	75.5	75.0
2.0	100.0	100.0

* The Calibration curve in fig. IV was obtained.

TABLE V

Calibrations for determining potassium by flame photometry and atomic absorption spectroscopy

Concentration of Standard Solution (ppm)	Flame Photometer readings	Atomic Absorption spectrophotometer readings
0.0	0.0	0.0
0.5	16.0	
1.0	33.0	1.0
1.5	49.0	
2.0	66.0	2.0
2.5	83.0	
3.0	100.0	3.0
4.0		4.0
5.0		5.0

Calibration curves were obtained as in Fig. III & Fig. VI.

TABLE Va

Determination of potassium - results for sample solutions

Sample No	Flame Photometer readings *	Corresponding concentration	% in Sample by Flame Photometry	Concentration read from AAS **	% in Sample by AAS
1	5.0	0.150	1.5	0.18	1.8
2	8.0	0.245	2.5	0.28	2.8
3	9.5	0.290	2.9	0.29	2.9
4	1.0	0.025	0.3	0.08	0.8
5	5.0	0.150	1.5	0.15	1.5
6	1.5	0.042	0.4	0.04	0.4
7	15.5	0.470	4.7	0.44	4.4
8	0.2	0.004	0.04	0.09	0.9
9	0.1	0.002	0.02	0.06	0.6
10	0.2	0.004	0.04	0.04	0,4

TABLE V(a) CONTD

11	3.0	0.086	0.9	0.11	1.1
12	3.5	0.102	1.0	0.11	1.1
13	1.0	0.025	0.3	0.04	0.4
14	0.5	0.012	0.1	0.04	0.4
15	65.0	1.960	19.6	1.89	18.9
16	2.0	0.057	0.6	0.07	0.7
17	13.0	0.394	3.9	0.38	3.8
18	12.0	0,365	36.5	3.05	30.5
19	13.5	0.410	4.1	0.44	4.4
20	12.0	0.365	3.7	0.38	3.8
21	9.5	0.290	2.9	0.26	2.6
22	8.5	0.260	2.6	0.20	2.0
23	5.0	0.150	1.5	0.11	1.1
24	7.0	0.210	2.1	0.17	1.7
25	8.0	0.245	2.5	0.20	2.0
26	8.0	0.245	2.5	0.20	2.0
27	9.5	0.290	2.9	0.20	2.0
28	2.5	0.075	0.8	0.06	0.6
29	3.5	0.102	1.0	0.07	0.7
30	3.0	0.086	0.9	0.04	0.4
31	1.5	0.042	0.4	0.09	0.9
32	10.0	0.305	3.1	0.26	2.6
33	4.0	0.119	1.2	0.06	0.6
34	5.0	0.150	1.5	0.13	1.3
35	3.0	0.086	0.9	0.27	2.7
36	11.5	0.352	3.5	0.34	3.4
37	4.0	0.119	1.2	0.13	1.3
38	1.0	0.025	0.3	0.04	0.4
39	3.5	0.102	1.0	0.09	0.9
40	4.0	0.119	1.2	0.04	0.4
41	0.5	0.012	0.1	0.04	0.4
42	1.0	0.025	0.3	0.04	0.4
43	14.0	0.424	4.2	0.36	3.6

* For flame photometric measurements the dilution factor was 1,000 for sample No. 18 and 100 for all others.

** For atomic absorption measurements the dilution factor was 100 for all samples.

TABLE VI(a)

Colorimetric determination of manganese - calibration of the colorimeter and spectrophotometer.

Volume Standard permanganate (ml.)	Colorimeter readings	Spectrophotometer readings
0.0	0.000	0.149
0.5	0.250	0.380
1.0	0.500	0.612
1.5	0.750	0.842
2.0	1.000	1.073

Calibration curves were obtained as in Fig. VII and Fig. VIII.

TABLE VI

Colorimetric determination of manganese - results from the colorimeter and spectrophotometer.

Sample No	Colorimeter readings	Equivalent Vol.(ml) of standard permanganate	% Mn in Sample ($x10^3$)	Spectro-photometer readings	Equiv. vol. of standard permanganate ml.	% Mn in Sample ($x10^3$)
5	0.060	0.1200	4.388	0.205	0.1225	4.479
13	0.069	0.1425	5.211	0.217	0.1500	5.485
28	0.022	0.0439	1.604	0.171	0.0475	1.737
29	0.067	0.1375	5.025	0.212	0.1375	5.025
38	0.062	0.1250	4.571	0.207	0.1250	4.571
40	0.062	0.1250	4.571	0.207	0.1250	4.571

TABLE VII

Absorbance measurements for untreated manganese cloride Solutions.

Concentration of Solution (g/l)	Colorimeter readings	Spectrophotometer readings
0.025	0.002	0.014
0.050	0.002	0.013
5.000	0.001	0.014
100.000	0.002	0.016

CALCULATIONS

The following are specimen calculations to show how the percentages in samples collected in Tables IV(a), V(a), and VI(a) were obtained:-

Sodium and Potassium Percentages

Absorbance reading from instrument = A
Corresponding ppm concentration from Calibration curve = C
Dilution factor applied = D
Then
Concentration of element in undiluted sample solution = C x D ppm

Wt. of element in 1 litre of sample solution = $\frac{C \times D \times 10^3}{10^6}$ g/l

i.e. $C \times D \times 10^{-3}$ g/l

But
Wt. of Sample in 1 litre of sample solution = 1.0000 g/l

% Element in dry sample = $\frac{C \times D \times 10^{-3}}{1.0000} \times 100\%$

= $C \times D \times 10^{-1}$ %

Percentage of manganese:

Absorbance reading from instrument = A

Corresponding volume of standardized permanganate = V ml.

Wt. of manganese per ml. of standard permanganate = 1097 ug

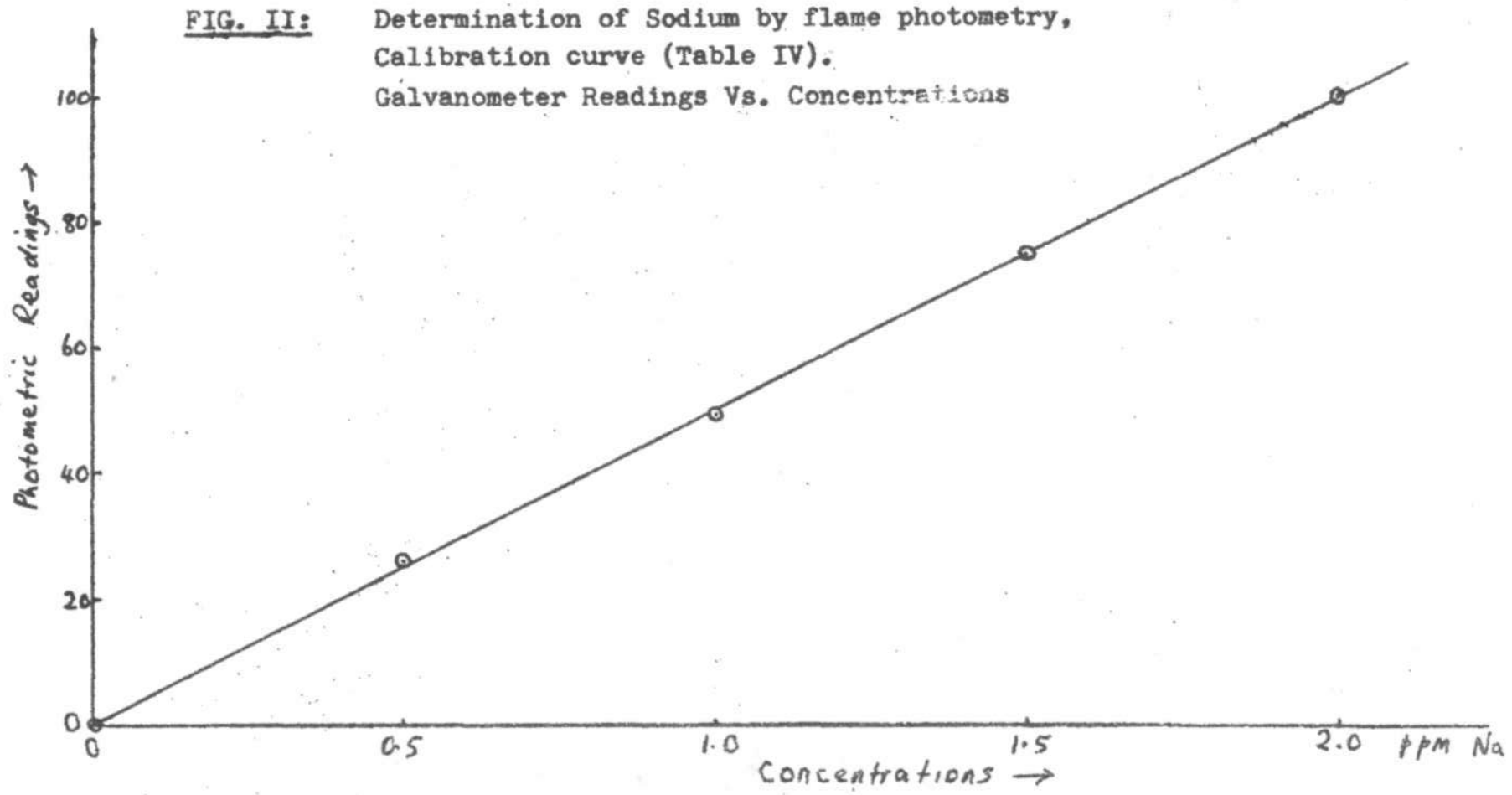
∴ Corresponding wt. of manganese analysed = 1097 V ug

Wt. of sample analysed = 3.0000 g

$$\% \text{ manganese in sample} = \frac{V \times 1097}{3 \times 10^6} \times 100 \%$$

i.e. $V \times 365.67 \times 10^{-4} \%$

FIG. II: Determination of Sodium by flame photometry, Calibration curve (Table IV). Galvanometer Readings Vs. Concentrations



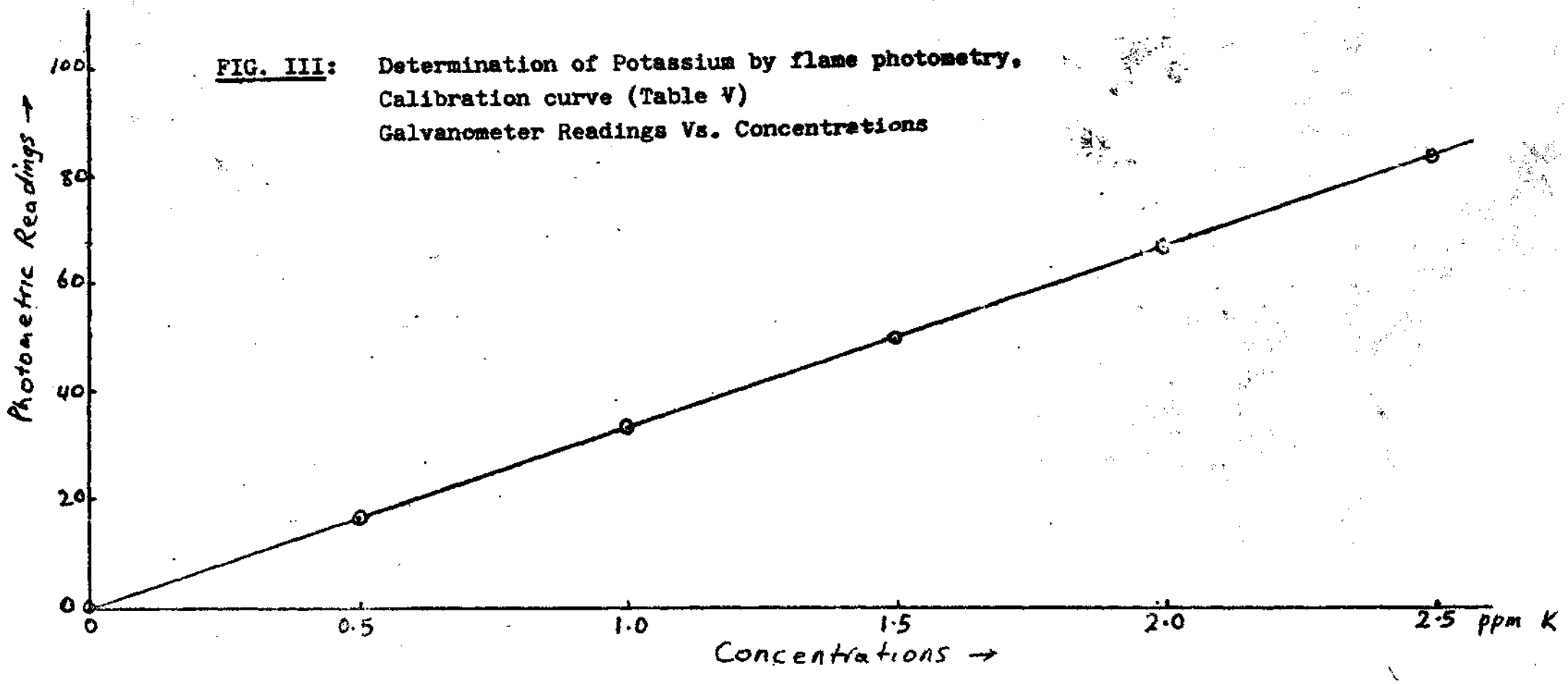


FIG. III: Determination of Potassium by flame photometry.
Calibration curve (Table V)
Galvanometer Readings Vs. Concentrations

FIG. IV: Determination of Sodium in presence of Potassium by flame photometer - calibration curve (Table IV b)
Galvanometer readings Vs. Concentrations

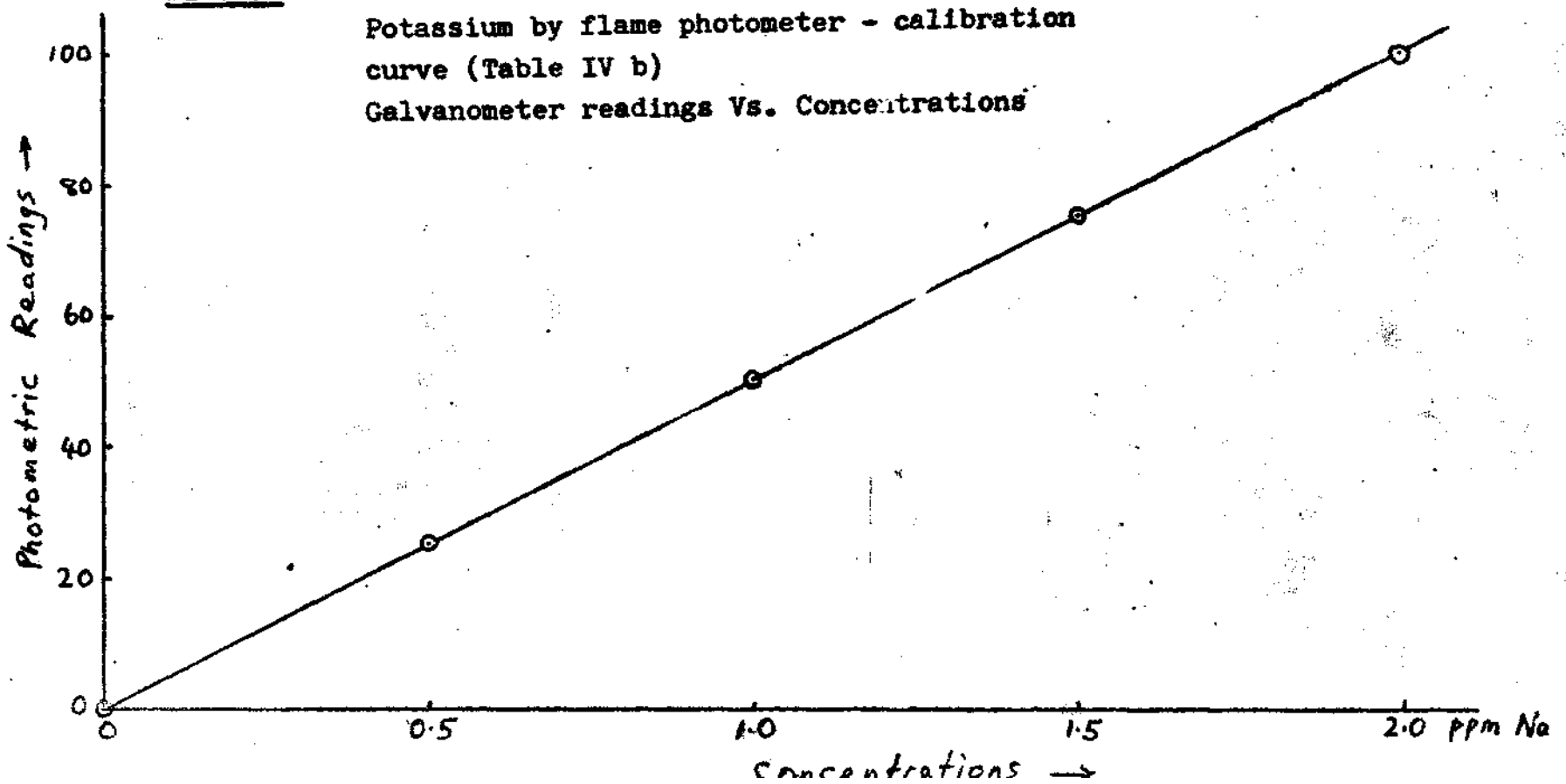


FIG. V: Determination of Sodium by AAS
Calibration curve (Table IV)
Absorbance Vs. Concentrations

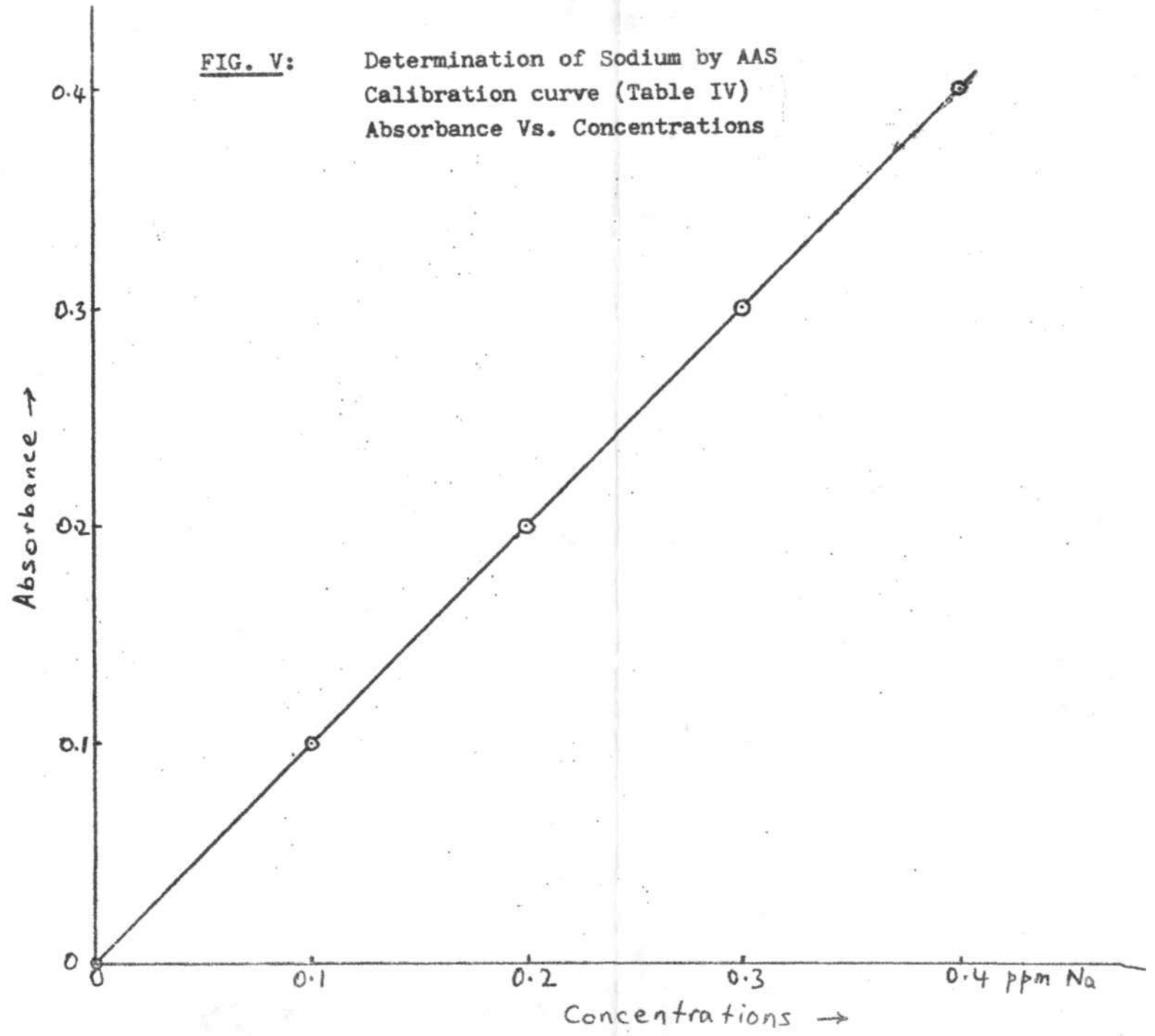


FIG. VI: Determination of Potassium by AAS
Calibration Curve (Table V)
Spectrophotometer readings Vs. Concentrations

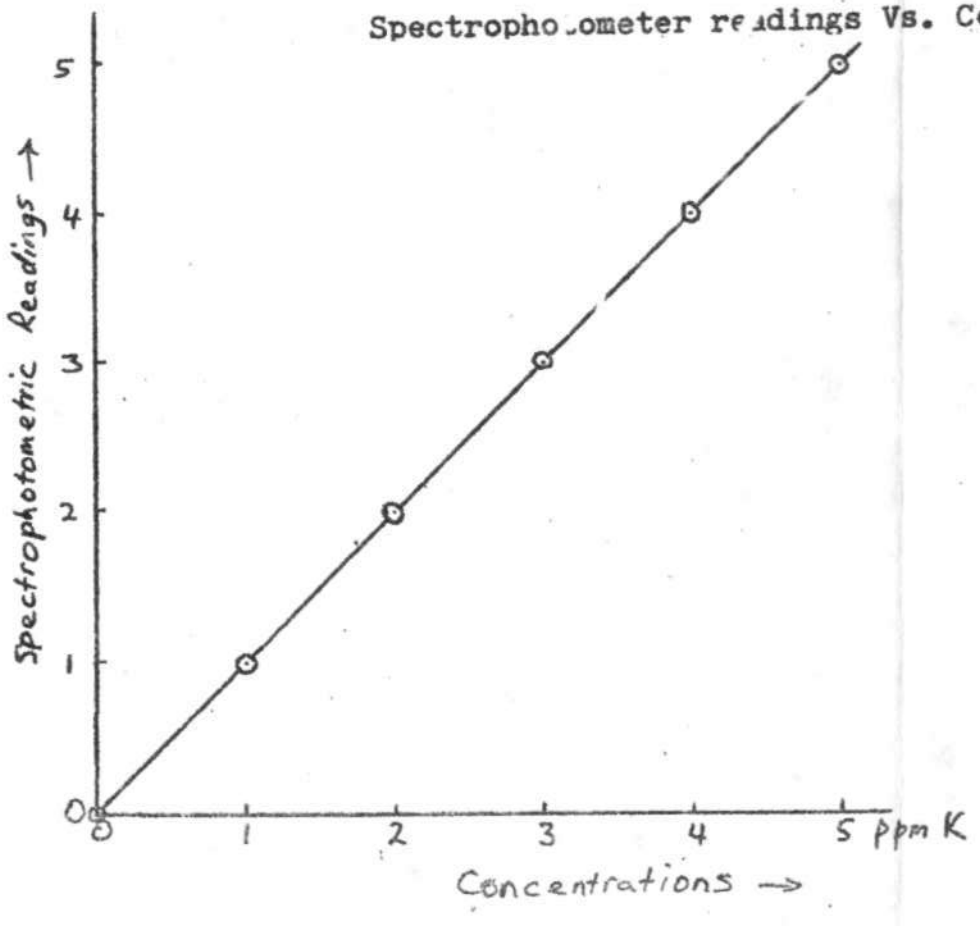


FIG. VII: Determination of Manganese using Colorimeter - Calibration Curve (Table VIa)
Absorbance Vs. Volume $KMnO_4$

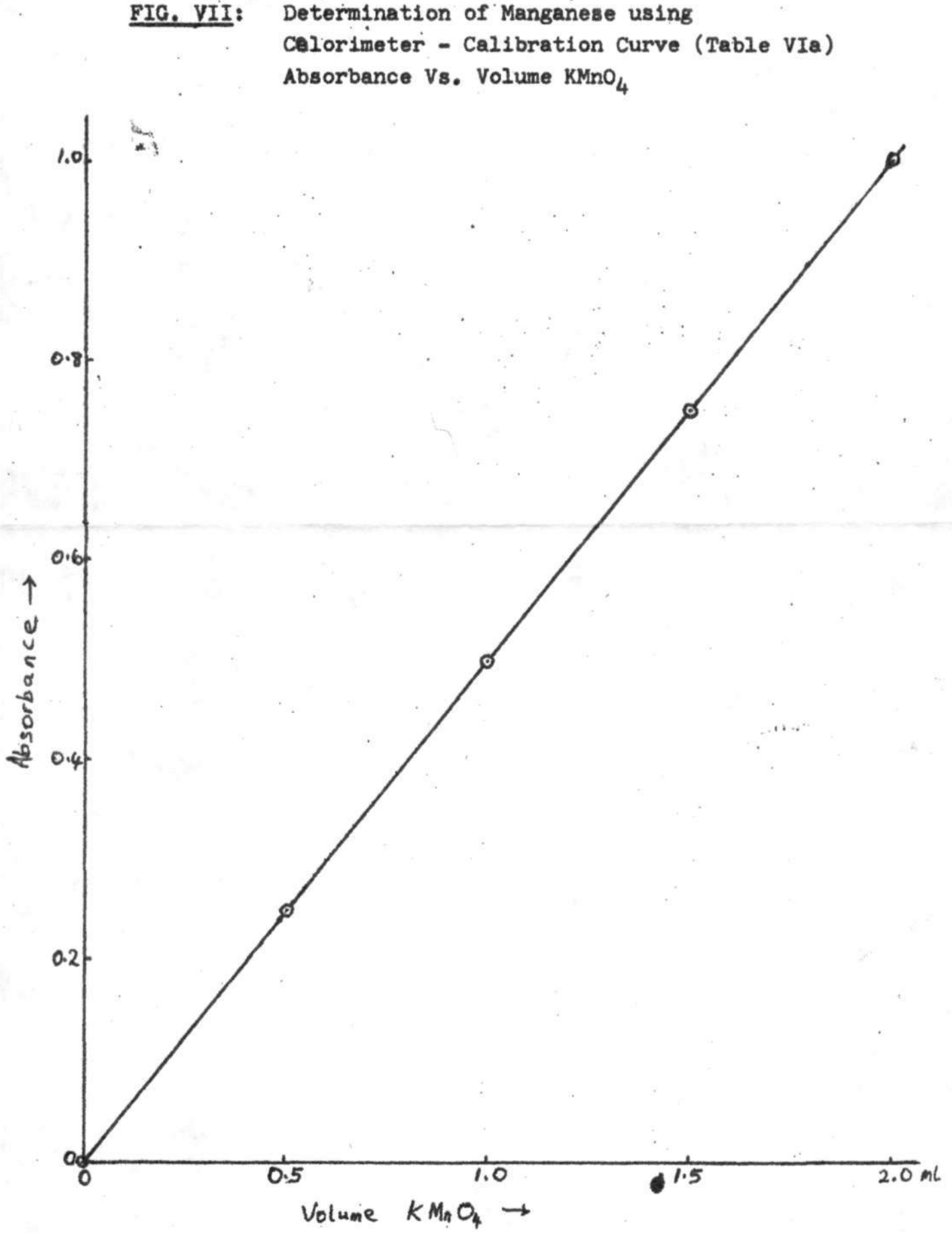
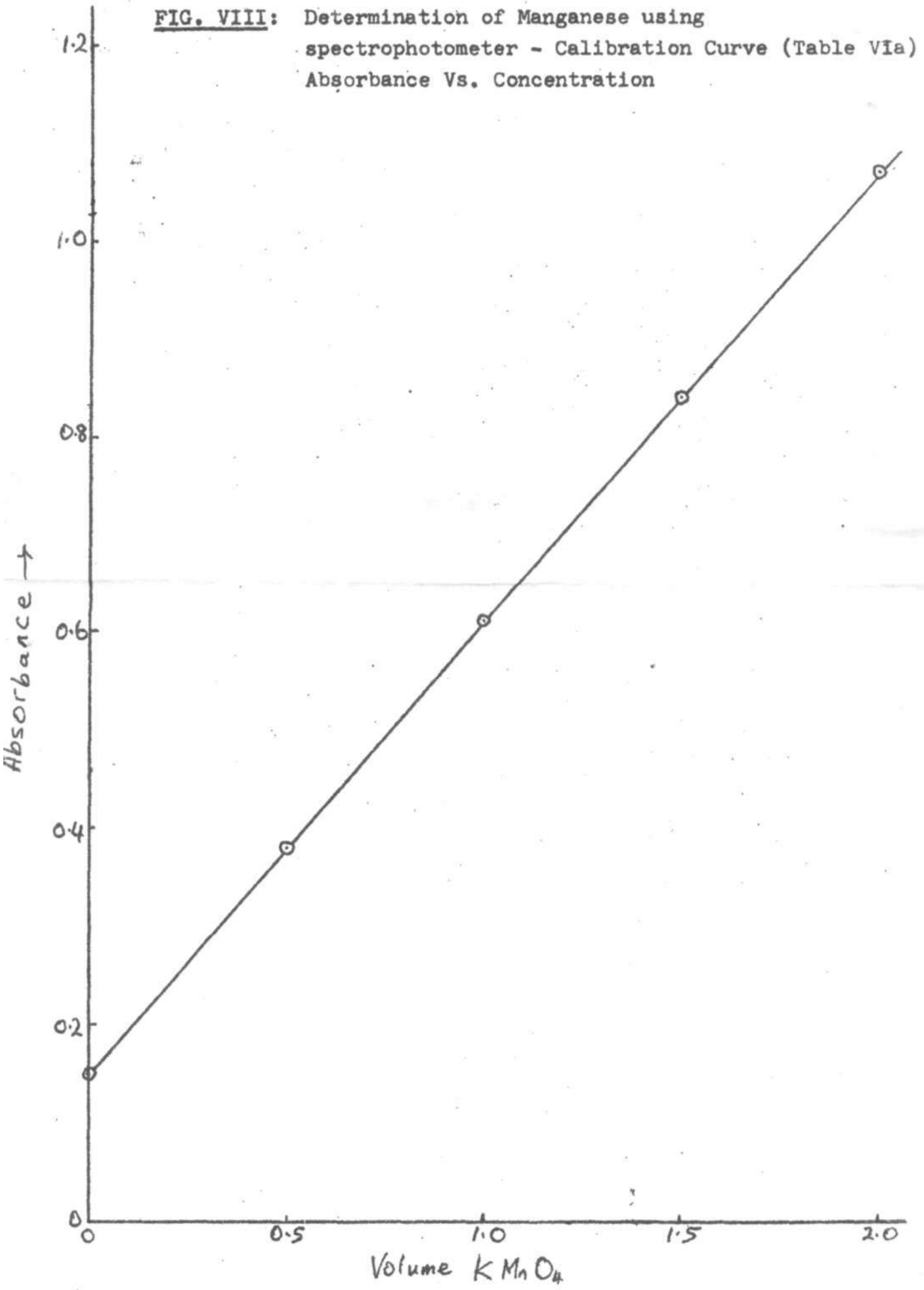


FIG. VIII: Determination of Manganese using spectrophotometer - Calibration Curve (Table VIa) Absorbance Vs. Concentration



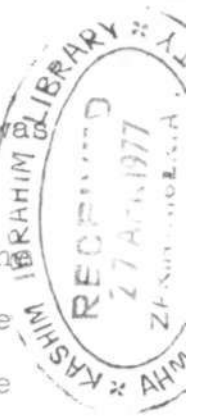
DISCUSSION

The results of qualitative tests (Table II) have shown that every sample of 'kanwa' analysed in this survey contained sodium and potassium together, that these elements occur in the samples probably as their carbonates, chlorides, or sulphates, that in those samples which possessed a bright pink colour, this colour was due to manganese. The Pavelka test for titanium was not effective; only this test suggested the presence of titanium in samples Nos. 13 and 40; this disagreed with all the other four tests which gave negative results for these two samples also. Results of quantitative analysis indicate a generally high proportion of sodium (Table IV(a) in a great majority of the samples and a very low content of potassium (Table V(a) in most of them; in all coloured samples manganese was found to occur to the same order of magnitude (Table VI(a).

In the determination of sodium and potassium by flame photometry and atomic absorption methods it was critical to get all sodium and potassium in the analysed samples into solution. It has been recommended (21) that the treatment of the sample with hydrogen fluoride would induce complete dissolution of the alkaline elements even if the sample was not completely soluble; then any residue could be filtered out and washed to leave the alkaline elements in the filtrate. In these analyses, however, complete dissolution

of sample was achieved in all cases. In both methods a majority of the samples had a sodium content of about 30% though few contained a much lower percentage. Both methods gave 2-4% of potassium for many samples and values of 1% and less for a significant number of samples; few samples contained over 10% of potassium. Except in very few cases the percentages of sodium determined by flame photometry and those determined by atomic absorption spectroscopy showed agreement within 0.5 - 2.0 %; the percentage difference in values obtained by the two methods was generally within 5%. In samples nos. 7, 15, 16, 33, 37, and 41, however, the percentage differences were rather high with values ranging from 10% to 30%. The cause for these high differences was not known. These differences were, however, mixed: the results from atomic absorption were higher in some cases, but in other cases they were lower than results obtained by flame photometry. In the determination of potassium, on the other hand, the agreement between the two methods was not as good as in the determination of sodium. Here (Table V(a) rather few results agreed exactly (sample nos. 3,5,6); about 90% of results agreed within 0.5% including many that agreed within 0.1%. These excluded sample nos. 8, 9, 15, 18, 27, 33, 35, 40, and 43 where the difference was 0.6 - 6.0%. The percentage differences between the values obtained by the two methods was generally between 10% and 20% but were much higher in about 25% of the cases. In these cases marked

differences occured in the order of magnitude of the measured values. The cause of these high differences was also not known.


KASHIM IBRAHIM LIBRARY
RECEIVED
ZARIA

A common method to correct for interferences in the flame methods is the addition of substances known to be present and to cause interference in the samples to the standard solutions so that the standards closely match the samples to be determined in composition. This method is encouraged only in cases where the sample compositions are accurately known and do not vary significantly from those of the standards; other measures are recommended because of the difficulty involved in this matching and the chances created for cross contamination from a mixture of salts involved in the process. In these analyses the samples were not analysed for other elements and this matching of standards was not performed. Other measures were, however, adopted to minimise mutual interference between sodium and potassium and that arising from other elements if any. One of these measures was to select a range of dilution at which these interferences were negligible (4,6,20). In the procedure included to assess the extent to which potassium might interfere in the determination of sodium by flame photometry the measurements (Table IVb) gave a calibration curve (Fig IV) which has the same slope as the curve (Fig. II) obtained with measurements in the absence of potassium; either calibration

curve would yield the same results for the samples. This suggests that potassium would not interfere in the determination of sodium, at least in this range of concentrations. The performance of the analysis at the experimental flame temperature ranges, in which the excitation of the alkaline elements selectively occured to the exclusion of other elements with higher excitation energies, provided on interference check intrinsic in the the procedure itself. The standard solutions were collected to yield a linear calibration curve and the sample solutions suitably diluted to concentrations that fell within this linear range.

In the qualitative tests for the transition elements which could give colour to the coloured samples most of the elements tested for were absent; only manganese was present in all the coloured samples. The literature suggestion (21) of transition elements which could occur with sodium and potassium in nature dictated the elements which were tested for in this group. Those suggested included titanium, zirconium, vanadium, cobalt, chromium, manganese; those tested for were titanium, vanadium, cobalt, manganese. It was unlikely that chromium and zircomium would be the cause of colour in the samples, as chromium salts are generally green in colour; chromates are yellow and dichromates red (35). Zirconium compounds are characteristically colourless (36). The colour of the samples did not also suggest nickel;

chromium and nickel were not suggested by the visible absorption spectra of the coloured samples. As titanium, nickel, and cobalt were not indicated in the samples, interferences due to them were not relevant in the determination of manganese by the persulphate oxidation method.

In the determination of manganese, results obtained from measurements on the colorimeter and spectrophotometer agreed exactly in half the cases; in other cases agreement was obtained within 0.0001% and within 0.0002% in some other samples.

The measurement of the absorbance of the solutions of coloured samples on the uv-visible spectrophotometer or on the colorimeter without first developing a colour raises doubts when two or more absorbing elements occur in the same sample. Difficulties arise when the colour exhibited and the absorption intensity are very weak, then the relationship between the concentration and absorption is not linear and comparison between samples and standards not satisfactory. In the special case of manganese II, which is usually in the form of the octahedral aquo ion $(Mn(H_2O)_6)^{2+}$, in neutral or acid solutions, the pink colour is very weak and gives correspondingly weak absorption bands in the 300-570 nm region (37), the band at 400 nm being characteristic. The weakness of the absorption and colour result from the fact that the d- d transitions which induce them are of the forbidden type.

This method for evaluating the level of manganese in the samples was considered unsatisfactory as both the colorimeter and the spectrophotometer could not discriminate between standard concentrations even for very concentrated solutions of manganese chloride (Table VII).

Conclusion

Evidence from these analyses would establish that most samples of "Kanwa" contain about 30% of sodium, 0.1 - 4.0% of potassium and that certain samples contain trace amounts of manganese. The problem of peripartum cardiac failure could be re-examined against the above composition of 'kanwa'. On the basis of a daily 'kanwa' **intake** of about 30g suggested by Davidson and his coworkers a nursing mother consumes about 10g of sodium and 0.3-1.2g of potassium daily; in addition a trace amount of manganese is also taken in. It would be interesting to know the medical implications of these results.

APPENDIX

SALT SAMPLES. Number refers to sample, each of which is identified by market, date of purchase, and place of origin if known.

1. Farar kanwa, white natron, obtained in Kano market. Origin is from Gashua or Nguru market. 12 March 1976.

2. Balma, salt from Bilma in the Kawar Oases, Niger. Obtained in Kano market, 12 March 1976.

3. Gari, powdered farar kanwa, obtained in Kano market, 12 March 1976, but imported from Gashua.

4. Farar kanwa, obtained in Geidam market, 17 March 1976, but came from Chilluma salt works, and bought initially in Togia market.

5. Jar kanwa, red natron, obtained in Geidam, 17th March 1976, but came from Kaitawa in Niger.

6. Ungurnu, obtained in Maiduguri market, 15 March 1976, brought from Kanem across Lake Chad.

7. Tsumbur tsumbur, obtained Kano market, but brought from Tahoua in Niger -- probably from Teggida N'tessoum. 12 March 1976.

8. Gwangwarasa, obtained in Kano market, 12 March 1976, brought from Gashua.

9. Beza, obtained in Kano market, 12 March 1976, claimed that this was brought from Mirria in Niger, but probably from Bilma.

10. Gallo, obtained in Kano market, 12 March 1976, but brought from Tahoua in Niger, and probably from Tegida N'Tessoum.

11. Kantu from Fashi, in Niger; obtained in Kano market, 12 March 1976.

12. Ungurnu, obtained from Kano market, 12 March 1976, but brought from Maiduguri and ultimately Lake Chad.

13. Jar kanwa na Auzin, obtained in Kano market, 12 March 1976, brought from Auzin - either from Tegidda N'Tessoum or from Bilma.

14. Gwangwarasa, obtained in Geidam market, 17 March 1976, brought from Adebur in Niger.

15. Manda chu or kigu; obtained in Maiduguri; brought from Geidam; 15 March 1976.

16. Bakin manda, obtained in Kano market, 12 March 1976, brought from Maigatari on Niger border, but probably brought from Wacha market in Niger.

17. Manguli, obtained in Kano, 12 March 1976, brought from Gashua or Geidam.

18. Manda chu or kigu, obtained in Geidam, 17 March 1976. Brought from Dakindiri, close to Goudamari in Niger.

19. Manguli, obtained in Geidam, 17 March 1976, produced at Fannamiram and brought from Togia market.

20. Manguli, obtained in Geidam, 17 March 1976, produced at Wadaram in Niger.

21. Manguli, obtained in Maiduguri, 15 March 1976, , brought from Geidam or Gashua.

22. Manguli, obtained in Geidam, 17 March 1976, produced at Tatekutu, brought to Togia market - from Niger.

23. Farar Kanwa, obtained at Jajimaji market, produced at Gatilla to the north; 20 March 1976.

24. Details of this sample were not certain.

25. Farar Kanwa, obtained at Jajimaji market, produced at Karagu, to the north, 20 March, 1976.

26. Gari, called tsumbar, obtained at Nguru but brought from Niger; 20 March 1976.

27. Bakin Manda, obtained at Jajamaji, brought from Karagu in the north via Mandaram in Niger, 20 March 1976.

28. Jar Kanwa, obtained from Maiduguri market but brought from Geidam, 15 March 1976.

29. Jar Kanwa, obtained in Tahoua, Niger, produced at Dirkou in the Kawar Oasis, 17 January 1976.

30. Red Salt from Tegidda N'Tessoum, obtained at Tahoua market, 27 January 1976.

31. Taoudeni salt, obtained from Tahoua, brought from Thoudeni, 27 January 1976.

32. Ungurnu, obtained in Kano Market, brought from Baga, 12 March 1976.

33. Bakin Manda, obtained at Nguru, 20 March 1976, brought from Wacha in Niger.

34. Manguli, obtained at Nguru, 20 March 1976, brought from Karagu.

35. Balma, obtained at Nguru, 29 March 1976; probably from Bilma.

36. Mangul, obtained at Nguru, 20 March 1976, from Tsumbar.

37. Mangul, obtained at Geidam, 17 March 1976 produced at Malaka.

38. Jar Kanwa, obtained at Jajimaji, 20 March 1976, from the north.

39. Gwangwarasa, obtained at Maiduguri, 15 March 1976, from Geidam.

40. Jar Kanwa, obtained at Kano, 12 March 1976, from Geidam.

41. Gajimarai, from Cameroons, from near Jimaita, an eye medicine; not known if this is salt, obtained 17 March 1976.

42. Gwangwarasa, from Geidam market, 17 March 1976; produced at Adebur in Niger.

43. Manguli, from manguli production; obtained at Geidam market, produced at Bizar, near Dara, 17 March 1976.

REFERENCES

1. Davidson, N. McD., Lorna Trevitt, and Parry, E.H.O., Bull. Wld Hlth Org. 51, 203-208 (1974).

2. Lovejoy, P.E., The Salt Industry of The Central Sudan A preliminary Survey, (Paper for the Seminar on Economic History of the Central Savanna of West Africa, Kano, 1976).

3. Buchanan, K.M. and Pugh, J.C., "Land and People in Nigeria", pp 193, 7th imp. London, University of London Press, (1969).

4. Kolthoff, I.M., and Philip J. Elving eds. assisted by Ernest B. Sandell "Treatise on Analytical Chemistry" Part I, Vol. 6, Interscience, John Wiley.

5. Foster Dee Snell, and C.L. Hilton "Encyclopaedia of Industrial Chemical Analysis", Vol.1, Interscience, John Wiley.

6. Snell, F.D., and Ettre, L.S., "Encyclopaedia of Industrial Chemical Analysis", Vol.2, Interscience, John Wiley.

7. Galen W. Ewing "Instrumental Methods of Chemical Analysis" International Student Edition, 3rd Ed., McGraw-Hill.

8. West, A.C., and W.D. Cooke, Anal. Chem, 32, 1471 (1960).

9. Reynolds, R.J., K. Aldons, and K.C. Thompson, "Atomic Absorption Spectroscopy" Griffin, London (1970).

10. Ramirez-Muriez, J., "Atomic Absorption Spectroscopy" Elsevier, Amsterdam (1968).

11. Bond, R.D., and H.C.T. Stace, Analyst, 83, 679 (1958).

12. Dean, J.A., "Flame Photometry", McGraw-Hill, New York(1960).

13. Collier, H.B., and R.P. Barschel, Anal. Chem., 24, 1030(1952

14. Charles N. Reilley "Advances in Analytical Chemistry and Instrumentation" Volume 3, Interscience, John Wiley, N. York.

15. Christian, G.D., and J.J. Feldmann, "Atomic Absorption Spectroscopy - Application to Agriculture, Biology and Medicine" Interscience, Wiley, N.Y. (1970).

16. West, P.W., P. Folse, and D. Montgomery, Anal. Chem., 22, 667, (1950).

17. Berry, J.W., D. G. Chappell, and R.B. Barnes, Ind. Eng. Chem., Anal. Ed., 18, 19 (1946).

18. Bills, C.E., F.G. McDonald, W. Niedermeier and M.C. Schwartz, Anal. Chem., 21, 1076 (1949).

19. Kingley, G.R., and R.R. Schaffert, Anal. Chem., 25, 1738 (1953).

20. Shellenberger, T.E., R.E. Pyke, D.B. Parrish, and W.G. Schrenk, Anal. Chem. 32, 210 (1960).

21. Vogel, A.I., "A Textbook of Quantitative Inorganic Analysis" 3rd Edition, Longman, London.

22. Peter Woodward, "Elementary Qualitative Analysis on the Small Scale" Oxford University Press.

23. Kolthoff, I.M., P.J. Elving, eds "Treatise on Analytical Chemistry" Part II, Vol.5, Interscience, John Wiley, New York (1961).

24. Foster Dee Snell, and Leslie S. Ettre, "Encyclopaedia of Industrial Chemical Analysis", Vol. 19, Interscience, John Wiley.

25. Van Nostrands's, "International Encyclopaedia of Chemical Science" Van Nostrand.

26. Kolthoff, I.M., and P.J. Elving eds "Treatise on Analytical Chemistry" Part II, Vol.8, Interscience, John Wiley.

27. Fritz Feigl, "Spot Tests in Inorganic Analysis" 5th, enlarged and revised edition, Elsevier Publishing Company.

28. Belcher, R., A.J. Nutten, and W.I. Stephen, Analyst, 76, 904 (1951).

Belcher, R., and A.J. Nutten, J. Chem. Soc. 154, 547 (1951).

Raquet, D., Chem. Abstracts, 42, 6698 (1948)

Foster Dee Snell, and Leslie S. Ettre, "Encyclopaedia of Industrial Chemical Analysis", Vol. 15, Interscience, John Wiley.

Foster Dee Snell, and C.T. Snell, "Colorimetric Methods of Analysis", vol.II, 3rd Edition, D. Van Nostrand Company, N. York.

33. Oscar Hackl, Z., Anal. Chem., 105, 182 (1936).

34. "Standard Methods for the Examination of Water and Waste Water", 13th Edition (1971), prepared and Published jointly by American Public Health Association, American Water Works Association, Water Pollution Control Federation.

35. Foster Dee Snell, and Leslie S. Ettre, "Encyclopaedia of Industrial Chemical Analysis", Vol.9, Interscience, John Wiley.

36. Kirk-Othmer "Encyclopaedia of Chemical Technology", Vol.22.

37. Cotton, F.A., and G. Wilkinson, "Advanced Inorganic Chemistry A comprehensive Text" Interscience, John Wiley.