

ANALYSIS OF NATURALLY OCCURRING WATERS FOR
TOXIC METALS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
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SCIENCE IN ANALYTICAL CHEMISTRY

BY

MR PAUL UKO ANYOGO B.Sc (Hons.) CHEMISTRY

DEPARTMENT OF CHEMISTRY
AHMADU BELLO UNIVERSITY
Z A R I A

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DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other University or Institution. Information derived from the published or unpublished work of others have been acknowledged in the text.

PAUL UKO ANYOGO
M.Sc. Candidate

Dedication

Dedicated to my wife and daughter, Christy
and Vivian Anyogo respectively.

Acknowledgement

I wish to use this opportunity to express my gratitude to my Supervisor, Dr. E.G. Kolawole, whose guidance, constructive criticisms and suggestions led to the successful conclusion of this work.

I also wish to thank the Acting Head of Department, Dr. H.T. Bozimo, the Technical and other supporting staff for their various contributions to the success of this work.

Abbreviations Used

APHA	=	American Public Health Association
AWWA	=	American Water Works Association
WPCF	=	Water Pollution Control Federation
APDC	=	Ammonium pyrrolidine dithiocarbamate
MIBK	=	Methyl isobutyl Ketone
AA3	=	Atomic Absorption spectrophotometer
NaDDTC	=	Sodium diethyldithiocarbamate
WHO	=	World Health Organization
EDTA	=	Ethylenediaminetetraacetic acid

Abstract

Samples of naturally occurring waters were analysed for toxic metals. The metals are cadmium, cobalt, copper, lead manganese and zinc. The analytical technique used here is a combination of methods recommended by APHA-AWWA-WPCF¹ and Reynolds and Aldous.² The samples were acidified with 5.0cm³ conc. HNO₃ per litre of sample, immediately after collection. At the time of analysis, they were acidified with 1:1 redistilled HCl heated for a given time on a steambath, cooled and filtered.

The analysis was done in two parts. In each case, 100.0 cm³ of samples were used. In the first part, the metal ions were chelated with APDC and extracted into MIBK at a given pH. The organic extracts were aspirated into an air-acetylene flame in AAS at the resonance wavelength of the metal. Already, analytical curves for the metals were prepared by extracting each metal from a solution of known concentration, determining their absorbances in AAS and plotting the same against concentrations. From these standard curves, the concentration of each metal in the water samples were determined,

In the second part of that analysis, the same metals

were chelated with sodium diethyldithiocarbamate and extracted into chloroform. The absorbances of the extracts were determined with a UV spectrophotometer and the concentrations were again determined from their Calibration Curves.

The results of these methods are a measure of the extractable metals in the water samples. Finally, the two methods of analysis are compared.

Introduction

Water is such a unique and multi-purpose substance that it needs no introduction. There is virtually no aspect of human endeavour that does not use water. These include drinking, cooking, laundry, agriculture, industry, medicine, transport, recreation etc. It is therefore not surprising that a lot of effort has been expended over the years, in the analysis of, among other things, trace metals in water (1,2,3,4,5,6,7,8 etc.)

In the present work, naturally occurring waters were analysed for toxic metals. The toxic metals analysed for are cadmium, cobalt, copper, lead, manganese and zinc. They are toxic to both humans and aquatic life when present in high concentration. For example cadmium is extremely toxic and has a long biological half-life in man. It is known to be deposited in various body tissues e.g. kidney and liver, and may be an etiological factor in various human pathological processes such as renal dysfunction, growth inhibition and arteriosclerosis.

Similarly the toxicity of copper to aquatic life is dependent on the alkalinity of the water as the cupric ion is complexed by anions present, which in turn affect toxicity. At lower alkalinity copper is generally more toxic to aquatic life. Concentrations of Copper found in natural waters are not known to have an adverse effect on humans. It has been reported by Train⁹ that copper exhibit toxicity to some agricultural plants when its concentration is 100 ug per litre.

Lead is a toxic metal that tends to accumulate in the tissues of man and other animals. Major toxic effects of lead include anaemia, neurological dysfunction and renal impairment. Lead enters the environment from pesticides, smelting industry, combustion of tetraethyl lead gasoline additives, leaching of soil etc. The distribution of lead in natural waters is not well known, but it is usually very low.

Manganese is not considered to be a problem in fresh waters, but very large doses of ingested manganese can cause some disease and liver damage.

The toxicity of zinc compounds to aquatic animals is influenced by such factors as hardness, dissolved oxygen

and temperature. An increase in temperature and reduction in dissolved oxygen increase the toxicity of zinc.

Table 1.1 below gives the criteria for domestic water supplies by WHO¹⁰.

Table 1.1: Criteria for domestic water supplies

Element	Concn. (µg/l)
cd	10
cu	1.0
Co	Not indicated
Pb	50
Mn	50
Zn	50

In using these criteria, local hydrological conditions, the natural quality of the water under consideration, the kinds of organisms and other factors should be borne in mind.

Previous Works

The literature on analysis of natural (as well as other) waters is so extensive that it will be impracticable to review it adequately in a limited work of this nature.

The author will therefore limit the review to the analysis of fresh waters which is what this work has covered.

A few general patterns emerge from the literature. One is that most of these toxic metals are usually present in very low concentrations in natural waters, and in order to determine them accurately, they are usually concentrated. Concentration may be by freezing, evaporation, ion exchange, solvent extraction or a combination of some of these methods. For example Korkisch¹¹, in analysing natural waters for these toxic metals, employed a combination of chelation and extraction (with NaDDTC/CHCl₃), evaporation (with infrared lamp), and ion exchange (Dowex 1, x8) for concentrating and separating the metals before they were analysed by A.A.S. and fluorimetry. The results showed that the metals were quantitatively extracted with the solvent (2:5 mixture of acetone and chloroform). The results also showed that neither did the volume of water has any effect in the volume range of 0.25cm³ to 1.0 litre nor did up to 10 mg of iron affect the recovery of the trace elements, except for uranium. But the most important of all, the results showed that none of the trace metals in seawater could be determined by direct atomic absorption measurement,

hence preconcentration is always desirable. The extraction method was thus shown to be more suitable for the determination of trace in natural waters.

Lacoste et al¹² used NaDDTC and chloroform for the determination of bismuth, cobalt, chromium, iron, nickel and uranium over a wide pH range (0.1 to 9). The results showed that, except for uranium complex, which did not extract well in acid solution and dichromate ion which extracted well up till pH 6.3 and decreased rapidly at higher pH, the other complexes were extracted almost quantitatively over the entire pH range which was investigated. The results also shown that CHCl_3 solution of the coloured diethyldithiocarbamate complexes obeyed Beer's Law of Linear proportionality between absorbancy and concentration.

Fishman and Midgett¹³ chelated cobalt, nickel and lead with APDC and extracted the chelates into MIBK. The metals were determined with AAS. They found that the results with this method agreed well with results obtained by spectrographic methods. They found pH 2.8 to be optimum for the extraction, especially for lead. No spectral interferences were found.

Boethner and Grunder¹⁴ found that the two instrumental components, affecting atomic absorption (AA) and flame

emission spectroscopy as techniques for analysis of water, are the burner and the hollow cathode lamps. The two components affect precision and limit of detection. Other authors like Slavin¹⁵ and Reynolds and Aldous¹⁶ have equally found AAS to be versatile, rapid, reproducible and almost free from spectral interferences. The combination of APDC and MIBK for chelation and extraction respectively are also very popular in trace ~~and~~ analysis.

Other chelating agents like 8-hydroxyquinoline, cupferon, dithizone, and ammonium diethyldithiocarbamate and solvents like carbon tetrachloride, benzene, xylene, toluene, isoamyl alcohol etc. are very popular and have been used extensively by Perrin¹⁷, Stary¹⁸, Landell and Onishi¹⁹ etc. in extractive works.

In all cases, the absorption obtained upon spraying the extract to an atomic absorption spectrophotometer is greatly enhanced by both concentration factor and greater volatility of the solvent.

The analytical techniques used here are based on AAS and UV spectrophotometry. Both techniques were used in combination with liquid-liquid extraction in order to preconcentrate the metals so that "improved detection limits and accuracy may be achieved".²⁰

Aims and Objectives

The main aim of this analysis is to determine the level or concentration of these toxic metals in some selected natural waters and thus ascertain whether their levels are within tolerable and acceptable limits.

To compare the analysis of trace metals by both AAS and the colorimetric methods using APDC/MIBK for AAS and NaDDTC/CHCl₃ for UV method and ascertain a better analytical technique.

It is also hoped that the information derived therefrom will bring to the attention of the authorities concerned, the need to provide clean and treated water to the populace, especially the rural areas where untreated water is consumed.

The natural waters analysed were from wells, streams, rivers and ponds at Makurdi, Kaduna, Jos, Zaria and Kano. A sample of water from the Atlantic Ocean, Lagos, was also analysed. The samples and the abbreviations used to identify them are shown below in table 1.2.

A Table 1.2 Samples for AAS Analysis

1. River Benue water at Makurdi - BW(MK)
 2. Well water from Makurdi - WW(MK)
 3. Spring water from North Bank Makurdi - NBS(MK)
 4. Well water from Kofa Kabuga Kano - WKK(KN)
 5. Pond " " Sane Mainege Kano - PW(KN)
 6. Stream Water from Airport Road Kano - SW(KN)
 7. Well water from Samaru Zaria - WWS(ZA)
 8. Well water from Zaria Town - WW(ZA)
 9. Dam water from A.B.U. Zaria - DW(ABU)
 10. Stream water from Bukuru near Jos - SWB(J)
 11. Atlantic Ocean Water, Lagos - AW(LA)
- B. Samples for UV spectrophotometry - all from Kaduna and its environs.
1. Rigachukun Stream - RCS
 2. River Kaduna near Stadium - RKT
 3. River Kaduna (Kaduna by-pass) - RKS
 4. Well Water from TV village - WTV₁
 5. Another Well water from TV village - WTV₂
 6. Stream water near F.T.C. - SW
 7. Kaura Stream Kaduna - KSK
 8. Gada Biu stream Jos - GBJ

Losses and Contaminations

Water is a complex solution containing either in a dissolved or particulate state, all the elements of the earth's crust. But most of these elements exist in trace amount, where trace amount is taken to mean a constituent that is less than 0.01% ($<100\text{ppm}$) of a sample²¹. For many of these elements, the literature contains a wide range of reported concentrations. One likely cause of these differences is contamination of the samples, either during collection and storage or subsequent analysis. Another source of error may be due to losses during the analysis. It is therefore necessary for the analyst to be aware of these sources of errors and how to eliminate or minimise them during sampling and analysis.

A sample can be contaminated by the air in the laboratory, from filter papers, the container, reagents and even the water used for preparing solutions and washing the container and apparatus. Losses may occur by absorption on the wall of the container, leaks etc. Most methods of analysis require chemical pre-separation for concentration or removal of interfering elements before an analysis can be performed. These procedures greatly increase the risks of contaminating the water sample.

In the case of airborne contaminants, the amount of contamination will vary with local conditions. For example, hydrogen sulphide in the air will greatly affect spectrophotometric determination of traces of metals, as it reacts with many metals to form insoluble sulphides.

According to Sandell and Onishi²², copper, manganese, lead, zinc, the rare earths and many other elements have been found in quantitative filter papers. There are therefore sources of contamination. Losses can also occur on filter paper through absorption of cations. Filter papers owe their absorptive properties to the presence of carboxylic groups, which allow cation exchange. Absorption of metals on filter paper can be reduced by filtering at very low pH.

In the present work, glass wool was used for filtration instead of filter paper. Preliminary washing of the wool with the sample to be used in the analysis was carried out.

Heavy metals may be absorbed on the walls of containers or they may be leached from the container into the sample. Losses may also occur by volatilization, co-precipitation and coextraction. Absorption of

container surfaces is largely prevented by adjustment of the pH to about 1.5 or less with Conc. HNO_3 . In acid medium, the cations are replaced by hydrogen ions.

Most of the purified solvent contain many trace elements at concentrations of the same order of magnitude as that of the sample. Therefore if large volumes of these solvents are used in preconcentration or chemical separation procedures, substantial contamination could result. The metal contents of water can be reduced to very low levels by passage of distilled water through a column of ion exchange. In practice, this was achieved by passing distilled water through an Elgastat Instant Water Purifier Type B102/MK II. The water was allowed to drop at a slow, but steady, rate to ensure complete purification.

Organic reagents used for analysis are also sources of contamination. Most contain metallic impurities in different proportions. Robertson²³ has reported that most chelating reagents contained significant concentrations of metals. According to him, the contamination which could result from the various chelating reagents, such as 8-hydroxyquinoline, dithizone, NaDDTC, 1-pyrrolidine carbothioic acid, 2-benzimidazolethiol and Nitroso-R

are zinc, cobalt, iron and silver.

Because very small amounts of these reagents are used, they may not contribute significantly to contamination. Recrystallisation from suitable solvents may reduce these contaminations. Liquid reagents, which are not of analytical grade, may be redistilled.

Other losses may occur during extractions, such as leakage from separatory funnels, incomplete separation of phases etc.

Sampling and preservation of Samples

Attempts were made to ensure that samples were as representative as possible. Whenever possible, samples were taken as far away from the banks as possible and a little distance from the surface. Treatment of the samples usually depend on the parameters to be determined. These parameters may be pH, dissolved oxygen, cyanide, phenolic substance, chlorides, chemical and biological oxygen demands, heavy metals etc.

In the atomic absorption spectrophotometric method, only the extractable metals were determined. These are the metals in solution and those lightly absorbed on

suspended materials. Thus samples were acidified without filtration at the time of collection²⁴. They were acidified with 1.50 cm³ conc. HNO₃ per litre. The acidification kept the metals in solution and minimized their absorption on the walls of the containers. This also prevented any form of chemical or biological reactions occurring between sampling and analysis. The samples were then put in the fridge until just before needed for analysis. According to Wilson²⁵, acidification of the sample to pH 1 ensures the stability of the trace metals for weeks. To prevent contamination of the sample by the container, the latter was thoroughly washed, first with soap solution, then with distilled water and finally with distilled, deionized and acidified water. The caps of the containers were similarly cleaned. These precautions were taken whenever new samples were taken. At the sampling site, each container was rinsed with the sample, before being filled up, and acidified.

During the analysis, the samples were pre-concentrated first by evaporation over a steam bath, then by chelation and extraction into the organic solvent.

In the UV spectrophotometric method, the sampling method, preservation and the pretreatment of the samples were the same as in the AAS method. The same metals were chelated by NaDDTC and extracted into chloroform. A combination of masking agents (EDTA or KCN) and pH control were employed to separate the metal ions before their eventual analysis. Sodium diethyldithiocarbamate forms complexes with many metals which are more or less soluble in various organic solvents. The purpose of the masking agents in solvent extraction is to retain unwanted metal ions in one solvent phase while permitting the transfer of the desired metal ion to a second solvent.

Finally, the determinations of cadmium, lead and zinc whose chloroform extracts are almost colourless, were backextracted into 0.1M HCl (for Pb and Cd) or weakly alkaline solution (for Zn) and shaken with cupric salt solutions. The absorbances of the resulting solutions were then measured at 436nm.

It may be observed that deviations may occur from the expected replacement reactions of cadmium, lead or zinc because of rate factors.

Theory of Extraction

The extraction of a metal from water to an organic solvent is based on the Nernst distribution law, which states that at a given temperature, a solute is distributed between two essentially immiscible solvents in such a way that the ratio of the concentrations of the solute in the two phases will be constant, provided the solute has the same molecular state in each solvent. In its simplest form, the law may be stated thus:

$$K_D = \frac{\text{total concn. of metal in org. phase}}{\text{total concn. of metal in aqueous phase}}$$

when K_D = the distribution coefficient.

The word "total" is used here to include the various forms of the metal in solution. K_D is approximately equal to the ratio of its solubilities in organic and aqueous phases. So metals that are sparingly soluble in water but readily soluble in organic solvent can easily be extracted.

Since metal ions are solvated by molecules of water, and will not be extracted into the organic solvent in that form, because of the high solvation energy involved, it is necessary to convert them into neutral extractable forms.

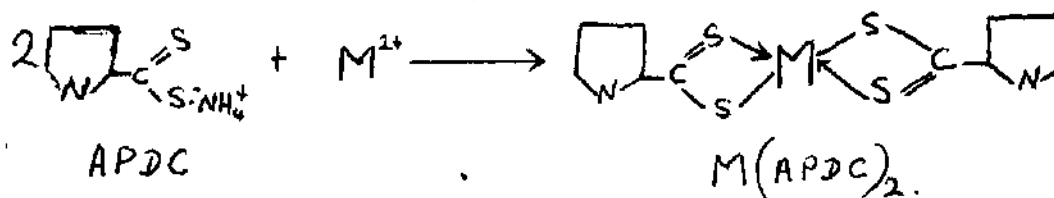
That means that some or all of the solvated water molecules must be removed to obtain an extractable form of the metal ion. The species must be neutral because of the low dielectric constants of the organic solvents.

According to Morrison and Freiser²⁶, the extraction process occurs in three stages.

(i) The first stage is the formation of the uncharged complex. A chelating agent or liquid, (L), reacts with the metal, M, to form a neutral complex.



In the case of APDC with the metal ions, the reaction can be represented thus;



Here the number of ligands attached to the extracted complex is equal to the valency of the metal. A similar reaction occurs with the diethyldithiocarbamates.

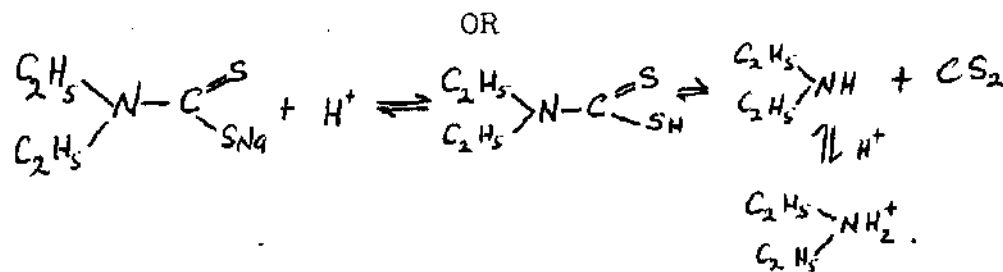
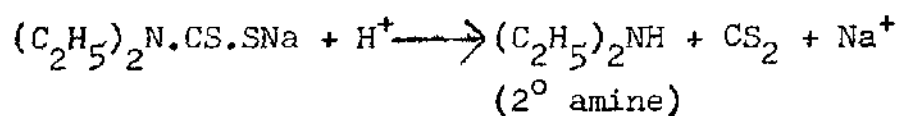
(ii) In the second stage, the complex becomes distributed between the two phases.

In practice, this is achieved by shaking one layer with a second immiscible phase until partition equilibrium has

been attained. The phases are allowed to settle out, and the layer containing the desired constituent is removed.

(iii) The final stage is the chemical interaction of the complex in the organic phase.

In the extractions with diethyldithiocarbamates, it is necessary to store the NaDDTC solution in dilute alkali, as NaDDTC decomposes in acid solution, forming diethylamine and carbon disulphide:



Among the factors affecting these extractions are the pH of the solution, the stability constant of the metal chelate and its relative stability in the organic phase.^{27,28}

Elements that form strong complexes react under acidic conditions, while elements that form weak complexes are not able to compete with hydrogen ions and do not react significantly. In all, the formation of an absorbing species is due to the effective deprotonation of the ligand.

Most of the metal dithiocarbamates investigated have low solubilities in water, but high solubilities in organic solvents, e.g. CHCl_3 , as shown below.²⁹

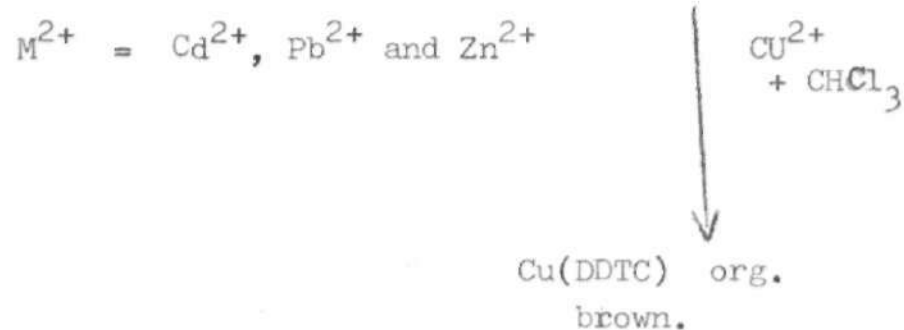
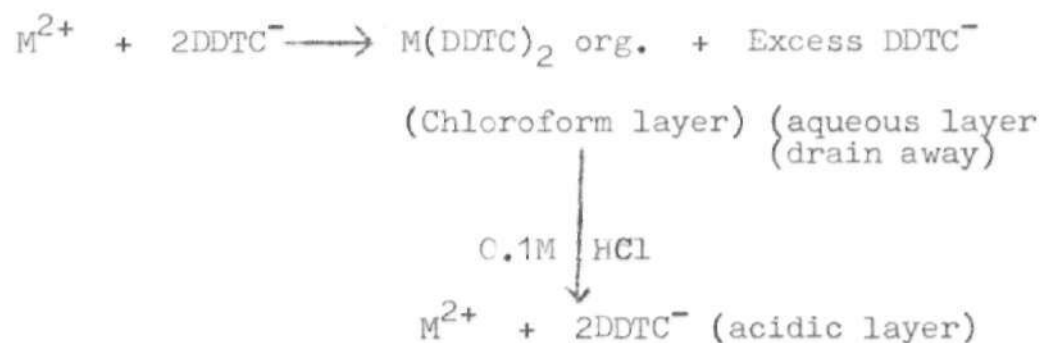
Table 2.1: Solubilities of some metal diethyldithiocarbamates in water and chloroform

Element	Water (M)	Chloroform (M)
Cd	1.8×10^{-7}	0.14
Co	1.3×10^{-7}	0.51
CU(II)	3.2×10^{-10}	0.70
Mn	1.5×10^{-4}	0.36
Pb	3.4×10^{-8}	0.89
Zn	2.6×10^{-6}	0.48

It is therefore expected that the distribution coefficient of these metals diethyldithiocarbamates will be high. Hence the extraction will be as quantitative as possible.

Lead, zinc and cadmium, whose diethyldithiocarbamates are colourless, were determined indirectly as copper diethyldithiocarbamate. For example, the colourless $\text{Pb}(\text{DDTC})_2$ was back-extracted into 0.1M HCl and shaken with a cupric salt (cupric nitrate) solution.

The organic solution of $Zn(DDTC)_2$ was washed free of excess DDTC with a weakly alkaline aqueous solution (pH 10) and then shaken with the aqueous solution of cupric salt solution in ~~excess to transform the colourless~~ $Zn(DDTC)_2$ into $Cu(DDTC)_2$. The reaction may be ~~repeated~~ ^{represented} as follows:



In the case of Zn^{2+} , 0.1M HCl is replaced by a weak alkaline solution (pH 10). The metal ion reacts with the reagent to form a complex, which is extracted into the chloroform layer. The excess reagent remains in the aqueous

layer. The organic layer is withdrawn and shaken with 0.1M HCl (for Cd and Pb) or weakly alkaline solution (pH 10 for Zn). The complex is decomposed. The reagent, which is water-soluble, goes to the aqueous layer where it reacts with Cu^{2+} to form a complex. The complex is again extracted with chloroform. Since only the reagent released by the decomposed complex is available for the reaction with Cu^{2+} , and since each of the three ions can each release two ligands per ion and Cu^{2+} can take two ligands per ion, it follows that the concentration of Cu^{2+} is equivalent to the concn. of either Cd, Pb or Zn, depending on which of them was being determined.

In practice, deviations from the expected replacement order may occur because of rate factors. For example, cobalt(II) diethyldithiocarbamate is transformed by oxidation to Co(III) diethyldithiocarbamate, which is very stable. Similarly Mn(II) is known to exist as Mn(III) and Mn(IV) diethyldithiocarbamates.³⁰ $\text{Cu}(\text{DDTC})_2$ is also known to be photochemically unstable in CHCl_3 . The decomposition products of the solvent is thought to act as the reducing agents.³¹

The stability of DDTC complexes with metals decrease in the series $\text{Hg} > \text{Ag} > \text{Co} > \text{Cu} > \text{Ni} = \text{Bi} > \text{Pb} > \text{Cd} > \text{Fe(III)} > \text{Zn} > \text{Mn}$.^{32,33,34} For this reason, the absorbances of $\text{Mn}(\text{DDTC})_2$ were determined as soon as they were extracted.

Principle of A.A.S.

When a solution containing a suitable compound of the metal is aspirated into a flame, the sample is converted to the gaseous form. Some of the atoms will absorb radiation and become excited. If the energy absorbed is sufficiently high, the excited atoms will emit the characteristic radiation of that metal. But the vast majority of the atoms will remain in the unexcited or ground state. When a light of the resonance wavelength, usually from a hollow cathode discharge lamp, is passed through a flame containing atoms of the element, part of the light will be absorbed, and the absorption will be proportional to the concentration of the atoms in the flame.

The relationship between the absorbance, the incident light, and the transmitted light is given by the expression³⁵.

$$A = \log \frac{I_0}{I_t} = KL N_0$$

Where

A = Absorbance

I_0 = incident light

I_t = transmitted light

N_0 = concn. of atoms in the flame

L = Path length (cm) through the flame

K = Constant

The Theory of UV Spectroscopy

The amount of radiation absorbed by a molecule depends upon the number (and structure) of molecules interacting with the radiation. Quantitative Spectroscopic analysis is based upon the relationship between the amount of light absorbed and the amount of absorbing species. When a monochromatic light passes through a homogenous solution, part of the incident light is reflected, a part is absorbed within the medium and the rest is transmitted. According to Lambert's Law,³⁶ the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically.

$$- \frac{dI}{db} = KI \dots\dots\dots (1)$$

- where I = intensity of the incident light
- b = thickness of the medium or pathlength
- k = Constant.

Similarly, Beer's Law³⁷ showed that the intensity of emitted light decreases exponentially with increasing concentration of the absorbing species.

A combination of the two laws, known as the Beer-Lambert's

Law, is given by the equation:

$$\log \frac{I_0}{I_t} = a.b.c.$$

$$\text{or } A = a.b.c.$$

where A = absorbance

a = Constant

c = Concn.

Thus the absorbance is directly proportional to the concentration of the absorbing species.

Deviations may occur due to dissociation, association in solution, complex formation and also if the light is not sufficiently monochromatic.

Chapter III: Experimental

Extractions with MIBK

Preparation of Stock Solutions

A 1000ppm stock solution of each metal was prepared as indicated below, and the standard solutions were made from the stock by appropriate dilutions. These standard solutions were chelated with APDC and extracted into MIBK at pH 2.8. The absorbances of the extracts were determined with Unicam SP 1900 AAS and calibration curves were obtained by plotting the absorbance against concentration.

Cadmium

A solution of cadmium was prepared by dissolving 2.1315g. of cadmium chloride, $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, in water and the solution was diluted to 1000cm^3 with distilled and deionised water. The solution was standardised by titrating 25.0cm^3 of it with 0.01M EDTA using xylenol orange as indicator. The solution was buffered with Hexamine to pH 5. From the result an appropriate volume of the solution was diluted to 250cm^3 to obtain a 100 ppm stock solution. Solutions of 1, 2, 3 and 4 ppm were then prepared from the stock solution by diluting 0.1, 0.2, 0.3, and 0.4cm^3 of the stock, with water, to 100cm^3 respectively.

Cobalt.

A stock solution of cobalt was prepared by dissolving 4.0380g of A.R. cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, in water and making the solution up to one litre. 25.0cm^3 of the solution was titrated with 0.01M EDTA at pH 6, using Hexamine and xylenol orange as buffer and indicator respectively. From the results the one litre solution contained 1000ppm of cobalt. Standard solutions of 1 to 5ppm were made from the stock by diluting appropriate volumes of the stock solution to 100cm^3 in volumetric flasks.

Copper

To make a 1000ppm stock solution of copper 3.8020g of cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, was dissolved in water and the solution was diluted to 1000cm^3 with distilled and deionised water. 25.0cm^3 of the solution was titrated with 0.01M EDTA using fast sulphon Black F as indicator. The end-point was indicated by the colour change from purple to dark green. A 1000ppm stock solution was then prepared by diluting an appropriate volume of the standardised solution to 250cm^3 . From the stock, solutions of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0ppm were prepared.

Lead

A stock solution of lead was prepared by dissolving 1.5980g of anhydrous lead nitrate, $\text{Pb}(\text{NO}_3)_2$, in about 200cm^3 of water and 1.5cm^3 of conc. HNO_3 was added and the solution was diluted to 100cm^3 with distilled and deionised water. Again, the solution was standardised with EDTA at pH 6, using Hexamine and sylenol orange as buffer and indicator respectively.

From the standardised solution, solutions of 1 to 5ppm were prepared.

Manganese

A solution of Manganese was prepared by dissolving 3.176g of A.R. manganous sulphate monohydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, in about 200cm^3 of distilled and deionised water. 1.5cm^3 of conc. HNO_3 was added and the solution was made up to the mark with the water. 25cm^3 of the solution was titrated with the standard EDTA solution at pH10, using $\text{aq. NH}_3/\text{NH}_4\text{Cl}$ and Eriochrome Black T as buffer and indicator respectively. From the result, a 1000ppm stock solution was prepared by diluting appropriate volume of the solution to 250cm^3 . From this standardised solution, solutions of 0.5, 1.0, 1.5, 2.0, 2.5 and 3 ppm were prepared.

Zinc

A 1000 ppm stock solution of zinc was made by dissolving 1.0g of A.R. zinc powder in 20cm³ of 1:1 HCl and the solution was made up to 1000cm³ with distilled and deionised water. Standard solutions of 1 to 5 ppm were prepared by dilution of appropriate volumes of the stock solution.

Extraction of Standard Solution

To extract the metal ion in each standard solution, the 100cm³ of the standard solution was poured into a small beaker. The pH of the solution was adjusted to 2.8 with pH meter. The pH was adjusted by the addition of either 1.0N NaOH or dilute HNO₃. The solution was transferred to a 250cm³ separatory funnel and shaken with 5.0cm³ of 1% APDC solution. Finally, 10cm³ of MIBK was added and the solution was vigorously shaken for about two minutes. It was then allowed to stand. The aqueous layer was drained off and discarded. The organic layer was collected in a small sample bottle and aspirated into an airacetylene flame in a Unicam SP1900 Atomic Absorption Spectrophotometer. The absorbances, measured, were plotted against concentration (ppm) and the graphs are shown in figs. 3.1 to 3.6.

Analysis of Samples

A. Apparatus

- (a) Unicam SP 1900 A.A.S.
- (b) Hollow Cathode discharge lamps
- (c) Separatory funnel
- (d) pH Meter.

B. Reagents

- (i) Acetylene gas (in cylinder)
- (ii) Air
- (iii) 1% APDC Solution
- (iv) MIBK
- (v) Conc. HNO_3
- (vi) Distilled, deionised and acidified water

C. Procedure

1. Preparation of Samples for analysis

At the time of analysis, 100cm^3 of the water sample was transferred to a 250cm^3 Conical flask which had been thoroughly cleaned.

5 ml of 1:1 redistilled HCl was added to the sample, which was then heated on a steam bath for 15 minutes. It was then filtered through glass wool which have been thoroughly washed with deionised water and then with the sample to be analysed. The

volume was adjusted to 100cm³ with the distilled and deionised water.

2. Chelation and Solvent extraction

To extract a given metal, the water sample was transferred to a beaker that was cleaned as above. The pH of the water was adjusted to pH 2.8³⁸ by either 1.0N NaOH solution or dil. HNO₃. The water was then transferred to a 250-cm³ separatory funnel. 5.0cm³ of a 1% solution of APDC was added to the water and shaken to mix. Finally 10.0cm³ of MIBK was added and the solution was shaken vigorously for two minutes. It was allowed to stand. The aqueous layer was drained off and discarded. Each organic extract was collected in a small sample bottle, and aspirated into a cool air-acetylene flame in a Unicam SP 1900 Atomic Absorption spectrophotometer (A.A.S.).

3. Determination of absorbance

Following the operating manual of the instrument, the instrumental conditions (for each metal) were set. MIBK (a blank) was aspirated into the flame and the fuel (C₂H₂) flow was reduced until the flame was similar to that before aspiration of the solvent. The absorbance of the metal was then determined by aspirating the organic

extract into the air-acetylene flame. The conc. of the metal was read from the standard calibration curve of the metal. The results are shown in table 4.1.

Each result is the mean of three determinations.

Chloroform Extractions

A. Apparatus

- (i) Unicam SP 1750 UV spectrophotometer
- (ii) Volumetric flasks
- (iii) Two curvettes
- (iv) pH meter
- (v) Pipettes and burettes

B. Reagents

- (i) 5% NaDDTC solution
- (ii) Amm. acetate - acetic acid buffer, pH 6.3
- (iii) 1.0M NH_4OH solution
- (iv) 0.006M EDTA solution
- (v) 0.03M KCN solution
- (vi) Cupric nitrate solution (1000ppm)

Preparation of reagents

1. Sodium diethyldithiocarbamate (NaDDTC).

A 5% solution of this salt was prepared by dissolving 5.00g of the NaDDTC (A.R) in distilled and deionized water. The solution was filtered and its pH adjusted to 10 by the addition of ammonium hydroxide solution. The solution was made alkaline to keep the salt in solution, as it decomposes easily in acidic medium.

2. Ammonium acetate - acetic acid buffer

The buffer solution was made by dissolving 27.0g ammonium acetate and 120 cm³ of glacial acetic acid (A.R.) in 1 dm³ of solution. This solution has a pH of 3.7. The pH was adjusted to 6.3 by the addition of NH₄OH solution.

3. Aqueous ammonia (I.ON)

This was prepared by diluting 71cm³ of ammonia (27% W/W) to 1 dm³ solution.

4. Masking agents

0.2233g of reagent grade EDTA and 0.1956g of reagent grade KCN were dissolved in water and made to 100 cm³ solutions in separate volumatic flasks to obtain 0.006M and 0.03M solutions respectively.

Preparation and extraction of standard solutions

Cobalt

Solutions of 0.2, 0.4, 0.6, 0.8 and 1.0ppm were prepared from a 1000ppm stock solution of Cobaltous Chloride. These solutions were made by diluting to 100cm³ 0.02, 0.04, 0.06, 0.08 and 0.1 cm³ respectively of the stock solution. To each of these solutions, 1.0cm³ of a 5% NaDDTC solution and 10.0cm³ of the ammonium acetate buffer, pH 6.3, were added. 2.0cm³ of the EDTA solution was also added as a masking agent. The pH was adjusted to 7 with the NH₄OH solution. The solution was left standing for about 30 minutes after the addition of the reagents before extraction.

The cobalt was extracted with two 10-cm³ portions of chloroform. The chloroform extract was withdrawn, each time, into a 25 cm³ volumetric flask. The solution was made to the mark with chloroform. The aqueous layer was drained and discarded.

The absorbance of the extract was read at 650nm with a Unicam SP 1750 UV spectrophotometer.

Cadmium

Standard cadmium solutions of 0.5, 1.0, 1.5, 2.0 and 2.5 ppm were prepared by diluting with water, 0.05, 0.1, 0.15, 0.2 and 0.25 cm³ of a 1000 ppm stock solution of A.R. cadmium chloride in a 100 cm³ volumetric flask.

The solution was transferred to a small beaker, and 1.0 cm³ of a 5% NaDDC solution and 10 cm³ of ammonium acetate - acetic acid buffer were added. The solution was shaken to mix and 0.5 cm³ of KCN solution was added, as a masking agent. The pH of the solution was adjusted to pH 11 by the addition of aqueous ammonia.

The solution was transferred to 250 cm³ separatory funnel. The metal was extracted with two 10 cm³ portions of chloroform. Because the cadmium complex in chloroform is colourless, it is back-extracted into 20 cm³ 0.1M HCl and shaken with 0.25 cm³ of (1000 ppm) cupric nitrate solution. The cupric complex was then extracted with chloroform and its absorbance measured at 436 nm, using a Unicam SP 1750 UV spectrophotometer.

Copper

Solutions of 0.2, 0.4, 0.6, 0.8 and 1.0ppm were prepared from the stock solution of cupric nitrate, as in cobalt. The cupric complex was extracted, as above, at pH 8 using EDTA as a masking agent. The extracts were combined and diluted with CHCl_3 to the mark. The absorbances were determined at 436 nm in the UV spectrophotometer.

Manganese

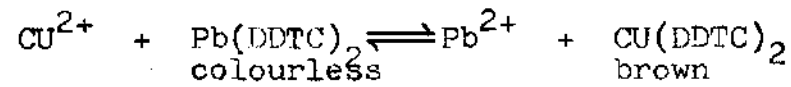
Standard solutions of 0.2, 0.4, 0.6, 0.8 and 1.0ppm were prepared from the stock solution of A.R. Manganous chloride, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, as in cobalt. (0.4cm^3 Conc. HNO_3 was added to the stock solution before it was made to the mark). To the solution was added 0.50cm^3 of the (0.03M) KCN as a masking agent. The pH of the solution was raised to pH 10.5 by the addition of aqueous ammonia.

The metal was extracted as before, and the absorbance of each extract was determined immediately as the solution decolourises on standing. The absorbance was determined at 520nm.

Lead

Standard solutions of 0.5, 1.0, 1.5, 2.0 and 2.5ppm were prepared from appropriate volumes of a 1000ppm stock solution of A.R. lead nitrate. The extractions were carried out as before with KCN as the masking agent. The pH was 9.5.

The colourless $Pb(DDTC)_2$ was shaken with $20cm^3$ 0.1M HCl. The chloroform layer was removed and discarded. The aqueous layer was shaken with $0.25cm^3$ of (1000ppm) $Cu(NO_3)_2$ solution.

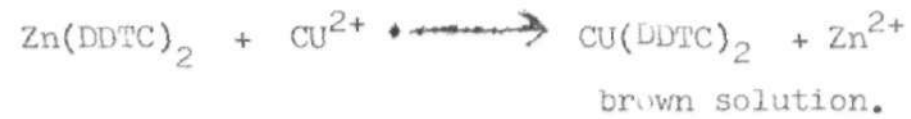


The absorbance was measured at 436nm with the SP 1750 UV spectrophotometer.

Zinc

Standard solutions of 1, 2, 3, and 4 ppm were prepared by diluting to $100cm^3$, 0.1, 0.2, 0.3 and $0.4cm^3$ of a 100ppm stock solution of zinc oxide. The stock solution was prepared by dissolving 0.3112g ZnO in $5cm^3$ of A.R. conc. HCl (S.gr.1.18) and the solution made to $250cm^3$ with distilled and deionized water. The chelate was back-extracted by shaking with $20cm^3$ of a weakly alkaline solution (pH 10). The alkaline aqueous layer was

finally shaken with cupric nitrate solution. The complex was again



extracted with two 10-cm³ portions of chloroform. The absorbance was measured at 436nm.

In all cases, the absorbances measured plotted against concentrations (ppm) to obtain the calibration curves.

Preparation and extraction of samples.

100cm³ of each sample was acidified with 0.5cm³ of 1:1 re-distilled HCl and heated on a steam bath for 15 minutes. It was then cooled and filtered through glass-fibres. The volume was made to the mark with distilled and deionized water.

The solution was transferred to a beaker. 10 cm³ of the ammonium acetate buffer pH 6.3 was added, followed by 1.0cm³ of a 5% NaDDTC solution and 2.0cm³ of EDTA or 0.5cm³ of (0.03M) KCN solution, depending on the metal being determined. The pH of the solution was adjusted to the appropriate value by the addition of aqueous ammonia.

The solution was then transferred to a 250-cm³ separatory funnel and 10cm³ of chloroform was added. It was shaken vigorously to mix, with the stopclock being opened occasionally to allow chloroform vapours escape. It was then allowed to settle and the chloroform layer was withdrawn into a 25-cm³ volumetric flask. The extraction was repeated with another 10cm³ of CHCl₃. The extracts were combined and diluted to the mark with chloroform. The aqueous layer was drained and discarded. As indicated before, the chloroform extracts for Cd and Pb were back-extracted into 20cm³ of 0.1M HCl solution. The aqueous layer was then shaken with 0.25cm³ of a 100ppm cupric nitrate solution and again extracted with two 10-cm³ portions of chloroform. The zinc extract was back-extracted with 20cm³ of a weakly alkaline solution (pH 10) and shaken with the cupric nitrate solution. Extraction was done with two 10cm³ portions of chloroform.

The absorbance of each organic extract was determined at the resonance wavelength of the metal, with the Unicam SP 1750 UV spectrophotometer.

The results are shown in table 4.2. Each result is the mean of three determinations.

CHAPTER 4

Results and Discussion

The results of the analyses of water samples for toxic metals are shown in tables 4.1 and 4.2. Table 4.1 gives the results of samples that were extracted with MIBK, while table 4.2 shows the results of the metals extracted with chloroform.

Figures 4.1 to 4.6 are the calibration curves for metals extracted with MIBK, while figures 4.7 to 4.12 are the calibration curves for metals extracted with chloroform.

Cadmium standard $\lambda_{max} = 228.8 \text{ nm}$ $I = 14 \text{ mA}$

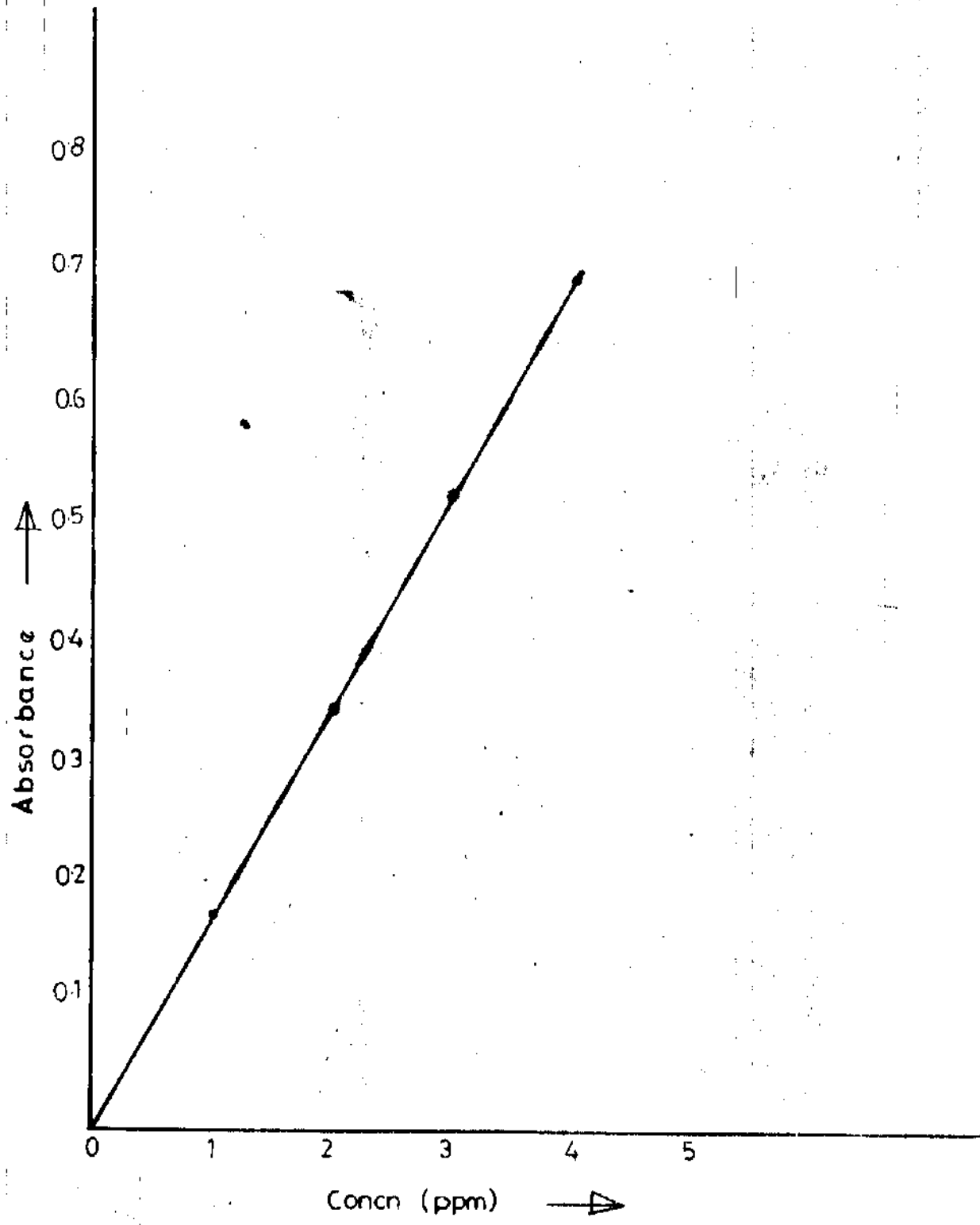


Fig 3.1

Cobalt standard $\lambda_{max} = 240.7nm$ $I = 25mA$

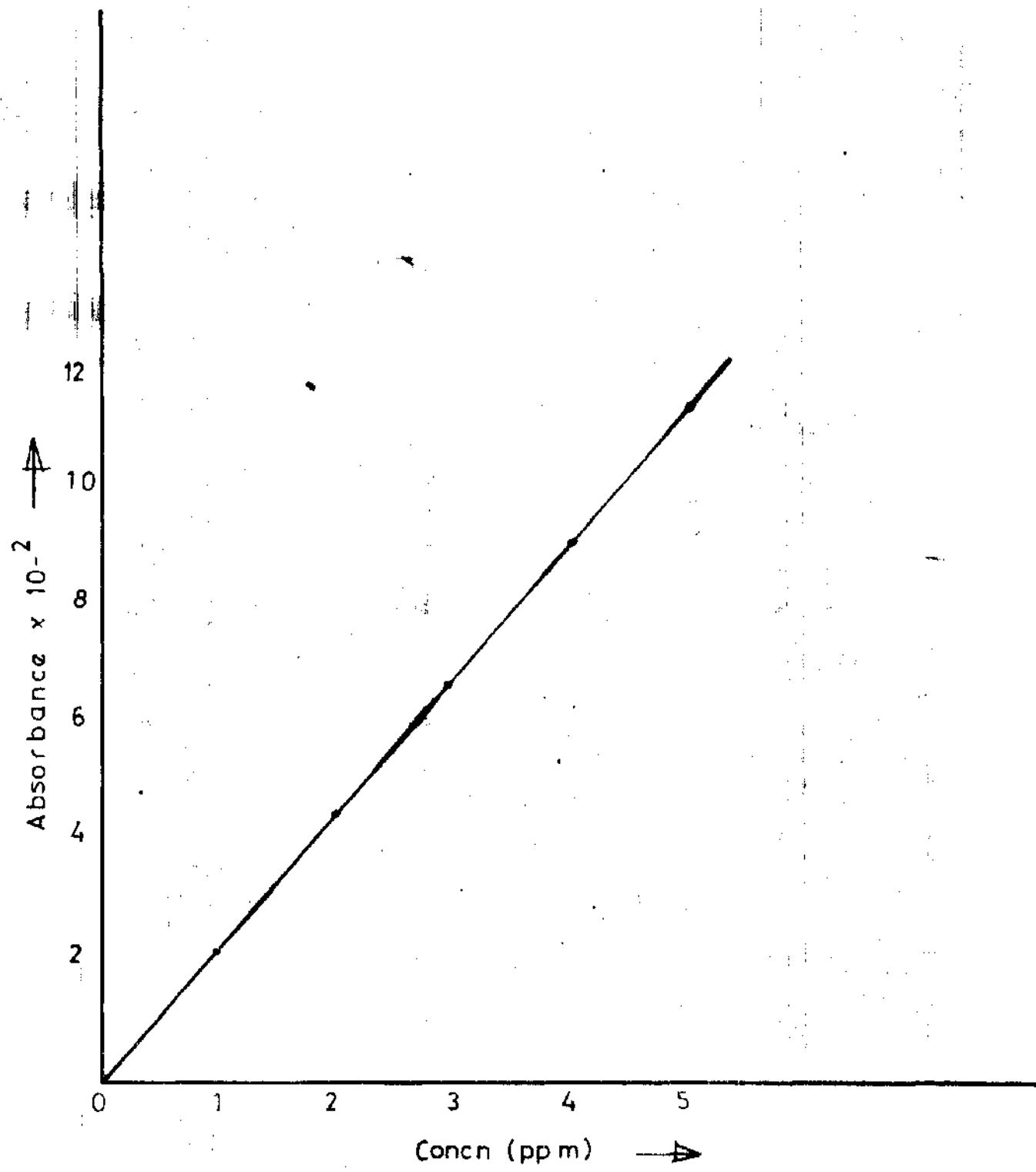


Fig 3-2

Copper standard $\lambda_{max} = 324.8 \text{ nm}$ $I = 5 \text{ mA}$

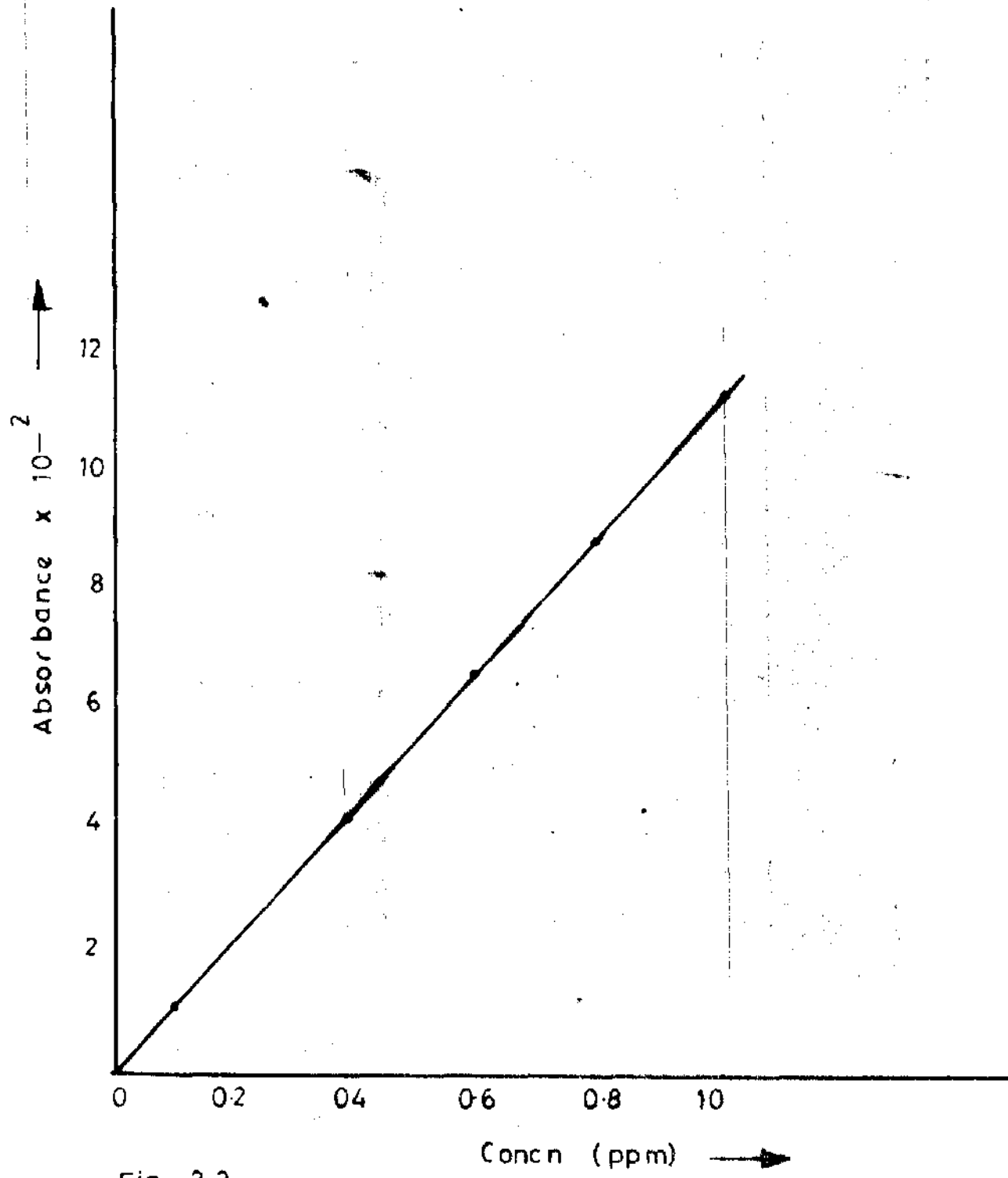


Fig 3-3

Lead standard $\lambda_{\text{max}} = 283.3 \text{ nm}$ $l = 5 \text{ mA}$

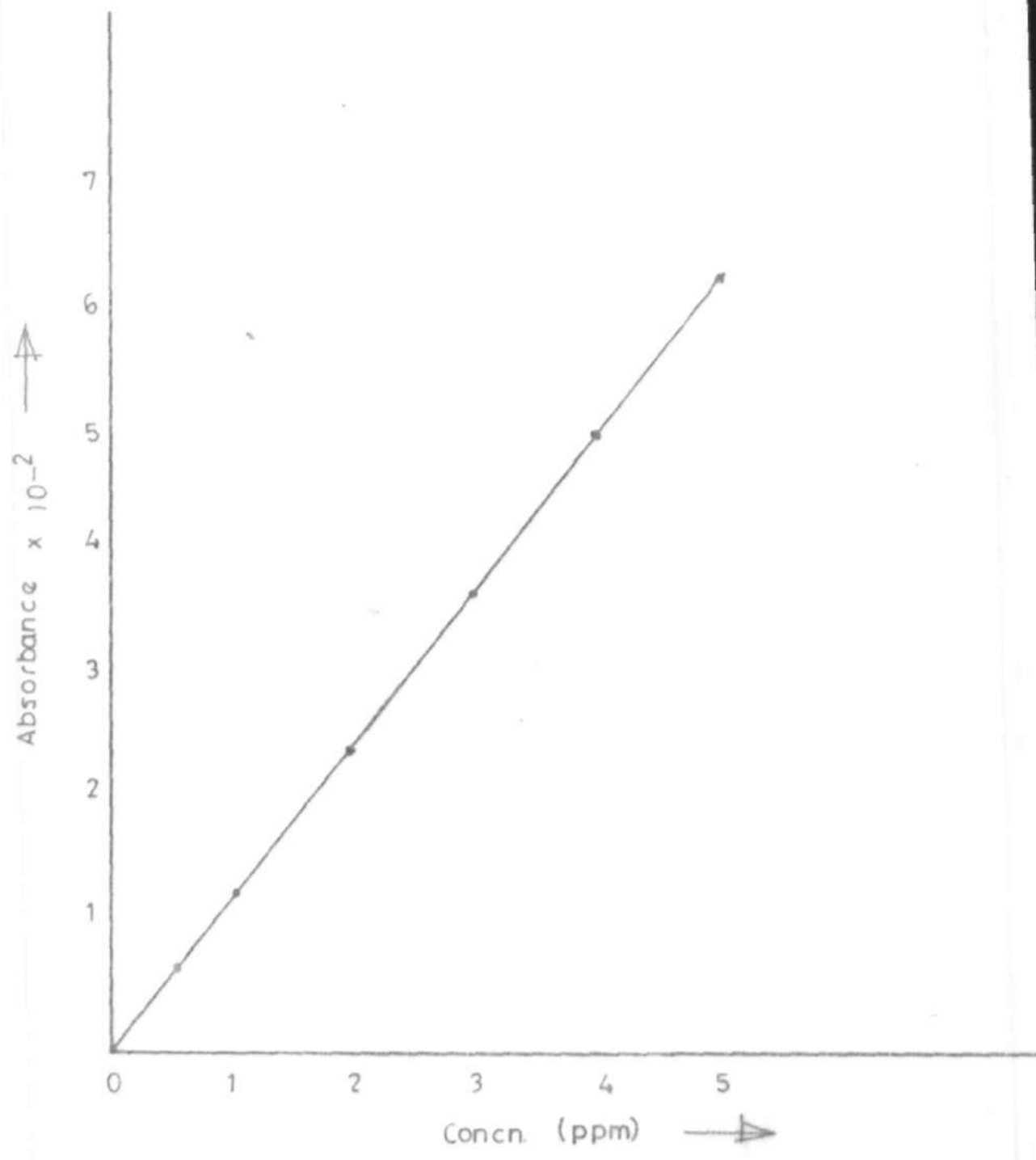


Fig. 34

Manganese standard $\lambda = 279.5 \text{ nm}$ $I = 11 \text{ mA}$

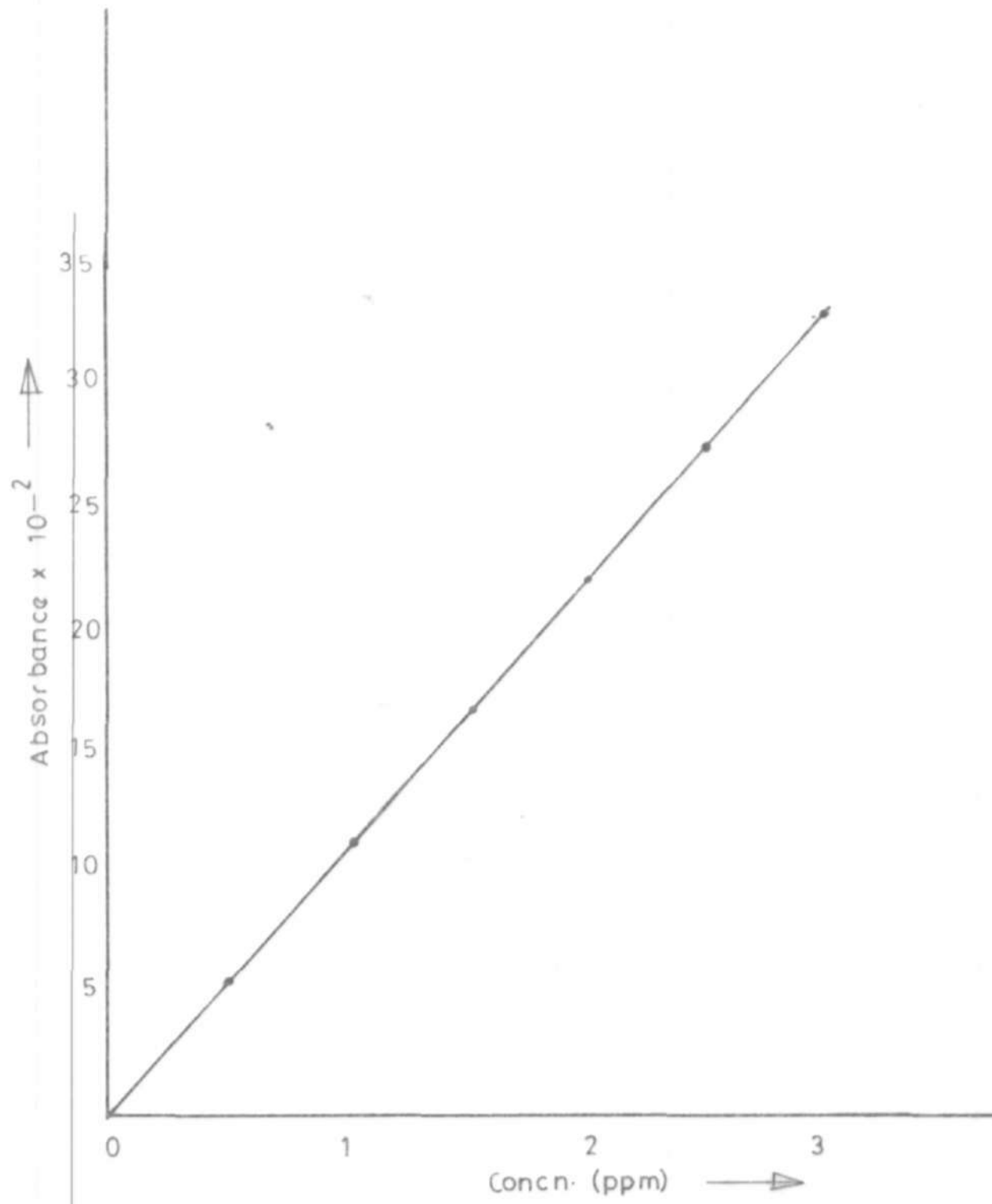


Fig 3-5

Zinc standard $\lambda_{max} = 213.9nm$ $I = 9mA$

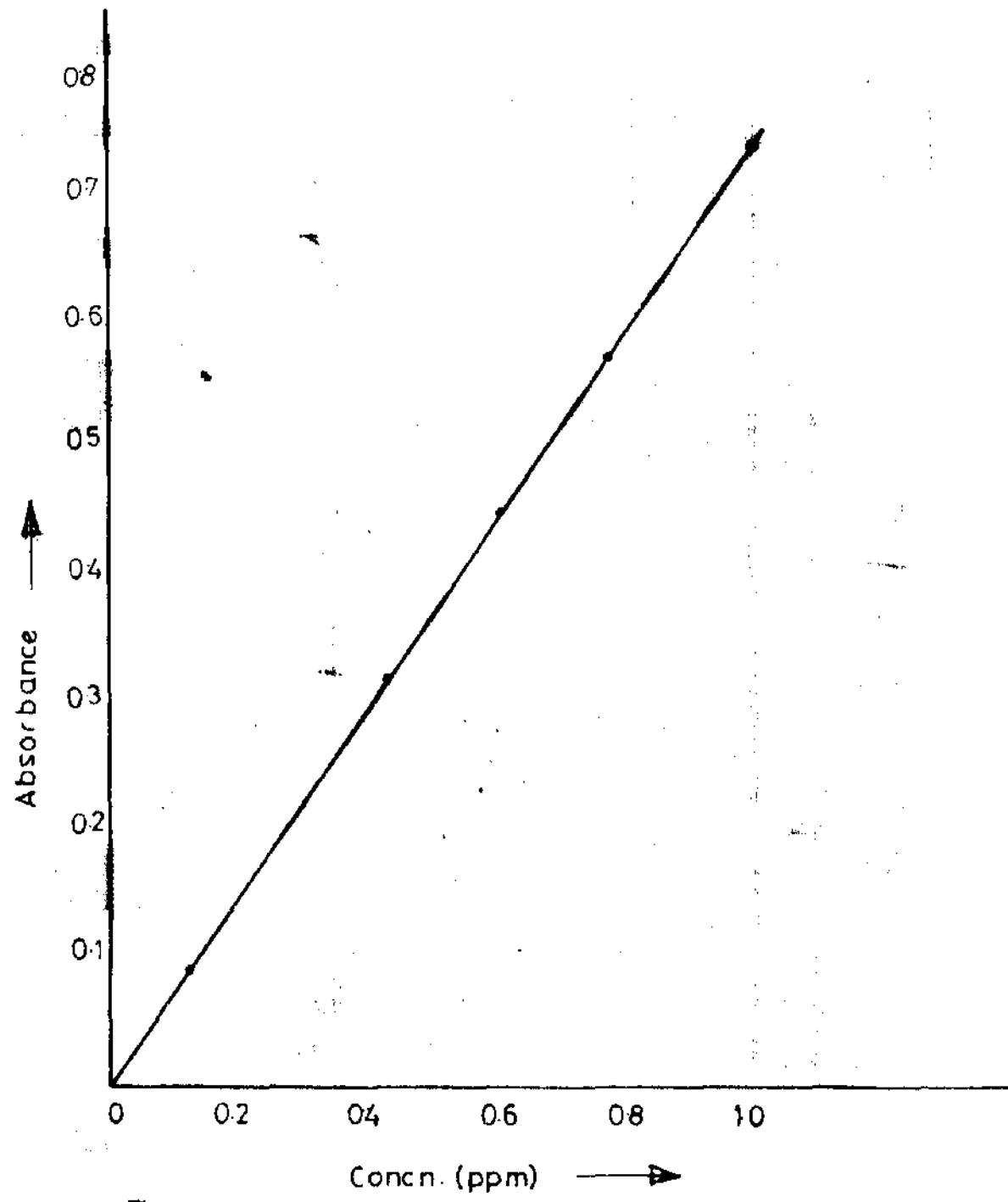


Fig 3-6

Copper standard extracted chloroform

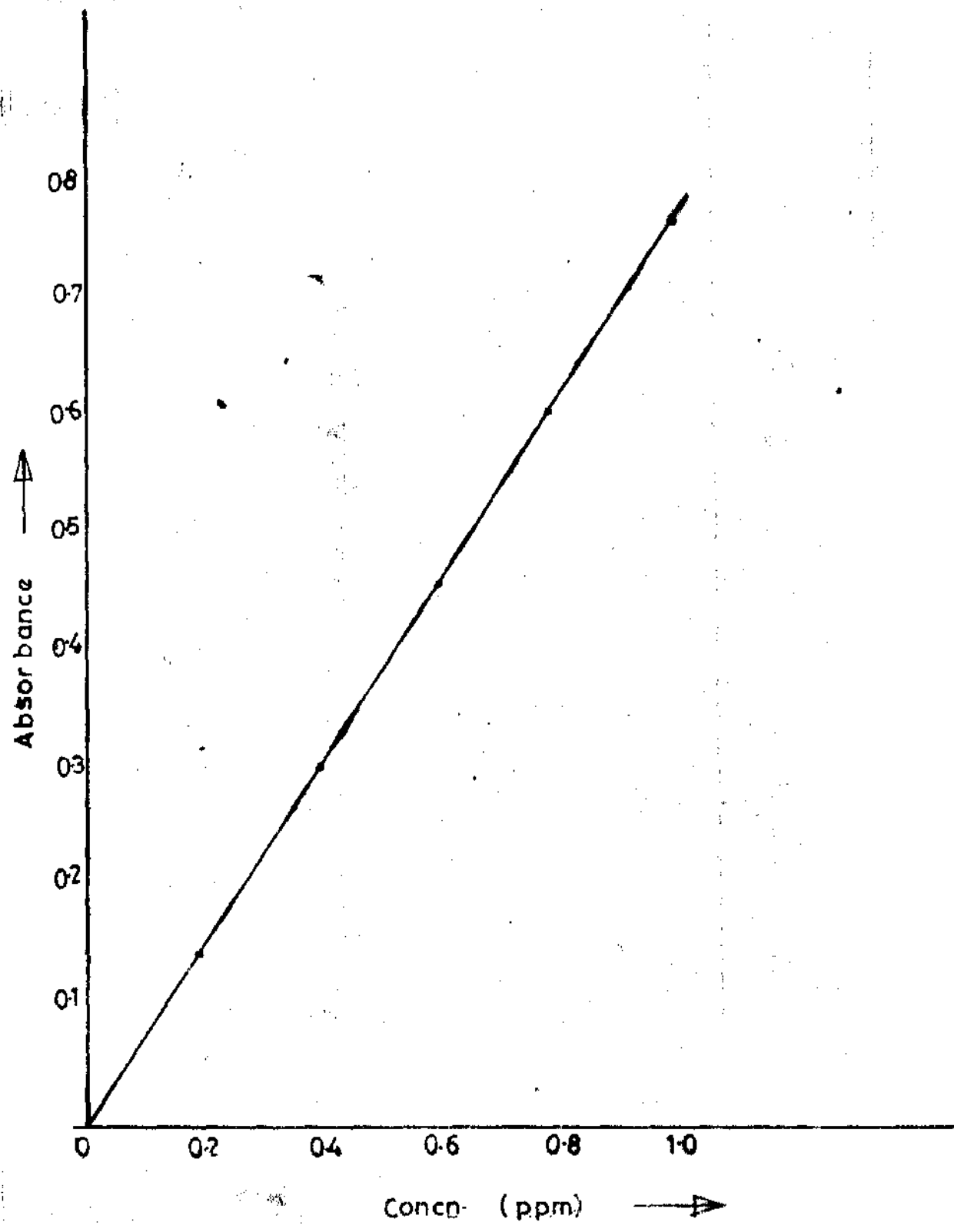


Fig. 3-7

Cadmium standard extracted with chloroform

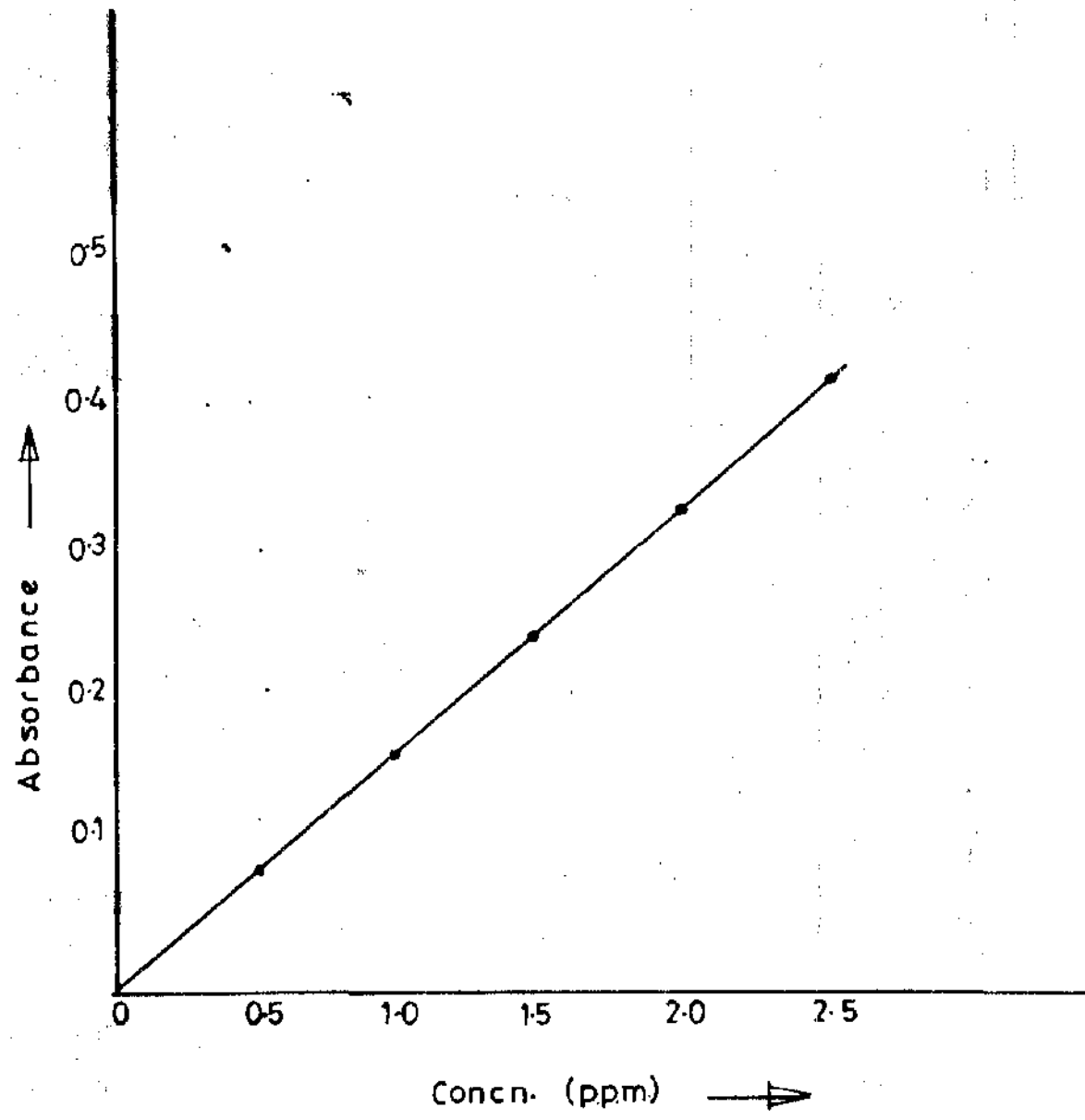


Fig. 38

Lead standard extracted with chloroform

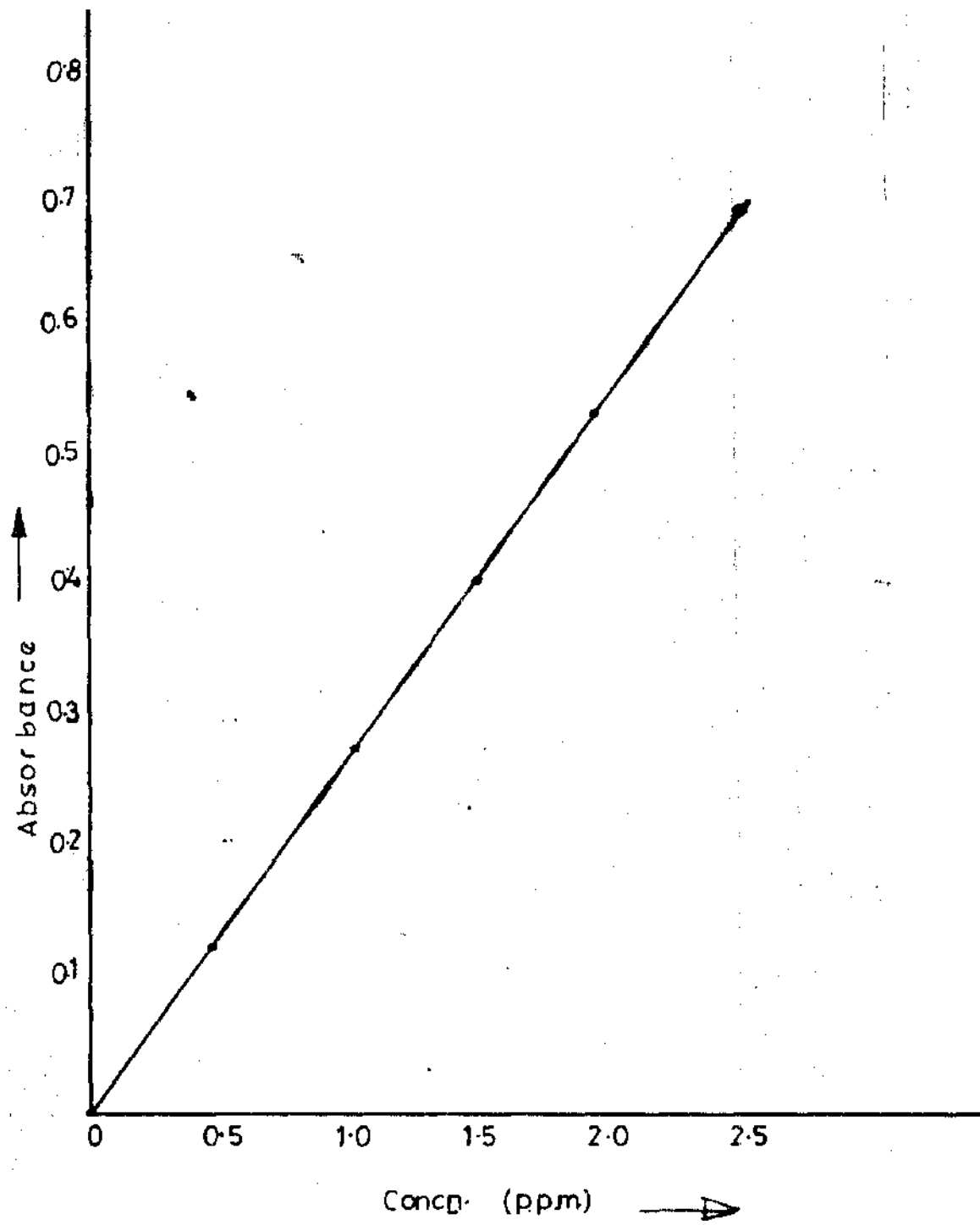


Fig. 3-9

Manganese standard extracted with chloroform.

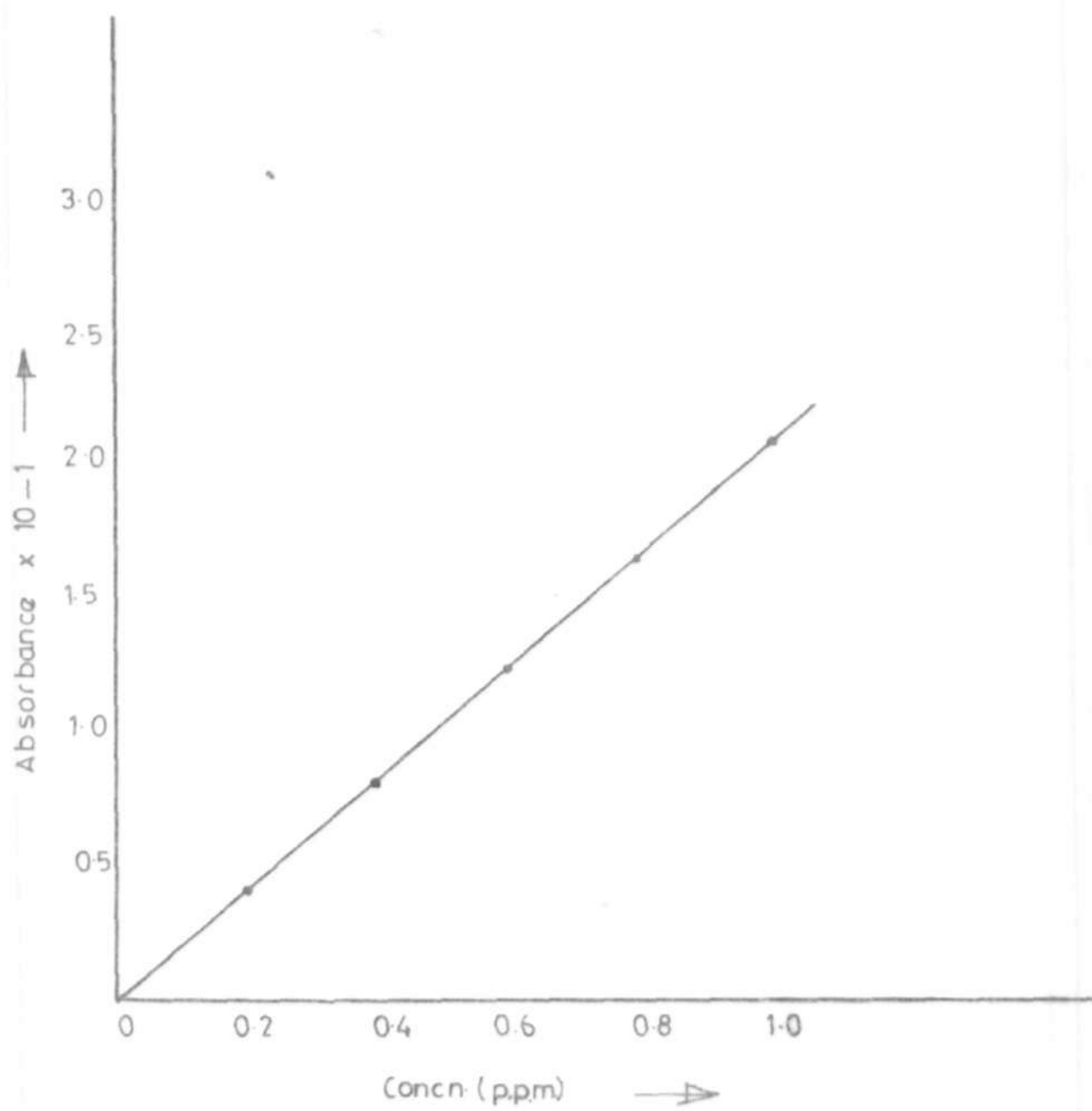


Fig. 3-10

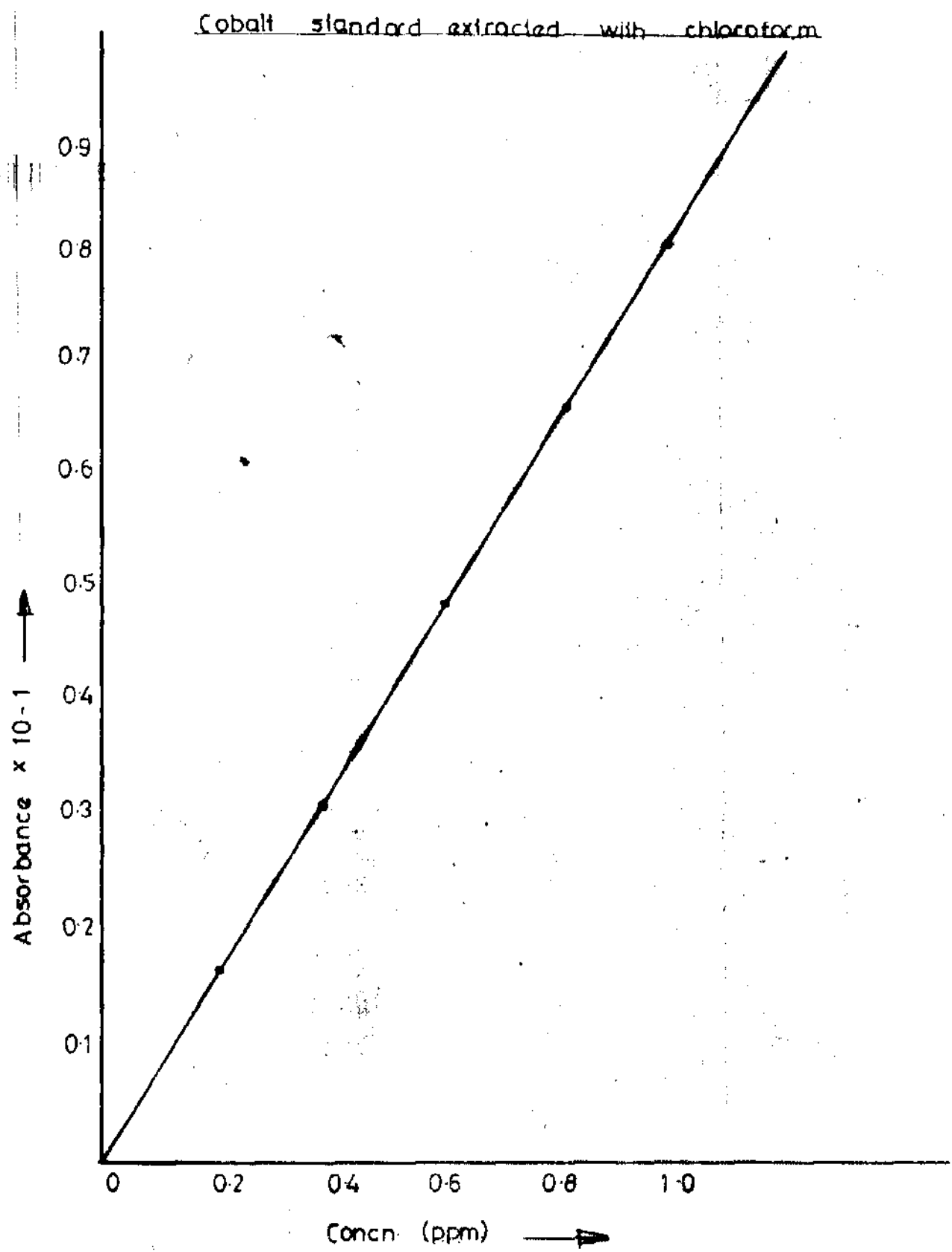


Fig. 311

Zinc standard extracted with chloroform

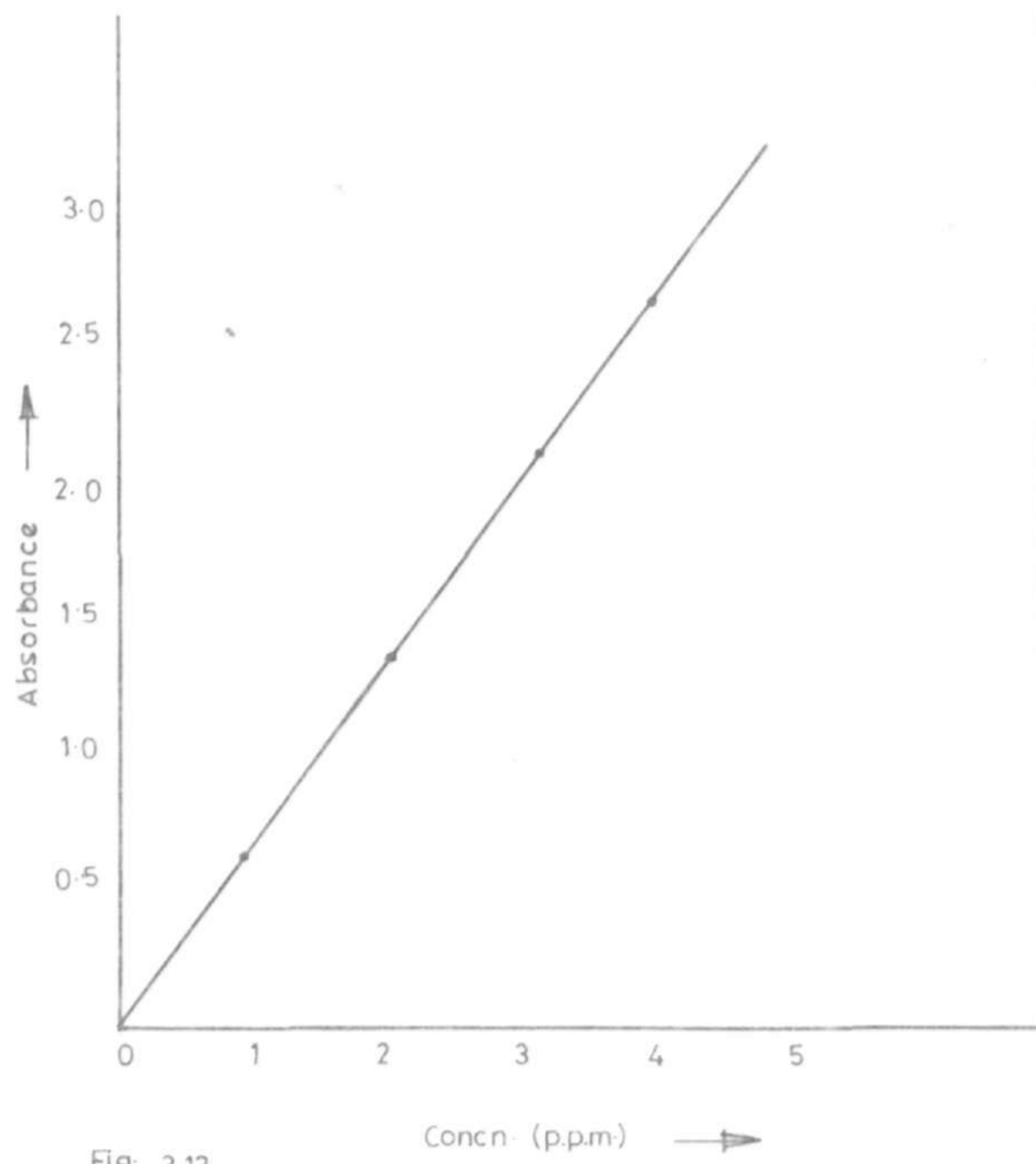


Fig. 3.12

The extractions of some metal pyrrolidindithiocarbamates from water into methyl iso-butyl ketone at pH 2.8.

Concentrations are in ppm

Table 4.1

Sample	Cd	Co	Cu
BW(MK)	0.07±0.001	-	0.017±0.01
WW(MK)	0.05±0.001	-	0.121±0.01
NBS(MK)	0.07±0.00	0.15±0.05	0.039±0.01
WKK(KM)	0.06±0.001	0.11±0.05	0.121±0.01
PW(KN)	0.06±0.00	0.19±0.05	0.054±0.01
SW(KN)	0.07±0.00	0.25±0.05	0.10±0.01
WWS(ZA)	0.06±0.001	0.19±0.05	0.025±0.01
VW(ZA)	0.05±0.00	0.13±0.05	0.04±0.03
DW(ABU)	0.05±0.00	0.11±0.05	0.014±0.01
SWB(J)	-	-	0.30±0.01
AW(LA)	0.10±0.001	0.25±0.00	0.09±0.01

Table 4.1 Cont...

Sample	Pb	Mn	Zn
BW(MK)	0.2 \pm 0.06	-	0.04 \pm 0.01
WW(MK)	0.25 \pm 0.15	-	0.06 \pm 0.001
NBS(MK)	0.94 \pm 0.01	0.04 \pm 0.00	0.42 \pm 0.08
WKK(KN)	0.06 \pm 0.00	-	0.395 \pm 0.07
PW(KN)	0.07 \pm 0.001	0.12 \pm 0.025	0.13 \pm 0.02
SW(KN)	0.37 \pm 0.06	0.07 \pm 0.03	0.772 \pm 0.01
WWS(ZA)	-	-	0.70 \pm 0.03
WW(ZA)	-	0.47 \pm 0.05	0.946 \pm 0.01
BW(ABU)	0.15 \pm 0.06	-	0.039 \pm 0.01
SWB(J)	-	0.87 \pm 0.025	0.061 \pm 0.001
AW(LA)	0.30 \pm 0.00	0.09 \pm 0.00	0.578 \pm 0.01

The extractions of the metal diethyldithiocarbamates
with Chloroform

Table 4.2

Samples	Cu	Co	Mn (mg/dm ³)
RCS	0.120±0.01	0.984±0.056	0.040±0.005
RKT	0.170±0.01	0.255±0.01	0.060±0.00
RKS	0.180±0.01	0.130±0.01	0.060±0.005
WTV ₁	0.480±0.01	0.770±0.01	0.037±0.005
WTV ₂	0.361±0.01	0.88±0.01	0.870±0.01
S.W.	0.520±0.01	0.61±0.01	0.487±0.05
KSK	0.150±0.01	0.965±0.01	0.030±0.005
GBJ	0.589±0.01	0.967±0.01	0.360±0.01

Table 4.2 Contd....

Samples	Pb	Cd	Zn (mg/dm ³)
RCS	-	-	0.950±0.05
RKT	-	0.59±0.01	1.29±0.05
RKS	-	-	0.450±0.05
WTV ₁	-	1.64±0.001	0.60±0.05
WTV ₂	0.075±0.01	-	1.80±0.29
S.W.	0.23±0.001	-	1.40±0.05
KSK	-	1.66±0.001	1.10±0.07
GBJ	0.09±0.001	-	0.36±0.01

The discussion of these results may be divided into three parts namely:-

- (a) Samples analysed by AAS
- (b) Samples analysed by UV and
- (c) a comparison of the two methods.

(a) Both the well water and the River Benue Water, from Makurdi, have no cobalt and manganese. But they contained the other metals in fairly comparable quantities. The water from the North Bank Spring (NBS (MK)) contained all the metals investigated. This perhaps is not unexpected as this water flows out from big rocks, and the underlying soil, from which these metals get into the water.

The samples from Kano contained all the metals, except WKK (KN) which did not contain manganese. In most cases their values are comparable to the values of samples from Makurdi. That means that stream and well waters from Kano town are similar to those from Makurdi. But the value for zinc from SW (KN) is rather high. The probable reason for that is that since this body of water is right in the heart of the town, there could be lots of industrial effluents in it. In fact, scraps of vehicles were seen submerged at several points in the water. These could contribute to the amount of metals analysed in this sample.

6 Both well waters from Samaru and Zaria town do not contain lead. Again the well water from Zaria town and the water from Ahmadu Bello University dam do not contain manganese. But all three samples contain all the other metals investigated, but their values are comparable to those from Makurdi and Kano town. This means that the quality of natural waters at Samaru and Zaria are not much different from those at Makurdi and Kano. Compared to the other water samples, the water from Ahmadu Bello University dam has the lowest amount of zinc. This is probably because this water is not near any town or industry and therefore it's less susceptible to contamination from these sources. The stream water from Bukuru, near Jos, contained no cadmium, cobalt, and lead, but has the highest amount of copper and manganese. The reason for this is not obvious. With the rocky terrain and the mining activity around this area, it was in fact expected that most of the metals investigated would be present. Since tin is mined in commercial quantity around this area, it will be quite instructive to determine its amount in water.

The water from the Atlantic Ocean has all the metals investigated. Apart from cadmium, the amount of other metals are lower than even the values for streams and wells. Again the reason is not apparent.

In all cases, except where metals are absent, the amount of these metals in water is higher than the maximum allowed for human consumption by W.H.O. (see p.5).

(b) In the UV spectrophotometric analyses, all the samples, except the well water from TV village, stream water, near F.T.C. Kaduna and Gada Biu stream Jos, all did not contain lead. Most samples did not also contain cadmium, except RKT, WTV₂ and KSK.

Unlike the samples analysed by the AAS method, where only about half the samples contain small amount of manganese, all the samples analysed by the UV method have large amounts of manganese. There can be two possible reasons for that.

Either there is too much manganese in the streams at or around Kaduna, possibly from industrial effluents, or the AAS method is not sensitive enough to detect the amount of manganese in those samples! A third possibility is that other metals, which were perhaps not completely separated from the manganese affected the results. Similarly all samples contain rather large amounts of cobalt and copper. Perhaps the two well waters (WTV₁ and WTV₂) from Kaduna deserve a special mention. Both well waters contain large amounts of almost all the metals investigated. This part of the town has no pipe borne water and most inhabitants of this village depend on wells for their drinking water.

This therefore poses a serious health hazard.

As in the AAS method, all the samples contain large quantities of zinc. In some cases, the amount of zinc doubles the amount of zinc in the samples analysed by AAS. One possible explanation is that zinc is present in rather large quantities in the water at Kaduna and its environs. The main source of such zinc may be from industrial discharges. But this is unlikely, as the sample, RKS, which was taken from river Kaduna at the Kaduna by-pass, has one of the lowest amount of zinc. This is inspite of the fact that most industries have discharged their effluents before this point or after this point.

It may be observed here that, at the Kaduna by-pass, the river water was dark-blue or black probably because of the dyes discharged into the river from the textile industries just ahead of the sampling point. It is possible that these dyes form complex compounds with zinc, thus accounting for the fact that this point has the lowest amount of zinc in the waters analysed. This view seem to be corroborated by the value for zinc in sample RKT which was well before the industrial effluents were discharged. Here the value for zinc is quite high.

As in AAS, the results show that all the water samples have too high amount of these toxic metals. They are therefore unfit for human consumption.

On the whole, the UV method gives higher values for all the metal investigated that the corresponding values by the AAS method. There are several explanations for this trend. It could mean that these toxic metals are more abundant at Kaduna and its environ than in those areas analysed by the AAS method. Another possibility is that the UV method is more sensitive than the AAS method and therefore gives higher values for the metals. Yet another possibility is that the separation of the metals, prior to their determinations, was not complete, and any metals co-extracted with the metal being investigated, could increase the absorbance, and therefore the amount, of the latter.

However, it should be borne in mind that since all samples were taken only once from the sampling points, the data represent judgement at the time of analysis. In a more systematic analysis, several samples should be taken from the same point over a given period.

Comparison

From the practical point of view, the AAS method is preferred to the UV spectrophotometric method. The AAS has several advantages over the UV method. Prior chemical separation of constituents is not required. AAS is free from spectral interference. The results are reproducible.

On the other hand, the colorimetric method involves separations of the species to be determined, with risk of errors through losses brought about by multiple operations. Because of the simplicity of sample preparation required, atomic absorption is much less liable to mechanical losses. When errors do occur, they are usually glaringly large and cause the analyst to check the instrument's operation and his standard and test solution - actions that can quickly be carried out.

Suggestions

To have a better or a more sound basis for comparison, sampling and analysis should be frequent and regular over a given period of time. This may necessitate reducing the number of sampling points. In addition, every sample should be analysed by both the AAS and the UV methods.

On the health side, the results of these analyses show that the amounts of these toxic metals in natural waters are much higher than the maximum allowed by the W.H.O. standards. And since the effects of some of them are cumulative, the health hazards these waters pose to the public becomes obvious. The only way out is for the authorities, at local, state or federal levels to make a more concerted effort at providing clean and potable water for the entire populace.

References

1. Standard Methods for the Examination of Water and Wastewater - APHA-AWWA-WPCF.
2. Reynolds, R.J. and Aldous, K. "Atomic Absorption Spectroscopy," Griffin, London 1970.
3. Winefordner, J.D. (ed), "Trace Analysis," John Wiley, 1976.
4. Gould, R.F. (ed), "Trace Inorganics in Water," Am. Chem. Soc., 1968.
5. Korkisch, J. "Pure & Appl. Chem. 50 371 (1978)"
6. Stary, J., "Solvent Extraction of Metal Chelates," Pergamon, 1964.
7. Wilson, A.L. "Chemical Analysis of Water," Soc. of Anal. Chem., 1974.
8. Irving, H. and William, R.J.P. "Liquid-Liquid Extraction" in "Treatise on Analytical Chemistry" Part I Vol.3 1st ed. Chap. 31 by I.M. Kolthoff, P.J. Elving and E.B. Sandell (ed).
9. Train, R.E. "Quality Criteria for Waters," Castle House Publication Ltd. 1979, p.62.
10. Train R.E. "Quality Criteria for Waters" Castle House Publication Ltd., 1979 various chapters of ref.9.

11. Korkisch, J., "Pure & App. Chem." 50 p.371 - 374 (1978).
12. Lacoste R.J., Laring, M.H. and Wiberley, S.E.
Anal. Chem. 23 871 (1971).
13. Fishman , M.J. & Midgett, M.R. "Extraction Techniques
for the Determination of Cobalt, ~~Nickel~~, and Lead
in Fresh Water by Atomic Absorption" in "Trace
Inorganics in Water" by Gould, R.F. (ed.), Am. Chem.
Soc., 1968 p.230.
14. Edward Boethner and Fred I. Grunder, "Water Analysis
by Atomic Absorption and Flame Emission Spectroscopy"
in "Trace Inorganics in Water" by Gould, R.F. (ed),
Am. Chem. Soc, 1968 p.236.
15. Slavin, W. "Atomic Absorption Spectroscopy,"
Interscience, 1968 p.67.
16. Reynolds, R.J. and Aldous, K. "Atomic Absorption
Spectroscopy," Griffin, London 1970 p.4
17. Perrin, D.D. "Organic Complexing Reagents,"
Interscience, 1964 p.176, p.205, p.206.
18. Stary, J. "Solvent Extraction of Metal Chelates,"
Pergamon, 1964 p.82.

19. Sandell, E.B. and Onishi, H. "Photometric Determination of Traces of Metal," Wiley-Interscience, 1978, p.910.
20. Korkisch, J. "Pure & Appl. Chem." 50 p.371.
21. Sandell, E.B. and Onishi, H. "Photometric Determination of Traces of Metal," Wiley-Interscience, 1978 p.2.
22. Sandell, E.B. and Onishi, H. "Photometric Determination of Traces of Metal," Wiley-Interscience, 1978 p.62.
23. Robertson, D.E. Anal. Chem. 40 1067 (1968).
24. Standard Methods for The Examination of Water and Wastewater -APHA-AWWA-WPCF.p.145.
25. Wilson, A.L. "Chemical Analysis of Water," Soc. of Anal. Chem., 1974, p.41.
26. Morrison, G.H. and Freiser, H. "Solvent Extraction in Analytical Chemistry," Wiley, N. York, 1957.
27. Basset, J. Denney, R.C. Jeffery, G.H. and Mendham, J. "Vogel's Textbook of Quantitative Inorganic Analysis," 4th ed., Longam, 1978 p.145.
28. Stary, J. "Solvent Extraction of Metal Chelates" Pergamon, 1964, p.21f.

29. Sandell, E.B. and Onishi, H. "Photometric Determination of Traces of Metals," Wiley-InterScience, 1978, p.517.
30. Sandell, E.B. and Onishi, E. "Photometric Determination of Traces of Metals," Wiley-InterScience, 1978 p.156.
31. Sandell, E.B. and Onishi, H. "Photometric Determination of Traces of Metals," Wiley-InterScience, 1978 p.523.
32. Sandell, E.B. and Onishi, H. "Photometric Determination of Traces of Metals," Wiley-InterScience, 1978 p.525.
33. Perrin, D.D. "Organic Complexing Reagents," InterScience, 1964 p.281.
34. Marczenko, Z. "Spectrophotometric Determination of Elements," Ellis Horwood, 1976 p.56.
35. Bassett, J. Denney, R.C., Jeffery, G.H. and Mendham, J. "Vogel's Textbook of Quantitative Inorganic Analysis," 4th ed., Longman, 1978 p.813.
36. Bassett, J. Denney, R.C., Jeffery, G.H. and Mendham, J. "Vogel's Textbook of Quantitative Inorganic Analysis," 4th ed., Longman, 1978 p.695.

37. Bassett, J. Denney, R.C., Jeffery, G.H. and Mendham, J. "Vogel's Textbook of Quantitative Inorganic Analysis," 4th ed., Longman, 1978 p:696.
38. Reynolds, R.J. and Aldous, K. "Atomic Absorption Spectroscopy," Griffin, London 1970 p:22.