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DETERMINATION OF TOTAL ARSENIC CONTENT OF SOME FOOD AND CASH CROPS, COOKED FOOD, VEGETATION FISH AND MEAT FROM KUMASI AND OBUASI

BY

EMMANUEL MELVIN KOFI AMEKOR

AUGUST, 1989

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CERTIFICATION BY SUPERVISOR

I CERTIFY THAT THIS WORK WAS DONE BY

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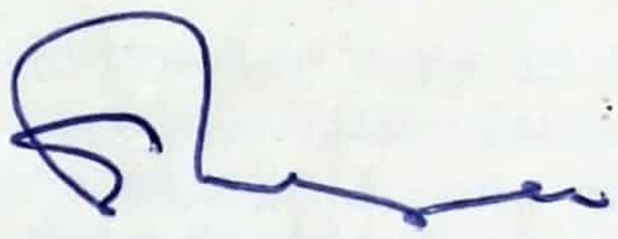

Prof E. H. AMONOO-NEIZER

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DEDICATION

This work is dedicated to my wife Theresa Amekor, my daughter Akpene Amekor, and all those engaged in working towards a better world environment.

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ABSTRACT

The total arsenic content of some food and cash crops from Kumasi and Obuasi farms and markets have been determined. Analyses were also conducted on vegetation, cooked food obtained from some homes, local fish, and meat as well as some soil and water samples. In all, 266 samples were examined . Sampling was random depending on which samples were available and obtainable at the different locations. Vegetation was as far as possible collected from sources of water utilized for domestic purposes.

KUMASI - food crops, 84 samples; cash crops, 8 samples; cooked food, 6 samples; vegetation, 6 samples; fish and meat, 2 samples.

OBUASI - food crops, 104 samples; cash crops, 11 samples; cooked food 9 samples; vegetation, 20 samples; fish and meat, 2 samples; soil, 7 samples; and water, 7 samples.

Two methods, Colorimetric and Atomic Absorption Spectrophotometric (A.A.S) techniques of analysis were employed for arsenic determination.

Arsenic concentration values for Kumasi ranged between 0.05 and 4.85 mg/kg with the colorimetric method while A.A.S gave a range of 0.07 to 7.20 mg/kg. In Obuasi ranges of 0.05 to 52.00 and 0.12 to 70.50 mg/kg were obtained for the colorimetric and A.A.S methods respectively.

The data showed that arsenic levels from Obuasi are much higher than those from Kumasi. Secondly the A.A.S method gave greater arsenic content than the colorimetric method for the same samples.

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CHAPTER 1

1. LITERATURE REVIEW

1.1 INTRODUCTION

Environmental science relates to the chemical, physical and biological changes on the environment through contamination or modification to the physical nature, biological behaviour of air, water, soil, food, and waste as they are affected by man's agricultural, industrial and social activities, and to the application of science and technology to the control and improvement of environmental quality.

The deterioration of environmental quality has existed as a serious problem under the ever-increasing impact of exponentially increasing population and of idustrialising society. Environmental contamination of air, water, soil, and food has become a threat to the continued existence of many plant and animal communities of the ecosystem and may ultimately threaten the very survival of the human race. It is obvious that civilization will continue to require increasing amounts of fuel, transportation, industrial chemicals, fertilizers, pesticides, and countless other products, and that it will continue to produce waste products of all descriptions. The dumping of these into the environment leads to pollution.

There are many forms of pollution and there are many pollutants. Classification varies according to whether they are air, water, or soil pollutants, depending on where they accumulate, and how they cause problems.

The Enviromental Pollution Panel of the President's Science Advisory Council (1) in the U.S.A defined pollution as " The unfavourable alteration of man's surroundings wholly or largely as a by-product of man's actions through direct or indirect effect of changes in energy patterns, radiation levels, chemical and physical constitution, and abundances of organisms. These changes may affect man directly or through his supplies of water and agricultural and other biological products, his physical possessions, or his opportunities of recreation and appreciation of nature". On a less limited scale, pollution can be defined as "the inability of plants to accommodate the conditions of the changed environment due to additional abnormal components of the environment in which plants have evolved and grown"(1).

Pollutants can be classified into two broad groups:

(i) Deliberate pollutants - these are chemicals such as agrochemicals released into the environment to achieve a specific purpose but which sometimes have secondary effects of undesirable nature e.g. fertilizers, pesticides etc.

(ii) Non-deliberate pollutants - these are unwanted by-products of industry released into the environment as a means of getting rid of them. It includes most gaseous air pollutants (CO, NO, NO_2, SO_2, CH_4 etc.) and particulate matter which are solids of very small particles (0.0002 to 500 pm diameter) consisting of carbon and oxides of many elements e.g. Fe_2O_3, Fe_3O_4, SiO_2, Al_2O_3, As_2O_3, K_2O, P_2O_5, Na_2O, CaO, MgO and TiO_2.

A number of chemicals that are sometimes referred to as pollutants may prove beneficial to or even essential for plant health when supplied in moderate amounts or useful industrially if collected. Such chemicals are not pollutants unless they reach toxic proportions as in the case of SO_2, NO_2, most agrochemicals, C_2H_4 (industrially beneficial if collected), and several heavy metals such as Fe, As, Cu and Zn. Therefore it is not the presence that is the critical consideration but such concepts as toxic levels, critical times of exposure, factors predisposing plants, animals, humans and structures to damage and interactions of various kinds of substances which influence plant, animal and human health, and structures indirectly.

There is therefore the need for continuous monitoring of all pollutants, deliberate and non-deliberate, in order to control their production, reduce their concentrations from reaching unwanted levels, and take measures to prevent their pollution of the environment.

In this study, an attempt has been made to monitor the total arsenic content of some food crops, cash crops and vegetation normally consumed by both human beings and animals in Kumasi and Obuasi.

In the extraction of gold from its ore, as is done at Obuasi gold mines, the roasting process results in the expulsion of arsenic and sulphur oxides into the atmosphere hence polluting the environment (air, soil and water). The arsenic oxide is known to possess toxic properties and it's ingestion beyond the human body's tolerable limit poses a health hazard to inhabitants. The monitoring of arsenic levels in these food crops, cash crops and vegetation will help to assess the extent of their arsenic contamination so that appropriate anti-pollution remedies may be recommended.

The data gathered in this study, it is hoped, will also serve as the basis for further research and lead to any other relevant information that will be useful scientifically, socially and economically to the nation.

1.2 NATURAL OCCURRENCE OF ARSENIC

1.2.1 ROCKS, SOILS AND SEDIMENTS

Arsenic is present in all soils in amounts varying from less than 10 ppm to 500 ppm (1).
Free or native arsenic occurs in small quantities usually in association with other metals and in crystalline rocks and schists. The arsenic content of the earth's crust is 1.5 to 20 mg/kg, it ranks 20th in abundance in relation to other elements (2). In combined state arsenic (As) is widely distributed, being present in certain mineral waters, coal, and in a variety of ores and minerals. The major arsenic containing minerals are arsenopyrites (FeAsS), realgar (As_2S_2), and orpiment (As_2S_3), and complexes with other metals; cobaltite (CoAsS), nickel glance (NiAsS) (3). Oxidized forms of arsenic e.g. arsenolite As_2O_3, are usually found in sedimentary deposits like limestone, shales and clay. The natural level of arsenic in sediments is usually contaminated by arsenic from man-made sources. Levels up to 10,000 mg/kg dry weight were found in bottom sediments near a copper smelter in Washington, U.S.A. (4).

1.2.2 AIR

Airborne particulate matter has been shown to contain both organic and inorganic arsenic compounds. In studies by Johnson and Braman (5) methylarsines made up approximately 20% of the total arsenic in ambient air from rural and urban areas. In unpolluted areas, airborne arsenic concentrations ranging from less than one to a few nanograms per cubic meter were reported.

Generally the concentration of airborne arsenic in a particular area depends to a large extent on the type of industry in the area, proximity of the area to an arsenic producing industry or the situation of the area relative to wind direction to such an industry, making possible the blowing of arsenic from the industry to the area.

1.2.3 WATER

Arsenic occurs in both inorganic and organic forms in water. The main organic arsenic species, methylarsonic acid $CH_3AsO(OH)$ and dimethylarsinic acid $(CH_3)_2\ AsO(OH)_2$ are generally present in smaller amounts than the inorganic arsenite and arsenate (salts of As(III) and As(V) (6).

The arsenic contents of surface waters (rivers, streams, lake, and well waters) in unpolluted areas vary but typical values seem to be a few micrograms per litre or less: river waters in U.S.A.- less than 0.01 mg/l (7); river water in Federal Republic of Germany - 0.003 mg/l (8); lake water in Federal Republic of Germany - 0.004 mg/l (8); Norwegian rivers - 0.0025 mg/l (9).

The oxidation state of arsenic in surface waters in various parts of the world remains largely unknown. Braman and Foreback (7) found that the ratio of inorganic As(III) to As(V) ranged from less than 0.06 to 6.7 in a few uncontaminated surface water samples containing between 0.0025 and 0.0030 mg/l of arsenic.

Analysis of two samples of well aerated stream water by Clement and Faust (11) (containing 0.014 and 0.06 mg/l respectively) showed that 8% of the total arsenic was in the trivalent state, whereas in anaerobic resevoir waters (containing 0.14 to 1.3 mg/l) all the arsenic present seemed to be in the trivalent state.

Penrose et.al. (12), reported that sea water ordinarily contains arsenic concentrations ranging from 0.001 to 0.008 mg/l.

The major chemical form of arsenic in sea water appears to be the thermodynamically stable As(V), even though As(III) often accounts for a third of the total arsenic (13).

1.2.4 PLANTS

The sorption of As^{5+} ions in the soil by iron and aluminium components greatly restricts the availability of arsenic to plants (14). The arsenic content of plants grown on soils that had never been treated with arsenic-containing pesticides varied from 0.01 to about 5.0 mg/kg dry weight (3). Plants grown on arsenic-contaminated soils may, however, contain considerably higher levels, especially in the roots (15). Some grasses growing on soils containing high levels of arsenic have been found to have elevated arsenic contents (16). Anderson and Nilsson (17) reported that arsenic in soils treated with sewage sludge was highly available to plants. Marine algae and seaweed usually contain considerable amounts of arsenic. Values of 10 - 100 mg/kg dry weight have been found by Lunde (18) in marine algae from the Norwegian coast.

1.2.5 FOOD CROPS AND CASH CROPS

There are two main sources of arsenic available to food and cash crops:

(i) Arsenic content of soil on which the crop grows, is obtained through the roots.
(ii) Airborne arsenic, is usually available to the crops through foliar uptake, which occurs through the pores in leaves (19). However, the amount of soil arsenic available to these crops is dependent on factors such as soil porosity, and presence of iron or aluminium in the soil.

High soil porosity facilitates arsenic leaching, this restricts availability of soil arsenic to surface growing and fibrous rooted plants while low soil porosity has the reverse effect. Adsorption of arsenic by iron and aluminium in the soil also restricts availability of arsenic to food and cash crops (14).

1.3 INDUSTRIAL PRODUCTION AND USES OF ARSENIC

1.3.1 PRODUCTION OF ARSENIC

Arsenic is not mined separately but recovered as a by-product when ores or concentrates of Cu, Pb, Zn, Sn and Au are smelted. Arsenic which does not melt at atmospheric pressure sublimes at $218^{o}C$, is liberated in the flue dust and separated by filters or electrostatic precipitators as an oxide, chiefly the trioxide, consisting of approximately 97% As_2O_3, its principal impurity being antimony(III) oxide, Sb_2O_3. Arsenic is obtained from the oxide by reduction with carbon and zirconium.

The main world producers (according to U.S. Bureau of Mines 1975) are China, France, Federal Republic of Germany, Mexico, Namibia, Peru, Sweden, U.S.A., and U.S.S.R. These countries together account for about 90% of the total world production.

1.3.2 USES OF ARSENIC

Arsenic is used widely in industry as follows:

INSECTICIDES AND WEED KILLERS: The largest quantity of arsenic is used in the form of chemical compounds. Calcium arsenate is used in the control of crabgrass and boll weevil which damage cotton crops, and lead arsenate is used to control fruit pest. Sodium arsenite finds use as weed killer, in control of undergrowth, as fungicide to control leaf-rot that attacks potato plants and as aquatic weed control to clear ponds and streams. It is also used to debark trees. Arsenic and dimethyl arsinic acids are widely used as dessicants which facilitate cotton harvesting and as sterillants for soils. The above uses of arsenic chemicals are now discouraged because of the toxicity of arsenic.

GLASS MAKING : White As_2O_3, in addition to being a basic chemical for the preparation of other arsenic salts, is used as a bronzing or decolourising agent in glass manufacture.

WOOD PRESERVATION : Sodium arsenate is an ingredient of Wolman salts used as wood preservatives.

METALLURGY: Because of its semi-metallic properties, arsenic is used in metallurgical applications as an additive metal to increase hardening and heat resistance e.g. additions of 0.5 to 2.0% of arsenic to lead assists in the manufacture of lead shot to improve its sphericity; while additions up to 3% arsenic to lead-base bearing alloys improves both mechanical and elevated temperature properties. In minor additions, arsenic improves the corrosion resistance and raises the recrystallisation temperature of copper. High purity arsenic is used in semi-conductor technology (for production of diodes, transistors and lasers).

MEDICINE : Arsenic is employed in the manufacture of arsenical organic compounds for therapeutic use e.g. Fowler's solution (1% or dilute neutral solution of As_2O_3) is used for the treatment of dermatoses and some forms of anaemia (2). Until recently, arsenicals were frequently used in the chemotherapy of syphilis and trypanosomiasis (20). Some phenylarsenic compounds such as p-aminophenylarsenic acid ($p\text{-}H_2NC_6H_4As(OH)_2$) commonly called arsanilic acid are used as feed additives for poultry and swine and to combat certain diseases in chicken.

OTHER USES: Arsenic sulphide is an ingredient in fire works. It is also used as the compound As_2S_3 in making infra red lenses. Indium arsenide is used for making infra red detectors.

CHAPTER 2

2. ENVIRONMENTAL POLLUTION BY ARSENIC

2.1 SOURCES OF ENVIRONMENTAL POLLUTION

The burning of coal, wood, and smelting of metals (especially copper) are the major sources of arsenic in air. These, together with the use of geothermal energy plants and the application of arsenic-containing agrochemicals serve as the main sources of arsenic in water and soil respectively.

2.1.1 BURNING OF COAL AND SMELTING OF METALS

In Prague, Vondracek found a winter mean concentration of 0.56 $\mu g/m^3$ of arsenic in air due to the burning of coal and a summer mean of 0.07 $\mu g/m^3$ (21). In 1974, about 200 of the 280 U.S. National Air Surveillance Network sites recorded quarterly average concentrations below 0.001 ug/m^3 (22). Only 13 sites, mainly highly urbanised areas and smelter locations showed levels exceeding 0.02 $\mu g/m^3$.

In the vicinity of smelters, levels of arsenic in air exceeding 1 $\mu g/m^3$ have been recorded (23), airborne arsenic concentration of 0.7 to 2.5 $\mu g/m^3$ given as As_2O_3 (i.e. 0.50 to 1.9 μg As/m^3 has been found within 4 km of copper smelter in the USSR. An annual mean arsenic concentration in ambient air ranging from 0.06 to 0.09 $\mu g/m^3$ were reported in the vicinity of a Canadian gold mine between 1975 due to roasting of gold ore (24). Creselius showed that in the stack dust from non-ferrous smelting operations, arsenic is predominantly in the trivalent inorganic form (5).

A thorough study made in the environs of a copper smelter near Tacoma (U.S.A.) showed that the arsenic build-up started with the operation of the smelter (5) and that less than 30% of the arsenic entering neighbouring waterways accumulated in the sediments. The remaining 70% presumably left the locations in solution. Elevated arsenic concentrations were found in water locations within 2-4 km of the smelter. Analysis of air, rain water, and snow all indicated elevated levels in the Tacoma area attributable to the smelter effluent. Levels of up to 380 mg/kg dry weight were found in top soil in the vicinity of the plant.

A similar pattern was observed in a study of the distribution of arsenic from a copper smelter in Sweden (25). The arsenic concentrations in air a few kilometers from the smelter were higher than normal, as were arsenic levels in the soil, moss and nearby natural water bodies.

2.1.2. BURNING OF ARSENIC TREATED WOOD

Burning of wood treated with arsenic-containing preservatives (mainly inorganic As(V) compounds) also results in the release of arsenic into the atmosphere. The concentration of arsenic released depends upon the temperature of burning, at 415^{o}C volatilisation of 8.6% of the total arsenic in treated wood occurred (26), at 700 to 800^{o}C about 50% of the arsenic was found in the ashes (the rest was mainly in the smoke) while at 1000^{o}C only 15% remained in the ashes (27).

2.1.3 GEOTHERMAL ENERGY PRODUCTION

The use of geothermal energy results in severe arsenic contamination. Crecelius and others in 1976 (28) found that the natural arsenic level of 0.002 mg/l had increased 1000 times in a water resevoir in which some discharge from a Mexican geothermal plant was emitted. Between 6 and 51% of the total arsenic in the reservior was present as As(III) and the rest as As(V). The emission of arsenic into the environment from the plant totalled about 60 kg/day.

2.1.4 USE OF AGROCHEMICALS

Arsenic is also present in trace amounts in fertilizers, pesticides, herbicides, silvicides, and feed additives hence their application in cultural, forestry and animal husbandry activities lead to pollution of soil, air, water and crops.

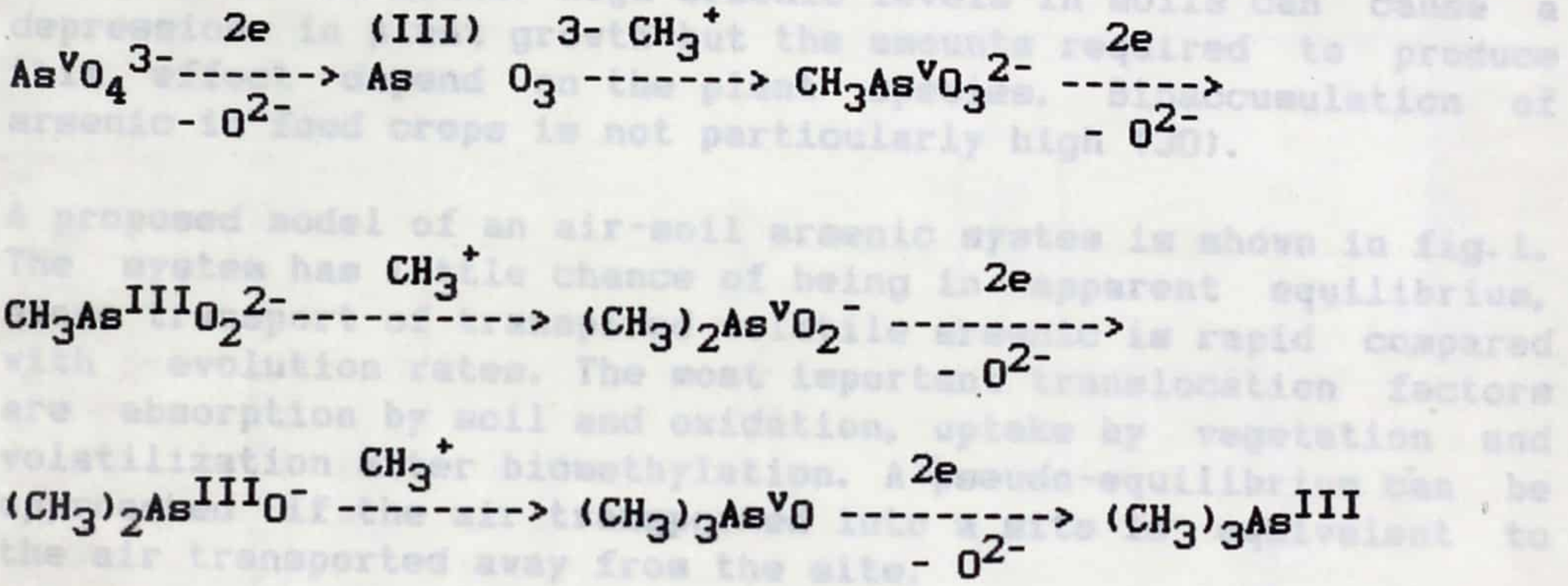
2.2 ENVIRONMENTAL TRANSPORT AND DISTRIBUTION OF ARSENIC

2.2.1 GENERAL

Most environmental transformations of arsenic appear to occur in the soil, sediments, plants and animals, and in zones of biological activity in the oceans.

Biomethylation and bioreduction are probably the most important environmental transformations of the element, since they produce organometallic species that are sufficiently stable to be mobile in air and water. However, the biomethylated forms of arsenic produced are subject to oxidation by bacterial demethylation back to inorganic forms.

The following mechanism for the methylation of arsenate has been proposed by McBride et al. (29).



The proposed mechanism indicates that As^{5+} has to be reduced to As^{3+} before being methylated.

2.2.2 AQUATIC SYSTEMS

Studies on the molecular forms of arsenic compound in sea water have been reported. In all these, variable As(III)/As(V) ratios have been reported, and these appear to be associated with phytoplankton and other biological activities.

In some instances, the As(III) concentrations exceeded those of As(V) (6). The same type of biological activity was observed in natural fresh waters (6). It is evident that the presence of As(III) compounds is the result of some reductive activity, which could be either a biological or a non-biological effect of dissolved organic matter on As(V). The presence of methylarsenate acids in sea water and fresh natural waters is evidence that arsenic goes through reactions other than simple oxidation and reduction.

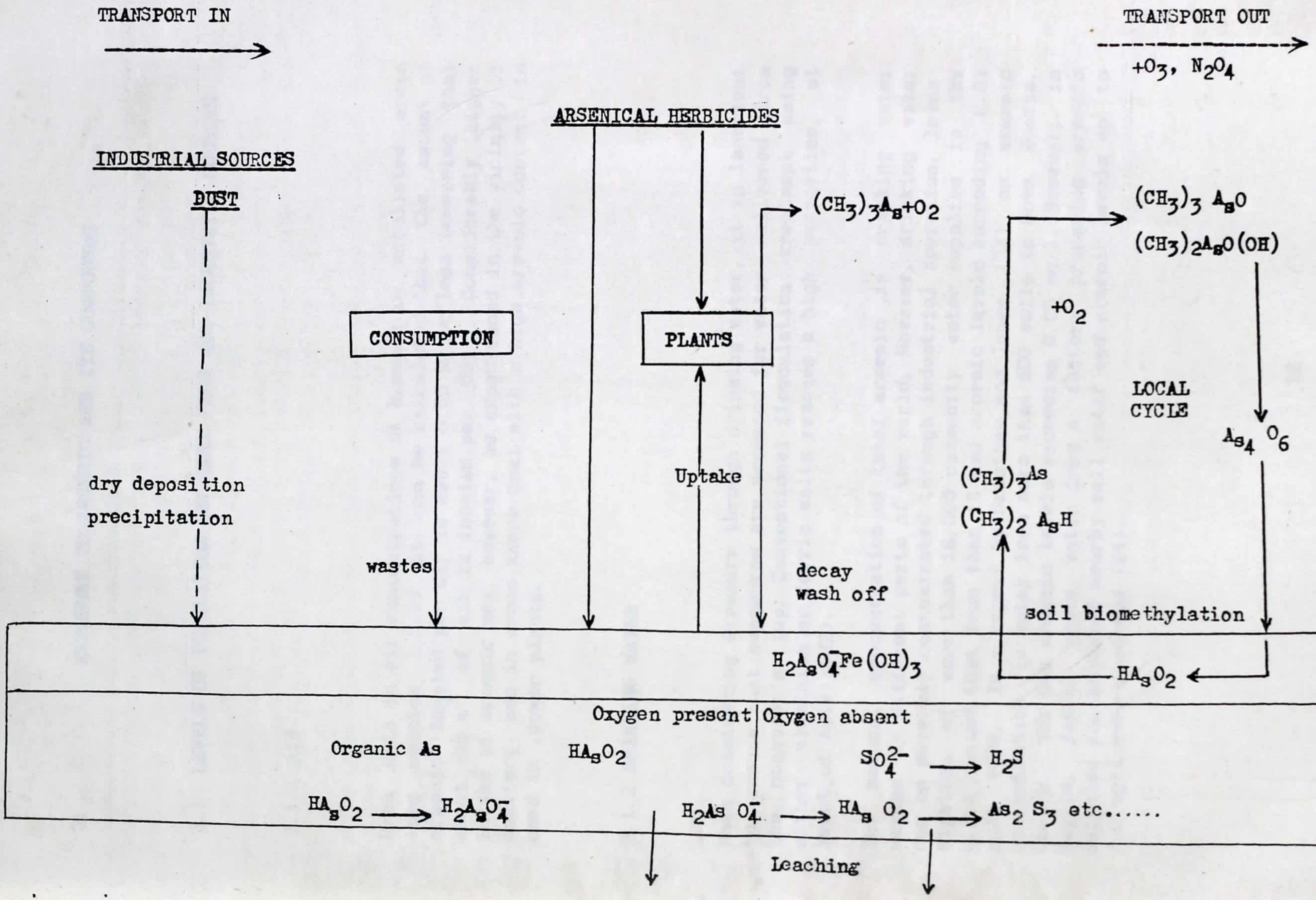
2.2.3 AIR-SOIL SYSTEMS

Large quantities of arsenic compounds used in agriculture are initially distributed in the soil, an important aspect of arsenic distribution in the environment (see sections 1.2.3 and 2.1.4).

In the soil arsenic is converted to arsenates except under highly reducing conditions. The arsenate ions (i.e. As^{5+}) are readily sorbed by hydrous oxides of iron and thus leaching of arsenic is slow. Absorption appears to be the major factor in the retention of arsenic in soils. High arsenic levels in soils can cause a depression in plant growth but the amounts required to produce this effect depend on the plant species. Bioaccumulation of arsenic in food crops is not particularly high (30).

A proposed model of an air-soil arsenic system is shown in fig.1. The system has little chance of being in apparent equilibrium, since transport of transpired volatile arsenic is rapid compared with evolution rates. The most important translocation factors are absorption by soil and oxidation, uptake by vegetation and volatilization after biomethylation. A pseudo-equilibrium can be approached if the air transported into a site is equivalent to the air transported away from the site.

Fig.1 - Local Soil-Air Cycle for Arsenic



CHAPTER 3

3. EXPOSURE TO ARSENIC AND ITS COMPOUNDS

3.1 LEVELS OF POPULATION EXPOSURE FROM NON-INDUSTRIAL SOURCES

3.1.1 AIR

From data on air concentrations of arsenic in unpolluted areas (see section 1.2.2) it can be calculated that the amount of arsenic inhaled per day is about 0.05 µg or less (assuming that about 20 m^3 of air is inhaled per day). Considerably higher intake of arsenic may, however, be experienced in the vicinity of smelters and in areas where coal with a high arsenic content is used in power plants.

3.1.2 DRINKING WATER

When considering exposure through drinking water, it is important to ensure that exposures are assessed for water delivered from the consumer's tap. Conventional flocculation treatment using either aluminium or ferric salts removes a high porportion, at least of As(V) (32).

The natural concentration of total arsenic in drinking water varies in different parts of the world. However, drinking water can be severely contaminated through industrial operation. Investigation of more than 18,000 community water supplies in the U.S.A showed that less than 1% had arsenic levels exceeding 0.01 mg/l (33). In a report by Grantham and Jones (34) on arsenic concentration in water from more than 800 wells in Nova Scotia, Canada, 13% had arsenic levels exceeding 0.05 mg/l. However, in Nigita, Japan, waste water from a factory producing arsenic sulphide contaminated nearby well water and arsenic levels up to 3.0 mg/l were recorded (34).

3.1.3 FOOD AND BEVERAGES

Arsenic levels in food, with the exception of some seafoods are generally well below 1 mg/kg wet weight. Certain bottom feeding fish, crustacea and shellfish may contain arsenic concentrations of several tens of milligrams per kg (6,36). Arsenic concentration of between 0.6 and 58 mg/kg dry weight have been found in some sea food supplements prepared from kelp (37). The use of some organic arsenic compounds as feed additives for poultry and swine may lead to accumulation of arsenic in certain organs hence limits of tolerance have been established in the U.S.A for edible by-products from chickens, turkeys, and swine (38).

Wine may contain appreciable amounts of arsenic. Most of the arsenic present in some U.S table wines was in As(III) form because considerable reduction from As(V) to As(III) occured during the fermentation of grape juice by wine yeast. Elevated arsenic levels (range 0.001 to 0.19 mg/l were reported in bottled mineral waters sold in E.E.C countries (39), however an investigation on lager beers from various countries showed that none of the samples contained more than 0.02 mg/l of As (40).

3.1.4 TOBACCO

The content of arsenic in tobacco grown on soils not treated with arsenic compounds is usually below 3.0 mg/kg (41) (the weight of a cigarette is approximately 1 g). Because of great reduction in the use of inorganic arsenic compounds in agriculture, former high levels (52 mg/kg as As_2O_3 in 1950's) in American cigarettes have decreased to 8 mg/kg over the last 20 years (42).The chemical form of arsenic in the smoke has yet to be elucidated.

3.1.5 DRUGS

Both inorganic and organic arsenic compounds have been used widely in medicine (sec. 1.3.2), and this serves as an avenue of the general population exposure to arsenic. Medical use is being discouraged because of arsenic toxicity.

3.1.6 TOTAL DAILY INTAKE OF ARSENIC IN THE GENERAL POPULATION

Daily intake of arsenic from ambient air will ordinarily be of the order of a few micrograms (about 0.05 µg or less), predominantly in the inorganic form (sec 3.1.1). Since the natural concentration of total arsenic in drinking water varies in different parts of the world, intake via water also vary accordingly.

The total daily dietary intake of arsenic depends to a great extent on the kind of foodstuff which forms the staple food of the individual, and on the amount of seafood in the diet (a seafood meal may lead to the ingestion of several milligrams of arsenic, predominantly in the organic forms). The U.S. Food and Drug Administration monitoring arsenic in foodstuffs showed from the data in the programme that, total daily intake of arsenic was 0.01 to 0.02 mg/day in 1972-74 (38). Most of the arsenic was found in the group "meat, fish and poultry". Values of between 0.07 and 0.17 mg/day have been reported for Japan (43), 0.025 to 0.035 mg/day for Canada (1972-1975) (44), and 0.01 mg/day for the United Kingdom (45).

Daily intake of arsenic through smoking of tobacco also varies according to the individual. However, the average smoker (1 packet a day) has been estimated to take in less than 0.02 mg arsenic per day (46), while through medicinal means, arsenic intake is minimal.

3.2 OCCUPATIONAL EXPOSURE THROUGH INDUSTRIAL MEANS

Occupational exposure to arsenic compounds takes place mainly among workers, especially those involved in the processing of gold, copper, and lead ores. Occupational exposure also occurs among workers using or producing arsenic-containing pesticides. Very little data exists on the actual air levels of arsenic to which persons in such occupations have been exposed. This is also the case for wood treatment plant workers and carpenters, who may become exposed to inorganic arsenic compounds (mainly As(V) through their use as wood preservatives (these react with wood to form insoluble compounds resistant to fungal attack).

Airborne arsenic particulate matter in smelters is generally assumed to consist primarily of arsenic (III) oxide which is released into the atmosphere. In the roasting of arsenopyrite (FeAsS) for example, arsenic is oxidised, sublimes, and combines to form the oxide As_2O_3.

$$2FeAsS + 5O_2 \text{ -------> } Fe_2O_3 + As_2O_3 + 2SO_2$$

The arsenic oxide together with sulphur dioxide gas and other fine particles are released in the resultant smoke and are breathed in by the workers. The form in which arsenic is present clearly depends to a great extent, on the characteristics of the industrial process involved, such as temperature, humidity and other elements present.

3.3 RECOMMENDED/MAXIMUM PERMISSIBLE ARSENIC LEVELS

The human body normally contains 0.3ppm (.3mg/l) arsenic and concentrations of 0.8 to 2.4 ppm are considered toxic (47). Because of rapidly accumulating epidemiological evidence that arsenic is a human carcinogen, most countries are dramatically lowering allowable or permissible concentrations of arsenic in the work environment. The U.S.A. has changed its recommendation for permissible worker "exposure to arsenic" without protective measures including medical evaluations from 0.1 mg As/m^3 in 1973 to .005 mg As/m^3 in 1978 (48).

The U.S.S.R and Czechoslovakia have 24 hour maximal atmospheric concentration recommendation of 0.003 mg/m^3 (48). The World Health Organisation (WHO) set the maximum allowable arsenic concentration in drinking water at 0.05 mg/l, and 1.0 mg/l for irrigation waters, river/dam water (for the protection of aquatic life), and live stock industry work (49).

CHAPTER 4

4. METABOLISM AND TOXICITY OF ARSENIC AND ITS COMPOUNDS

4.1 METABOLISM OF ARSENIC

Owing to its wide distribution in nature, arsenic is constantly taken into the human body in very small quantities and is therefore regarded by most authorities as a normal constituent of the body, the normal value being 0.3 ppm with concentrations 0.8 to 2.4 ppm considered toxic (2). Both trivalent and pentavalent inorganic arsenic compounds in solution are readily absorbed after ingestion. The metabolism of arsenic in man is very complex since the fate of arsenic compounds in the human body varies with the type of compound. The metabolism of inorganic arsenic depends on its chemical form.

About 4/5 of the arsenic absorbed is stored and widely distributed in the tissue (2) including the liver, abdominal viscera, bone, and particularly the hair and nail where it may be detected many months later after it has disappeared from the urine and the feaces. Hair and nails have higher values due to their richness in disulphides which has higher binding capacity for arsenic. The normal arsenic content of hair has been used as indicator of suspected poisoning on several occasions, values in excess of 2 ppm indicates possibility of poisoning.

Arsenic is excreted from the body slowly, some appearing in the urine and to a smaller extent in the feaces within 24 hours but a large proportion of absorbed arsenic is stored in tissues and eliminated at varying time intervals. Since the major excretion route for arsenic is the urinary tract (48), measurement of urinary arsenic concentration is the method most often chosen for biololgical monitoring. Normal urinary values reported by most laboratories lie within the range 0.01 - 0.15 ppm (47). Depending on the amount of arsenic in foodstuffs urinary arsenic concentrations can vary from 0.01 to 1.0 ppm, levels being highest after consumption of sea food.

4.2 TOXICITY OF ARSENIC

In industry acute poisoning from solid arsenic is rare, subacute and chronic poisoning usually arise from exposure to arsenic-containing dust and fume. In man, acute poisoning leads to abdominal pain and vomitting usually within an hour of ingestion due to inflamation of mucous membrane of the stomach and upper gastrointestinal tract. Symptons of chronic poisoning include loss of weight, gastrointestinal disturbances in the form of loss of appetite, nausea and diarrhoea alternating with constipation, pigmentation and erruptions of the skin, falling out of the hair and peripheral neuritis (2).

A wide variation of toxicity has been reported in various animal species. Sheep, goat and horses (as a group) are 20, 100 and 200 times more resistant than pigs, dogs and poultry respectively (2). Cattle are the most resistant while rats are the least. Both particle size and amount of impurity influence the toxic dose in animals. Gastrointestinal damage evidenced by severe convulsions, retching and haemorrhage of the stomach and intestines are observed when animals ingest arsenic (as As_2O_3 in acute toxicity. In chronic toxicity there is profound effect on fat metabolism, infiltration of liver, kidneys, spleen, bronchial and intestinal mucosa (2).

The effect of arsenic on plants is usually dose related but variables such as type of arsenic compound, plant species, geographic location, soil type, and climate can strongly modify the response. For example, most vegetables do not develop significant arsenic content when grown on soils having high concentration of applied As_2O_3 but it is the opposite when lead arsenate is applied to the soil (48). Usually, fibrous-rooted plants taking arsenic from the top soil tend to develop high arsenic content in contrast to the tap-rooted which get access to only the leached arsenic in the rainy season. The effect of arsenic contamination in plants ranges from withering to death. In many cases damage to plants is due to the deposition of As_2O_3 on the vegetation from smelting plants.

CHAPTER 5

5. REVIEW OF ANALYTICAL METHODS FOR THE TOTAL ARSENIC DETERMINATION

5.1 SAMPLING AND SAMPLE TREATMENT

The American Society for Testing of Material (A.S.T.M) outlines three types of sampling methods for arsenic, particularly in water as follows (50):

(i) Grab sampling - represents the conditions existing only at the point and time of sampling.
(ii) Composite sampling - sampling at a specific site, portions of which are collected at varied time intervals. Alternatively the composite may consist of portions collected at various sites or a combination of both site and time interval.
(iii) Continual sampling - sampling on a continuous basis (with a fixed equipment) from wells, rivers, lakes, streams, oceans, reservoirs, pipelines etc.

Arsenic poses some special problems in sampling not experienced in the determination of other trace elements. Water, urine and biologically active samples should either be analysed within a few hours or frozen and stored (51). This is because low concentrations of arsenic compounds found in natural waters for example decrease with time, unless stabilised in some manner to prevent adsorbtive losses. Moreover the biomethylation of inorganic arsenic in a biologically active sample can cause a change in its composition.

Since environmental analysis often involve trace concentrations, sample treatment frequently includes some type of preconcentration prior to analysis. Typical examples of pre-concentration methods are: conversion of arsenic to arsine, co-precipitation with iron (III) hydroxide, distillation as arsenic (III) chloride and extraction.

Sea and fresh natural waters are generally analysed without oxidative treatment prior to a preconcentration step, when the molecular forms of arsenic are to be analysed. However, if the preconcentration step or the final steps in the analytical method require the conversion of organo-arsenic compound to an inorganic form, oxidative procedures (such as acid-persulphate or acid-permangante oxidation) may be necessary. Arsine generation followed by cold trapping in liquid nitrogen, volatilisation as trichloride or tribromide as well as coprecipitation with hydroxide are techniques commonly used in preconcentrating arsenic in sea and natural fresh waters before analysis. Air

sampling for trace amounts of arsenic in the environment has mainly been confined to sampling the particulate phase. Many different types of particulate filters are used for this type of sampling, though arsenic is usually associated with small size particles. The saturated concentration of As_2O_3 in air at 25^oC is about $600mg/m^3$ hence when air concentrations fall below this level, As_2O_3 collected on a filter may evaporate or may be incompletely collected. Nevertheless, using a filter impregnated with ethylenediamine in glycerol (which is 65% efficient in trapping As_2O_3 vapour), it was shown that the major portions of arsenic in air (78-99%) could be collected on untreated 0.4 um pore size polycarbonate type filters (52).

Vapour forms of arsenic in air, particularly the arsines can be preconcentrated from air onto silver-coated glass beads (6). Even if oxidized after adsorption the identity of the compound is not lost, adsorbed compounds can be desorbed using dilute NaOH.

The pretreatment of biological samples is very essential to the successful determination of their trace arsenic contents. Hence recommended methods have been set out for the preparation of analytical samples for AAS (53):

PLANTS - All foreign matter such as adhering soil and dust should be removed by rinsing with distilled water. However prolonged rinsing should be avoided to minimise the leaching of soluble mineral constituents. Drying should then be carried out at room temperature or in an oven at $35-40^oC$ until the sample is sufficiently dry to be ground; so that the ground sample can pass an 0.5 mm mesh sieve and stored in an air-tight container.

MEAT - A representative sample free of bone should be rendered uniform by passing it at least twice through a food chopper with plate openings not larger than 4mm, mixing thoroughly after each grinding.

FISH - A representative sample of the fish with or without head, skin and bones is cut and ground several times using a meat chopper with 1.5-3.0mm holes, each time removing unground material and mixing the ground material.

FRUIT - Fresh fruit samples should be pulped using a food chopper or suitable mixer or by grinding in a large mortar and mixing thoroughly.

Samples of biological materials to be analysed for total arsenic are generally digested i.e. completely oxidised (mineralised) prior to analysis. A number of digestion methods have been studied, the majority of which involves the use of oxidising acids or persulphate and is called wet decomposition. The completeness of the oxidation has however seldom been checked. Because of the strong CH_3-As bond found in methylated arsenic compounds, complete mineralisation is difficult to achieve. Dry

decompostion which involves ashing the sample with MgO or $Mg(NO_3)_2$ (which forms magnesium arsenate thus preventing volatility of arsenic) is successful for the determination of most common metals in a variety of biological samples. The approach of analysis without oxidation is applied whenever molecular forms of arsenic present in a sample are to be identified. No available system has been found that will digest tissue without changing the original valence state i.e As(III) to As(V), therefore only total arsenic can be measured with accuracy in biological systems.

The efficiency and dependability of three methods of digestion have been compared by measuring their recovery rate of added arsenic (54). Arsenic in form of sodium arsenate and dimethyl arsenic acid (DMAA) were thoroughly mixed with commercially obtained special diet for rats. 1g of each mixture was digested with HNO_3, $Mg(NO_3)_2$ and by total digestion method which consists of oxidation with conc HNO_3 followed by ashing in an oven. The following results were obtained:

Method of Digestion	Arsenic Recovery	
	Na-arsenate	DMAA
HNO_3 Digestion	100.4 %	67.5 %
$MgNO_3$ Digestion	100.8 %	73.7 %
Total Digestion	101.2 %	98.7 %

From the result it can be observed that while recovery of arsenic in the inorganic form is comparable for all three methods, for the recovery of methylated arsenic the total digestion method is superior to the other two methods.

The best wet digestion method involves the use of a mixture of H_2SO_4, HNO_3 and $HClO_4$ (55). Perchloric acid is used to speed up the digestion and hence reduce the volume of nitric acid used and shorten the time taken to complete the destruction of all organic matter. There is considerable risk that in the absence of sulphuric acid the digest may boil dry, thus increasing hazards due to possible explosion.

5.2 REVIEW OF ANALYTICAL METHODS USED FOR ARSENIC DETERMINATION

5.2.1 GUTZEIT METHOD

This was one of the very early common methods employed for the determination of total arsenic. Very small quantities (0.01 to 0.1mg) of arsenic may be determined by volatilising the element as arsine (AsH_3). In the Gutzeit generator, hydrogen generated by the reaction between Zn and HCl converts all As(III) in the solution to arsine.

$$Zn + 2HCl \text{ ------> } ZnCl_2 + H_2$$

$$H_3AsO_3 + 3H_2 \text{ ------> } AsH_3 + 3H_2O$$

The arsine is brought into contact with a filter paper impregnated with $HgCl_2$ or $HgBr_2$. A stain or coloration which may vary from pale yellow to dark brown is produced on the paper. The intensity of this coloration, in comparison with those produced by known amounts of arsenic are then used as an approximate quantitative measure of arsenic concentration in the sample. The method has the disadvantage of too much dependence on the rate of evolution of arsine, which is not necessarily the same as that of hydrogen, and it is doubtful whether the accuracy exceeds 10% of the true value.

5.2.2 MOLYBDENUM BLUE METHOD

The method is suitable for the analysis of most types of organic materials, and it is specific for arsenic in all ordinary circumstances.

The sample is treated with acids to convert the arsenic compound to either arsenate(III) acid (H_3AsO_3) or arsenate(V) acid (H_3AsO_4).

$$2M_3AsO_3 + 3H_2SO_4 \text{ ------> } 3M_2SO_4 + 2H_3AsO_3$$

$$2M_3AsO_4 + 3H_2SO_4 \text{ ------> } 3M_2SO_4 + 2H_3AsO_4$$

The solution is digested, and organic matter is destroyed, leaving the arsenic in solution. The digestate is treated with $SnCl_2$ solution and HCl to reduce all As(V) to As(III):

$$2M_3AsO_4 + SnCl_2 + 2HCl \text{ ------> } H_3AsO_3 + SnCl_4 + H_2O$$

Zn metal is added to the resultant solution to generate the arsine gas (distillation) as shown in section 5.2.1. The arsine is absorbed in an I_2 - KI solution where As^{3+} is oxidised to As^{5+} by triiodide ion ($I_2 + I^- \longrightarrow I_3^-$). Hence the decolorisation of of the iodine solution.

$$AsO_3^{3-} + I_3^- + H_2O \Longleftrightarrow AsO_4^{3-} + 3I^- + 2H^+$$

since the reaction is reversible, $NaHCO_3$ is added to the I_2-KI solution to act as a buffer and remove the H^+ ions formed so that the reaction goes to completion. When the solution is treated with ammonium molybdate solution, the arsenic as arsenate, As^{5+} combines to give an arseno-molybdenum complex.

$$AsO_4^{3-} + 12MoO_4^{2-} + 3NH_4^+ + 24H^+ \longrightarrow (NH_4)_3AsMo_{12}O_{40} + 12H_2O$$

The complex actually contains the trimolybdate ion $Mo_3O_{10}^{2-}$ in which molybdenum is in the oxidation state of +6. Hence its composition should be written as $(NH_4)_3As(Mo_3O_{10})_4$. Some of the Mo(VI) in the complex is reduced by the hydrazine (from the added hydrazine sulphate $N_2H_4.H_2SO_4$) to Mo(V). Charge transfer between Mo(VI) and Mo(V) results in the blue colour, the intensity of which is dependent on the concentration of arsenic in the complex. The absorbance of the blue complex which has maximum absorption at 840nm and shows no appreciable change in 24h, is spectrophotometrically determined and hence the concentration of the arsenic in the sample calculated by the interpolation on a calibration curve prepared using standard arsenic solutions of known concentrations.

The molybdenum blue method has the chemical problem of the conversion of all the arsenic in the sample into the coloured complex. With very small amounts of arsenic the conversion may not be rapid or stoichiometric. Interference from other substances present in the sample e.g. phosphate which also forms blue coloured complex with molybdenum has to be taken into consideration.

BLANK DETERMINATION A blank solution is prepared by taking the same volume of the oxidising acid, but without sample through the process of digestion, distillation and reduction with $SnCl_2$ solution at the same time with the sample solution. It is treated with ammonium molybdate and hydrazine sulphate solutions as in the actual procedure, and its absorbance is determined on the spectrophoto- meter. This absorbance value is used as a correction factor for the readings obtained for the sample solutions i.e it is subtracted from the absorbances given by the sample solutions.

5.2.3 SILVER DIETHYLDITHIOCARBAMATE (SDDC) METHOD

In this method, arsenic in the sample is distilled as arsine and this is made to react with a solution of SDDC,

$$\left(AgS\text{-}C\text{-}N\text{-}C_2H_5 \right)$$
$$\quad\ S\ C_2H_5$$

in pyridine to form a soluble red complex with maximum absorption at 540nm. The absorbance of the complex is spectrophotometrically determined and referred to a calibration curve to obtain the concentration of the arsenic in the sample. A blank determination is performed as described earlier.

As a colorimetric method, it is also has the problem of not rapidly or stiochiometrically converting all the arsenic in the sample into the coloured state. Heating is at times used to reduce the time required for development of maximum colour. Interference from antimony which also forms stibine SbH_3 a red coloured compound with maximum absorption at 510 nm has to be taken into consideration.

5.2.4 ATOMIC ABSORPTION SPECTROPHOTOMETRIC (A.A.S) METHOD

Chemical analysis by AAS technique involves converting the sample, at least partially, into an atomic vapour and measuring the absorption of this vapour at a selected wavelength which is characteristic for each individual element (193.7nm for As).

The measured absorbance is proportional to the concentration of the element, and analyses are made by comparing this absorbance with that given by reference samples of known composition under the same experimental conditions.

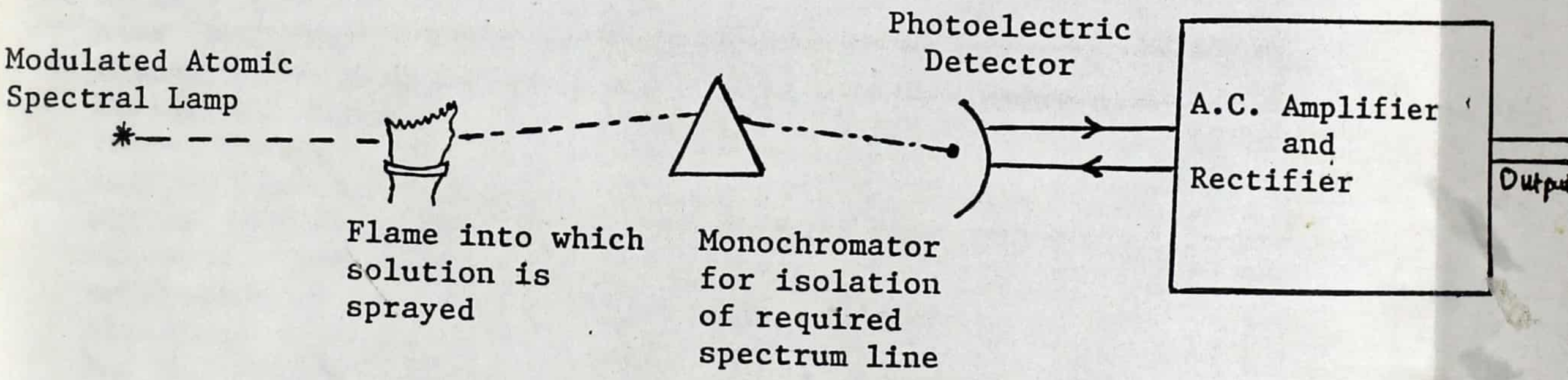


Fig 2: Schematic diagram of the mode of operation of an Atomic Absorption Spectrophotometer

Samples to be analysed by AAS are usually made into solution and sprayed into the flame as such or after appropriate dilution (when reference samples record lower absorbance) with water. For most accurate results, it is desirable that the metal to be determined should produce absorption between 20% amd 80% (i.e. an absorbance between 0.10 and 0.70). However latest trends of research are directed towards the analysis of solid samples (56). Electrothermal Atomic Absorption Spectrometry (EAAS) with use of solid sampling technique is one of the most attractive methods for determining trace elements in a solid biological sample. There can be advantages in introduction of the sample into the furnace as a powder rather than in the form of a solution. It eliminates many steps for sample pretreatment such as dissolution and dilution or enrichment which increases the risks of contamination and loss of analyte. Although many works have been carried out to analyse various solid samples directly with EAAS one of the most serious problems to be solved is to prepare a standard for calibration. The authors (57) employed the use of a metal powder and an aqueous solution as standards for preanalysis of alloys, while Atsuya, I. et. al. (58) also investigated the suitability of the direct calibration procedure using simple reference solutions for the determination of trace elements in biological samples. Analytical results for Cu, Cr and Mn gave lower results than the certified values. The method of standard addition has been employed for the analyses of biological samples (58). However it is often difficult to verify that a substance for standard addition behaves in the same way as an analyte in an unknown sample. Many standard reference materials (SRM) are available now from the U.S.A and several other countries. They are prepared from various naturally occuring materials, however for concentrations less than several mg/g there is a scarcity of SRMs that could be applied for the calibration. Trace element standards must have small sampling error (in the mg and sub mg region) and thus must be homogenous at these levels. Synthetic reference materials (SyRM) such as phenolformaldehyde resin, silica, gelatin ion exchange beads and copolymerisate of acrylamide have been reported (59), but there are few SyRM for multi-element analysis of biological materials by EAAS with the solid sampling technique. Akatsuka & Atsuya (55) have proposed a powder SyRM prepared by coprecipitation with magnesium(II)-8-quinolinate for solid sampling EAAS analysis of biological samples. The procedure is the preconcentration of trace elements in natural waters involving the quantitative introduction of 8 elements in the same SyRM. The powder SyRM is stable and suitable for use at sub-mg and mg weights for the 8 elements. Additionally this SyRM is highly accurate for the determination of trace elements in different kinds of solid biolgical samples. The limits of detection for Al, Cd, Co, Cu, Mn, Ni, Pb and Zn in solids were found to be 0.087, 0.008, 0.012, 0.05, 0.003, 0.043, 0.14 and 0.013 µg/g respectively.

5.2.4.1 INTERFERENCES IN A.A.S.

A.A.S analysis suffers the disavantage of interferences of various kinds, viz spectral, flame emission, chemical, matrix, scatter and ionisaton interferences. The majority of difficulties arise from the last four mentioned interferences.

SPECTRAL AND FLAME EMISSION INTERFERENCES

These are instrument related interferences, and with the continuous improvement on the make, model and function of instruments, these interferences have virtually been eliminated. Flame emission interference, for example, which is caused by emission of the elements at the same wavelength at which absorption occurs is corrected by increasing source current or by closing down the slit, implying an increase in signal-to-nose ratio (SNR). There is no simple way to greatly reduce analyte flame emission noise short of replacing the hollow cathode lamp with an electrodeless discharge lamp, which will increase interferences. O'Haver **et. al.**(60) revealed that the radiance of a prefocussed Xe arc contniuum lamp source, measured over the spectral width of a corresponding hollow cathode lamp, was significantly greater than every cathode lamp tested. The ratio (continuum/line source) varied from 2.5 for As at 193.696 nm to 107 for Ca at 422.673 nm. Therefore a continuum-source based Flame Atomic Absorption Spectrometry (FAAS) system such as the the wavelength-modulated spectrometer with a Cermax Xe arc continuum source system should possess a SNR advantage over conventional line source atomic absorption (AAL) instrumentation for FAAS measurements of high concentrations of emissive elements in high temperature atomizers. This hypothesis was demonstrated and verified for Ca in a study by Messman and O'Haver (61). Calcium was selecteld as test analyte because of (i) its low excitation potential, (ii) high FAAS sensitivity, and (iii) presence as a major constituent in many sample types. The measurement precision obtained using wavelength - modulated (echelle spectrometer with a Cermax Xe arc) continuum source (WM-ACC) was found to be superior to that obtained with an instrument using a hollow cathode lamp line source when the Ca concentration exeeds 5 mg/l.

CHEMICAL INTERFERENCE

Usually caused by any substances that prevents or suppresses the formation of ground state atoms in the flame. It can be corrected by application of the following techniques: (i) A compound is added which leads to the release of the element of interest by formation of a preferential complex e.g. ethylenediamine tetraacetic acid, EDTA is used to complex cations such as Co Fe Ni Zn

etc preventing their association with anion, or lanthanum chloride solution is added to a calcium solution containing phosphate to enable release of Ca due to the preferential formation of lanthanum phosphate. In a study by Boampong **et. al** (62) Fe(II) has been used as a releasing agent in As and Se determinations. It behaves as an oxidising agent and the reduction of Fe(III) to Fe(II) is kinetically favoured over the reduction of Ni(II) to Ni(O). Thus the formation of As hydride is essentially complete before the strongly interfering, low oxidation state Ni has had an opportunity to form and interact with the arsine. L-cysteine was chosen as a reagent that might have an effect on the interference from transition metals. It is cheap and readily available, and gives a low blank for As and has much lower toxicity than, for example thiourea. (ii) Virtually all chemical interference may be overcome by using the high-temperature nitrous oxide - acetylene flame.

MATRIX INTERFERENCE

Includes enhancement of sensitivity due to the presence of an organic solvent in aqueous solution as well as depression of sensitivity due to the sample having greater viscosity than the standard solution. This interference can be corrected by (i) method of additions; (ii) matching the matrix of the standard with that of the sample; (iii) solvent extraction to remove the cations to be determined from the interfering matrix; (iv) relating the erroneous value obtained to an accurate value by using a factor determined by other means.

NON-SPECIFIC SCATTER INTERFERENCE

This results in the enhancement of analytical results at ppm and sub-ppm levels due to solution containing high concentration of of dissolved salts. It is more pronounced at shorter wavelenghts and most significant below 250 nm. It can be corrected by solvent extraction to remove the element from the interfering matrix, repeating the determination at a nearby non-absorbing line, or using a deuterium backgrounds corrector.

IONISATION INTERFERENCES

They arise from the energetic nature of the flame which gives ground state atoms but also excite some atoms to such an extent that one or more electrons are lost and ionisation occurs. This problem is usually overcome by the selection and optimisation of furnace operating conditions.

5.2.4.2 HYDRIDE GENERATION TECHNIQUE

The occurence of more severe chemical intreference in the cooler Ar-H_2 entrained air flame is reduced by the necessary resort to more selective technique of hydride generation. Through this process an analyte is simultaneously concentrated as its hydride and separated from the sample matrix. Reduction of As to AsH_3 with its subsequent release from solution and transport to the flame leaves behind many potential interferants and substantially increases detectivity. Sensitivity and detection limit are improved and spectral interference is reduced. Ian D. Brindle and Xiao-Chun Le (63) found that if the hydride is introduced to the DC-plasma while a solution of easily ionised element (EIE) such as KCl or CsCl with constant concentration is separately nebulised and transported to the plasma jet, it is possible to obtain an improved (SNR) which is beneficial to trace analysis. Hydride generation is an ideal situation where interference by EIEs could become an advantage by increasing the sensitivities and improving the detection limits of the hydride-forming element. The replacement of distilled water by solutions of EIEs allows the signal enhancement effect of EIEs to be put to advantage. The authors (62) have determined Sb, As, Ge, Pb and Sn by hydride generation coupled with DC plasma in Atomic Emission Spectrophotometer (AES). Detection limits, defined as 3 times the noise for the determination of As, Sb, Ge and Pb were 230, 200, 12 and 140 pg/ml respectively with the introduction of 0.1M EIE solution (KCl or CsCl) whereas they were 360, 360, 20 and 250 pg/ml respectively in the absence of EIE. For Sn the detection limit was limited by the reagent blank to 20pg/ml although the introduction of EIE further enhanced the signal.

Hydrides may be decomposed by atomisation techniques other than the flame such as He or Ar plasmas, tube furnaces (electrically heated with or without use of H_2 diffusion flame, externally flame-heated, tube confined H_2-O_2 or air flames) and a graphite furnace of the type used for EAAS.

Hydride generation technique however is associated with high instrument-related imprecision and suggests the need for caution in applying the technique.

5.2.4.3 ADVANTAGES OF THE AAS METHOD

Despite the many problems mentioned earlier, the AAS has advantages over other methods. Its principal advantages include :

(i) High sensitivity for a wide range of metals, including many which are difficult or impossible to determine by flame photometry,

(ii) It is highly specific,
(iii) Any one metal can normally be determined in the presence of large amounts of other substances,
(iv) It is rapid and requires only small amounts of material,
(v) The small amount of pretreatment and handling of samples normally minimises the risk of contamination.

5.2.5 OTHER METHODS

A variety of other analytical methods have been successfully used for the determination of trace amounts of arsenic. Among these are Atomic Emission Spectroscopy (AES), X-ray Fluorescence (XFS), Neutron Activation Analysis (NAA), Differential Pulse Polarography, Anodic Stripping Voltametry and Isotope Dilution Mass Spectrometry. All these have detection limits in the nanogram range.

An enzyme method reported recently by Goode and Mathews (64) gave reasonable results in the 0.02 to 2.0 mg/kg range. An Electron Spectroscopic method (ESCA) with detection limit within the ppb range (65) and Direct Current Plasma Atomic Emission Spectroscopy (DCP-AES) (61) have also been reported.

CHAPTER 6

6. EXPERIMENTAL DETERMINATION OF ARSENIC

Two analytical methods were employed to experimentally determine the total arsenic contents of the sample :

i. the molybdenum blue method which involves colorimeter spectrophotometric technique.
ii. the atomic absorption spectrophotometric (AAS) technique.

The determination of arsenic was initially being carried out with the colorimetric method because of the unavailabilty of an atomic absorption spectrophotometer. (The AAS used for this work was made available by the Ashanti Goldfield Corporation at its analytical laboratory at Obuasi).

PRECAUTIONS: Certain essential precautions were taken to minimise errors and to avoid contamination :

i. All glass and plastic vessels were washed, rinsed and soaked in 2% v/v HNO_3 for at least 24h then thoroughly rinsed with double-distilled water.
ii. A clean bench area was reserved for solution preparation.
iii. Volumetric and storage ware were kept separate from those used for conventional laboratory work.
iv. The same apparatus was used for preparing the same solution.

6.1 MOLYBDENUM BLUE METHOD

6.1.1 REAGENTS

NaOH pellets, $N_2H_4.H_2SO_4$, HNO_3, H_2SO_4, $NaHCO_3$, $SnCl_2.2H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ all of Analar grade, as well as HCl (Spectrolsol grade, for AAS) were all obtained from BDH, England.

Lead acetate and $Na_2S_2O_5$ were obtained from Merck, Darmstadt, FRG. $HClO_4$ was obtained from Aldrich Chemical Company Ltd, USA, while resublimed I_2 and KI came from Sigma Chemical Company, USA and M&B, England respectively. Powdered zinc metal was obtained from East Anglia Chemicals, USA. All these were used without further purification. Double-distilled water was used for the preparation of all solutions.

I_2- KI (0.02M)(66) - 2.54g (19.7 mMol) I_2 and 8.0g (49.4 mMol) KI were dissolved in water and made up to 1 litre in a volumetric flask.

$Na_2S_2O_5$(0.02M), $NaHCO_3$(0.05M), $N_2H_4.H_2SO_4$(0.15% w/v), KI (15% w/v), $SnCl_2.2H_2O$ (40% w/v), saturated lead acetate, all prepared fresh as needed.

AMMONIUM MOLYBDATE (66) - 5.0g of the solid were dissolved in 300ml of distilled water containing 70ml of conc H_2SO_4, the solution was made up to 500ml.

ACID MIXTURE (66) - From concentrated stocks, HNO_3, H_2SO_4 $HClO_4$ (10:1:1).

PREPARATION OF ARSENIC STOCK SOLUTION (66)

1.320g (6mMol) As_2O_3 were added to 500ml water and the solution was made basic with 10ml of 70% (w/v) NaOH solution. After the As_2O_3 had dissolved, the solution was neutralised with 70% v/v H_2SO_4 and diluted to 1 litre with distilled water. 1 ml of this solution contained 1 mg of As i.e 1mg/ml or 1000 ppm. From this stock, suitable dilutions could be made to give desired working standards.

APPARATUS

(i) Digestion flask : Kjeldahl or 250 ml round-bottom flask
(ii) Distillation flask : Kjeldahl or 250 ml round-bottomed flask (long neck type).
(iii) Funnel trap and bent dispersion tube.
(iv) Variable micropipette (Eppendorf) with disposable tips.

6.1.3 EXPERIMENTAL WORK

Samples of food crops and cash crops were obtained directly from the farms. These were sealed in plastic sachets and stored in the laboratory (average temperature was 26^{o}) until required. Market samples were bought and treated as above. Cooked food samples were obtained from homes and sealed in plastic sachets and kept under laboratory conditions until analysis.

6.1.3.1 SAMPLE PREPARATION

Vegetation (i.e grass and leaves) were initially rinsed with distilled water to remove adhering soil and dust. The samples were cut into small pieces and dried in the oven at $50^{o}C$ for 3 days. The dried sample was then ground to powder and sieved with a 20 - 30 mesh sieve.

Oil palm fruit was sun dried for 7 days and the fleshy part was ground to a friable mass from which a representative sample was taken for analysis.

Fresh samples of all the food crops as well as cassava and plantain peels were each cut into small pieces and ground to a friable mass using mortar and pestle. Weighed quantity of this wet sample was used for As determination.

Fish and meat were rendered uniform using a food chopper with about 3.0 mm holes. These were then oven dried, ground and sieved with 20-30 mesh sieve.

Cocoa and Tobacco which were obtained in the dry state were cut into pieces, oven dried, ground and sieved with 20-30 mesh sieve before analysis.

6.1.3.2 DIGESTION

The destruction of organic matter (digestion) was carried out by the method of wet decomposition - action of various acids with conditions adjusted to prevent loss of volatile arsenic.

PROCEDURE:

To a Kjeldahl flask containing 1g of finely ground sample, 3 ml of distilled water and 10 ml of conc HNO_3 were added, the flask stoppered and the mixture allowed to stand overnight. After the addition of 10 ml of the acid mixture, the flask was equipped with a reflux condenser and slowly heated at first and then the temperature gradually increasd until the solution boiled. Heating was continued at this temperature for about 30 min after which the digestion mixture became straw-coloured.

The flask was cooled and 3 ml of 70 - 72% perchloric acid and boiling chips (glass beads) were added. Heating was slowly increased until the mixture boiled, and heating was done at this temperature for 30 min after which period sulphur trioxide fumes appeared. The flask was allowed to cool, 5 ml distlled water added and heated until SO_3 appeared. Again the flask was allowed to cool, 5 ml distilled water added, and the temperature was increased slowly until the mixture boiled. To achieve a good recovery this temperature was maintained for 2h.

6.1.3.3 DISTILLATION

After the digestion was complete, the flask was allowed to cool. About 20 ml distilled water were added to the contents, washed well and filtered into a 100 ml volumetric flask and made to the mark. An aliquot of 25 ml was pipetted out into a distillation flask (250 ml round-bottomed flask). 10 ml of arsenic-free conc HCl, 2 ml of KI solution and 0.5 ml of $SnCl_2$ solution were added, mixed well and allowed to stand at room temperature for 20-30 min to permit complete reduction of all As(V) to As(III).

The flask was connected to a funnel trap containing cotton wool saturated with lead acetate (to remove H_2S and trap any acid spray). The other end of the funnel trap was connected to a bent glass dispersion tube, the fritted end of which was submerged in a mixture of 10 ml of 0.001M iodine-iodide solution and 2 ml of sodium hydrogen carbonate (to displace any air bubbles), in a test tube immersed in an ice bath (see fig. 3).

About 5g of powdered zinc added to the flask and quickly reconnected, and the distillation was allowed to proceed for an hour when all arsenic generated as arsine AsH_3 gas was collected in the iodine-iodide solution. The dispersion tube was removed from the collection solution and a drop or two of sodium disulphite solution was added to the collection solution and mixed to remove any iodine colour still remaining.

6.1.3.4 COLOUR DEVELOPMENT AND QUANTITATIVE MEASUREMENT OF ARSENIC

To the test tube containing the arsenic distillate, 2 ml of the ammonium molybdate solution were added. After mixing, 0.8 ml of a 0.15 % hydrazine sulphate solution was added and mixed. The tube was immersed in a boiling water bath for 10 min, removed and allowed to cool.

The absorbance of the resulting blue coloured complex solution was determined on a spectrophotometer manufactured by V.E.B Carl Zeiss, Jena, GDR at 840nm with 100% transmission set with distilled water. (Preliminary investigations with solutions containing 20 and 40 ug of arsenic showed that a minimum transmission occured at 840 mn). The colour of the arsenomolybdenum blue complex was stable for at least 24h.

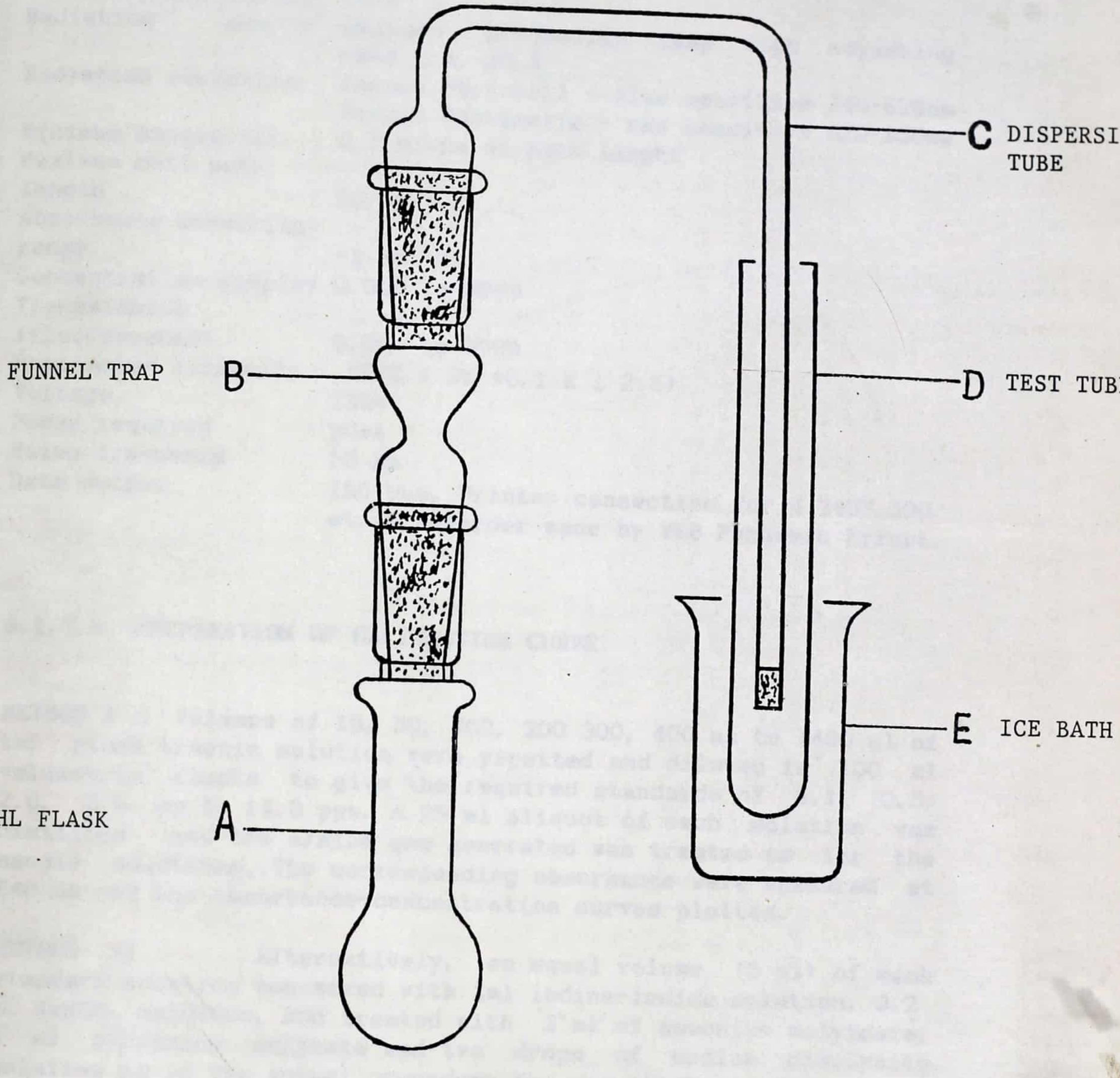


Fig.3 : Schematic Diagram of Arsenic Distillation Apparatus

SPECIFICATIONS OF THE SPECTROPHOTOMETER (SPEKOLL 11)

Monochromator	Precision diffraction grating with 651 grooves/nm
Wavelength	340 to 850 nm at 1 nm interval graduation
Repeatability of wavelenght setting	± 0.2 nm
Spectral bandwidth	11 nm
Scatter light(340nm)	0.5%
Radiation source	Halogen projection lamp with adjusting base 6 V, 20 W
Radiation recievers	Vacuum Photocell - blue sensitive 340-620nm Vacuum Photocells - red sensitive 620-850nm
Minimum sample vol.	0.1 ml/cm of path lenght
Maximum cell path length	50 mm
Absorbance measuring range	-2 to +2
Concentration display	0.000 to 9999
Transmission (fluorescence)	0.000 to 9999
Photometer linearity	?E/E ≤ 2% (0.1 E ≤ 2.5)
Voltage	240V
Power required	90vA
Mains frequency	50 Hz
Data output	IBC bus, Printer connection for G 3407.500 strip recorder made by VEB Funkwerk Erfurt.

6.1.3.6 **PREPARATION OF CALIBRATION CURVE**

METHOD I - Volumes of 10, 50, 100, 200 300, 400 up to 1400 ul of the stock arsenic solution were pipetted and diluted in 100 ml volumetric flasks to give the required standards of 0.1, 0.5, 2.0, 3.0 up to 14.0 ppm. A 25 ml aliquot of each solution was distilled and the arsine gas generated was treated as for the sample solutions. The corresponding absorbance were measured at 840 nm and the absorbance-concentration curves plotted.

METHOD II - Alternatively, an equal volume (5 ml) of each standard solution was mixed with 1ml iodine-iodide solution, 0.2 ml $NaHCO_3$ solution, and treated with 2 ml of ammonium molybdate, 1 ml hydrazine sulphate and two drops of sodium disulphite solution as in the actual procedure. The resultant solutions were heated to 95-100^{o} in a boiling water bath. The absorbances of the resulting blue solutions were measured at 840 nm and the absorbance-concentration curve plotted.

6.1.3.7 CALCULATION OF TOTAL ARSENIC CONTENT OF SAMPLE

The total arsenic content of the aliquot (25ml) taken was found from the absorbance-concentration calibration curve prepared from standard arsenic (III) oxide solutions. The total arsenic content of 1g sample (expressed in mg/kg) was calculated using the following equation:

$$\text{TOTAL ARSENIC CONCENTRATION} = \frac{C \times V_T \times D}{V_d \times W}$$

where C = Corresponding concentration value from calibration curve

V_T = Total volume of distillate solution (1000 ml)

D = Dilution factor (1)

V_d = Volume of distillate aliquot used (25 ml)

W = weight of sample

SAMPLE CALCULATION

If arsenic concentration read from the calibration curve C = 0.075ug/ml, V_T = 100ml, V_d = 25ml, D = 1 and W = 1g the Total Arsenic concentration is given by

$$\frac{C \times V_T \times D}{V_d \times W}$$

$$= \frac{0.075 \times 100 \times 1 \text{ ug/g}}{25 \times 1}$$

$$= 0.075 \times 4 \text{ ug/g}$$

$$= 0.300 \text{ ug/g}$$

$$= 0.300 \text{ mg/kg}$$

6.2 ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD

This method was used to determine the total arsenic content of food, cash crops and vegetation in both Kumasi and Obuasi area as well as soil and water from Obuasi.

Water samples were collected in well washed and clean 1000ml glass bottles. Small quantities of sample water were used to rinse the flask three times before fetching the water for analysis. The arsenic concentration was determined without any pretreatment within 1h.

Soil samples were collected in clean glass containers (1 litre wide mouth bottles with stopper) at about 5-10 cm depth, i.e from the second layer after the top soil.

DIGESTION OF THE SOIL 1 g of soil, ground and sieved with a 3.0 mesh sieve, and 2 ml concentrated H_2SO_4 were added to the digestion flask and mixed. Heat was applied slowly at first and gradually the heat was increased until the acid fumed. The flask was rotated during the heating to prevent caking of the acid-soil mixture. Heating was continued with rotation of flask at intervals until the soil became light grey in colour (i.e. when all the organic matter had been oxidised). The flask was cooled, 3 ml of 70 - 72% perchloric acid were added, as well as some boiling chips. The heating was continued until boiling started and the temperature was maintained for about 2h. Following this period of digestion the contents of the flask became almost white. The solution was filtered with a glass frit (G2) and transfered into a 100 ml volumetric flask and made to the mark with distilled water.

6.2.1 RECOVERY STUDIES ON THE A.A.S

Measurements were carried out on an Instrumentation Laboratory AAL/AE spectrophotometer 357 manufactured by Thermo Electron. Recoveries for various concentrations of arsenic (III) oxide standard solutions were made (see Table below).

X_o = Concentration of standard As_2O_3 solution

X_m = Measured concentration of As_2O_3 solution with AAS

X_o [ppm]	X_m [ppm]	$X_m - X_o$	$\frac{(X_m - X_o)}{X_o}$	$\frac{(X_m - X_o)}{X_o} \times 100\%$
1.00	1.018	0.018	0.018	1.80
2.00	2.023	2.023	0.012	1.20
3.00	3.025	0.025	0.009	0.90
4.00	4.106	0.016	0.004	0.40
5.00	5.082	0.082	0.016	1.60
6.00	6.066	0.066	0.011	1.10
7.00	7.108	0.108	0.016	1.60
8.00	8.088	0.088	0.011	1.10
9.00	9.121	0.121	0.014	1.40
10.00	10.098	0.098	0.010	1.00

Total deviation = 0.121

average Deviation = 0.012

= 1.2%

=====

This implied that for amounts between 1 and 10.0ppm the instrument gave readings which were 1.2% higher than the actual values. Hence all measured values were accordingly corrected for by reducing measurements by a factor of 1.2%.

PROCEDURE : In this method, portions of the digested solutions of the sample were aspirated into the flame of the AAS and the absorbance of the arsenic solution was measured. A standard arsenic solution containing 25 ppm (µg/ml) arsenic was used for the calibration of the instrument, its absorbance also being determined.

Distilled water was aspirated into the flame after measurement of each sample in order to remove all traces of this solution before proceeding to the next solution.

The total arsenic concentrations of the sample solution were then calculated using the following equation:

$$\text{TOTAL ARSENIC CONCENTRATION} = \frac{A_{sp} \times C_{st}}{A_{st}}$$

where A_{sp} = Absorbance of sample solution

A_{st} = Absorbance of standard solution

C_{st} = Concentration of standard solution, 25ppm

SAMPLE CALCULATION : For the sample solution which gave absorbance of A_{sp} = 0.009, and the standard solution with concentration C_{st} = 25 ppm and absorbance A_{st} = 0.307,

$$\text{TOTAL ARSENIC CONCENTRATION} = \frac{A_{sp} \times C_{st}}{A_{st}}$$

$$= \frac{0.009 \times 25}{0.307} \text{ ppm}$$

$$= \frac{225}{307} \text{ ppm}$$

$$= 0.700 \text{ ppm}$$

$$= 0.700 \text{ mg/kg}$$

6.2.2 PARAMETERS OF THE AAS USED

Light sources	= Hollow cathode/EDL
Lamp current	= 8 mA
Wavelength	= 193.7 nm
Slit width	= 320 µm
Burner head	= single slot
Bend pass	= 1 nm
Pin-voltage	= 700 V
Integration time	= 4 s
Aspiration rate	= 5 ml/min
Flame	= Air-Acetylene, 2300°C

Sensitivity (at 0.0044 absorbance = 1% absorption) = 0.4 µg/ml for the instrumental parameters described above.

A standard solution containing 10 µg/ml of As gave a reading of approximately 0.1 absorbance.

CHAPTER 7

7. EXPERIMENTAL RESULTS

The results of the experimental work are presented in the tables below. Arsenic concentrations obtained using the molybdenum blue method are presented under the column designated "COLORIMETRIC" or "COL" whereas those obtained by employing the atomic absorption spectrophotometric technique are presented under the column designated "AAS".

The result presented in the following tables are average vaues of triplicate determinations.

TABLE 1 : CALIBRATION CURVE (Molybdenum Blue Method)

ARSENIC CONCENTRATION (PPM)	ABSORBANCE	
	METHOD I	METHOD II
0.10	0.012	0.010
0.20	0.024	0.025
0.25	0.029	-
0.30	0.036	0.040
0.40	0.048	0.052
0.50	0.060	-
1.00	0.120	0.121
2.00	0.232	0.260
3.00	0.380	-
4.00	0.450	0.503
5.00	0.600	-
6.00	0.711	0.680
8.00	0.940	0.962
10.00	1.206	1.200
12.00	1.440	-
14.00	1.701	-

ARSENOMOLYBDENUM BLUE COMPLEX
(LOWER CONCENTRATIONS – METHOD 1)

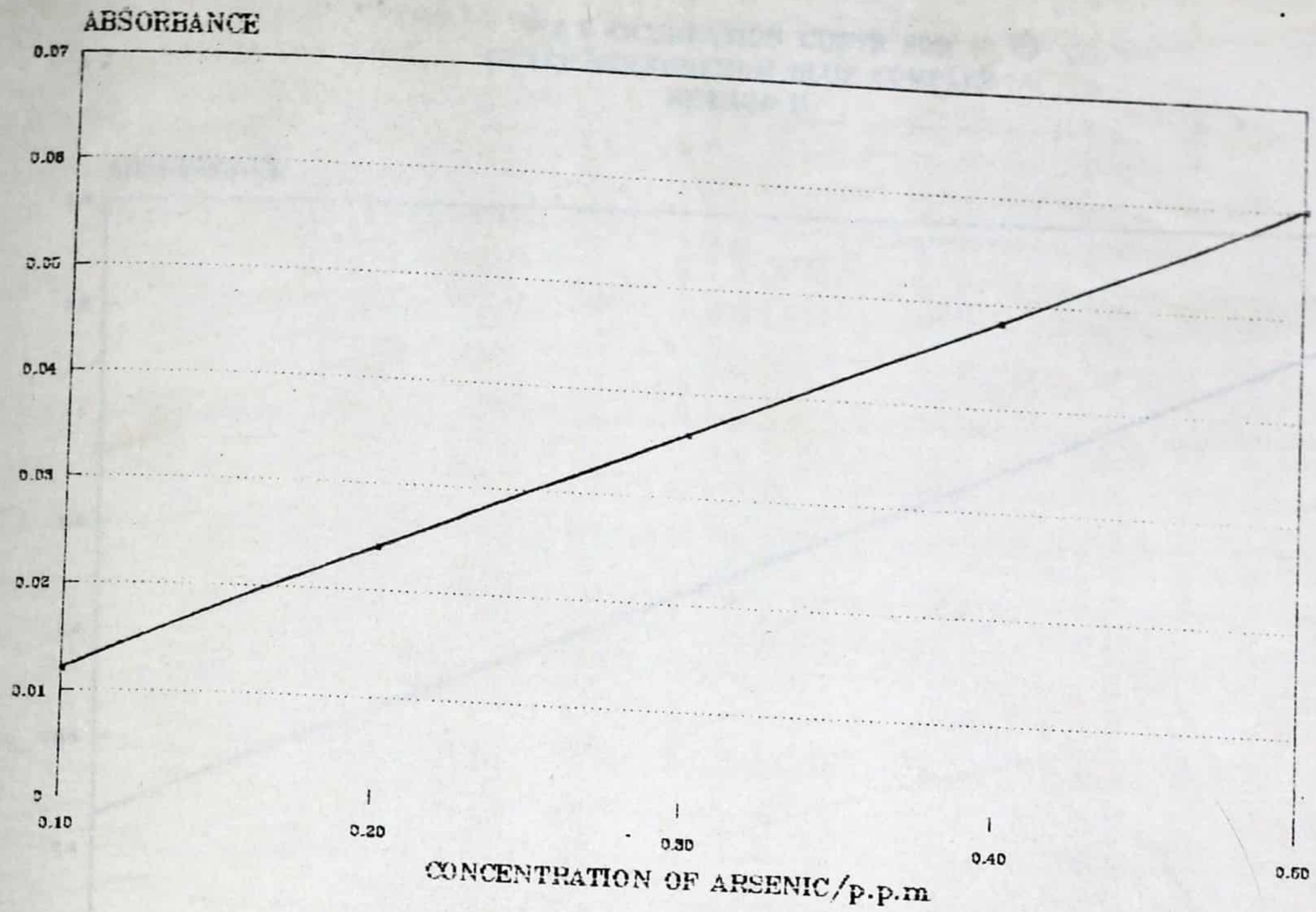


Fig4b CALIBRATION CURVE FOR
ARSENOMOLYBDENUM BLUE COMPLEX
(HIGHER CONCENTRATIONS – METHOD 1)

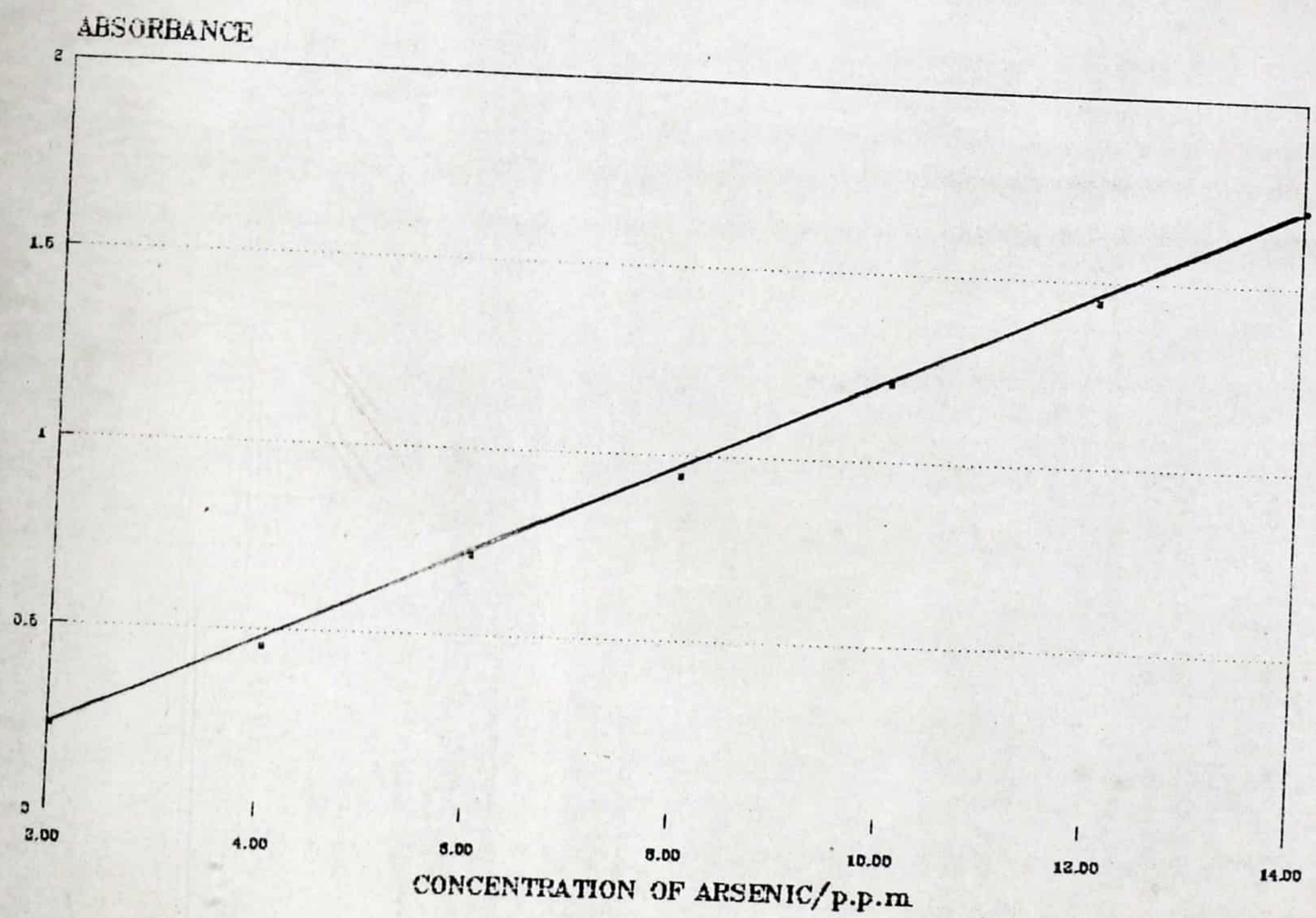


Fig 5 CALIBRATION CURVE FOR
ARSENOMOLYBDENUM BLUE COMPLEX
METHOD II

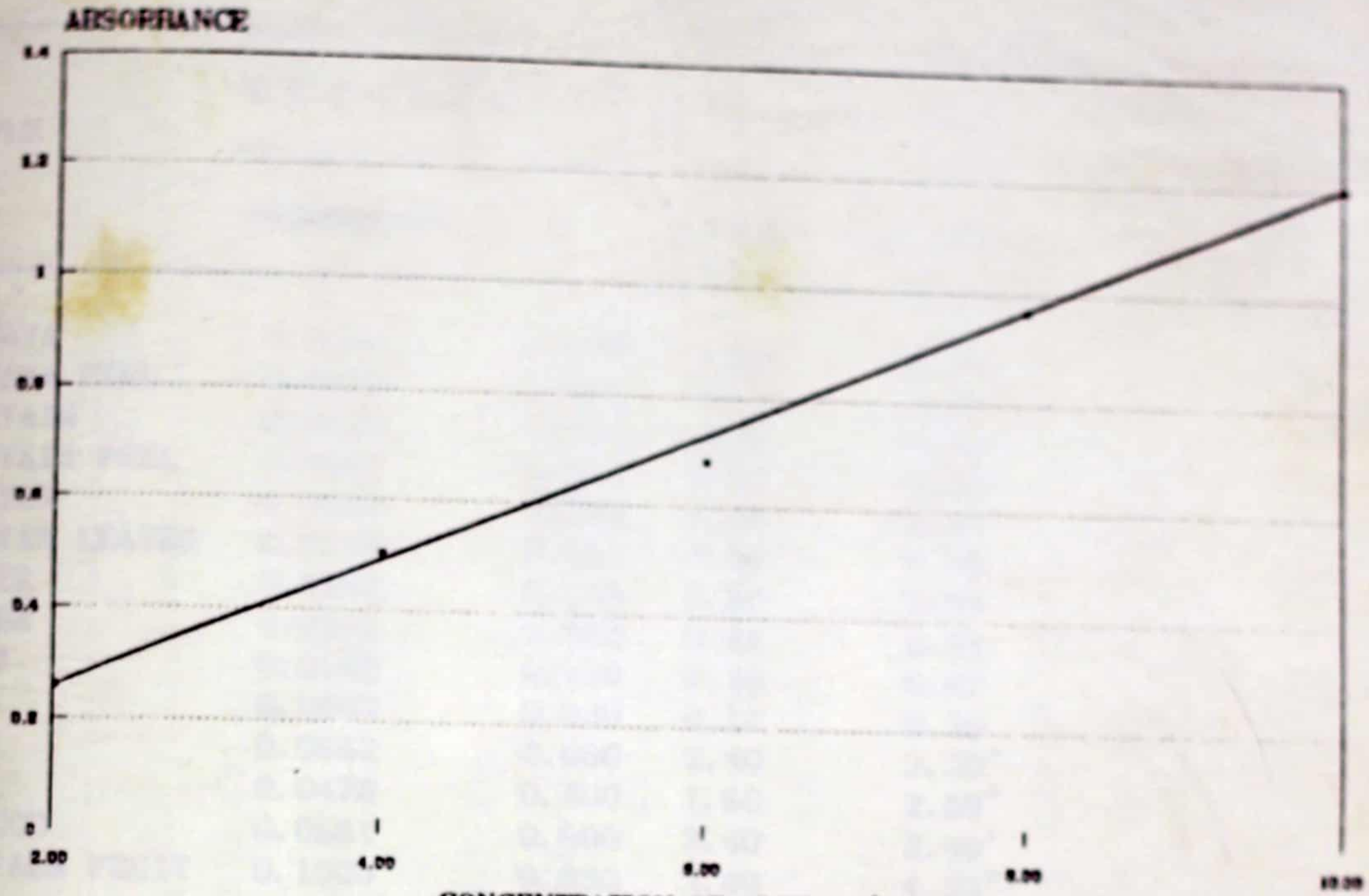


TABLE 2: TOTAL ARSENIC CONCENTRATION IN SAMPLES FROM KUMASI MARKET (mg/kg wet weight)

SAMPLE	COLORIMETRIC			A. A. S
	ABSORBANCE	C	As conc	As conc
CASSAVA	0.0090	0.075	0.30	0.70
CASSAVA PEEL	0.0052	0.040	0.16	0.26
PLANTAIN	0.0122	0.083	0.33	0.51
PLANTAIN PEEL	0.0060	0.043	0.17	0.28
COCOYAM	0.0085	0.065	0.26	0.47
COCOYAM LEAVES	0.0020	0.015	0.06	0.10
PEPPER	0.0183	0.153	0.61	0.97
ORANGE	0.0132	0.103	0.41	0.54
BEANS	0.0145	0.120	0.48	0.62
PEAR	0.0040	0.030	0.12	0.20
FISH	0.0662	0.600	2.40	3.30*
MEAT	0.0478	0.400	1.60	2.59*
TOBACCO	0.0661	0.600	2.40	2.40*
OIL PALM FRUIT	0.1003	0.850	3.40	4.53*

C = Arsenic conc. from calibration curve
* = Values given in mg/kg dry weight.

TABLE 4: TOTAL ARSENIC CONCENTRATION IN SOME COOKED FOOD FROM KUMASI HOMES (mg/kg dry weight)

SAMPLE	COOKED CASSAVA		COOKED PLANTAIN		FUFU	
LOCATION	COL	AAS	COL	AAS	COL	AAS
ASAWASI	1.40	1.94	2.20	2.86	1.24	1.53
UST	1.20	1.81	2.60	3.24	0.80	1.26
AVERAGE	1.30	1.91	2.40	3.03	1.02	1.40

TABLE 3: TOTAL ARSENIC CONCENTRATION IN SOME FOOD CROPS FROM KUMASI FARMS (mg/kg wet weight)

SAMPLE	CASSAVA		CASSAVA PEEL		PLANTAIN		PLANTAIN PEEL		COCOYAM		COCOYAM LEAVES		PEPPER		ORANGE		BEANS		PEAR	
LOCATION	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS
U.S.T.	0.23	0.28	0.11	0.15	0.20	0.28	0.12	0.16	0.25	0.38	0.06	0.10	0.17	0.24	0.08	0.10	-	-	0.09	0.11
AHINSAN	0.30	0.45	0.20	0.30	0.26	0.32	0.01	0.14	0.26	0.39	0.06	0.10	-	-	-	-	-	-	-	-
KAASE	0.30	0.46	0.16	0.25	0.33	0.48	0.18	0.27	0.35	0.54	0.10	0.12	-	-	0.16	0.23	-	-	0.12	0.19
AHODWO	-	-	-	-	-	-	-	-	-	-	-	-	0.17	0.24	-	-	-	-	-	-
DABAN	0.32	0.47	0.21	0.31	0.33	.047	0.18	0.22	0.43	0.49	0.10	0.14	0.24	0.32	-	-	0.20	0.30	0.12	0.16
KWADASO	0.23	0.33	0.11	0.17	0.33	0.38	0.13	0.18	0.26	0.38	0.10	0.13	0.17	0.27	0.06	0.09	0.10	0.20	0.12	0.13
TANOSO	0.26	0.35	0.16	0.22	0.26	0.45	0.13	0.18	0.26	0.35	0.09	0.12	-	-	0.13	0.16	0.20	0.27	0.08	0.13
ABUAKWA	0.30	0.36	0.16	0.23	0.26	0.30	0.13	0.16	-	-	-	-	0.17	0.22	0.05	0.07	0.10	0.37	0.12	0.14
TAFO	0.30	0.39	0.21	0.27	0.22	0.30	0.13	0.18	0.35	0.40	0.10	0.12	-	-	0.10	0.15	0.10	0.18	-	-
BUKROM	0.24	0.37	0.11	0.16	0.20	0.28	0.12	0.16	0.26	0.43	0.06	0.11	-	-	-	-	-	-	0.10	0.17
TOTAL	2.48	3.46	1.43	2.06	2.36	3.26	1.21	1.65	2.42	3.36	0.67	0.94	0.92	1.29	0.58	0.80	0.70	1.32	0.75	1.03
AVERAGE	0.28	0.38	0.16	0.23	0.26	0.36	0.13	0.18	0.30	0.42	0.08	0.12	0.18	0.26	0.10	0.13	0.14	0.26	0.11	0.15

TABLE 5: TOTAL ARSENIC CONCENTRATION IN SOME CASH CROPS FROM KUMASI FARMS (mg/kg dry weight)

SAMPLE	LOCATION	COLORIMETRIC			AAS
		ABSORBANCE	C	As conc.	As conc
Tobacco	Tanoso	0.0360	0.30	1.20	2.14
Palm Fruit	Tanoso	0.0802	0.65	2.60	3.70
Palm Fruit	Kwadaso	0.0645	0.55	2.20	3.56
Palm Fruit	Tafo	0.0603	0.50	2.00	3.24
Cocoa	Ayeduase	0.0405	0.35	1.40	2.42
Cocoa	Kaase Depot	0.0402	0.35	1.40	2.46

TABLE 6: TOTAL ARSENIC CONCENTRATION IN SOME GRAZING VEGETATION FROM KUMASI (mg/kg dry weight)

SAMPLE	LOCATION	COLORIMETRIC			AAS
		ABSORBANCE	C	As conc.	As conc.
Star grass+	UST*	0.1324	1.05	4.20	6.00
Star grass	Airport	0.1442	1.21	4.85	7.20
Star grass	Ahinsan	0.1200	1.00	4.00	6.80
Elephant grass	UST*	0.0802	0.65	2.60	4.40
Elephant grass	Airport	0.1134	0.85	3.40	5.54
Elephant grass	Ahinsan	0.0680	0.60	2.40	4.60

+ = Eleusine Indica

* = Behind Chemistry Department Building

TABLE 7: TOTAL ARSENIC CONCENTRATION IN SOME SAMPLES FROM OBUASI MARKET (mg/kg wet weight)

SAMPLE	LOCATION	COLORIMETRIC			AAS
		ABSORBANCE	C	As conc	As conc
Cassava	Tukuta	0.0135	0.11	0.45	0.80
Cassava Peel	-do-	0.0060	0.05	0.21	0.30
Plantain	-do-	0.0261	0.22	0.86	1.14
Plantian Peel	-do-	0.0134	0.11	0.42	0.67
Cocoyam	-do-	0.0135	0.11	0.43	0.89
Cocoyam Leaves	-do-	0.0072	0.06	0.25	0.47
Pepper	-dO-	0.0180	0.15	0.60	0.58
Beans	-dO-	0.0160	0.13	0.50	0.55
Orange	-do-	0.0010	0.08	0.32	0.52
Pear	-dO-	0.0073	0.06	0.23	0.43
Palm Fruit	-dO-	0.1012	0.90	3.60+	5.71+
Mutton	Market*	0.0480	0.40	1.60+	3.48+
Palm Fruit	-do-	0.0800	0.65	2.60+	3.02+
Tobacco	-do-	0.0415	0.35	1.40+	2.34+
Cassava	-dO-	0.0120	0.10	0.38	0.62
Cassava Peel	-do-	0.0070	0.06	0.21	0.38
Plantain	-do-	0.0123	0.10	0.40	0.65
Plantain Peel	-do-	0.0035	0.03	0.13	0.19
Cocoyam	-dO-	0.0010	0.08	0.32	0.49
Cocoyam Leaves	-dO-	0.0050	0.04	0.16	0.25
Pepper	-do-	0.0034	0.03	0.10	0.12
Beans	-do-	0.0158	0.13	0.50	0.63
Orange	-do-	0.0134	0.11	0.44	0.42
Pear	-do-	0.0060	0.05	0.19	0.39
Fish	Lake water (Fresh)	0.0650	0.60	2.40	2.60+

* = Obuasi Central Market + = Values given in mg/kg dry weight

TABLE 8: *TOTAL ARSENIC CONCENTRATION IN SOME FOOD CROPS FROM OBUASI (mg/kg wet weight)*

SAMPLE	CASSAVA		CASSAVA PEEL		PLANTAIN		PLANTAIN PEEL		COCOYAM		COCOYAM LEAVES		PEPPER		ORANGE		BEANS		PEAR	
LOCATION	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS	COL.	AAS
AKAPORISO	0.91	1.19	0.53	0.78	0.92	1.29	0.51	0.70	1.12	1.51	0.32	0.45	0.15	0.60	0.41	0.56	0.42	0.67	0.19	0.43
POMPOSO	0.60	0.92	0.27	0.57	0.86	1.20	0.47	0.65	0.86	1.28	0.22	0.38	0.22	0.52	0.35	0.56	0.40	0.51	0.17	0.30
K.K.*	0.45	0.72	0.27	0.40	0.79	0.99	0.34	0.56	0.35	0.53	0.10	0.14	0.52	0.19	0.38	0.46	0.30	0.44	0.12	0.20
P.T.P.ESTATE	-	-	-	-	1.32	1.86	0.68	0.92	-	-	-	-	-	-	-	-	-	-	-	-
KWABRAFOSO	-	-	-	-	0.86	1.19	0.47	0.63	-	-	-	-	-	-	-	-	-	-	-	-
TUTUKA	-	-	-	-	1.07	1.40	0.34	0.44	-	-	-	-	-	-	-	-	-	-	-	-
BOETE	0.91	1.17	0.53	0.78	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
KWAMEDUKROM	0.76	1.15	0.43	0.70	0.92	1.26	0.55	0.67	1.14	1.40	0.38	0.47	0.44	0.87	-	-	-	-	0.27	0.47
ABOAGYEKROM	-	-	-	-	0.53	0.85	0.17	0.23	-	-	-	-	0.13	0.97	-	-	-	-	-	-
AKROFUOM	0.76	1.04	0.32	0.52	0.86	1.39	0.26	0.44	0.54	1.02	0.13	0.32	0.05	0.40	-	-	-	-	0.15	0.26
NANTRIN	0.30	0.55	0.16	0.34	0.33	0.68	0.17	0.32	0.52	0.97	0.16	0.32	0.35	0.86	-	-	-	-	-	-
NHIESO	0.38	0.60	0.21	0.29	0.46	0.78	0.21	0.42	-	-	-	-	0.52	0.94	0.32	0.48	0.20	0.38	0.12	0.18
KYEKYEWERE	0.83	1.32	0.53	0.90	0.26	0.67	0.13	0.32	0.26	0.52	0.06	0.14	-	-	0.35	0.49	0.30	0.47	-	-
NNIRIWA	-	-	-	-	-	-	-	-	0.35	0.59	0.10	0.15	-	-	-	-	-	-	-	-
BIDIESO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.38	0.62	-	-	-	-
BOGOBRI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.47	0.65	-	-	-	-
TOTAL	5.90	8.66	3.25	5.28	9.18	13.56	4.30	6.30	5.14	7.82	1.15	2.37	2.38	5.35	2.66	3.82	1.62	2.47	1.02	1.84
AVERAGE	0.66	0.96	0.36	0.59	0.77	1.13	0.36	0.53	0.64	0.98	0.19	0.30	0.30	0.67	0.38	0.55	0.32	0.49	0.17	0.31

* = KWABENA AKWAKROM

TABLE 9: TOTAL ARSENIC CONCENTRATION IN SOME COOKED FOOD FROM OBUASI HOMES (mg/kg dry weight)

SAMPLE LOCATION	COOKED CASSAVA		COOKED PLANTAIN		FUFU	
	COL.	AAS	COL.	AAS	COL.	AAS
TUTUKA	1.80	2.65	2.60	3.14	1.60	2.43
WAWASI	1.60	2.53	2.80	3.81	1.40	2.04
KWABRAFOSO	2.00	2.84	2.64	3.21	1.80	2.65
AVERAGE	1.80	2.67	2.68	3.39	1.60	2.37

TABLE 10: TOTAL ARSENIC CONCENTRATION IN SOME CASH CROPS FROM OBUASI FARMS (mg/kg dry weight).

SAMPLE	LOCATION	COLORIMETRIC			AAS
		Absorbance	C	As conc.	
Cocoa	Cocobod Depot	0.0400	0.30	1.20	2.23
Oil Palm Fruit	Akaporiso	0.0803	0.65	2.60	4.63
-do-	Kwabena Akwakrom	0.0240	0.20	0.80	1.16
-do-	Akrofuom	0.0650	0.55	2.20	3.44
-do-	Nhieso	0.0300	0.25	1.00	1.75
-do-	Pomposo	0.0401	0.30	1.20	2.24
-do-	Kwamedukrom	0.0402	0.30	1.20	2.10
-do-	Nantrin	0.1200	1.00	4.00	5.87

TABLE 11: TOTAL ARSENIC CONCENTRATION IN SOME VEGETATION FORM OBUASI (mg/kg dry weight)

SAMPLE	LOCATION	COLORIMETRIC			AAS
		Absorbance	C	As conc	
STAR GRASS	FRESH WATER DAM - (A)	0.2500	2.05	8.20	10.17
-do-	OPPOSITE P.T.P AT 450m - (B)	0.9200	8.10	32.40	39.30
-do-	POMPORA PUMP HOUSE - (C)	0.3050	2.60	10 .40	12.41
-dO-	SUPER MAMBO HOTEL BRIDGE (D)	0.0650	0.55	2.20	3.75
-do-	B/N SLIME DAMS N.5 or 8 - (E)	0.1804	1.50	4.20	5.99
-do-	GYIMI RIVER PUMP HOUSE - (F)	0.1200	1.00	4.00	5.65
-do-	AKROFUOM (BRIDGE) - G	0.0360	0.30	1.20	2.23
ELEPHANT GRASS	KWABRAFOSO - (H)	0.1180	0.95	3.80	5.10
-do-	TUTUKA - (I)	0.1202	1.00	4.00	5.50
-do-	AKROFUOM (BRIDGE) - (G)	0.0420	0.35	1.40	2.36
FERN	FRESH WATER DAM - (A)	1.2002	10.13	40.50	48.50
-do-	1.5 km NORTH OF P.T.P. - (J)	1.4413	12.00	48.00	58.00
-do-	1.0 km NORTH OF P.T.P - (K)	1.5224	12.70	50.81	62.40
-do-	OPPOSITE P.T.P AT 450m -(B)	1.5631	13.00	52.00	70.50
-do-	POMPORA PUMP HOUSE - (C)	1.4451	12.13	48.53	59.60
OIL PALM TREE LEAVES	SITE A	0.0601	0.50	2.00	3.50
-do-	SITE J	0.0360	0.30	1.20	2.20
-do-	SITE K	0.1124	0.90	3.60	4.20
-do-	SITE B	0.0604	0.50	2.00	3.70
-do-	SITE C	0.0670	0.55	2.20	3.80

A, B, C, D.....K = Exact locations as shown on attatched maps.

TABLE 12: TOTAL ARSENIC CONCENTRATION IN SOME SOIL AND WATER SAMPLES FROM OBUASI (AAS METHOD)

LOCATION	S O I L (mg/kg dry wt)	W A T E R (ppm)
A	21.50	4.40
B	29.60	10.40
C	21.90	5.60
D	21.30	4.70
E	19.80	4.90
F	5.40	2.80
G	16.20	3.50

CHAPTER 8

8. DISCUSSION OF RESULTS

It is difficult to ascertain the extent of arsenic contamination of food on a global basis because of the following reasons:

(i) There is disparity between countries in the number and type of food items.

(ii) The vast number of individual foods in existence makes it difficult to present a data in a summary fashion or to draw conclusion from it.

(iii) The arsenic content of a particular food item is to a large extent dependent on factors such as soil arsenic content and its availability to the plant involved, proximity to arsenic producing industries and wind direction among many other factors. However, a lot of research work has been carried out in various countries to determine the arsenic content of some food crops, cash crops, vegetation etc.

The following discussion is based on the total arsenic concentrations obtained for the different samples analysed using the AAS technique because of its greater precision and accuracy over the colorimetric method, (i.e. the Molybdenum Blue Method) which gave lower values of arsenic concentration for each sample.

Total arsenic concentrations obtained for the various food crops, cash crops, cooked food, fish, meat and vegetation from Kumasi and Obuasi markets and farms will be compared with values from literature. These results will be discussed in terms of pollution. An attempt will be made to see if there is any correlation between market and farm values. Finally the results for Obuasi will be compared with those from Kumasi which is a non gold mining town.

8.1.1 FOOD CROPS - KUMASI MARKET

The total arsenic concentrations in different food crop samples from Kumasi market are presented in Table 2. The lowest value was obtained for cocoyam leaves (0.10 mg/kg wet weight) while the highest arsenic level was found in pepper (0.97 mg/kg wet wt).

Westoo, G. and Rydalv, M. (36) showed that arsenic levels in food, with the exception of sea foods, are generally well below 1.0 mg/kg wet weight. This implies that the food crops which constitute the major daily food intake by Kumasi residents i.e. cassava, plantain, cocoyam and cocoyam leaves ("Kontomire"), sold on the Kumasi market are not arsenic contaminated beyond that normally encountered in foods.

8.1.2 FOOD CROPS - KUMASI FARMS

Table 3 shows the total arsenic concentrations in food crops from farms in and around Kumasi. Sampling areas include non-industrial/residential areas like University of Science and Technology (UST) as well as industrial areas such as Ahinsan, Kaase, Dabaan, Ahodwo and other suburbs in the Kumasi metropolis. The table also shows the average arsenic content for each food crop. Cocoyam from Kaase appears to have the highest arsenic level (0.54 mg/kg wet weight), while orange from Abuakwa shows the least value of 0.07 mg/kg wet weight. The average values indicate that cocoyam has the highest arsenic concentration of 0.42 mg/kg wet weight and cocoyam leaves contain the lowest arsenic concentration of 0.12 mg/kg wet weight. Since all the values obtained are below 1.0mg/kg, it can be said that food crops from Kumasi farms are not arsenic contaminated beyond that normally encountered in food stuffs.

8.2 COOKED FOOD - KUMASI HOMES

The cooked food items analysed for arsenic are cassava, plantain and fufu, which are the major meals for Kumasi residents. Form table 4 it is observed that these samples showed quite high arsenic concentrations with cooked plantian contianing the highest, followed by cooked cassava and fufu in that order. The results of the analyses show that cooked food from Kumasi residents contain considerable amount of arsenic up to about 3 ppm and the cooking process did not eliminate all the arsenic, though the possibility exits that some might have been vapourised or leached during the cooking.

8.3 FISH AND MEAT - KUMASI MARKET

Marine fish are known to contain arsenic concentrations up to 5.0 mg/kg wet weight, and concentrations in some crustacea and bottom feeding fish reach several tens of milligrams per kilogram usually in the form of organic arsenic (55). By contrast fresh water fish in uncontaminated waters usually have arsenic concentrations less than 2 ppm (48).

Comparing the value of 3.30 mg/kg (3.30 ppm) with the above 2 ppm, it can be said that the local fresh water fish bought on the market contains considerable amount of arsenic which on consumption is likely to pose toxicity problems.

Accumulation of arsenic in the tissues of poultry and swine can result from the use of organic arsenic compounds as feed additives (55). Grazing animals, on the other hand obtain most of their body arsenic from the vegetation and other foods such as cassava and plantain peels which they feed on. In the absence of any literature values for comparison, it can still be observed that the value of 2.59 mg/kg obtained for mutton (Table 2) bought from the market is not so alarming. This is because after exposure to a single dose of As(III), both animal and human data indicate an initial elimination of about 75% in the urine and a few per cent in the faeces within the first week. For pentavalent arsenic, As(V), a few animal experiments have indicated that 80-90% of a single dose is eliminated during the first two days, human data indicate a slower rate of elimination (4). Applied to the above therefore, ingestion of about 1kg of goat meat (containing 2.59 mg As) will lead to retention of only about 0.50 mg of arsenic after two days.

8.4 CASH CROPS - KUMASI MARKET AND FARMS

From Tables 2 and 5, the following arsenic levels were found after analysis of the market and farm samples respectively: Tobacco = 2.40 and 2.14 mg/kg, oil palm fruit = 4.53 and 3.24 - 3.70 mg/kg, cocoa = 2.42 and 2.46 mg/kg (farm only)

The sorption of arsenate ions in the soil by iron and aluminium components, greatly restricts the availability of arsenic to plants (14). There is great variability in the arsenic content of plants. A National Academy of Sciences (N.A.S) study in Washington D.C. (3) showed that the arsenic content of plants grown on soils that had never been treated with arsenic containing pesticides varied from 0.01 to 5.0 mg /kg dry weight. Plants grown on arsenic - contaminated soils may, however, contain considerably higher levels, especially in the roots (14). In the light of the above the total arsenic levels obtained for oil palm fruit and cocoa are well within the normal expected for plants growing on untreated soils. This therefore helps to dispel any fear of arsenic poisoning resulting from the eating of oil palm fruit and cocoa-derived products from these crops cultivated in and around Kumasi or sold on the open market in Kumasi.

According to Griffin et al., the content of arsenic in tobacco grown on untreated soils is usually below 3.0 mg/kg dry weight (41). The arsenic content of tobacco quoted above are all well below 3.0 mg/kg. Snuffing or smoking 10g of Kumasi grown tobacco is equivalent to inhaling between 21.4 and 24.0 mg of arsenic into the lungs. Small as these values may seem there is the threat of arsenic poisoning through using this tobacco because

studies in rats on the elimination of arsenic via the lungs seem to indicate that little, if any, of arsenic is eliminated by this route (68). Secondly another study using chickens also indicated a very low elimination of arsenic ^{74}As through the lungs, following exposure to ^{74}As-arsenate (69).

8.5 VEGETATION - KUMASI

The two types of vegetation analysed are star grass (Eleusine indica) and elephant grass (Paniacum maximum) which are grazing leaves. For all the locations, the elephant grass showed lesser arsenic concentration than the star grass (Table 6). The results also show lesser values of arsenic in the two grasses from the residential area (UST) than at the industrial Ahinsan and airport areas. According to Porter and Peterson (16) some grasses growing on soils containing high levels of arsenic contain elevated arsenic concentrations above 5 mg/kg for untreated soil plants (3). Apart from elephant grass from Ahinsan (4.60 mg/kg) and UST (4.40 mg/kg), all the samples analysed showed values above 5.0 mg/kg dry weight, an indication that these grass samples may be arsenic-polluted and grazing animals feeding on them may be in danger of arsenic poisoning.

8.6. FOOD CROPS - OBUASI MARKET

There are two major markets in Obuasi: Obuasi central market and Tutuka market situated at the centre and east respectively. Available samples of food crops, cash crops and meat were purchased from these markets randomly and analysed for arsenic. The total arsenic concentrations for the various food crop samples is shown in Table 7.

Apart from plantain from Tutuka market with arsenic concentrations of 1.14 mg/kg wet weight, all samples analysed showed arsenic levels below 1.0 mg/kg. For Tutuka market the highest arsenic concentration was found in plantain (1.14 mg/kg) whilst pear showed the least value of 0.43 mg/kg wet weight. From the Obuasi central market while plantain with 0.65 mg/kg was highest, pepper with 0.12 mg/kg was the lowest arsenic level obtained. The high arsenic level found in plantain could be explained on the basis of the fact that plantain is known to contain a lot of iron which has a high affinity for arsenic (66) and hence concentrates the arsenic.

On the basis of the results obtained for the market samples it can be concluded that these food crops sold on the market Obuasi do not pose any toxicity problems.

Comparison of the results for the two markets shows higher arsenic levels for samples from Tutuka than the Obuasi central market. This observation can be explained by noting that food crops in Tutuka market come mostly from villages to the north and east of P.T.P. (the gold treatment plant) where the effect of the arsenic-laden smoke from P.T.P. are most felt due to foliar uptake of arsenic as it falls on the plants (19). The central market receives food crops mostly from the food producing villages to the west of Obuasi scattered along the Dunkwa - Kumasi lorry road, where the effect of the smoke from the gold mining activities is not very significant.

8.6.2 FOOD CROPS - OBUASI FARMS

About 84 samples from various locations within the Obuasi municipality and surrounding villages were analysed and the results are shown in Table 8. Sampling was done on the basis of which food crops were available at particular locations. Secondly sampling was done so as to cover as much as possible all geographical directions in relation to the treatment plant at P.T.P. This led to sampling sites such as the following (see attached maps).

(a) Nantrin - 6.4 km north of P.T.P.
(b) Akaporiso, Pomposo, Kwabena Kwakrom - about 3.2, 4.8, and 7.2 km respectively to the east of P.T.P.
(c) P.T.P. Estate, Kwabrafoso, Tutuka - predominantly residential areas in the immediate vicinity and to the east of P.T.P.
(d) Boete (1.6 km), Kwameduokrom (3.2 km), Aboagye-krom (2.4 km) - to the south-east of P.T.P.
(e) Akrofuom - about 16 km south of P.T.P.
(f) Nhieso - about 4.8 km to south-west of P.T.P.
(g) Bidieso (2 km), Bongobri (2.5 km) - residential areas to the west of P.T.P.
(h) Kyekyewere (about 4 km along the Kumasi-Obuasi lorry road), Mmiriwa (about 5.0 km) to the north-west of P.T.P.

From the mean or average arsenic concentrations calculated for each sample it is observed that plantian shows the highest value of 1.13 mg/kg wet weight and cocoyam leaves with 0.30 mg/kg wet weight as the least. Plantain taken from a backyard garden in P.T.P. Estate (adjacent to the Pompora Pump House) about 500 metres from P.T.P contained the highest arsenic concentration 1.86 mg/kg. This can be accounted for with the reason that maximum fall out of smelter discharge, which is in the form of plume occurs in nearby settlements such as P.T.P. Foliar uptake as well as uptake of soil arsenic through the roots account for the elevated arsenic contents of the plantain samples from these

locations. The arsenic is then concentrated in the plantain fruit which contains a lot of iron with a high affinity for arsenic.

The results obtained for samples analysed from the three towns Akaporiso, Pomposo, and Kwabenaakwakrom in the east of P.T.P - the prevalent wind direction to which the arsenic-laden smoke is blown, show that the arsenic concentration decreases with distance away from the treatment plant. This is due to the fact that the volume of smoke taken along by the wind decreases with distance away from the source of emission because of deposition and wind scattering.

Cassava, plantain and cocoyam from Kwamedoukrom show arsenic levels beyond 1.0 mg/kg probably because it is located to the south east of P.T.P. and experiences maximum dustfall of P.T.P. smoke. On the other hand only uptake of soil arsenic can be used to account for the arsenic levels in these samples at Akrofuom as the result of the soil analysis for Akrofuom (Site C in Table 12) shows.

The arsenic concentrations obtained for the samples for Nhieso are either the lowest (viz pear, beans cassava) or next to the lowest (viz plantain, orange). Similar observations were made for cocoyam and cocoyam leaves from Mmiriwa which is far beyond the hills in the north-western direction from P.T.P.

These observations result from the fact that the smoke from the P.T.P. chimney is not blown very much to these areas so as to cause excessive arsenic contamination.

With reference to the average arsenic concentrations for each sample, it can be deduced that food crops from Obuasi and surrounding villages are not arsenic-contaminated beyond what is normally encountered in food crops.

8.7 COOKED FOOD - OBUASI HOMES

The cooked food samples were obtained from private homes in Wawasi, Kwabrafoso and Tutuka. Results of the analysis as presented in Table 9 again show that cooked food items in Obuasi contain arsenic. Though the sources of these food items are unknown and since cooking which involves high temperatures may lead to the vapourisation and leaching of some arsenic, the levels of arsenic contents are a good indication of the extent to which food crops in the Obuasi area are arsenic - contamimated. Moreover, the presence of arsenic in these cooked food items (cassava, plantain, and fufu) - the major food items in the meal of Obuasi residents, shows that they are ingesting considerable quantities of arsenic in their daily meals - a health hazard.

8.8 CASH CROPS - OBUASI FARMS AND MARKET

Tobacco from Obuasi central market (Table 7) analysed for arsenic showed a concentration of 2.34 mg/kg dry weight - a value below the 3.0 mg/kg limit (41). This is probably due to the fact that there are no tobacco farms in the Obuasi area and those on the market have been brought in from other parts of the country.

Cocoa obtained from the Obuasi Cocobod Depot showed an average arsenic content of 2.23 mg/kg (Table 10). This value is far below the 5.0 mg/kg generally accepted as the normal value for plants grown on soils untreated with arsenic (2). Because of the constant befouling of the atmosphere by the smoke from P.T.P. former cocoa farms have now ceased to exist because of short lives of the cocoa trees and the long time they took to bear fruit.

Hence cocoa beans obtained for analysis are not representative of the sampling area, but locations beyond, which also fall under Obuasi district. The above quoted arsenic content for cocoa shows, however, that it is quite safe for consumption and export without danger of arsenic poisoning.

All the oil palm fruit samples analysed from the various locations show arsenic levels far below 5.0 mg/kg weight) (Table 10). The only exceptions come from Mantrin (5.87 mg/kg dry weight) and Tutuka (5.71 mg/kg dry weight) market. The very low levels of arsenic in the other samples led to the conclusion that on the whole oil palm fruit from farms around Obuasi are safe for human consumption and possible export so far as arsenic contamination is concerned.

8.9 FISH AND MEAT - OBUASI

Local fish (Tilapia) was obtained from an artificial fresh water lake created by the Ashanti Gold fields Corporation as a result of building a dam across the streams issuing from the hills towards the north of P.T.P. Analysis showed that it contained 2.60 mg/kg wet weight. Comparing this to 2.0 ppm quoted earlier (48) it can be adduced that this local fish is not too arsenic contaminated beyond that fit for human consumption.

Mutton was obtained from the Obuasi central market and analysed for arsenic to 3.48 mg/kg. Since the source of the goat (i.e. its breeding place) is unknown it cannot be concluded that the value of arsenic is due to the gold mining activity in Obuasi, but rather due to the grazing leaves and other feed on which the goat might have been fed.

8.10 VEGETATION - OBUASI

The sites for samples of the grazing vegetation (which are concentrated in the north, east, south-east and southern directions from P.T.P) were chosen with the following reasons in mind:

(i) To assess the extent of pollution of the environment through the arsenic-laden smoke from the treatment plant.

(ii) To determine whether residual arsenic from the P.T.P treatment plant and the slime dams flowing into the Kwabrafo stream was taken up by grasses growing just at the edge of the streams.

(iii) To monitor the levels of arsenic in the grasses along the stream with distance as far as possible.

(iv) Availability of the grasses growing in these areas to the grazing animals in order to assess their safety.

8.10.1 STAR GRASS (Eleusine indica)

The arsenic content of the samples analysed are shown in Table 11. The highest value was found at site B opposite slime dam number 3 and situated about 450 m from the P.T.P. treatment plant (39.30 mg/kg).

This particular location is the meeting point of different sources of arsenic-carrying water, viz the effluent from the ore treatment plant, water issuing from slime dams numbers 3 and 4, the Kwabrafo stream flowing from the hills towards the north-east, and the fresh water dam overflow taking its source from the polluted hills to the north of P.T.P. The arsenic content of all these sources are added up at Site B hence contributing to the increased arsenic concentration available to the grass growing at the edge of the stream at this point. Grass at site C (Pompora Pump House) registered the next higher arsenic content. This observation can be explained by the fact that the location is just about 200m down-stream from site B along the Kwabrafo stream. This means that some of the arsenic has been deposited along the stream bed hence the lower concentration available to the grass at this point (12.41 mg/kg). The grass sample beside the fresh water lake showed 10.17 mg/kg of arsenic and is the third highest.

Water supply for the lake comes from the hills to the north of P.T.P. which have been polluted over the years with arsenic, hence so much is available to the grass growing at the edge of the lake. From Table 12 it can be observed that sites A, B, C show arsenic in concentrations far above the 2 ppm expected in normal untreated soil (48) and 0.05 - 1 ppm for protection of aquatic life (49) - contributing to the high arsenic concentrations

registered by grass at these sites. Moreover the above three sites lie within 1 km radius of the treatment plant at P.T.P. towards the north and east directions. As noted earlier, areas in this vicinity receive the maximum of dustfall from the smoke emitted from the P.T.P. chimney because they lie in the prevalent wind direction. Therefore grass in these areas receive arsenic from the soil, water and the arsenic-laden smoke leading to their arsenic contents being above 5.0 mg/kg expected in grasses (16).

Site D is located further downstream along the Kwabrafo stream, and the 3.75 mg/kg arsenic concentration registered for grass at this point reflects the fact that with distance, the arsenic available to the grass at the banks decreases because of deposition on the stream bed.

Grass taken beside the Kwabrafo stream flowing between slime dams numbers 5 and 8 show arsenic value of 5.99 mg/kg. This value is due to the fact that remnant arsenic carried along by the stream from earlier pollution together with that added to it from adjoining slime dams are to some extent available to the grass at site E.

At Site F (Gyimi River Pump House) the lower arsenic content of the grass (5.65 mg/kg) is not too greater than 5.0 because the Gyimi river along which the sample was collected is not contaminated by arsenic from the ore treatment plant at P.T.P. The least value of 2.23 mg/kg found in grass growing beside the Kwabrafo stream at Akrofuom further south shows that the majority of the arsenic in the stream due to the discharge of P.T.P effluent has been deposited on the stream bed.

Once more, evidence from the soil and water arsenic concentrations (Table 12) confirm the fact that the farther away from P.T.P. a site is, the lower the arsenic concentration in soil, water , and vegetation.

8.10.2 ELEPHANT GRASS

Arsenic concentration in elephant grass samples are generally lower than those found in the star grass (Table 11). For Kwabrafoso and Tutuka - residential areas in the prevalent wind direction from P.T.P. the arsenic contents are 5.10 and 5.50 mg/kg respectively. The least value was detected in the sample taken from Akrofuom which is very far removed from P.T.P. and hence not affected by polluted smoke from the chimney.

From the above analytical results, it can be safely concluded that these two grazing vegetation in Obuasi, north and east of P.T.P. are not fit for consumption by grazing animals. Animals

which feed on them (even if these were their only sources of feeding) are liable to serious arsenic pollution because of the high arsenic levels obtained in these samples.

8.10.3 FERN

The fern plants growing along the lorry road running from P.T.P/Estate to the Fresh Water Dam were analysed for arsenic, and the results shown in Table 11. It can be observed that arsenic content decreases with distance as one moves away from P.T.P. towards the Fresh Water Dam i.e. from B, K and J to A. The arsenic level in the fern at site C is also comparably high.

From preliminary analyses of soil and water for sites A, B and C (Table 12) it can be concluded that those elevated arsenic concentrations found in the fern samples are due primarily to arsenic received from the smoke coming from the treatment plant which falls in these areas. Secondly because of deposition and wind scattering, the arsenic available to the vegetation through the smoke decreases with distance away from the source P.T.P.

8.11 PLANTAIN AND CASSAVA PEELS, COCOYAM LEAVES

According to a study by Woolson and Pyles (70) into the arsenic content of vegetables grown on arsenic - treated soils, the peels of root crops such as potatoes, beets, carrots, and turnips contain much higher residues than do the flesh. On the contrary, for all cassava samples analysed in this study, the arsenic contents obtained for the cassava peels are lower than those obtained for the cassava flesh.

Also the arsenic contents of plantain flesh showed higher values than the peels as expected, due to the presence of iron, which is known to concentrate arsenic.

All cocoyam samples analysed also showed higher arsenic contents than the cocoyam leaves.

In Kumasi average arsenic concentrations of 0.23, 0.18 and 0.12 mg/kg wet weight were obtained for cassava peel, plantain peel and cocoyam leaves respectively

For Obuasi values of 0.59, 0.53 and 0.30 mg/kg wet weight were obtained for cassava peel, plantain peel and cocoyam leaves respectively for the farm samples whilst the market samples showed 0.34, 0.43 and 0.36 mg/kg respectively.

8.12 SOIL AND WATER

For a meaningful evaluation ofthe concentrations found in the samples analysed it is important to have an idea of the arsenic content of the soils and waters in the areas under investigation. As this was not available, preliminary experiments were designed to provide the necessary data. The results are presented in Table 12.

The arsenic contents of the soil samples from sites A to G ranges between 5.40 and 29.60 mg/kg dry weight. For all the locations the arsenic concentration is above the 2-5 ppm range expected in normal uncontaminated soil (48). Such high values can only be attributed to the constant befouling of the Obuasi environment by the smoke emitted from the gold treatment plant since no pesticides or weedicides are used in the sites indicated for farming purposes. This is evidenced by the fact that the lowest value was obtained for soil at site F (beside the Gyimi river) where there is no arsenic contamination by water from the treatment plant. Secondly the arsenic content decreased with distance away from the treatment plant at P.T.P.

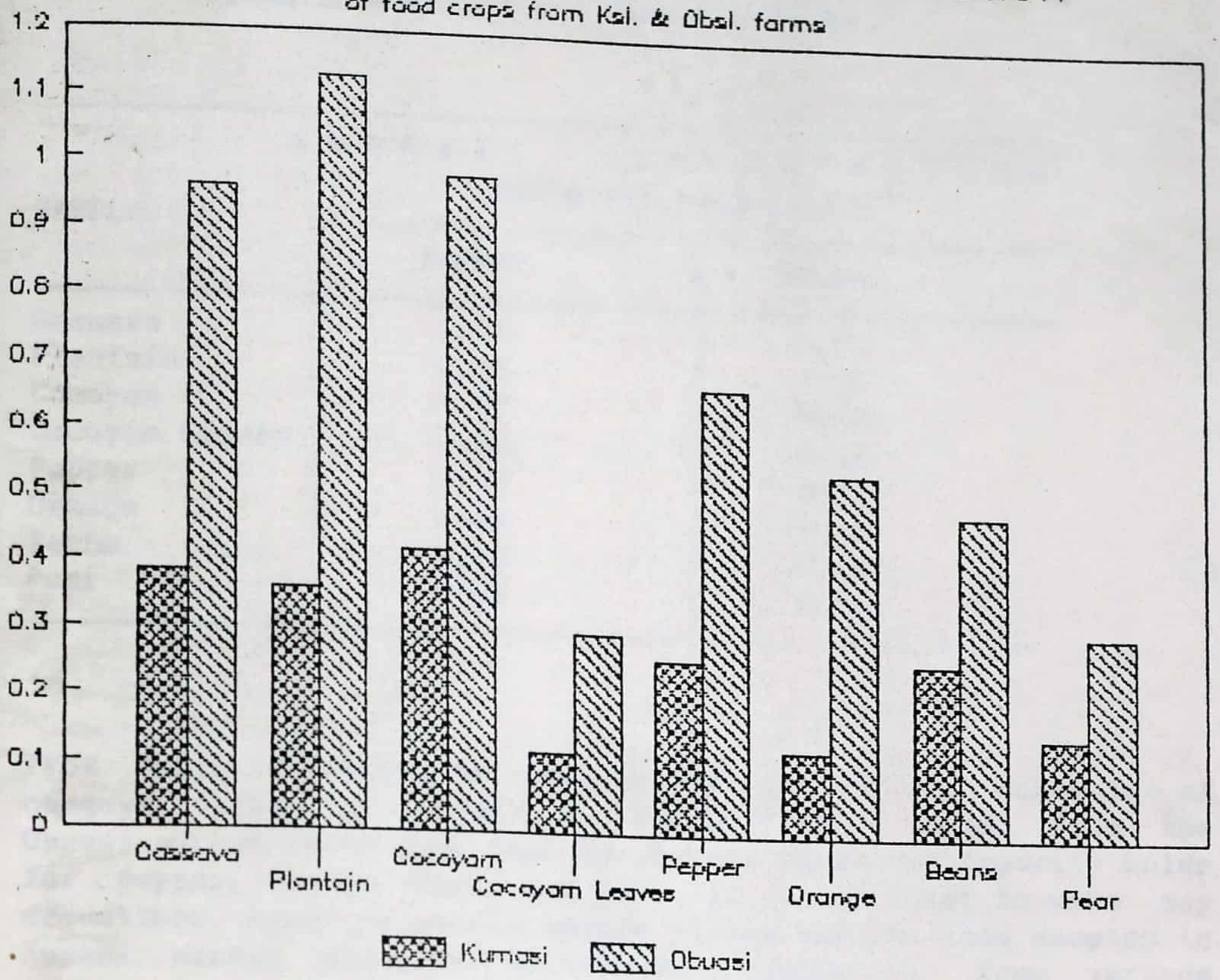
Water sample were taken from the Kwabrafo stream (A,B,C,D,E and G) and the Gyimi river (Site F). A range of 3.50-10.40 ppm was obtained for the Kwabrafo stream and a value of 2.80 ppm for the Gyimi river. Comparing these values to the WHO International Standard for drinking water (0.50 ppm) and water for agricultural purposes and production of aquatic life (1.0 ppm) (49), it can be concluded that the Kwabrafo stream is highly arsenic contaminated (by the P.T.P effluent being discharged into it). This has therefore rendered the water unfit for drinking, irrigation as well as for use in the livestock industry.

8.13 COMPARISON OF ARSENIC LEVELS - KUMASI AND OBUASI

Because of the large number of samples and the variety, it is difficult to do any meaningful comparison with the individual arsenic levels. Hence a mean or average value is calculated for each sample from the sampling sites at Kumasi and these are compared with the values obtained from Obuase for each food crop. However, in the case of the cash crops, individual values are compared because of the smaller number of samples; the same method was used to compare the arsenic levels in fish, meat and vegetation.

Comparison of mean As. Concentration

of food crops from Kai. & Obai. farms



Comparison of mean As. Concentration

in food crops from Kumasi & Obuasi Markets

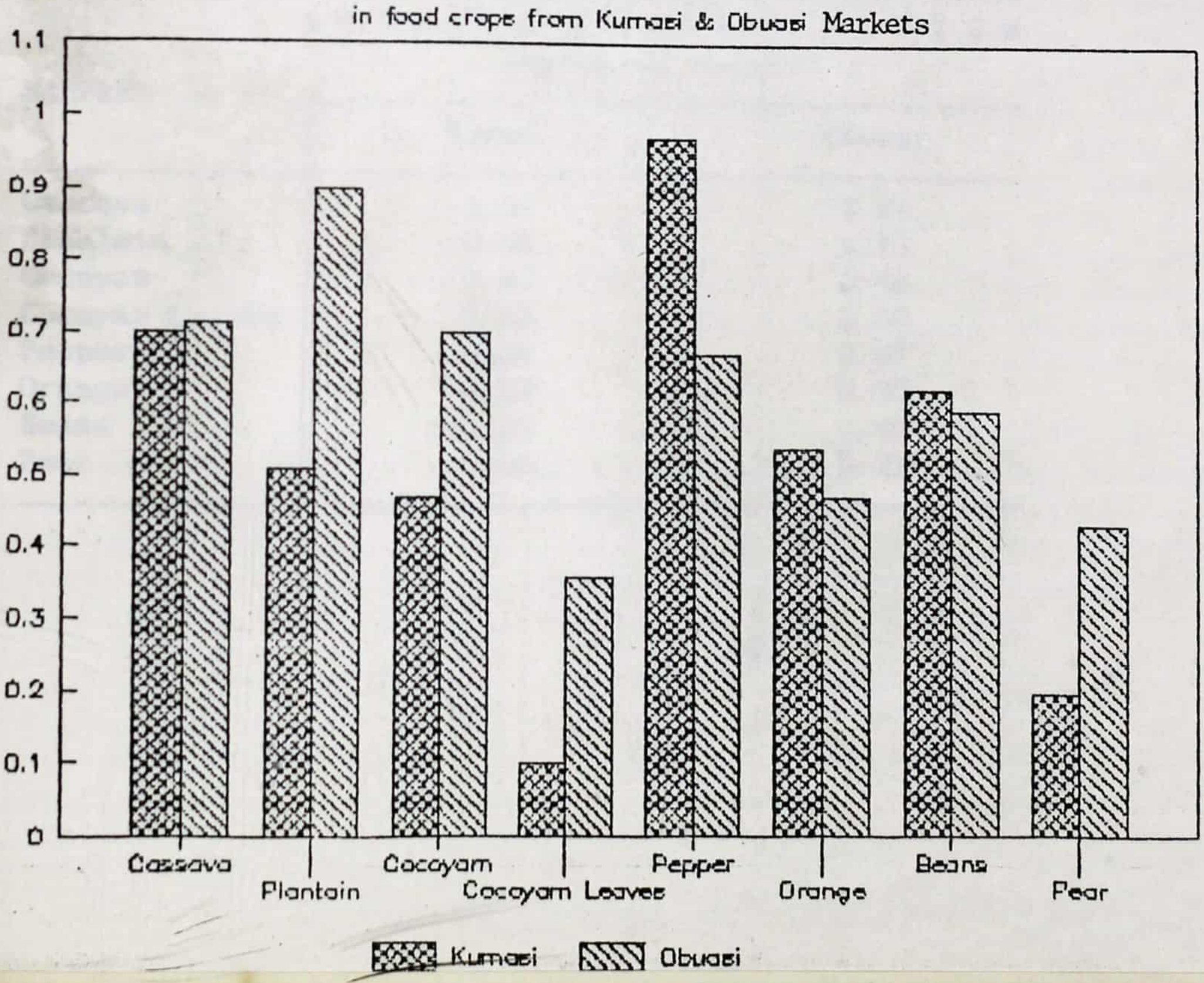


Table 13 Comparison of mean arsenic contents of food crops from Kumasi and Obuasi markets

SAMPLE	ARSENIC CONCENTRATION (mg/kg wet weight)	
	Kumasi	Obuasi
Cassava	0.70	0.71
Plantain	0.51	0.90
Cocoyam	0.47	0.70
Cocoyam Leaves	0.10	0.36
Pepper	0.97	0.67
Orange	0.54	0.47
Beans	0.62	0.59
Pear	0.20	0.43

From Table 13 it can be observed that the arsenic contents of cassava, plantain, cocoyam and cocoyam leaves bought from the Obuasi market are higher than for Kumasi while the opposite holds for pepper, orange, beans and pear. It is difficult to make any deductions based on market sample values because food samples in Kumasi market are known to have been brought in from various parts of the country (including Obuasi) where environmental conditions vary and affect the arsenic content also variedly.

Table 14 Comparison of mean arsenic contents of food crops from Kumasi and Obuasi farms

SAMPLE	ARSENIC CONCENTRATION (mg/kg wet weight)	
	Kumasi	Obuasi
Cassava	0.38	0.96
Plantain	0.36	1.13
Cocoyam	0.42	0.98
Cocoyam Leaves	0.12	0.30
Pepper	0.26	0.67
Orange	0.13	0.55
Beans	0.26	0.49
Pear	0.15	0.31

From Table 14 shown above, it can be observed that for all the food crops, the arsenic content of the Obuasi sample is more than double the concentration determined in the sample from Kumasi farms. As noted earlier, the arsenic released into the Obuasi atmosphere from P.T.P. settles on vegetation and soil hence increasing the arsenic available to these food crops from Obuasi as evidenced from the analysis. The bigger size of Kumasi compared to Obuasi as well as the absence of such arsenic producing industry like that existing at Obuasi account for the lower values obtained from the Kumasi farms.

8.13.1 COOKED FOODS - KUMASI AND OBUASI HOMES

Tables 4 and 9 show the actual and average arsenic levels in the cooked samples for both Kumasi and Obuasi respectivley. From both the raw values as well as the average values , cooked cassava and fufu show arsenic concentrations below 2.0 mg/kg at Kumasi while the corresponding values for Obuasi are above this value. On the other hand, the total arsenic content of cooked plantain from Kumasi and Obuasi are comparable (3.03 and 3.39 mg/kg respectively) though that for Obuasi is still higher. In the absence of any gold mining activity in Kumasi, it is reasonable to attribute the higher content of arsenic in these food items from Obuasi to the mining activity which is releasing tons of arsenic-laden smoke into the Obuasi environment.

8.13.2 CASH CROPS FROM KUMASI AND OBUASI FARMS

From Tables 5 and 10 calculated average arsenic content of oil palm fruit for Kumasi and Obuasi are 3.50 and 3.03 mg/kg respectively. For locations such as Nantrin and Akaporiso, which lie in the prevalent wind direction from P.T.P at Obuasi and experience maximum fallout of chimney smoke, the arsenic levels in the oil palm fruits are far higher (5.87 and 4.63 mg/kg) than those from Kumasi (3.70, 3.56, 3.24 mg/kg) whereas arsenic levels in sites at Obuasi where effect of arsenic smoke are insignificant, (viz Pomposo, Kwabenakwakom, Kwameduokrom and Nhieso) are lower than the Kumasi values. The higher average value for Kumasi could be due to the less number of samples analysed.

Cocoa shows an average of 2.44 mg/kg for Kumasi and 2.23 mg/kg for Obuasi, while tobacco from Obuasi market, 2.34 mg/kg, (Table 7) compares favourably with 2.40/kg from Kumasi market (Table 2). Though the values for Kumasi are higher than those for Obuasi, there is no significant difference in arsenic concentrations.

8.13.3 GRAZING VEGETATION - KUMASI AND OBUASI

So far as grazing vegetation are concerned Tables 6 and 11 reveal that for both star grass and elephant grass, the samples from Obuasi gave considerably higher arsenic concentrations than Kumasi (especially at locations not far removed from P.T.P (A, B, C, H and I). This observa-tion is invariably due to the rich supply of arsenic received by these Obuasi samples from the surrounding environment (soil, water and air) as a result of the mining activity there.

8.13.4 FISH AND MEAT - KUMASI AND OBUASI

While local fish from Kumasi market shows an arsenic concentration of 3.30 mg/kg, that from the artificial fresh water lake in Obuasi contained 2.60 mg/kg (Tables 2 and 7). It is difficult to make any meaningful comparison and deduction from these values because the source of the fish sold on the Kumasi market and the sources of arsenic available to it are unknown.

Mutton shows arsenic concentrations of 2.59 and 3.48 mg/kg for Kumasi and Obuasi respectively (Tables 2 and 7). The higher value for Obuasi can be attributed to the feeding sources of the grazing animals. As far as the comparison of grazing vegetation (sec. 8.12.6) reveals, coupled with the fact that arsenic content of cassava peel and plantain peel from Obuase are higher than from Kumasi (Tables 3 and 8), it can be concluded that the higher value for meat from Obuasi is due to the higher arsenic content of the sources of food for the animals.

8.14 COMPARISON OF ARSENIC CONTENT OF SOME SAMPLES WITH THOSE OBTAINED BY S. K. AMASA IN A PREVIOUS STUDY IN 1975

In Table 15 below is presented a summary of some of the results from S.K. Amasa's study (Appendix 3) and the present study for comparison.

Table 15: SUMMARIZED ARSENIC LEVELS FOR 1975 AND 1989 FOR SIMILAR SAMPLES

SAMPLE DESCRIPTION	ARSENIC CONCENTRATION (PPM)			
	Amasa's Study (1975)	Present Study (1989)		
		VALUE	SD	VC
Cocoyam leaves (Obuasi)	4.80	1.15	0.85	46%
Cassava, 500m from Chimney	0.65	N.A.	-	-
Orange (Obuasi)	2.29	1.69	0.06	11%
Cassava (Obuasi) Market	2.65	1.10	-	-
Cassava (Obuasi Farm)	1.83	1.73	0.26	27%
Cocoyam (150m from mine)	1.89	N.A.	-	-
Plantain (Obuasi Market)	0.615	1.90	0.34	30%
Obuasi-Kwabrafoso Dam River	2.25	4.40	-	-

N.A = Samples are no more available at these sites.
SD = Standard deviation VC = Variation of coefficients

From Table 15 it can be observed that for all the food crops except plantain, arsenic levels are lower than the 1975 results. This is due to the fact that food crops are harvested after they have matured. However, for the Kwabrafaoso dam water, the results show accumulation of arsenic over the years due to the continuous discharge of residual arsenic from P.T.P into the Kwabrafo stream.

CONCLUSION

From the above discussion the following conclusions can be drawn:

Food and cash crops from Kumasi and Obuasi are arsenic contamimated but the arsenic levels are not beyond what is expected for those plants grown on soils not treated with arsenic-containing compounds. These food items are therefore safe for human consumption without encountering toxicity problems.

Grazing vegetation (i.e. star grass and elelphant grass) analysed showed arsenic concentrations beyond what is expected for Kumasi. In Obuasi, elevated levels were found in locations within 400-600 metres of the gold treatment plant, and the concentration decreased with distance away from P.T.P. It can therefore be concluded that these vegetation are unfit for grazing animals. Ferns analysed showed unusually high arsenic contents, an indication that the smoke from P.T.P is polluting the environment.

Evidence from the soil and water analyses coupled with that from the vegetation leads to the conclusion that the Obuasi environment is polluted with arsenic, ostensibly due to the effect of mining activities in the town.

Moreover, the comparison with work done in 1975 by S.K. Amasa as presented in section 8.14 shows that the Kwabrafo stream into which residual arsenic from P.T.P is discharged is arsenic polluted.

Though similar trends are observed for arsenic contents of the various samples using the Gutzeit - Molybdenum Blue Method i.e. the colorimetric technique, the A.A.S technique is a better method for arsenic analysis in the samples analysed in this study.

RECOMMENDATIONS

In the light of the above conclusions, the following recommendations are made:

1. The Ashanti Goldfields Corporation (A.G.C.), the mining company at Obuasi should set up an Environmental Impact Assessment Unit, a sort of Environmental Directorate within the Corporation which will be charged with constant monitoring of the extent of pollution of the Obuasi environment.

2. The Company, as a matter of urgency should adopt one of the many recycling processes available to recycle or clean the flue dust with the aim of reducing, if not completely eliminating, its arsenic content before discharging it into the atmosphere.

3. Programmes to continuously monitor the arsenic levels in the finger nails of Obuasi residents should be instituted with the view to assess the extent of human poisoning in the area.

4. The type of study presented in this thesis should be extended to other mining and industrial communities in the country.

5. The Environmental Protection Council should establish maximum permissible levels or standards for various environmental pollutants for all industrial areas in the country.

6. The Kwabrafo Stream in Obuasi should be desilted to reduce arsenic pollution of other water sources.

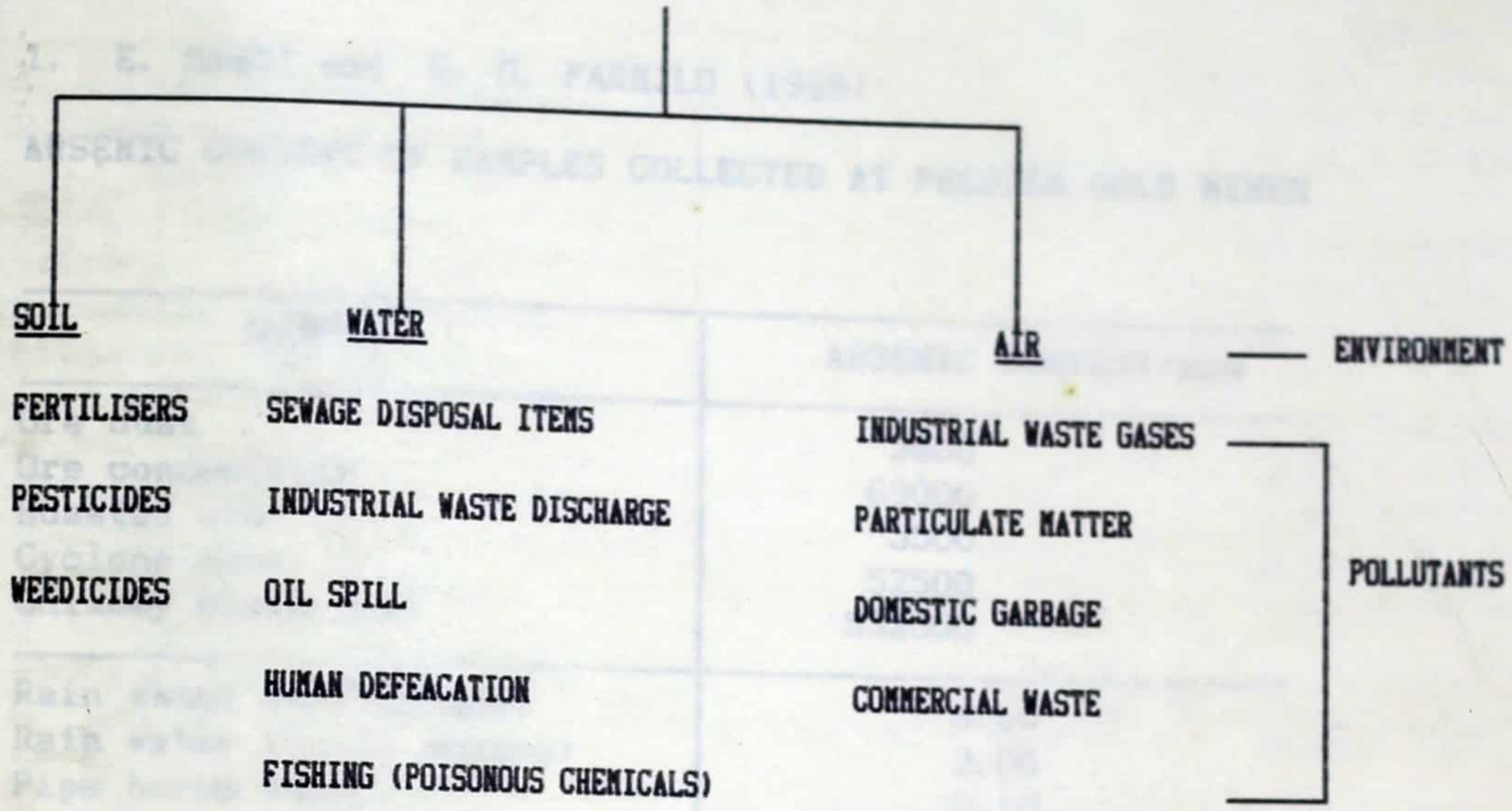
APPENDIX 1

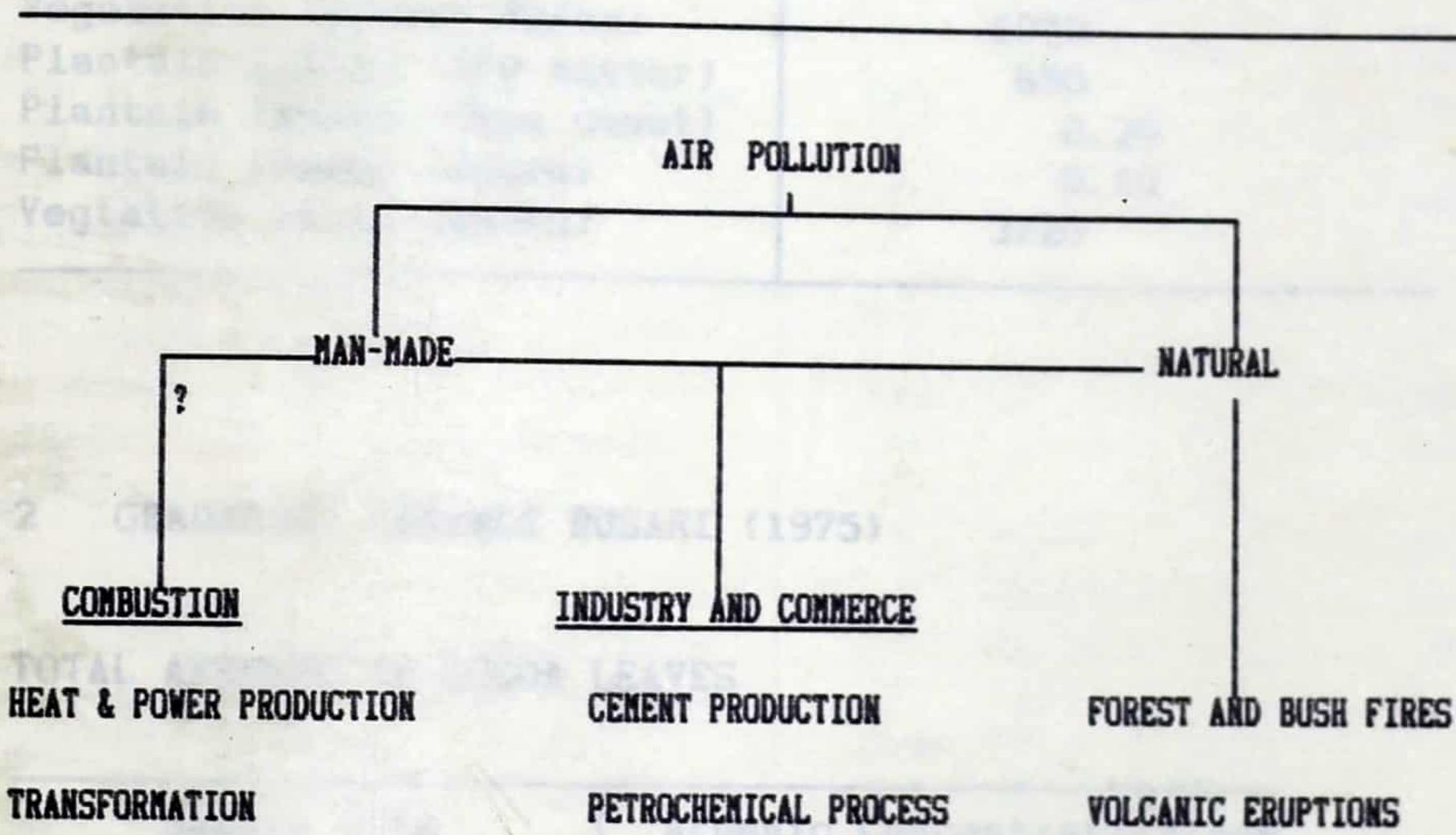
ENVIRONMENTAL PROTECTION COUNCIL - GHANA
PROPOSED AMBIENT AIR QUALITY STANDARDS

POLLUTANT	EFFECTIVE AREA	MAXIMUM PERMISSIBLE LEVEL	AVERAGE TIME
Total suspended Particulates	Residential	260 $\mu g/m^3$	24 hours
	Industrial	290 $\mu g/m^3$	24 hours
Respirable	Residential	150 $\mu g/m^3$	24 hours
Non-Toxic dust		260 $\mu g/m^3$	24 hours
Total Nuisance	Work and	10 mg/m^3	
Dust	Public places	10 mg/m^3	8 hours
Dust fall	Residential	8 tonnes/km^2	1 month
	Industrial	10 tonnes/km^2	1 month
Sulphur Dioxide	Residential	250 mg/m^3	24 hours
	Industrial	300 mg/m^3	24 hours
Total Flourides	All Areas	10 mg/m^3	
Asbestos	All Areas	2 fibre/cm^3	8 hours

APPENDIX 2

POLLUTION CHARTS





APPENDIX 3

PREVIOUS WORK ON ARSENIC POLLUTION

1. E. SANDI and G. G. FARMILO (1969)

ARSENIC CONTENT OF SAMPLES COLLECTED AT PRESTEA GOLD MINES

SAMPLE	ARSENIC CONTENT/ppm
Ore dust	3600
Ore concentrate	69000
Roasted ore	5500
Cyclone dust	52500
Chimney stack dust	532000
Rain water (dry season)	6.60
Rain water (rainy season)	3.00
Pipe borne water	0.10
Well water	0.10
Vegetation (mostly ferns)	6000
Plantain leaves (dry matter)	650
Plantain leaves (Cape coast)	0.20
Plantain leaves (Accra)	0.10
Vegtation (fine leaves)	3720

2 GBADAMOSI LAKUNLE BUSARI (1975)

TOTAL ARSENIC IN COCOA LEAVES

Sample site	Arsenic Concentration/ppm
Dakabuoso	5.7
Adaitu	4.5
Konongo Gold mines	11.3
Pentebuom	7.8

3 S.K. Amasa (1975)

ARSENIC CONTENT IN FOOD ITEMS, WATER, VEGETATION, SOIL AND MINE MATERIALS FROM OBUASI GOLD MINES AND SURROUNDING COUNTRYSIDE

SAMPLE DESCRIPTION	METHOD	ARSENIC CONTENT (BY WEIGHT) [%]	[ppm]
1. Cocoyam leaves (Obuasi)	Col		4.80 ± 0.22
2. Cassava 500 yd from Chimney	"		0.61 ± 0.035
3. Sugar cane (Obuasi)	"		14.75 ± 0.035
4. Orange (Obuasi)	"		2.29 ± 1.10
5. Cassava (Obuasi Market)	"		2.65 ± 0.09
6. Cassava (Obuasi farm, 4 miles from mine)			1.83 ± 0.06
7. Cocoyam 150 yd from mine	"		1.89 ± 0.07
8. Plantain (Obuasi market)	"		0.61 ± 0.50
9. Obuasi-Kwabrafoso dam water	"		2.25 ± 0.08
10. Obukasi-Kwabrafoso drinking water			1.40 ± 0.05
11. Fern (Pteris Vitatae) 100 yd from Chimney	Vol	0.47 ± 0.10	4700 ± 110
12. Fern(Pteris Vitatae) 150 yd from chimney	"	0.125	1252 ± 113
13. Fern (Pteris Vitatae) 220 yd from Chimney	"	0.110	1100 ± 100
14. Grass 200 yd from chimney	Col		14.14 ± 1.50
15. Bahama grass 150 yd from chimney	"		20.90 ± 0.50
16. Bahama grass 250 yd from chimney	"		11.60 ± 0.25
17. Palm tree 150 yd from chimney	Vol		2875 ± 25
18. Soil 30 yd from chimney	"		147 ± 2.5
19. Soil 2.5 miles from Chimney	"		67.2 ± 1.8
20. Soil 1.5 miles from chimney	"	21.10 ± 0.87	96.5 ± 1.7
21. Soil 5 miles from chimney	"	21.80 ± 0.25	19.45
22. Soil 9 miles from chimney	"	17.6 ± 1.12	11.15 ± 0.32
23. Chimney dust (Obuasi)	Grav	17.5 ± 0.59	
24. Ore concentrate(Obuasi)	Vol	15.5 ± 0.41	
25. Ore dust (Obuasi)	Grav	14.4 ± 0.35	

Col = colorimetric Vol = volumetric Grav = gravimetric

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MAP OF KUMASI INDICATING SAMPLING SITES OF ENVIRONMENTAL MONITORING

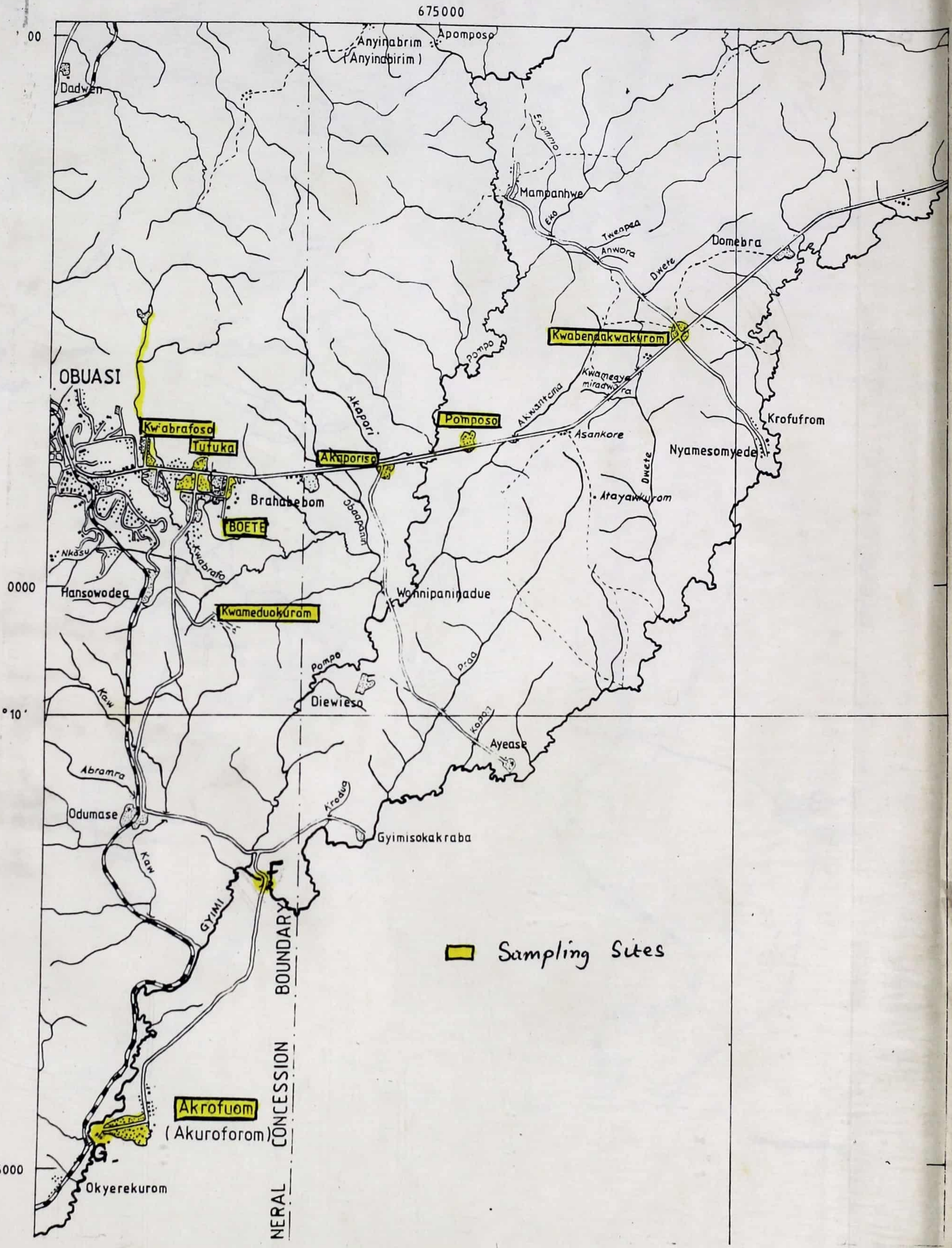
— SAMPLING SITE

TO OFFINSO
TO TAMALE
Pankronu
Boachire
Breman
Esuoja
Mpatasie
Makro
Tafo
Buokrom
Abrepo
Tarkwa
CEMETERY
Apraprem
Bohen
Ampabami
Kokoso
WESLEY COLLEGE
New Tafo
Sipe Wusuansa
AIR PORT
STATE SCHOOL
MENHYIA EXT
Sipe Tinpom
Asokori Mampong
Abasi
Prempe College
North Suntreso
Mbrom
Kontomponaferi
Kejetia
Menhia
Bantama
Asawasi
Adukrom
Abaakwa
Tanoso
CENTRAL HOSPITAL
Nsenie
Kwadaso
South Suntreso
South Zongo
Aboabo
Akrom
TO ACCRA
Asuabua
N.I.E.R.
Kantinkronu
Ehwemasi
Oforikrom
Aketego
Ayija
Benimasi
Anwuma
POLICE DEPOT
Ridge
New Asafo
Sisaso
Bomso
Old Amakom
Dadiesoaba
Patasi
Residency
Asukwa Res. Area
SISA
UNIVERSITY OF SCIENCE & TECHNOLOGY
Ayeduasi
Opoku Ware
KUMASI FIREWOOD PLANT RESERVE
Fanchinibra
Adiebeba
Ahinsan
KBL
Kotei
Adiembra
Ahojo
Asukwa Industrial Area
SLAUGHTER HOUSE
Jinyasi
Santasi
Atasomansokuma
TO BEKWAI
Kasi
Agogo
Atasomanso
Atonsu
Chirapatre
N
0 1/5 2/5 3/5 4/5 1 Mile

A. G. C. (GHANA) LTD.

GYIMI — POMPO RIVER CATCHMENT AREA

SCALE 1 : 50000



MAP OF OBUASI GOLD MINE SHOWING SAMPLING SITES