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DETERMINATION OF ARSENIC IN WATER, SEDIMENTS AND FISH IN SOME RIVERS
AT KONONGO AND ITS SURROUNDING TOWNS AND VILLAGES
BY NEUTRON ACTIVATION ANALYSIS

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BY
MARY ASSIAMAH, BSC (HONS) CHEMISTRY, U.S.T.

DETERMINATION OF ARSENIC IN WATER, SEDIMENTS AND FISH IN SOME RIVERS
FOUND AT KONONGO AND ITS SURROUNDING TOWNS AND VILLAGES
BY NEUTRON ACTIVATION ANALYSIS

A THESIS PRESENTED TO THE UNIVERSITY OF SCIENCE AND TECHNOLOGY,
IN PARTIAL FULFILMENT FOR THE DEGREE OF

MASTER OF SCIENCE
IN
ANALYTICAL CHEMISTRY

MARY ASSIAMAH, BSC (HONS) CHEMISTRY, UST

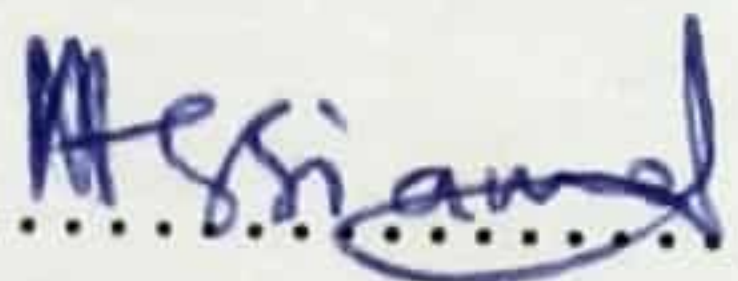
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AUGUST, 1999

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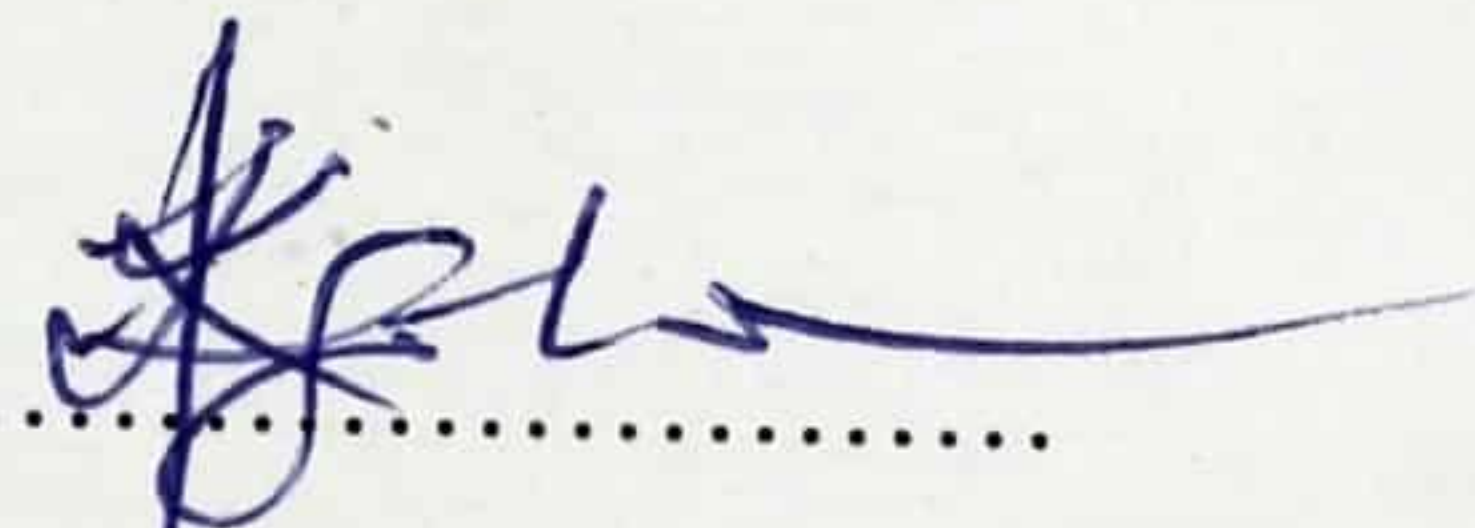
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PROF. E K OSAE

CO-SUPERVISOR

DATE: 30/8/99.....

ACKNOWLEDGEMENT

The author of this work wish to acknowledge all those who assisted her in diverse ways and have made the completion of the work possible but whose names are too many to list.

DEDICATION

THIS DISSERTATION IS DEDICATED TO THE ONE

WHO WAS, AND WHO IS AND IS TO COME.

IN HIM ALONE I LIVE, MOVE AND HAVE MY BEING.

To Professor A. A. Adumado, head of the Department of Chemistry, I say thank you very much for your advice, encouragement and thoughtfulness. May the Good Lord bless and guide you in all your endeavours.

To my Co-supervisor, Prof. E. K. Osei of the Ghana Atomic Energy Commission, (GAEC) I will say thank you very much for all the support and advice you gave me. I cannot end without extending my appreciation to Prof. C. Schandorf, Director of the Radiation Protection Board of GAEC whose understanding and advice saw to the completion of this work.

The list would be long but I cannot fail to extend my warmest appreciation to all my colleagues at the Radiation Protection Board and the Reactor Centre of GAEC, notably Mr. E. K. Osei, Mr. K. D. Asamoah, Mr. J. Yeboah, Mr. E. O. Darko, Mr. B. J. B. Nyarko, Mr. K. Serfor-Armah and Mrs. Cora Asamoah. May the Lord of Hosts bless you for all that you have lost to make this project what it is now. To the Technicians at both the Radiation Protection Board and Reactor Centre of GAEC, I say thank you very much for all the support you accorded me in this work. To all my siblings, friends and church members I say, thank you and may God bless you for your prayer support and everything.

Special thanks also go to the staff of the Water and Soil Research Institute of the Council for Scientific and Industrial Research for the assistance they gave in the water quality and soil

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I would like to express my gratitude to my supervisor, Dr. A. A. Golow, whose fatherly guidance, understanding, help and above all dedication to this work cannot be over-emphasized. Dr. Golow, may the Almighty Lord bless and restore onto you all that you have lost through this work.

To Professor A. A. Adimado, head of the Department of Chemistry, I say thank you very much for your advice, encouragement and thoughtfulness. May the Good Lord bless and guide you in all your endeavours.

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composition analysis respectively.

ABSTRACT

I would like to express my gratitude to the Ghana Atomic Energy Commission and the University of Science and Technology for all the assistants received.

Finally, I would like to express my profound gratitude to my parents, Mr. J. K. Assiamah and Madam Rebecca Ntosour whose love, care and support has brought me this far. Thank you dear Dad and Mum and may the Almighty Father keep and strengthen you. Last but not the least, I would like to acknowledge Elder Francis Boadu, my husband, whose advice and thoughtfulness was a great booster to the completion of this work.

"I will praise my maker while I have life and my thought is lost in depth", for He holds all things together by the power of His word. Therefore to him who was, and who is and is to come, Him will all the glory, praise and adoration be given.

ABSTRACT

Neutron Activation Analysis (NAA) method has been employed for arsenic determination in water, sediments and fish in water bodies at Konongo and its surrounding villages. The work was carried out at the Ghana Atomic Energy Commission, Accra. Water, fish and sediment samples were collected from Konongo and its surrounding towns and villages as well as those from the site of the mining company, Obenemase Gold Mine (OGM), notably the ores and the tailing dams and analysed for the presence and level of arsenic. The samples were also analysed for other parameters including gold. The general water quality of the water samples were carried out.

In some of the water samples, the results showed the presence of arsenic while others did not give any indication of the metal. Some of the water samples gave significant levels of arsenic. For sediments and fish samples, arsenic was found in all the sampling sites. The arsenic level found in the fish samples were low but that of the sediments were very high. The average arsenic level found in the water samples analysed ranged between 0.04 and 12.2 ppm while that in the sediment ranged between 31 and 4626 ppm. The average arsenic concentration found in the fish samples ranged from 0.96 to 1.72 ppm.

The sediments showed level of gold compared to that reported elsewhere. However, the water as well as the fish did not give any indication of gold contrary to expectation. The untreated ore showed the highest arsenic and gold contents compared to any of the sediments. At one of the sampling sites, sediments were collected from different sinks. It was observed that the upper sink (i.e. the surface portion) showed higher level of arsenic than the lower sink (i.e. bottom portion). For most of the water samples, the general water quality were found to be within the acceptable range recommended by the World Health Organization (WHO).

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CHAPTER 1

INTRODUCTION

1.1 Background

Konongo is one of the old mining settlements in Ghana. The mining activities came to a standstill in the late 80's and early 90's. Currently, mining activities in the area has begun. It was suspected by the Authorities of the Obenemase Gold Mine (OGM) that there may be arsenic present in the gold ore as against the earlier notion that, the Konongo gold fields are basically gold finely dispersed in quartz veins or lodes

Industrial processes have resulted in the introduction of metals into the environment, generally from the processing of ores to the manufacture of finished products containing metals. In 1975, world production of arsenic was estimated around 60 000 tonnes (EHC, 1981). Metal processing result in contamination of air, water and soil which can be ingested by humans and other animals. The development of most countries is vitally linked among other factors with the development of their mineral resources. Ghana is one of the leading countries with mineral deposits. The Obuasi gold mine is the largest gold mine in Africa aside Transvaal, South Africa (Kesse, 1980). In Ghana, presently, the mining industry is second to no other industry in terms of its contribution to the total export earnings of the country. Current Statistics show that mining continue to play a leading role in the country's foreign exchange earnings (Table 1). In 1995, out of the total foreign exchange earnings of 1.5 billion US dollars (\$1,500,000,000), 682.2 million US dollars (\$682,200,000) of it was from the mining sector (Minerals Commission of Ghana, 1995). Gold mining is the most important mineral industry in the country. In the early 80's, it accounted for 89.00% of the value of total mineral exports (Int. Conf. on the Geol. of Gh., 1988). Presently, however, gold accounts for 94.44% of the total mineral exports (Min. Comm. of Gh., 1995). Currently, there are eight major gold mines in Ghana operated by five corporations.

TABLE 1: MINERAL EXPORTS COMPARED TO TOTAL EXPORTS (1983-1995)

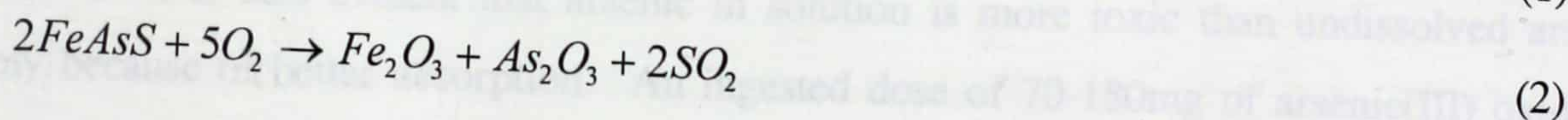
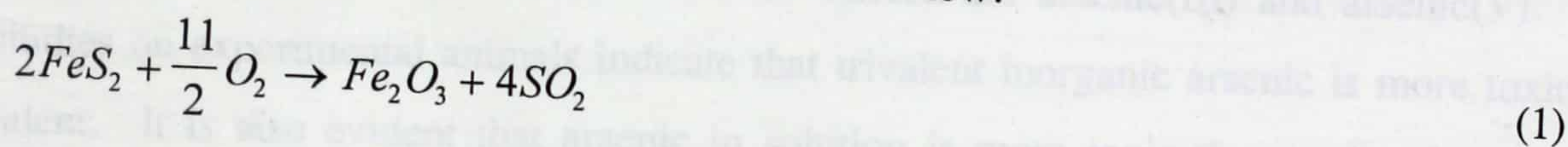
<u>EXPORTS</u>	<u>UNITS</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>	<u>1986</u>	<u>1987</u>	<u>1988</u>	<u>1989</u>	<u>1990</u>	<u>1992</u>	<u>1993</u>	<u>1994</u>	<u>1995</u>
Gold	Mil.\$	114.1	103.3	90.6	106.4	142.5	168.5	159.9	201.6	343.4	415.7	548.7	651.1
Diamonds	Mil.\$	2.8	2.8	5.5	4.8	4	3.5	5.2	16.5	19.3	14	20.4	13.8
Manganese	Mil.\$	3.1	8.3	9	8.2	7.8	8.9	11.7	14.2	16.4	13.5	9.6	6.8
Bauxite	Mil.\$	1.7	0.9	2.7	5	5.2	6.9	9.1	10	9.5	10.4	9.6	10.5
Total Minerals Exports	Mil.\$	121.7	115.3	107.9	124.4	159.4	187.8	185.9	242.3	388.6	453.4	588.2	682.2
Total Merchandise Exports	Mil.\$	439	567	632	749	874	880.7	808.2	896.7	986.3	1020.1	1214.8	1500
(Minerals/All Merchandise) Exports	%	27.70%	20.30%	17.10%	16.60%	18.20%	21.30%	23.00%	27.00%	39.40%	44.50%	48.40%	45.48%
Gold/Minerals	%	93.76%	89.59%	83.97%	85.53%	89.40%	89.72%	86.01%	83.20%	88.37%	91.64%	93.28%	95.44%
Diamonds/Minerals	%	2.30%	2.43%	5.10%	3.86%	2.51%	1.86%	2.80%	6.81%	4.97%	3.09%	3.47%	2.02%
Manganese/Minerals	%	2.55%	7.20%	8.34%	6.59%	4.89%	4.74%	6.29%	5.86%	4.22%	2.98%	1.63%	1.00%
Bauxite/Minerals	%	1.40%	0.78%	2.50%	4.02%	3.26%	3.67%	4.90%	4.13%	2.44%	2.29%	1.63%	1.54%

Source: Minerals Commission, Accra (1995)

They are:

- (i) The deep level mines at Tarkwa, Prestea, Konongo and the Dunkwa gold dredges on the Ofin and Jimi rivers, operated by the State Gold Mining Corporation;
- (ii) The deep level mine at Obuasi, operated by the Ashanti Goldfield Corporation (Ghana) Limited;
- (iii) Teberebie gold mine operated by Teberebie Goldfield;
- (iv) Iduaprim gold mine operated by the Ghana-Australian Goldfield;
- (v) The Bogoso mine operated by Billiton-Bogoso Goldfield.

Gold, usually finely dispersed in quartz vein or lodes may be free (free-milling gold) as occurs in the ores of Tarkwa and Konongo fields or contained within mineralized rock in association with sulphide particularly pyrites (FeS_2) and arsenopyrites (FeAsS). At Prestea, the sulphide ores form the bulk of the treated ore, while at Obuasi, both gold-in-quartz as well as sulphide-bearing ores form the major gold deposits. A wide range of technologies are employed in the extraction and processing of gold from its ore resulting in the release of poisonous gaseous substances such as sulphur dioxide (SO_2), arsenic(III) oxide, (As_2O_3), and other arsenic compounds into the atmosphere. The equations for the reactions are shown below:



The released substances find their way into air, water, soil, plants, animals and human beings in the neighborhood of the stack with consequent adverse effects. The release of sulphur and arsenic compounds from the processing of gold ore pose pollution problems in the environs of the goldmine. In the present studies, the focus is on arsenic released from gold mining and processing.

1.2 Literature review of Arsenic

Arsenic, with symbol As, has atomic number 33 and atomic mass 74.9216 a.m.u. Arsenic belongs to the same group as Nitrogen(N), Phosphorus(P), Antimony(S), and Bismuth(Bi). It has metalloid properties typical of Group VA elements. Arsenic binds covalently with both non-metals and metals and thus forms many different organic and inorganic compounds. In these compounds, the arsenic can exist in the metalloid (As^0), the trivalent (As^{3+} and As^{3-}) or the pentavalent (As^{5+}) states. The element occurs in different solid states, yellow and grey or metallic with specific gravities 1.97 and 5.73 respectively.

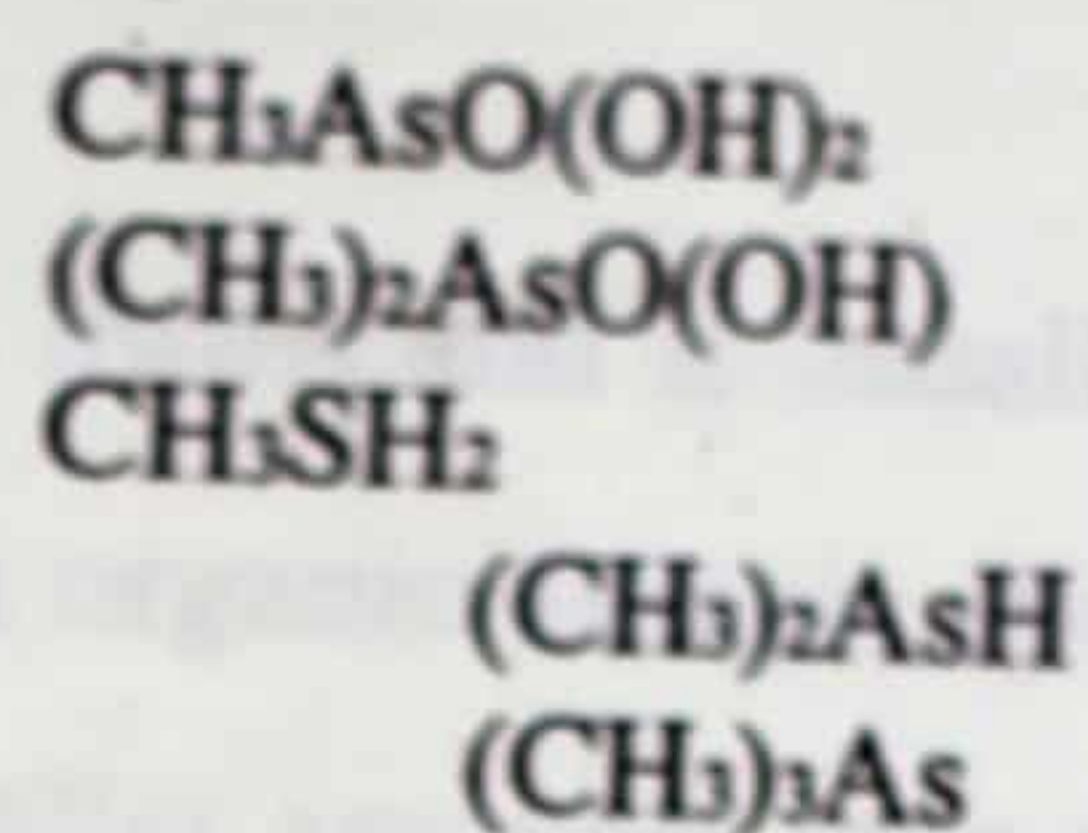
Arsenic is an ubiquitous element. In nature, arsenic is distributed in a number of minerals, mainly as the arsenide of copper, nickel, and iron, or as arsenic sulphide or oxide. Arsenic is regarded as an important environmental toxicant due to its general toxic properties and extensive presence in the environment. It is said to be a common environmental toxicant in soil, water and air (Schroeder & Balassa, 1966). Arsenic oxide, one of the released substances during mineral processing, is of environmental concern due to its notoriety. The two most important inorganic arsenic compounds which are of environmental concern are arsenic(III) and arsenic(V). Data from studies on experimental animals indicate that trivalent inorganic arsenic is more toxic than pentavalent. It is also evident that arsenic in solution is more toxic than undissolved arsenic, probably because of better absorption. An ingested dose of 70-180mg of arsenic(III) oxide has been found to be fatal in man (Schoeder & Balassa, 1966). Some common inorganic and organic arsenic compounds are shown in Table 2 below.

TABLE 2: SOME COMMON INORGANIC AND ORGANIC ARSENIC COMPOUNDS

Name	Formula(e)
Inorganic arsenic,	
Arsenic(III) oxide	As_2O_3 or As_4O_6
Arsenous acid	H_3AsO_3
Arsenic(V) oxide	As_2O_5
Arsenic acid	H_3AsO_4
Arsenenic acid	HAsO_3

Organic arsenic,

Methylarsonic acid
Dimethylarsinic acid
Methylarsine
Dimethylarsine
Trimethylarsine



Source: Environ. Health Criteria, 1981.

1.2.1 Sources And Occurrence Of Arsenic In The Environment

1.2.1.1 Natural Source

Rocks, Soils, and Sediments

Arsenic is widely distributed in a large number of minerals. Major minerals containing arsenic are arsenopyrites, (FeAsS); realgar, (As_4S_4) and orpiment, (As_2S_3). The arsenic content of the earth's crust is 1.5-2.0mg/kg and it ranks 20th in abundance in relation to other elements (NAS, 1977). Surface soil tends to adsorb pollutants which settle on it more than on vegetation. Oxidized forms of arsenic are usually found in sedimentary deposits. In USA the average content in coal mine was estimated between 1-10 mg/kg (Davis et al, 1971). High levels of arsenic may occur in some coal. In some coal mines in Czechoslovakia, the concentration of arsenic has been shown to be as high as 1500 mg/kg (Cmarko, 1963).

Uncontaminated soils usually contain arsenic levels between 0.2 and 40mg/kg, while arsenic-treated soils contained levels up to 550mg/kg (Walsh & Keeney, 1975) and levels up to 10,000mg/kg has been found in sediments near a copper smelter in Washington, USA (Crecelius, 1974). Methylated arsenic compounds occur naturally in the environment as a result of biological activity (EHC, 1981).

Air

Airborne particulate matter has been shown to contain both inorganic and organic arsenic compounds. In an unpolluted area, airborne concentrations ranging from less than one to few nanogram per cubic metre have been reported (Beavington & Cawse, 1978; Brimblecombe, 1979).

In water, arsenic occurs in both the inorganic and organic forms and is usually found in the form of arsenate or arsenite i.e. the +5 or +3 state. The main organic arsenic species, methylarsonic acid and dimethylarsinic acid, are present generally in smaller amounts than the inorganic forms, arsenite and arsenates (Crecelius, 1974). The arsenic contents of surface waters in unpolluted areas vary but typical values have been found to be a few orders of micrograms per litre. In well-aerated streams, greater proportion of the arsenic is in the pentavalent form whiles in anaerobic reservoirs, all of the arsenic is present in the trivalent form. It has been reported by Penrose et al (EHC, 1981) that sea water, ordinarily contains arsenic concentrations ranging from 0.001-0.008mg/litre. The major chemical form of arsenic in sea water being the thermodynamically stable arsenate ion; while arsenite accounts for about a third of the total arsenic. Arsenic concentrations as high as 224 and 280mg/litre have been found in groundwater supplies of which about 50% was found to be in the +3 state (Clement & Faust, 1973).

1.2.1.2 Anthropogenic Sources

Some activities of man contribute to the release of arsenic into the environment. These activities include the utilization of natural resources (coal, petroleum, minerals), the application of insecticide, herbicide, and pesticide in farming activities. Arsenic salts are used in the manufacture of glassware and ceramics, tanning and in some chemical manufacturing processes. In some countries, arsenic is used as a desiccant for cotton prior to machine picking. The anthropogenic sources of arsenic exceed natural sources in the environment (Woolson, 1983). Mining operations are a major source of release of arsenic into the environment. This source of arsenic however, is confined to specific parts of the world unless the tailings are transported elsewhere.

1.2.2 Occurrence of Arsenic in Ghana

Some of the gold deposits found in the country is associated with arsenic. The gold deposits found in Tarkwa and Obuasi contain arsenopyrites ores. The roasting of these ores constitute the main source of arsenic pollution in the country. Particularly areas close to the stack of the mine. The Obuasi gold fields, being a large gold mine, releases large quantities of gaseous arsenic into the atmosphere during processing of the ores. The released arsenic, finds its way into the air, soil, water, plants, animals and humans in the neighborhood of the stack (Amonoo-Neizer & Busari, 1980). Another form of arsenic pollution from the mines is through the discharge of mining effluent into water bodies. For example, the Kwabrafoso river near Obuasi, is found to have a high arsenic content which is basically due to the discharge of effluent from the Pompora Treatment Plant(P.T.P.) of the mine into the river. High levels of arsenic have been reported from surveys conducted in the mining communities. They include hair samples, various food items, drinking and washing water, vegetation and soils and geological materials from the mining process (Amasa, 1975; Manful & Verloo, 1990).

1.2.3 Toxicological Effects of Arsenic on Human

Arsenical toxicity is highly dependent on chemical form, oxidation state and route of exposure. It is also related to how fast it is eliminated or excreted from the body. The relative toxicity of arsenic to human is dependent on the chemical form in which it is inhaled or ingested. The toxicity of arsenic compounds decreases in the following order: Arsine (AsH_3), > arsenite (As^{3+} , Inorganic), > arsenoxide > arsenate (As^{5+} , inorganic) > penta-valent arsenical such as arsenic acids, arsonium compounds and metallic arsenic (Penrose, 1974). Acute and sub-acute effects of arsenic may involve many organ systems including the respiratory, gastro-intestinal, nervous, and hematopoietic systems. Arsenic poisoning in human beings produces diseases of the nerves and skin, leading to serious tissue damage (carcinoma of the liver, skin and lung).

Other effects are itching of the skin, stomach upset, nausea and diarrhoea. Arsenic poisoning can damage bone marrow resulting in secondary anemia and cirrhosis of the liver. The soluble

arsenic compounds such as sodium arsenite is readily and rapidly absorbed through the skin, and are highly toxic. Unfortunately, in most cases of human intoxication, the doses and valence states of arsenic have not been determined. With a strong predilection for kidney and liver, arsenic tends to accumulate in them in high concentrations. Arsenic also combines with sulphhydryl group of sulphur containing proteins, which includes the skin, hair, nails and other keratin-containing tissues. Long-term ingestion of arsenic through drinking water produce increased risk of cancer, dermatitis and loss of hair (EHC, 1981; Peoples Daily Graphic, 1993). More concentrated arsenic exposures can lead to perforation of the nasal septum. Skin irritation is prevalent in smelter workers who are exposed to dust with high arsenic content (Newland, 1982; Waldbolt, 1982).

1.2.4 Toxicological Effects of Arsenic on Plants and Animals

Arsenic has also been found to have adverse effects on both plant and animal life. Excess of arsenic in soil may arise from the use of arsenic containing fertilizers, application of insecticides, herbicides or fungicides in the form of arsenite. Atmospheric arsenic which arises as a result of industrial processes return to the soil in the form of soluble oxides. The arsenic that has been introduced into the soil is taken up by the roots of the plants and their effect manifested as retardation in growth or outright burning of the plant. The amount required to produce this effect is dependent on the plant species. It has been found out by Copper et al (1980), that the application of small quantities of arsenic to light soils decreased yields of cotton and cowpea, two important crops in the economic and dietary sense respectively of the Ghanaian populace. Earlier works by Madhee et al (1960); Jones & Hatch, have shown that increased concentration of arsenic in the soil resulted in increased accumulation of the element in plant. It has been found out that plants in the vicinity of the treatment plants of the Obuasi goldfields have been rendered brown and unfruitful due to excess arsenic released into the atmosphere which finally settles in the soil. The adsorption of arsenate ions in the soil by iron and aluminium greatly restricts the availability of arsenic to plants (Walsh et al, 1977). Thus soil with high content of iron and aluminium, has little effect of arsenic on the plants.

A lot of research carried out on the effects of arsenic on animals indicate that they are not spared by the toxicological effects of the element. High body weight (7.6mg/kg) of arsenic in rats results in the loss of the glossy appearance in their pelage, especially of the back and nape of the neck. At high levels of arsenic, moist eczema which developed into severe skin changes with ulcerations and crust formation was observed in the rats. Histopathological findings including ulcers and scarring of the epidermis and subcutaneous tissue hyperkeratosis, enlargement and hyperplasia of the hair bulbs were also observed (EHC, 1981).

1.2.5 Uses of Arsenic

Arsenic was used both as a therapeutic agent and poison in the ancient Greek and Roman times. The element in the form of arsenous oxide has continued to exceed all poisons in this respect. More recently (until the advent of penicillin), arsenic was used in the treatment of syphilis as a tonic commonly known as Fowler's solution (1% potassium arsenite). Its only therapeutic use today is in the treatment of trypanosomiasis involving the nervous system.

Nearly sixty thousand tonnes of arsenic were produced yearly in the world from 1967-1973. About 50% of this amount was used non-medically in the manufacture of pesticides and wood preservatives, while other minor applications are in the production of metallic arsenic, especially alloys, catalysts, pigments and in the glass industry (Buralti, 1984).

Currently, arsenic is used in the electronic industry as gallium arsenide and its alloys to make semi-conductors for constructing lasers, solar cells, microwaves devices, photoemissive surfaces and light-emitting diodes. Arsenic is also used as antifouling paints and materials to control sludge formation in lubricating oils. Organic arsenic are still being used as food additives to promote growth in farm animals (Wilardson, 1983) and also to combat certain diseases in chicken.

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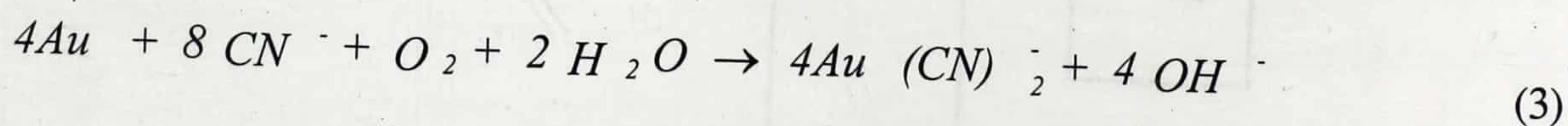
1.2.6 Regulations on Arsenic

There is international concern about human intake of toxic trace elements such as cadmium, lead, mercury, and arsenic. Intake of relatively low doses of these elements over a long period can lead to malfunction of organs and chronic toxicity.

The Environmental Protection Agency (EPA) estimate for cancer risk due to arsenic in air for a lifetime exposure to a concentration of $1 \mu\text{g}/\text{m}^3$. The concentration of arsenic in water of health significance is given as $0.01 \text{ mg}/\text{l}$. The World Health Organization (WHO) Guideline Value for arsenic in water is $0.05 \text{ mg}/\text{l}$. Chronic toxicity reference value of arsenic in water as given by WHO is same as the Guideline Value, $0.05 \text{ mg}/\text{l}$, but Regulatory level is $5.0 \text{ mg}/\text{l}$ (FAO, 1984). The Food and Agriculture Organization (FAO) has a maximum level of arsenic in fruits and vegetables as $0.2 \text{ mg}/\text{kg}$ whiles cocoa powders and dry cocoa-sugar mixtures as $1.0 \text{ mg}/\text{kg}$ (WHO, 1989). The acceptable daily dietary intake of arsenic for an adult man as recommended by the National Academy of Sciences is $2.0 \mu\text{g}/\text{kg}$ per body weight (WHO, 1989).

1.3 Treatment Process of the Obenemase Gold Mine

The main activity at the Konongo Goldfield currently known as Obenemase Gold Mine (OGM) is based on the exploitation of lode ores. Presently, the project is being undertaken by the Ghana Mines Limited (GGML). Figure 1 shows the mining operations of OGM. The run-off-mine ore (oxide ore) from open pit is conveyed to the Oxide-Treatment Plant to be crushed and grounded into fine powder. The free gold is precipitated by gravitation. The gold ore is then leached by cyanidation with dilute excess sodium cyanide (NaCN) and lime (CaO) in five(5) successive tanks. The equation for the cyanidation reaction is shown below.



The gold is then adsorbed on an activated carbon and the pulp sent out as tailings into the Tailings Dam. The loaded carbon is washed with dilute hydrochloric acid (HCl) to remove any

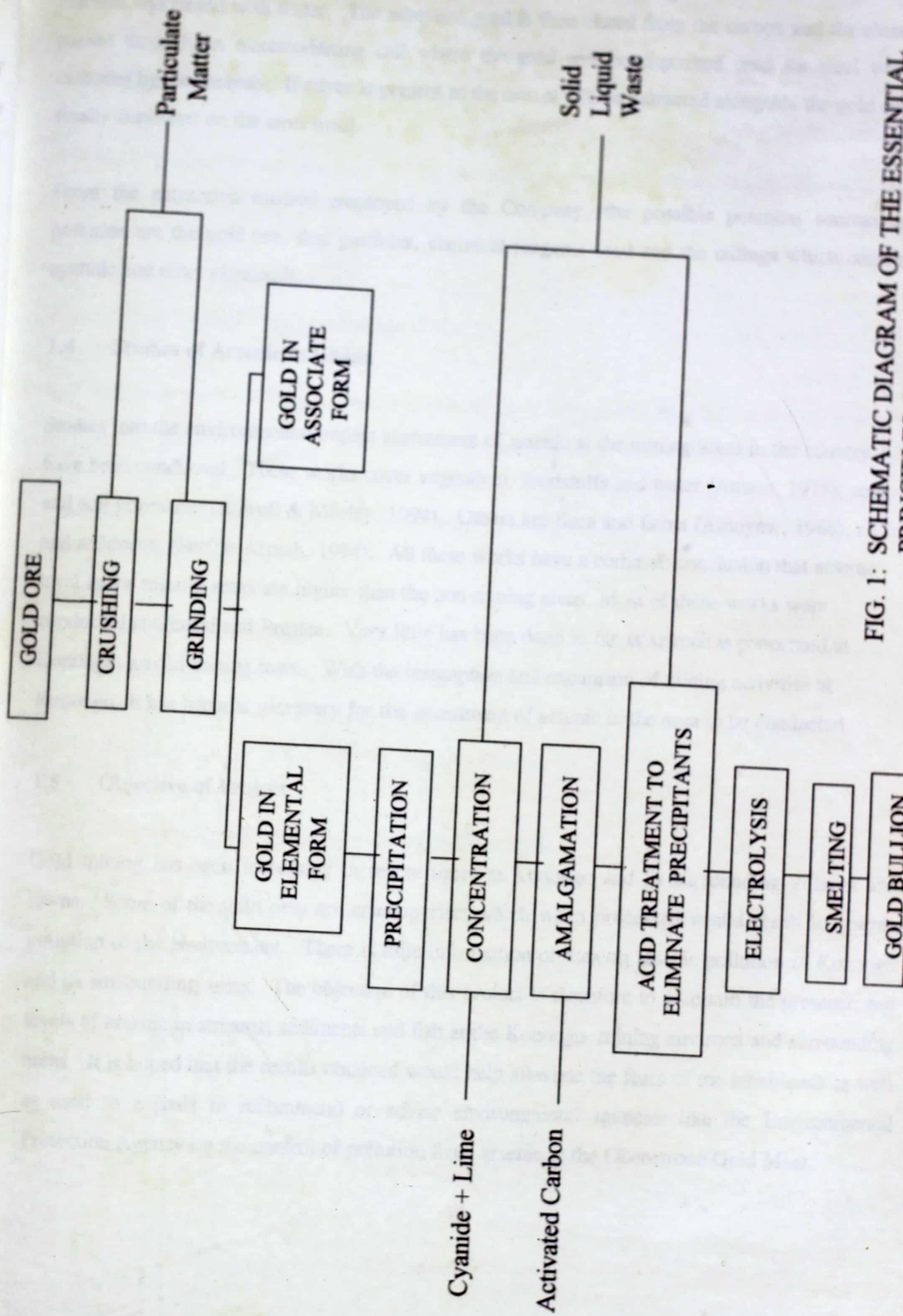


FIG. 1: SCHEMATIC DIAGRAM OF THE ESSENTIAL

calcium and rinsed with water. The adsorbed gold is then eluted from the carbon and the eluate passed through an electrowinning cell where the gold will be deposited onto the steel wool cathodes by electrolysis. If silver is present in the ore, it will be extracted alongside the gold and finally deposited on the steel wool.

From the extraction method employed by the Company, the possible potential sources of pollution are the gold ore, dust particles, chemical reagents used and the tailings which contain cyanide and other chemicals.

1.4 Studies of Arsenic in Ghana

Studies into the environmental impact assessment of arsenic at the mining areas in the country have been conducted. These works cover vegetation, foodstuffs and water (Amasa, 1975), soils and soil porewater (Bowell & Morley, 1994). Others are flora and fauna (Amoyaw, 1986), river and sediments (Serfoh-Armah, 1994). All these works have a common conclusion that arsenic level in the mining areas are higher than the non-mining areas. Most of these works were conducted at Obuasi and Prestea. Very little has been done as far as arsenic is concerned at Konongo, an old mining town. With the resumption and expansion of mining activities at Konongo, it has become necessary for the assessment of arsenic in the area to be conducted.

1.5 Objective of Project

Gold mining has been increasing in recent times at Konongo and its surrounding villages and towns. Some of the gold ores are arsenopyrites which when processed would result in arsenic pollution of the environment. There is little information or data on arsenic pollution of Konongo and its surrounding areas. The objective of this project is therefore to ascertain the presence and levels of arsenic in streams, sediments and fish at the Konongo mining environs and surrounding areas. It is hoped that the results obtained would help alleviate the fears of the inhabitants as well as used as a basis to recommend or advise environmental agencies like the Environmental Protection Agency on the control of pollution from arsenic at the Obenemase Gold Mine.

CHAPTER 2

LITERATURE REVIEW OF METHODS FOR ARSENIC DETERMINATION

Arsenic determination can be carried out by two major analytical methods, namely Chemical and Instrumental analytical methods.

2.1 CHEMICAL METHODS

2.1.1 Silver Diethyl Dithiocarbamate (SDDC)

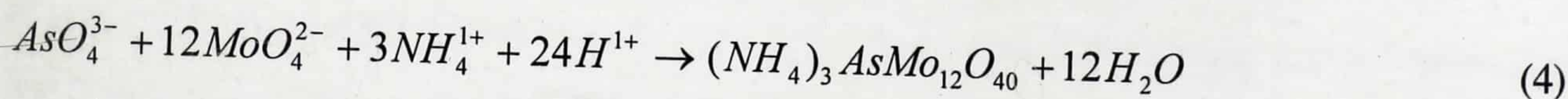
The method is used for total arsenic. In this method, arsenic is reduced to arsine by granular zinc in hydrochloric acid (HCl). The arsine generated reacts with a solution of silver diethyl dithiocarbamate ($\text{AgS.CS.N(C}_2\text{H}_5)_2$) in pyridine to form a red complex, with an absorption maximum of 540nm on a spectrophotometer Powers et al, 1959).

Disadvantages of the Method

- (i) For low arsenic concentration, conversion to arsine may be slow or non-stoichiometric.
- (ii) Converting all arsenic into solution has a chemical setback.
- (iii) Antimony forms a red complex, stibine, which absorbs at the same wavelength 540nm as arsenic and therefore causes interference in the analysis.

2.1.2 Molybdenum Blue (Kingsley-Schaffert) Method

The molybdenum blue method is used for total arsenic analysis. Arsenic as arsenate, reacts with ammonium molybdate solution to form arseno-molybdenum complex. The complex formed is reduced with hydrazine sulphate or tin(II) chloride, forming a blue soluble complex, "molybdenum blue" (Kingsley-Schaffert, 1951). The reaction equation is:



The complex actually contains the trimolybdate ion $\text{Mo}_3\text{O}_{10}^{2-}$ with the molybdenum having an oxidation state of +6. The composition of the complex can therefore be written as $(\text{NH}_4)_3\text{As}(\text{Mo}_3\text{O}_{10})_4$. The complex absorbs at 845nm in a spectrophotometer.

Disadvantages of the method

- (i) For low arsenic concentration, conversion to arsine may be non-stoichiometric.
- (ii) Conversion of all arsenic into arsine has a chemical setback.
- (iii) Interference from other substances like phosphate which also forms blue complex with molybdenum.

2.1.3 Gutzeit Method

This method also determines total arsenic. Nascent hydrogen is generated from zinc and hydrochloric acid. The hydrogen generated is used to convert all arsenic into arsine (Std. Mtd. for the Exam. of Waste Water, 1985). The equations for the reaction are:



Disadvantages of the Method

- (i) There is too much dependence on the rate of arsine generation which is not necessarily equal to the rate of evolution of hydrogen.
- (ii) Low accuracy.

2.2 INSTRUMENTAL METHODS

There are a number of instrumental analytical methods for arsenic determination. For this work Neutron Activation Analysis would be used for arsenic determination.

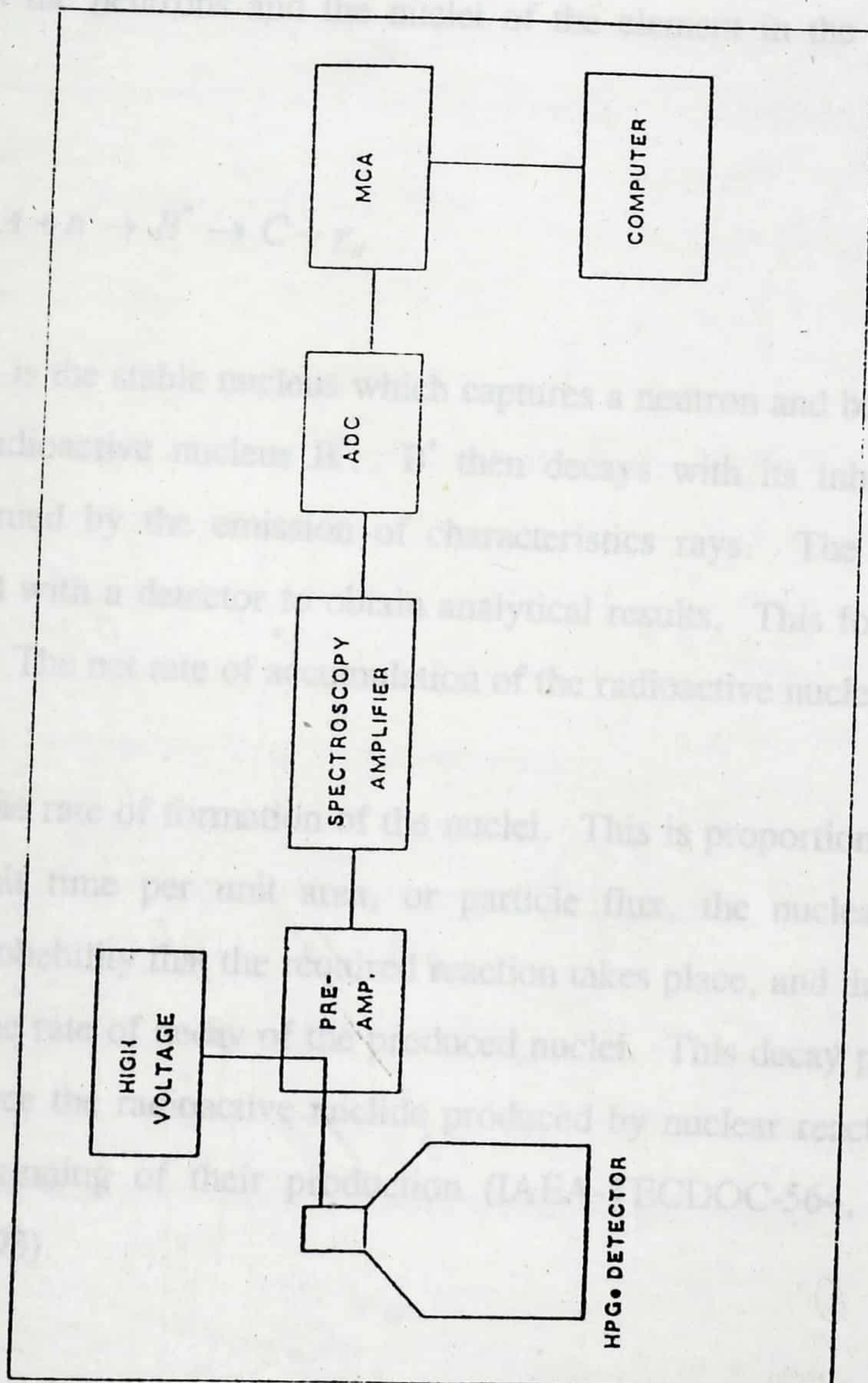
2.2.1 NEUTRON ACTIVATION ANALYSIS

Activation analysis techniques include those methods that use nuclear reactions to form product radionuclides or excited states of target nucleus as the basis for the analytical determination. An element is bombarded with either neutrons, charged particles or photons to induce a nuclear reaction resulting in the formation of a radioactive product which then decays by emitting radiation such as gamma, beta or an alpha particles. The radiation emitted are measured to obtain both qualitative and quantitative analytical results. Neutron activation analysis (N.A.A.) is the most common form of activation analysis. It is one of the expanding analytical techniques and currently has become an important means for the super-trace, trace, semi-micro and normal analysis. In N.A.A., neutrons are the activating particles. Neutrons induce different kinds of nuclear reactions, depending on their energy. For most applications, it is the delayed gamma radiation from the radioactive product that is detected after activation for qualitative and quantitative information (Ehmann-Vance, 1991). Fig. 3 show a typical set-up for NAA.

Neutron activation analysis can be divided into three categories according to the energy of the activating neutrons:

1. Thermal neutron activation analysis, the most common of the three, employs neutrons with energy of about 0.025 eV.
2. Epithermal neutron activation analysis employs neutrons with energies between 0.1eV and 1.0 MeV.
3. Fast neutron activation analysis is NAA with neutron energy greater than 0.5 MeV.

Neutron activation analysis can also be classified into another three groups depending on the need for chemical separations and the time of the separation. The three groups are:



KEY

ADC = ANALOG-TO DIGITAL CONVERTER

MCA = MULTICHANNEL PULSE-HEIGHT ANALYZER

FIG. 3: SCHEMATIC DIAGRAM OF NAA

1. Instrumental neutron activation analysis (INAA). In INAA, no chemical treatment is carried out. The sample is irradiated with little handling.
2. Radiochemical neutron activation analysis (RNAA). For the RNAA chemical separations are done after irradiation to remove interference or to concentrate the radionuclide of interest.
3. Chemical neutron activation analysis (CNAA). In CNAA, chemical separations are carried out before irradiation.

2.2.1.1 Basic Principles of Reactor NAA

When a sample is irradiated with neutrons in the nuclear, reactor nuclear reactions take place between the neutrons and the nuclei of the element in the sample. The reaction is shown as below:

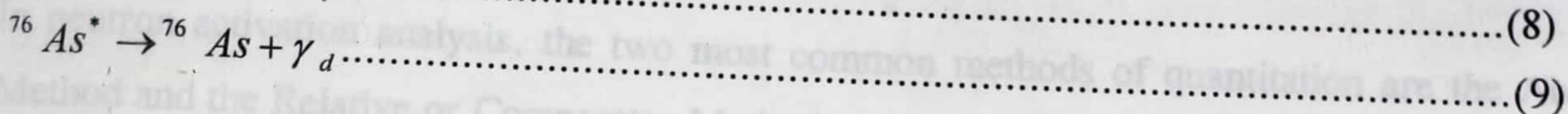
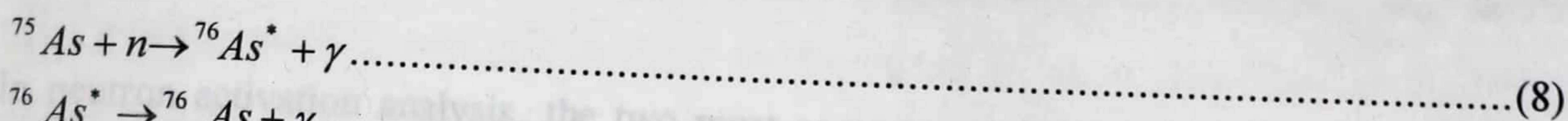


where A is the stable nucleus which captures a neutron and becomes activated and it is converted into a radioactive nucleus B*. B* then decays with its inherent half-life, $T_{1/2}$, and is always accompanied by the emission of characteristics rays. The emitted rays and its intensities is measured with a detector to obtain analytical results. This forms the basis of neutron activation analysis. The net rate of accumulation of the radioactive nucleus is dependent on two factors:

1. The rate of formation of the nuclei. This is proportional to the number of projectiles per unit time per unit area, or particle flux, the nuclear reaction cross-section, i.e. the probability that the required reaction takes place, and the number of target nuclei, N
2. The rate of decay of the produced nuclei. This decay possesses the property of statistics, since the radioactive nuclide produced by nuclear reactions decay continuously from the beginning of their production (IAEA-TECDOC-564, 1990; MNSR Training Manual, 1993).

2.2.1.2 Theory

The equations for the irradiation or activation of Arsenic are as follows:



A stable arsenic nucleus (^{75}As) captures a neutron and becomes activated or radioactive arsenic nucleus ($^{76}\text{As}^*$). The $^{76}\text{As}^*$ produced then decay by emitting gamma radiation (γ_d) to a stable or ground state. The intensities of the emitted gamma radiation is measured with a detector. From the measured intensities of the gamma radiation, the amount of the radioactive arsenic is determined which consequently gives the amount of the stable arsenic present. The basic equation for activation analysis of an element X is as follows:

$$A = N_v \theta \phi \sigma \frac{W}{M} [1 - e^{-\lambda t_i}] e^{-\lambda t_d} \quad (10)$$

where:

- A = activity of the produced nucleus,
- N_v = Avogrado's constant
- ϕ = neutron flux, $\text{ncm}^{-2}\text{s}^{-1}$,
- σ = effective activation cross-section of nuclear reaction,
- θ = isotopic abundance of target nuclei,
- W = weight of the element to be measured,
- M = atomic weight of the element to be measured,
- t_i = irradiation time,
- t_d = time interval from stopping irradiation to beginning of measurement,
- λ = decay constant = $0.693/T_{1/2}$
- $T_{1/2}$ = half life for the radioactive nucleus of the element to be measured.

The above equation is derived based on two premises:

1. The number of target nuclei remain basically unchanged during irradiation.
2. The number of product nuclei is reduced only through decay, without consideration of them being reactivated.

In neutron activation analysis, the two most common methods of quantitation are the Absolute Method and the Relative or Comparator Method.

1. Relative or Comparator Method

In the Relative or Comparator Method, a standard containing the element to be determined and of a matching matrix is prepared and irradiated along with the sample. The sample and the standard are counted under identical conditions. The concentration of a particular element of interest is evaluated by comparing the activities of known masses of the sample and the standard (IAEA-TEC-REP-197, 1990; IAEA-TECDOC-564, 1993). Thus when the above equation is written for both sample and standard, and one is divided by the other, a much simpler comparison equation, (11) results:

$$\frac{A_o(\text{Sample})}{A_o(\text{Standard})} = \frac{W(\text{Sample})}{W(\text{Standard})} \quad (11)$$

The Comparator Method appears to be simple but has a major set-back since obtaining standards for each element is difficult. The problem becomes compounded if a multi-elemental analysis is involved, because preparing a multi-element standard of the same matrix and concentration as the sample under investigation is not an easy task.

2. The Absolute Method

The Absolute Method uses the basic neutron activation equation (equation 10). For practical purposes, the amount, m_j , of an element j in a sample, which has been irradiated in a neutron flux, ϕ , for a time T , can be calculated by modifying equation (10) (Osae et al, 1996). The modified equation is:

$$m_j = C_j \lambda_j M_j / [\theta_j (\phi_t \sigma_{tj} + \phi_e \sigma_{ej}) f_j \epsilon(E_j) N_A K_j] \quad (12)$$

where $K_j = (1 - \exp(-\lambda_j T))(1 - \exp(-\lambda_j t_c)) \exp(-\lambda_j t_d) \quad (13)$

and $\phi \sigma_j = \phi_t \sigma_{tj} + \phi_e \sigma_{ej} \quad (14)$

C_j is the photopeak counts, f_j is the branching ratio of identifying gamma ray (gamma yield i.e. the number of gamma-rays/ 100 disintegrations) and $\epsilon(E_j)$ is the efficiency of the gamma detector. The nuclear constants in equation (12) are λ , M , σ , θ , f and N_A . The Absolute Method depends on the nuclear constants obtained from literature in addition to an accurate knowledge of the efficiency of the gamma detector and the neutron flux at the irradiation position. The accuracy of the method therefore depends on the accuracy of the nuclear constants, the accurate knowledge of the efficiency of the detector, the neutron flux and the counting statistics. For most elements the errors in nuclear constants are less than 5% (IAEA-TECREP-273, 1987). The overall error using the Absolute Method is about 10-15% (Erdmann, 1989). Equation (12) may be expressed in a simple form as:

$$m_j = D_j C_j / (\phi \epsilon(E_j) K_j) \quad (15)$$

where $D_j = \lambda_j M_j / (\theta_j \sigma_j f_j N_A) \quad (16)$

The constant D may be calculated for any element by obtaining the nuclear constants from any current nuclear data books such as IAEA-TECREP-273, 1987; IAEA-TECDOC-564, 1993. Knowing D , ϕ , $\epsilon(E_j)$ and K , and also by measuring the photopeak counts C , the amount, m , of any element in the sample may be obtained using equation (15).

To reduce the overall error to less than 10%, the Absolute Method is standardized (Osae et al, 1996). The standardization of this procedure is to irradiate known standard reference material (SRM) of the element of interest and determining the experimentally measured value. The correction factor, F , for the measured value is given by:

$$F = m_j / m_{std} \quad (17)$$

where m_j = experimentally measured value m_{std} = quoted concentration

The correction factor takes into account the errors in the nuclear constants, the efficiency of the detector system for the particular sample-to-detector geometry and the neutron flux at the irradiation position. The correction factors for forty one (41) elements of interest in the Instrumental Neutron Activation Analysis (INAA) covering a wide range of the Periodic Table including Arsenic have been obtained using 5 standard reference materials, 6 pure elements and 5 chemically pure compounds for INAA with the Absolute Method. The results from the standardization have been validated using a NBS (National Bureau of Standards) SRM 1663a Coal Fly Ash, compared very well with the certified or quoted values (Osae et al, 1996).

The correction factor for an element was obtained by the ratio of certified values to the measured ones. With this method, there is no need for the irradiation of a sample and its standard anytime measurements are to be made.

2.2.1.3 Neutron Sources

2.2.1.3.1 Radioisotopic Neutron Source

Radioisotopic neutron sources rely on spontaneous nuclear processes for neutron production. The radioisotopic sources include γ -emitter sources, photon sources, and californium-252 sources. They are quite simple in design and operation compared to other sources of neutrons. The source consists of an alpha or gamma emitting radioisotope thoroughly mixed with a target element capable of interaction. The only requirement of the target source is that the emitted radiation has an energy above the reaction threshold. In the γ -emitter sources of neutrons, beryllium is thoroughly mixed with an γ -emitter such as americium-241, plutonium-239 or radium-226 as it used to be. The reaction that occurs is ${}^9\text{Be}(\gamma, n){}^{12}\text{C}$. The (γ, n) reaction forms

the basis of the neutron emission in many radioisotopic neutron sources. The neutrons produced are of varying energies, mostly at higher energies (approximately 3-4 MeV) and must be moderated for use in NAA, and neutron flux ranging from 10^5 to $10^7 \text{ ns}^{-1}\text{Ci}^{-1}$. The neutron flux produces low analytical sensitivity when used for NAA. The γ -emitter sources are the simplest and least expensive of the neutron sources. They require relatively little shielding, and their neutron yield per curie is better than photon sources. Light elements such as lithium and aluminium mixed with beryllium by an γ -irradiation can be used to produce neutrons but the fluxes are smaller. Beryllium is used mainly because of its low (γ, n) reaction threshold (Ehmann-Vance, 1991; De Soete et al). Table 3 shows some isotopic neutron sources. Photon sources of neutrons rely on the $^9\text{Be}(\gamma, n)^8\text{Be}$ reaction. Both the neutron energies and fluxes produced by these sources are low, 26keV and $10^5 \text{ ns}^{-1}\text{Ci}^{-1}$ respectively. The γ -ray must have an energy of at least 1.67 MeV to induce this nuclear reaction. The most widely used photon emitter to produce energy greater than 1.67MeV is ^{124}Sb . ^{124}Sb has a natural setback of low half-life of 60.2days and a low flux. The high-energy γ -ray requires heavy shielding in contrast to the easily shielded γ -emitter sources.

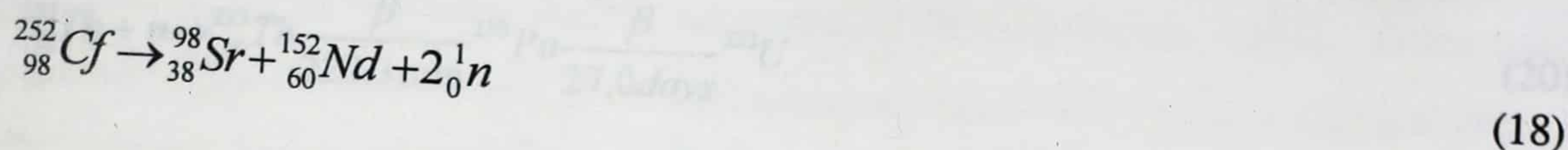
TABLE 3: ISOTOPIC NEUTRON SOURCE

Source Isotope	Half-life (years)	Target	Neutrons Emitted ($\text{ns}^{-1}\text{Ci}^{-1}$)
^{227}Ac	22	Be	1.5×10^7
^{226}Ra	1620	Be	1.3×10^7
^{228}Th	1.9	Be	2.0×10^7
^{229}Pu	2.4×10^4	Be	1.4×10^7
^{241}Am	458	Be	2.5×10^6
		B	5.0×10^5
		F	1.5×10^5
		Li	4.0×10^4

Source: De Soete et al,1972

2.2.1.3.2 Nuclear Reactor Source (Ehmann-Vance, 1991)

An unstable heavy nucleus spontaneously breaks into two smaller nuclei with the release of large amount of energy and two or three neutrons. An example of spontaneous fission decay process is:



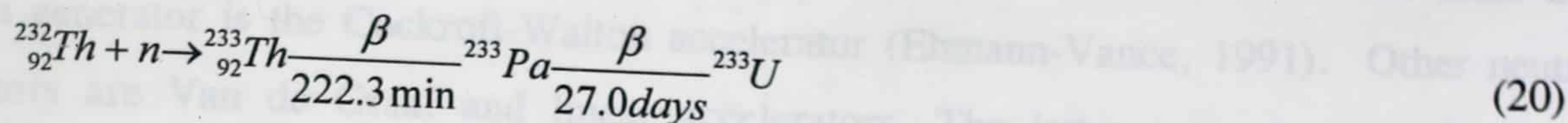
Nuclear reactors are devices in which controlled nuclear fission occurs. The fission that takes place in a reactor is largely not spontaneous but is neutron-induced. In a neutron-induced fission a neutron is captured by a high-mass nucleus which subsequently splits into two smaller nuclei with the release of about 200 MeV of energy and two or three neutrons. An example of neutron-induced fission reaction.



There are two competing forces at work in the target nucleus namely: binding force that holds the nucleons together and the Coulomb force that tends to push them apart. In a stable nucleus, the binding force is stronger. For low-mass nuclide, the binding force is much larger than the repulsive force while for heavier nuclide, the two forces are more equal in magnitude and it is possible to shift the balance in favour of the repulsive forces by addition of a neutron. The added neutron provide internal excitation energy that deforms the nucleus into a transition state and consequently split it into two fragments if the deformation is severe enough. The fission fragments are repelled away from each other with considerable kinetic energy due to the coulomb repulsive forces. The fragments are neutron-rich, so they will decay by negatron emission and often followed by a gamma transition, until a favorable N/Z (neutron/proton) ratio is attained and a stable products results. All these occur in an extremely short time (nanoseconds).

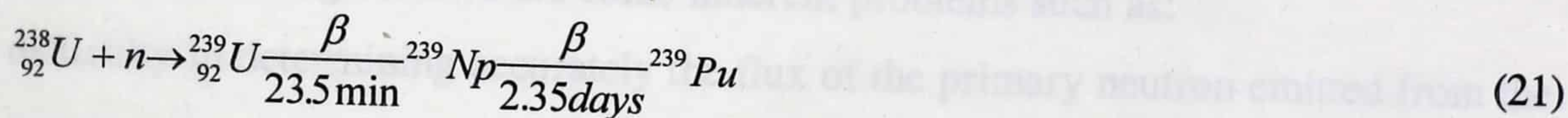
In a nuclear reactor, neutrons are produced as a by-product of uranium fission processes

occurring within the reactor core. Natural uranium fission consists of 99.2745% ^{238}U and 0.720% ^{235}U . Depending on the design of the reactor, uranium fuel may consist only of the naturally occurring isotopes, or it may be enriched in the ^{235}U isotope. The enrichments may vary from a few percent up to about 90% range. The uranium may be used as the pure metal,



Other fissile nuclide that can be used as fuel in reactors are thorium-232, uranium- 233 and plutonium- as uranium dioxide (UO_2), or as uranium carbide (UC). The UO_2 has the best overall (mechanical strength, chemical stability and resistance to radiation damage) characteristics, and is the most commonly used form. Uranium-233 is radioactive and is produced by the irradiation of thorium-232 as shown below:

239. Of the fissile nuclide uranium-233, uranium-235 and plutonium-239 have high cross-section for fission induced by thermal neutrons. Uranium-238 and thorium-239 undergo fission induced by fast neutrons (1MeV or greater). The distinction between fuel that fission with either fast or thermal neutrons is one of the ways that reactors can be classified. ^{239}Pu used as a nuclear fuel is not naturally occurring, but is produced from the chemical processing of irradiated uranium fuel rods.



Plutonium is used in the form of the oxide (PuO_2) for nuclear reactors. The metal is not used directly as fuel element because its mechanical and chemical properties are poor and it is also toxic. Thorium, like uranium is best used as a fuel element in either the oxide (ThO_2) or carbide (ThC_2) form. Primarily, thorium is used to produce the fissile uranium-233 as shown earlier.

2.2.1.3.3 Accelerator Neutron Source

In recent times, accelerator produced neutrons have played an important role in nuclear physics research and neutron activation analysis. Accelerators have been used to produce either charged particles or energetic neutrons as a result of nuclear reactions. The most used neutron generator is the Cockroft-Walton accelerator (Ehmann-Vance, 1991). Other neutron generators are Van de Graaf and linear accelerators. The latter generators are large and expensive devices hence are primarily constructed for nuclear physics research. A typical research neutron generators produces analytically useful flux density of $10^9 \text{ ncm}^{-2}\text{s}^{-1}$ at the sample irradiation position and an energy of 14.7 MeV. The research neutron generator usually consists of deuterium ions accelerating toward a tritium-containing target. The nuclear reaction that takes place is:



The application of neutron generators has a couple of advantages:

- (i) ability to turn the neutron beam off by simply de-exciting the acceleration high voltage.
- (ii) possibility of threshold reactions provide a unique solution to certain nuclear interference problems.

In spite of these advantages, there are some inherent problems such as:

- (i) difficulty in determining accurately the flux of the primary neutron emitted from the target;
- (iii) inhomogeneity of the neutron flux;
- (iii) short life span of the target material meaning frequent replacement (Nargolwall-Przybylowicz, 1973).

2.2.1.3.4 Fission Neutron Source (Ehmann-Vance, 1991)

Some transuranic elements that are unstable spontaneously break up into smaller fragments, with the emission of neutrons. The spontaneous fission of ${}^{252}\text{Cf}$ provides an alternative isotopic

fission neutron source. The emitted neutrons produced in the spontaneous decay of ^{252}Cf have energy in the range of 1.0 - 3.0 MeV. The neutron yield depends on the size and age of the ^{252}Cf source. Californium-252 is the most commonly used nuclide for the production of neutrons among available fission sources. The neutrons produced through ^{252}Cf have neutron flux of $2.3 \times 10^{12} \text{ ns}^{-1} \text{ cm}^{-2}$.

The choice of any of the above sources of neutrons depends on:

- (i) cost
- (ii) source handling facilities
- (iii) physical dimensions and shielding requirement
- (iv) source strength.

2.2.1.4 Interferences in Activation Analysis

Activation analysis, when properly performed can be among the most precise and accurate of all analytical methods for the determination of trace elements. However, there are potential interference and problems associated with the method. These include Interference reactions, Gamma-ray spectral interference and others (De Soete et al; Ehmann, 1991).

2.2.1.4.1 Interference Reactions

Three types of interference reactions can be encountered in activation analysis:

Primary Interference Reaction which is the most significant among the three, is when the desired or indicator radionuclide is produced by a reaction on an element in the matrix other than the analyte. An example of this would be the determination of Si. The desired analytical reaction is $^{28}\text{Si}(n,p)^{28}\text{Al}$ but phosphorus will produce ^{28}Al if present with the reaction $^{31}\text{P}(n,\alpha)^{28}\text{Al}$. Therefore, if a significant proportion of P were present in the Si-containing sample, the measured ^{28}Al activity would be greater than that due only to the presence of ^{28}Si , and the results would be in error.

Secondary Interference Reaction occurs when particles resulting from primary reactions produce the desired radionuclides by nuclear reaction with other elements in the matrix. This type of interference is less common than the primary interference reaction one, because the flux of secondary particles is quite small and can hardly initiate a nuclear reaction.

Second Order Reaction occurs when there is an enhancement of the desired product, through a nuclear reaction on some matrix element, producing a measurable quantity of the stable trace element that is being determined by the analytical nuclear reaction. For example, P may be determined via the radiative capture reaction on ^{31}P with a reaction $^{31}\text{P}(n, \gamma)^{32}\text{P}$. ^{30}Si forms the reaction $^{30}\text{Si}(n, \gamma)^{31}\text{Si}$. The ^{31}Si that is formed will decay by β emission to form ^{31}P , which is the target of the original analytical reaction. This type of interference is rather a rare one. Because it is very unusual for a significant amount of the stable target nuclide to be formed during the irradiation process.

2.2.1.4.2 Gamma-Ray Spectral Interference

This type of interference occurs when two radionuclides emit γ rays of the same, or nearly the same energy. An example of gamma-ray spectral interference would be the 846.8keV γ ray emitted by manganese-56 and the 843.8keV γ ray emitted by magnesium-27. The spectral interference have been overcome by the introduction of high-resolution detectors (High Purity Ge) and the continual improvement in software. Spectral interference problem can also be overcome by utilizing the difference in half-lives between the two mutual interference.

2.2.1.4.3 Other Interference

Two types of interference occur during the irradiation process itself. They are self-shadowing (or self-shielding) and resonance capture interference. The former takes place when one part of the sample shields another part from the incident neutron flux. This is overcome by simply reducing sample size. Resonance capture interference on the other hand, occurs in elements with

extremely large neutron cross-section in the Epithermal neutron energy range. Like the self-shielding interference, resonance capture interference can be overcome by minimizing the sample size.

EXPERIMENTAL

2.2.1.5 Advantages of Reactor NAA (IAEA-TECDOC-564, 1990)

In spite of the above set backs, Neutron Activation Analysis has the following advantages:

- (i) High sensitivity. The analytical sensitivity for most elements in the periodic table ranges between 10^{-6} to 10^{-13} g.
- (ii) High accuracy and precision: Accuracy indicates the deviation of the experimental value from the real value.
- (iii) No reagent contamination: In non-destructive activation analysis, no chemical treatment of the sample is made before irradiation, therefore there is no contamination caused by reagents.
- (iv) Multi-elemental analytical method. Several elements can be measured in the same sample at a time.
- (v) Non-destructive activation analysis can be used, in many occasions, to perform the determination of multi-elements, thus avoiding the errors caused by the sample dissolution and separation. This method is very important for the samples which are limited in quantity or are valuable to be kept, such as archaeological or forensic samples.
- (vi) A small sample amount.

2.2.2 Other Instrumental Methods

A number of other instrumental methods which have been reported for the determination of trace amount of arsenic are: Atomic Absorption Spectrometry (AAS), Atomic Emission Spectroscopy (AES), X-ray Fluorescence (XRF) and Isotope Dilution Mass Spectroscopy. Others include: Electron Spectroscopy Method (ESM), Anodic Stripping Voltametry, Direct Current Plasma Atomic Emission Spectroscopy (DCP-AES) and Differential Pulse Polarography.

CHAPTER 3

EXPERIMENTAL

This chapter describes the study area, sampling sites, sampling methods, parameters determined, sample treatment, sample preparation, analytical procedures, reagents used and other miscellaneous activities conducted to determine the effect of the gold mining practice on the various water bodies, fish and sediments of surface waters at Konongo and surrounding towns.

All reagents used were of analytical grade except otherwise stated.

3.1 STUDY AREA

Konongo is located between latitudes $6^{\circ}35'$ and $6^{\circ}40'N$ and longitudes $1^{\circ}10'$ and $1^{\circ}15'E$ (Fig. 4). It lies about 50 kilometres east of Kumasi, the Administrative Capital of the Ashanti Region. Konongo is a fairly large town. The town lies on the main Accra Kumasi trunk road. Vegetationally, Konongo lies in a rich agricultural area extending northwards to Agogo and therefore is well supplied with food. Major economic activity is food crop farming. Other economic activities include crafts, gold and black smithing, kente weaving and petty trading.

3.2 SAMPLING SITES

Sampling was conducted at Konongo, Odumasi, Patriensa and Obenemase towns. The sampling sites were selected along the course of the Owerri river and its tributaries, streams, wells, boreholes and pipe-borne water within the study area. Konongo receives its water supply from Kumasi. Pipe borne water was therefore added to serve as a control analysis. The sampling points were selected to coincide with agricultural and urbanized areas of the study area in order to assess possible deleterious effects of the gold mining practices in the area on water quality. A total of eighteen (18) sampling sites were covered.

TABLE 3: SAMPLING SITES AND THEIR LOCATIONS

SITE	DESCRIPTION
1.	An underground water from the old mine shaft. It is not used for drinking but for laundry and other domestic purposes. It is also used for irrigation purposes.
2.	River Owerri. At this point, the water is not used for drinking. However, during the dry seasons, it is used for laundry purposes.
3.	River Owerri. Does not serve any domestic purpose at this point except for dry seasons. It is drunk by grazing animals.
4.	River Owerri. Main source of drinking water for the inhabitants of Patriensa (a village along the Konongo-Obenemase road). The river is not protected, hence grazing animals also drink from it.
5.	River Owerri. This part of the river is close to a spring called Amosua. The river at this point serves only laundry purposes.
6.	River Awerekye, North Pond. It is close to the mining operations. Wastes from abandoned heaps may wash into it. Does not serve any domestic purposes. Farmers used it for swimming or washing themselves. Grazing animals do not get near it.
7.	River Awerekye, South Pond. This part of the river is the main source of water for the operations of the Obenemase Gold mine. Wastes from abandoned heaps may wash into it. The river is close to a cocoa farm. Thus some of the farmers drink from it as well as use it to irrigate their crops.
8.	Tailings Dam. Mainly discharge of waste from the mining processes are stored here to be re-used. Does not serve any domestic purposes.
9.	Tailings Seepage Dam. Tailings Dam's water allowed to seep through rocks and gravel is collected at this point. The Dam does not serve any domestic purposes.
10.	Processed Dam. This is where water from the Tailings Seepage Dam left alone for some time for the cyanide concentration to reduce to an acceptable level is collected.
11.	Borehole No. 1. This borehole is near Pinnamang school at Konongo and it is used for both drinking and other domestic purposes.

12. Pipe borne water. Konongo receives its source of pipe borne water from Kumasi.
 13. Amosua (an underground water in the form of a spring), at Obenemase. The source is not known. Amosua is the main source of drinking water for the inhabitants of Obenemase and workers of OGM. It is not protected from grazing animals.
 14. River Owerri. At this point the water is not used for drinking. It is used for domestic purposes. Grazing animals also drink from it since it is not protected.
 15. Basel well. An underground water (in the form of a well) near the Presbyterian Church and School premises. It is used for drinking and other domestic purposes.
 16. Borehole near the Low Cost houses, Konongo. It is used for drinking and other domestic purposes.
- X. Raw ore or untreated ore from the surface of the trench.
- Y. Raw ore or untreated ore from the bottom of the trench.
-

3.3 SAMPLING

Sampling was done on four occasions. The first was from 25-27th November 1995, second was on 11th March, 1996, the third on 15th July, 1996, and the fourth was on 15 November, 1996. Table 3 shows the sampling points as indicated on the map (Fig. 4).

3.3.1 Water

Water constitutes the most important route of entry of element into plants, animals and humans. The sample containers were pre-conditioned as follows: washing with a detergent, followed by rinsing with tap water, then soaked in 1% nitric acid, HNO_3 , for 24 hours and finally rinsed thrice with deionized water (X-ray Spectrometry, 1993). Rivers, wells and surface water samples were sampled using a plastic bucket attached to a rope and put into pre-conditioned air-tight 1-litre plastic bottles. Sample container was rinsed twice with some of the sample before filling it. The containers were filled to the brim. At a sampling site, four samples were collected. Prior to the sampling of pipe-borne and borehole water, the pipes were flushed

sufficiently to avoid contamination of the samples. Rivers and well water were sampled at a place where the water body is fully mixed and the exact location of the sampling point could be made (GEM, 1987).

3.3.2 Sediment

Sediments were taken at the same points as the water samples. Samples were taken from the bottom of the river with an Eckman bottom sampler and placed in clean polyethylene bags.

3.3.3 Fish

The fish samples were caught with hooks. The quantity of fish caught was not as much as one would wished for. This was due to the method and the absence of abundant fish in the streams. Private people were engaged to do the angling or they bought from those who have caught them. At times there was no body to catch the fish and also many a times they were reluctant to sell their catches. The samples were kept in ice chest during transportation. In the laboratory, the samples were stored in a deep freezer at a temperature of -15°C until time of analysis.

3.4 **SAMPLE TREATMENT**

Water samples were filtered soon after sampling using a pre-conditioned Millipore filter unit and a vacuum pump. For suspended and total solids determination, the water samples were not filtered. The size of the Millipore filter used was 0.45 μm . The filtrate was put in clean plastic bottles and stored in a refrigerator or acidified with 10cm³ concentrated nitric acid (HNO_3) per litre of sample if not immediately analyzed.

Sediments were emptied and spread onto flat glass trays. Stones and macro-organisms were hand picked out from the samples and sample dried in an oven to a constant weight, at a temperature of 40°C . The dried sample was ground in an agate mortar and sieved through a 0.5mm (40-

mesh) sieve. The ground samples were stored in air-tight polyethylene bags and kept in a cool dry place. Portions of this fine homogenized powder were taken for analysis.

The fish samples were dried at 48°C to a constant weight in an oven. The dried sample was broken into the various parts (muscle, skin, bone and gill). Each part was homogenized and analyzed separately.

3.5 PARAMETERS DETERMINED

The following parameters were determined for the water samples: arsenic, total alkalinity, and total hardness. For the sediment samples, the parameters determined were arsenic, potassium, sodium and phosphorus. The main parameter determined from the fish was arsenic.

3.6 ANALYTICAL PROCEDURE

Description of the Ghana Research Reactor-1 (GHARR-1)

The Ghana Research Reactor-1 (GHARR-1) Centre, where this work was carried out, employs purely Instrumental Neutron Activation Analysis, and the Absolute Method of quantitation has been adopted. The GHARR-1 is a Miniature Neutron Source Research Reactor. It was manufactured in China and installed in 1994 by the China Institute of Atomic Energy. The fuel is 90.2% uranium-235 enriched.

3.6.1 Sample Preparation

Arsenic poses some special problems not experienced in the determination of other trace elements. Water and biologically active samples are analyzed immediately. An 0.5cm³ of the filtered water sample was placed in a 1cm³ polyethylene vial and weighed. The weight was recorded and the vial sealed with a hot soldering iron. The sealed vial was placed in a polyethylene capsule and sealed with the hot soldering iron. For each sampling site, three analyte samples were prepared.

For sediment analysis, analyte samples were taken from the homogeneously ground sample. About 0.1g of sediment sample was weighed on a polyethylene foils. The samples were then wrapped with the polyethylene foils and sealed with the hot soldering iron. They were then placed in a polyethylene capsules and sealed with the hot soldering iron. For each sampling site, three analyte samples were prepared.

For the fish analysis, analyte samples were taken from the homogeneously ground sample. About 0.5g of fish sample was weighed on a polyethylene foils. The samples were then wrapped with the polyethylene foils and sealed with the hot soldering iron. They were then placed in a polyethylene capsules and sealed with the hot soldering iron. For each sampling site, three analyte samples were prepared.

3.6.2 Sample Irradiation and Counting

Reactor source of neutron was employed in the activation of the samples. Irradiation of the sample was done using the Ghana Research Reactor-1, operating between 10-15kW and at neutron flux in the range of $1-5 \times 10^{11} \text{ ncm}^{-2} \text{ s}^{-1}$. Each of the capsules was sent into the reactor for irradiation by means of a pneumatic transfer system operating at a pressure of 65psi. The samples were irradiated for 1 hour. At the end of the irradiation, the capsules were returned from the reactor, allowed to cool down for about 24 hours until the activities had reached the acceptable level for handling. Each of the samples was then placed on the detector for counting. The irradiation scheme for some radionuclides including arsenic are shown in Table 3C.

The samples were counted on a PC-based gamma-ray spectroscopy system which consists of an N-type High Purity Germanium (HPGe) detector model GR2518, an HV Power Supply Model 3103, a Spectroscopy Amplifier Model 2020, all manufactured by Canberra Industries Inc., a Silena EMCAPLUS Multi-Channel Analyzer (MCA) Emulation Software card and a 486 micro-computer for data evaluation and analysis. The detector operates on a bias voltage of 3000(-ve)V, and has a resolutions of 0.85keV and 1.8keV for cobalt-60 gamma-ray energies of

122keV and 1332keV respectively (Germanium Detectors, 1993). The relative efficiency of the detector is 25%. By means of the MCA, the spectra intensities for the samples were accumulated for some pre-set times.

The energy calibration of the spectroscopy system was performed with sealed point sources, namely cobalt-60, caesium-137 and barium133.

3.6.3 Qualitative and Quantitative Analysis

The qualitative analysis involves the determination of the various elements in the samples by identifying the spectra peaks and assigning corresponding radionuclides and hence the elements present. The quantitative analysis involves the calculation of the areas under the peaks of the identified elements and converting them into concentration using equation (15). The qualitative analysis was achieved by means of a Silena EMCAPLUS Multi-Channel Analyzer (MCA) Emulation Software. The quantitative measurements was done using the Gamma Spectra Analysis Software SPAN 5.0 (Liyu, 1995). Spectra data for some of the samples have been shown in chapter 4.

The efficiency of the detector was experimentally measured using IAEA (International Atomic Energy Agency) mixed standard solution. The solution contains ten (10) radionuclides. Table 3B shows the list of the ten radionuclides. The neutron flux was obtained from the reactor control console.

CERTIFICATE NO. DM/42/0/95/EX

TABLE 3B: RADIOACTIVE CONCENTRATION AND ITS OVERALL UNCERTAINTY OF TEN RADIONUCLIDES CONTAINED IN STANDARD MIXED SOLUTION

REFERENCE TIME: 1 March, 1995
 AMPOULE NUMBER: 42/95
 DENSITY: 1.057 g/cm³ at 20°C

Radionuclide	γ -ray Energy [MeV]	Gamma-rays Per Second Per Gram of Solution	Radioactive Concentration [kBq/g]	Overall Uncertainty [%]
Am-241	0.060	1552	4.31	1.0
Cd-109	0.088	737	20.04	4.5
Co-57	{0.122 {0.136	{663 {82	0.775	1.7
Hg-203	0.279	3270	4.02	1.2
Sn-113	0.392	2293	3.53	4.6
Sr-85	0.514	2966	3.01	1.5
Cs-137	0.662	3397	4.00	2.4
Mn-54	0.835	5116	5.12	1.8
Zn-65	1.115	5378	10.7	2.5
Co-60	{1.173 {1.333	{5944 {5949	5.95	1.0

Source: Radioisotope Production and Distribution Centre
 Laboratory of Radioisotope Metrology
 05-400 Swierk, Poland
 March, 1995

3.6.4 DETERMINATION OF ARSENIC AND GOLD BY NEUTRON ACTIVATION ANALYSIS

In this section the actual or practical determination of arsenic in water, sediments and fish samples by neutron activation analysis using the absolute method of quantitation would be described. The samples are prepared, irradiated and counted as has been described earlier in sections 3.6.1 and 3.6.2 respectively. After the sample is irradiated by neutrons in the reactor, it is allowed to cool down or decay for a time period of 24 to 48 hours until the activities of the irradiated samples have reached an acceptable level for handling. The sample is then counted on the detector. For arsenic content, samples are counted at a pre-set time of 1000 to 3000 seconds depending on its activity. Lower activity samples were counted for 3000 seconds while higher activity ones are counted for 1000 seconds. The major photopeak counting for arsenic occurs at 559.1keV, see figures 5-7. The areas under the peaks of the spectra are then calculated and converted into activity in counts per second. This represents C_j in equation (15). Having obtained the activity in counts per second, the concentration of arsenic m_j in the sample is then calculated using (15). The equations for the calculation of concentration m_j are shown below.

$$m_j = D_j C_j / (\phi \epsilon(E_j) K_j) \quad (15)$$

M_j is the atomic weight, θ_j is the isotopic abundance, σ_j is the effective activation cross-section, D_j and K_j have been defined in equations (16) and (13) respectively. λ_j is the decay constant, f_j is the gamma yield, N_A is the Avogadro's constant, C_j is the counts per second, ϕ is the neutron flux, $\epsilon(E_j)$ is the efficiency of the detector and K_j is the counting statistics (T is the irradiation time, t_c is the counting time and t_d is the decay time). Table 3D shows the nuclear constants data for arsenic and gold. The major photopeak counting for gold occurs at 411.8keV, see figure 6.

TABLE 3D: NUCLEAR CONSTANTS DATA FOR ARSENIC AND GOLD

Nuclear Constant	Numerical Value	
	Arsenic	Gold
λ	0.693/T _{1/2} , T _{1/2} for arsenic is 26.32 hours	0.693/T _{1/2} , T _{1/2} for gold is 2.70 days
θ	1.0 or 100%	1.0 or 100%
σ	4.58 barns (1 barn=1 x 10 ⁻²⁴)	120 barns
M	74.9216 a.m.u.	196.9665 a.m.u.
F	0.446 or 44.6% for 559.1keV	0.955 or 95.5% for 411.8keV
N _A	6.023 x 10 ²³ atoms/mole	6.023 x 10 ²³ atoms/mole
ϕ	5 x 10 ¹¹ ncm ⁻² s ⁻¹	5 x 10 ¹¹ ncm ⁻² s ⁻¹
$\epsilon(E)$	5.017 x 10 ⁻³ for 559.1keV	6.6895 x 10 ⁻³ for 411.8 keV

Sources: IAEA-TECREP-273

IAEA-TECDOC-564

The neutron flux ϕ is obtained from the reactor control console. The efficiency of the detector $\epsilon(E_j)$ is experimentally measured using IAEA mixed standard solution.

HOW TO CALCULATE THE CONCENTRATION

To calculate the concentration of an element in a material, the values of D_j and K_j were calculated and substituted into the equation (15) together with the counts C_j, neutron flux ϕ and efficiency $\epsilon(E)$.

Calculation of D_j

D_j is calculated using the parameters in Table 3D in equation (16). Putting the parameters into equation (16), D_j for arsenic is calculated as:

$$D_{As} = \lambda_{As}M_{As} / (\theta_{As}\sigma_{As}f_{As}N_A) \tag{16}$$

Thus
$$D_{As} = (0.693/(26.32 \times 3600)) \times 74.9216 / (1 \times 4.58 \times 10^{-24} \times 0.446 \times 6.023 \times 10^{23})$$

$$= 4.454 \times 10^{-4}$$

$D_{As} = 4.454 \times 10^{-4}$ is a constant as stated earlier. It is therefore used anytime the concentration of arsenic is to be calculated by the absolute method of quantitation. As an illustration, the calculation of the concentration for three samples representing the three sampling types have been shown below. The samples to be used for this exercise are water sample from site 1 November, 1996, sediment from site 8 November, 1995 and fish sample from site 2. Table 3E below indicates other parameters needed for the calculation of arsenic and gold concentration in the selected samples.

Example 2: Calculation of arsenic concentration in sediment sample from site 8

TABLE 3E: SOME PARAMETERS NEEDED FOR THE CALCULATION OF ARSENIC AND GOLD CONCENTRATION IN SOME SELECTED SAMPLES

Sample & Site	Counts, C_j		Decay time, t_d (hours)	Counting time, t_c (seconds)
	Arsenic	Gold		
Water 1	7020	-	23.8	1000
Sediment 8	3.96×10^5	705.3	40.9	600
Fish 2	1290	-	22.5	600

Irradiation time, $T = 60$ minutes

$$D_{As} = 4.454 \times 10^{-4}$$

Thus the concentration of arsenic in the sediment sample from site 8 is 1780.1 ppm.

Example 1: Calculation of arsenic concentration in water sample from site 1.

The concentration is calculated by the equation

$$m_j = D_j C_j / (\phi \epsilon(E_j) K_j)$$

For arsenic concentration, the equation becomes

$$m_{As} = D_{As} C_{As} / (\phi \epsilon(E_{As}) K_{As})$$

The parameters in m_{As} are all known except K_{As} . K_{As} is calculated using the irradiation T , decay t_d and counting times t_c for the sample, in Table 3E in the equation (13).

$$K_{As} = (1 - \exp.(-\lambda_{As}T))(1 - \exp.(-\lambda_{As}t_c))\exp.(-\lambda_{As}t_d)$$

K_{As} for the water sample at site 1 therefore is:

$$K_{As} = (1 - \exp.(-(0.693/26.32) \times 1))(1 - \exp.(-(0.693/26.32) \times 0.28))\exp.(-(0.693/26.32) \times 23.8)$$

$$= 1.02 \times 10^{-4}$$

Having calculated K_{As} for the water sample, it is used together with the values of the counts per

second C_j , the constant D_{As} , the neutron flux ϕ and the efficiency $\epsilon(E_j)$ in equation (15) to calculate the concentration of arsenic in the water sample at site 1.

$$\text{i.e. } m_{As} = D_{As} C_{As} / (\phi \epsilon(E_{As}) K_{As})$$

$$m_{As} = (4.454 \times 10^{-4} \times 7020) / (5 \times 10^{11} \times 5.017 \times 10^{-3} \times 1.02 \times 10^{-4}) = 12.22 \text{ ppm}$$

Thus the concentration of arsenic in the water sample from site 1 is 12.22 ppm.

Example 2: Calculation of arsenic concentration in sediment sample from site 8

The calculation follows similar pattern as in example 1 above. First, K_{As} is calculated using the irradiation, decay and counting times for the sample in Table 3E.

K_{As} for the sediment sample at site 8 was calculated to be 3.95×10^{-5} .

The K_{As} value calculated, the counts per second per second C_j , the constant D_{As} , the neutron flux ϕ and the efficiency $\epsilon(E_j)$ are used in equation (15) to calculate the concentration of arsenic in the sediment sample at site 8.

$$\text{i.e. } m_{As} = D_{As} C_{As} / (\phi \epsilon(E_{As}) K_{As})$$

$$\text{Thus } m_{As} = (4.454 \times 10^{-4} \times 3.96 \times 10^5) / (5 \times 10^{11} \times 5.017 \times 10^{-3} \times 3.95 \times 10^{-5})$$

$$m_{As} = 1780.1 \text{ ppm}$$

Thus the concentration of arsenic in the sediment sample from site 8 is 1780.1 ppm.

Example 3: Calculation of arsenic concentration in the fish sample from site 2

The calculation follows similar pattern as in examples 1 and 2 above. First, K_{As} is calculated using the irradiation, decay and counting times for the sample in Table 3E.

K_{As} for the fish sample at site 2 was calculated to be 6.42×10^{-5}

The K_{As} value calculated, the counts per second per second C_j , the constant D_{As} , the neutron flux ϕ and the efficiency $\epsilon(E_j)$ are used in equation (15) to calculate the concentration of arsenic in the fish sample at site 2.

$$\text{i.e. } m_{As} = D_{As} C_{As} / (\phi \epsilon(E_{As}) K_{As})$$

$$m_{As} = (4.454 \times 10^{-4} \times 1290) / (5 \times 10^{11} \times 5.017 \times 10^{-3} \times 6.42 \times 10^{-5}) = 3.57 \text{ ppm}$$

Thus the concentration of arsenic in the fish sample from site 2 is 3.57 ppm.

Example 4: Calculation of gold concentration in sediment sample 8

The calculation follows similar pattern used to calculate the arsenic concentration in the three examples shown above. The equation used is:

$$m_j = D_j C_j / (\phi \epsilon(E_j) K_j) \quad \text{i.e. } m_{Au} = D_{Au} C_{Au} / (\phi \epsilon(E_{Au}) K_{Au}), \text{ for gold.}$$

D_{Au} and K_{Au} were calculated in like manner as in the three examples and found to be 8.477×10^{-6} and 1.25×10^{-5} respectively. The D_{Au} , K_{Au} calculated, the counts (from Table 3E), ϕ and $\epsilon(E_{Au})$ (from Table 3D) for gold are substituted into the m_{Au} equation to calculate the concentration.

$$\text{i.e. } m_{Au} = (8.477 \times 10^{-6} \times 705.3) / (5 \times 10^{11} \times 6.6895 \times 10^{-3} \times 1.25 \times 10^{-5}) = 0.143 \text{ ppm}$$

Thus the concentration of gold in the sediment sample from site 8 is 0.143 ppm.

The concentration of arsenic and gold in the samples calculated above were found to be comparable to the arsenic and gold concentration of the same samples obtained by the SPAN 5.0 software see Table 3.I. It was also found out that the errors associated with the manual calculations were even smaller than the SPAN 5.0 software. It can therefore be said that the concentration of elements in materials can be correctly calculated manually as shown above and also using the SPAN 5.0 software. To save time SPAN 5.0 was used for the calculation of the concentration of the elements.

TABLE 3.I: COMPARISON OF ARSENIC AND GOLD CONCENTRATION FROM THE SPAN 5.0 SOFTWARE WITH THAT FROM THE MANUAL CALCULATION

SAMPLE	CONCENTRATION (ppm)			
	Arsenic		Gold	
	SPAN 5.0	MANUAL	SPAN 5.0	MANUAL
Water 1	12.22 ± 0.21	12.22 ± 0.15	-	-
Sediment 8	1781 ± 16.0	1780.1 ± 2.8	0.143 ± 0.04	0.143 ± 0.01
Fish 2	3.58 ± 0.55	3.57 ± 0.1	-	-

3.6.5 Recovery

The reliability of Neutron Activation Analysis method was determined by a recovery test. An already prepared arsenic trioxide (As_2O_3) in approximately 1M Hydrochloric acid (HCl) standard solution with concentration 1000 ppm was used for this test. The arsenic standard solution was manufactured by Fisons Scientific Equipment. From the standard arsenic solution, 10cm^3 was taken and diluted to 100cm^3 in a volumetric flask with distilled water. 1cm^3 of this solution contains $100\mu\text{g}$ or 0.1mg of arsenic (100 ppm). From this arsenic solution 1.0, 5.0, 10.0 and 50.0cm^3 aliquots were taken into four (4) separate 100cm^3 volumetric flasks and diluted to the mark with distilled water. The solutions prepared contained 1.0, 5.0, 10.0 and 50.0 ppm of arsenic respectively. A 0.5cm^3 each of the 1.0, 5.0, 10.0 and 50.0 ppm arsenic solutions were taken into separate 1cm^3 polyethylene vials and weighed. The weights were recorded and the vials sealed with a hot soldering iron. The sealed vials were then placed in polyethylene capsule and sealed with a hot soldering iron. The capsules were then sent into the reactor for irradiation by means of a pneumatic transfer system. The samples in the capsules were irradiated for 1 hour. At the end of the irradiation, the capsules were returned from the reactor, allowed to decay for 24 hours and then counted. The 1.0, 5.0 and 10.0 ppm arsenic solutions were counted for 3000 seconds while the 50.0 ppm was counted for 1000 seconds. The counting was carried out on an N-Type High Purity Germanium (HPGe) detector with a Silena EMCAPLUS Multi-Channel Analyzer (MCA) Emulation Software card and a 486 micro computer for data evaluation and analysis. By means of the MCA the spectra intensities for the solutions were accumulated for the pre-set times. The spectra intensities for the emitted gamma radiation for arsenic occurs, at an energy level of 559.1keV . The spectra intensities accumulated were then analysed for the arsenic concentrations using the Gamma Spectra Analysis Software, SPAN 5.0.

The mean, percentage recovery, standard deviation and coefficient of variation were calculated. The recoveries ranged from 92.4 to 93.0% of the expected level. The mean recovery for all the solution analysed was 92.75%. The coefficient of variation between the replicates ranged from 0.04 to 0.51%. The relative error averaged 7.24%, see Table 3.II below.

3.6.6 Reproducibility

Reproducibility tests were also performed to determine the consistency of the method. Some of the sediment samples already measured were randomly selected and remeasured repeatedly for arsenic. The samples used for this exercise were from site 4, 13, X and Y. About 0.1g of each sample was separately weighed on polyethylene foils and the weights recorded. The samples were then wrapped with the polyethylene foils and sealed with the hot soldering iron. They were placed in a polyethylene capsules and again sealed. The capsules were sent into the reactor for irradiation by means of a pneumatic transfer system. The irradiation was carried out for an hour. At the end of the irradiation, the capsules were returned from the reactor, allowed to decay for 24 hours and then counted. The samples were counted for 1000 seconds using the N-Type High Purity Germanium detector as described in section 3.6.5. The spectra intensities accumulated were also analysed for arsenic concentrations using the Gamma Spectra Analysis Software, SPAN 5.0. The samples were analysed in triplicate.

The mean, standard deviation and the 95% confidence limits of the reproducibility tests are presented in Table 3.III below. The confidence limits μ , for n replicate measurements are given by the expression:

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} \quad (24)$$

Where $\bar{x}$ is the mean, s is the standard deviation and t is a parameter that depends on the degrees of freedom ($n-1$) and the confidence level required. The t values could be found in quantitative analytical textbooks such as Vogel's Textbook of Quantitative Chemical Analysis. As an illustration, the 95% confidence limit for site 4 sample is calculated below. The mean ($\bar{x}$) of the three determinations of arsenic content was 393.07 with a standard deviation $s = 0.21$. From the t -tables, the value of t for the 95 percent confidence level with $(3-1)$ i.e. 2 degrees of freedom, is 2.920.

Within 95% (CL),

$$\mu = \bar{x} \pm ts/\sqrt{n}$$

$$= 393.07 \pm 2.920 \times 0.21\sqrt{3}$$

$$= 393.07 \pm 0.35$$

Thus, within 95 percent confidence the true mean of arsenic content in the sediment sample from site 4 lies in the range 392.72 to 393.42 and the coefficient of variation (cv) is 0.09. The reproducibility was found for the others and the cv are between 0.01 and 0.49% see Table 3.III. There was good agreement between the replicate measurements since the variability of the results are low. The instrument could measure as low as 0.01mg/ L (ppm) of arsenic.

Concentration of Arsenic used (ppm)	Mean recovered (ppm)	Mean (ppm)	Mean Percentage Recovery (%)	σ	cv (%)
10.0	9.28 9.27 9.28	9.29	92.8	4.71×10^{-1}	0.05
50.0	46.20 46.19 46.16	46.18	92.4	0.02	0.04

σ = Standard Deviation

cv = Coefficient of variation

TABLE 3.II: RECOVERY OF SOME STANDARD ARSENIC SOLUTION

Concentration of Arsenic used (ppm)	Arsenic Recovered (ppm)	Mean (ppm)	Mean Percentage Recovery (%)	σ	cv (%)
1.0	0.93 0.93 0.94	0.93	93.0	4.71×10^{-3}	0.51
5.0	4.64 4.63 4.64	4.64	92.8	4.71×10^{-3}	0.10
10.0	9.28 9.27 9.28	9.29	92.8	4.71×10^{-3}	0.05
50.0	46.20 46.19 46.16	46.18	92.4	0.02	0.04

σ = Standard Deviation

cv = Coefficient of variation

TABLE 3.III: REPRODUCIBILITY OF ARSENIC CONCENTRATION FOR SOME SEDIMENT SAMPLES BY NAA

Site	Known Arsenic Concentration (ppm)	Measured Arsenic Concentration (ppm)	Mean (ppm)	σ	cv (%)	95% C.L. Mean Value Range
4	393.0	393.3 392.8 393.1	393.07	0.21	0.05	392.72 to 393.42
13	67.8	67.2 66.7 67.5	67.1	0.33	0.49	66.54 to 67.66
X	4624	4623.7 4624.3 4623.5	4624	0.34	0.01	4623.43 to 4624.57
Y	2968	2968.2 2967.9 2968.1	2968	0.12	0.01	2967.80 to 2968.20

σ = Standard Deviation
cv = Coefficient of variation
CL = confidence limit

CHAPTER 4

RESULTS

In this chapter the experimental results are presented in Tables 4.1 to 4.7 below. The results presented are the average of the three analyte samples prepared. WHO and Canadian Standard guidelines (Table 4.0) for water quality is also presented for comparison purposes.

TABLE 4.0: GUIDELINES FOR DRINKING WATER QUALITY

PARAMETER	CANADIAN STANDARD	WHO STANDARD
	Maximum acceptable ^a	Maximum acceptable
Arsenic	0.05	0.05
Boron	5.0	-
Cyanide	0.2	0.1
Hardness (as mg CaCO ₃ /L)	-	500
Alkalinity (as mg CaCO ₃ /L)	-	500
TDS ^b	500	400
Lead	0.05	0.05
Manganese	0.05	0.1
Mercury	0.001	0.001
pH	6.5-8.5	6.5-8.5
Temperature	15°C	No guideline value set
Turbidity	5NTC ^c	5NTC
Colour	15TCU ^d	15TCU
Silver	0.05	No guideline value set
Sulphate	500	400
Zinc	5.0	5.0
Sodium	-	200
Magnesium	-	150
Calcium	-	200

Sources: 1. WHO, Geneva, 1985.
2. Guidelines for Canadian drinking-water quality.

a Maximum acceptable concentration in drinking water (mg/L)

b Total dissolved solids,

c Nephelometric turbidity units,

d True colour unit

TABLE 4.1: THE ALKALINITY AND TOTAL HARDNESS MEASUREMENTS IN THE WATER SAMPLES

Site	TOTAL ALKALINITY (mgCaCO ₃ /L)						TOTAL HARDNESS (mgCaCO ₃ /L)						
	Nov. '95	Mar. '96	Jul. '96	Nov. '96	Mean	σ	Nov. '95	Mar. '96	Jul. '96	Nov. '96	Mean	σ	cv (%)
1.	84.0	90.0	95.0	98.0	91.0	5.31	438.0	489.2	474.2	462.0	465.9	8.74	4
2.	56.3	50.1	44.4	64.4	53.8	7.43	71.0	42.3	37.0	68.8	54.8	15.26	28
3.	51.6	43.2	45.1	70.2	52.5	10.67	62.0	49.2	43.0	67.0	55.3	9.62	17
4.	41.2	51.2	43.0	40.7	44.0	4.23	41.0	26.3	28.2	44.6	35.0	7.91	23
5.	41.0	42.1	32.0	49.0	41.2	6.05	40.0	25.0	29.0	45.0	34.8	8.07	23
6.	98.7	103.4	109.1	101.5	103.2	3.41	98.0	104.2	101.0	109.2	103.1	4.15	4
7.	74.5	79.0	80.2	76.2	77.5	2.25	79.5	77.2	74.0	83.5	78.6	3.46	4
8.	76.0	80.0	73.0	68.7	74.4	4.13	63.0	72.5	68.9	70.5	68.7	3.54	5
9.	70.0	65.0	61.0	59.2	63.8	4.15	77.0	94.0	89.2	81.2	85.4	6.64	8
10.	138.0	146.0	140.0	132.1	139.0	4.97	133.0	158.3	151.3	141.5	146.0	9.60	7
11.	60.0	58.0	51.0	56.3	56.1	3.34	60.0	51.8	60.1	55.8	56.9	3.41	6
12.	55.0	56.0	50.0	51.2	53.1	2.51	73.0	83.0	85.4	79.0	80.1	4.69	1
13.	15.2	17.1	14.0	16.0	15.6	1.13	8.6	20.1	12.5	9.8	12.8	4.47	35
14.	43.7	37.5	40.5	66.1	47.0	11.27	59.0	50.2	41.5	64.8	53.9	8.83	16
15.	23.0	26.0	28.1	22.0	24.8	2.42	18.0	30.1	24.0	20.2	23	4.59	20
16.	105.0	99.0	91.0	102.0	99.3	5.21	84.0	94.2	96.3	93.6	92.0	4.74	5

σ = Standard deviation
cv = Coefficient of variation

TABLE 4.2: THE NAA MEASUREMENTS OF ARSENIC IN THE WATER SAMPLES

SITE	ARSENIC CONCENTRATION (ppm)			
	Nov.'95	Mar.'96	Jul.'96	Nov.'96
1.	11.8 ± 0.17	11.7 ± 0.18	11.9 ± 0.17	12.2 ± 0.21
2.	0.34 ± 0.04	0.31 ± 0.04	0.33 ± 0.04	0.29 ± 0.04
3.	0.35 ± 0.03	0.38 ± 0.02	0.36 ± 0.03	0.43 ± 0.03
4.	0.24 ± 0.02	0.24 ± 0.02	0.24 ± 0.03	0.25 ± 0.02
5.	0.13 ± 0.03	0.13 ± 0.03	0.13 ± 0.03	0.13 ± 0.03
6.	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.04 ± 0.01
7.	0.04 ± 0.01	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01
8.	6.70 ± 0.18	6.70 ± 0.17	6.80 ± 0.17	6.70 ± 0.17
9.	6.50 ± 0.14	6.40 ± 0.23	6.50 ± 0.20	6.40 ± 0.27
10.	6.10 ± 0.25	6.04 ± 0.26	6.02 ± 0.28	6.13 ± 0.27
11.	ND	ND	ND	ND
12.	ND	ND	ND	ND
13.	0.22 ± 0.02	0.21 ± 0.02	0.23 ± 0.02	0.23 ± 0.02
14.	0.27 ± 0.04	0.26 ± 0.03	0.26 ± 0.03	0.26 ± 0.04
15.	ND	ND	ND	ND
16.	ND	ND	ND	ND

ND = Not Detected

The detection limit for Arsenic in water using NAA = 0.01 ppm

TABLE 4.3: SOME HEAVY METALS ALSO IDENTIFIED IN THE WATER SAMPLES BY NAA

SITE	LANTHANUM (ppm)		CERIUM (ppm)	
	Nov. '95	Nov. '96	Nov. '95	Nov. '96
1.	0.19±0.06	0.20±0.06	226.9±14.8	223.6±15.0
2.	0.12±0.04	0.13±0.04	240.6±14.7	242.0±14.2
3.	0.14±0.04	0.13±0.04	251.8±15.9	251.1±15.5
4.	0.13±0.04	0.15±0.04	247.9±14.6	244.8±15.4
5.	0.11±0.03	0.10±0.03	232.4±14.6	233.6±14.0
6.	ND	ND	241.3±14.7	238.5±15.0
7.	0.18±0.05	0.16±0.05	245.0±14.0	249.3±14.3
8.	0.17±0.04	0.16±0.04	246.0±14.8	244.0±14.9
9.	0.14±0.04	0.16±0.04	243.5±14.4	246.3±14.1
10.	0.13±0.04	0.14±0.04	236.0±14.2	234.4±14.5
11.	0.17±0.04	0.16±0.04	211.7±13.3	213.4±13.2
12.	ND	ND	105.5±9.9	107.2±9.7
13.	0.19±0.05	0.21±0.05	228.3±14.4	226.1±15.0
14.	0.12±0.04	0.14±0.04	234.0±13.8	238.7±13.8
15.	0.13±0.03	0.15±0.04	233.0±14.0	237.2±13.5
16.	0.14±0.04	0.15±0.04	247.9±14.9	250.1±14.8

ND = Not Detected

TABLE 4.4: THE NAA MEASUREMENTS OF ARSENIC AND GOLD (ppm) IN THE SEDIMENT SAMPLES

SITE	ARSENIC CONCENTRATION (ppm)				GOLD CONCENTRATION (ppm)			
	Nov.'95	Mar.'96	Jul.'96	Nov.'96	Nov.'95	Mar.'96	Jul.'96	Nov.'96
1.	NA	NA	NA	NA	NA	NA	NA	NA
2	514 ± 6	518 ± 6	515 ± 6	516 ± 6	0.50 ± 0.11	0.49 ± 0.11	0.50 ± 0.11	0.51 ± 0.11
3.	387 ± 5	390 ± 5	383 ± 5	386 ± 5	0.71 ± 0.11	0.72 ± 0.11	0.72 ± 0.11	0.72 ± 0.11
4.	393 ± 5	389 ± 5	393 ± 5	389 ± 5	0.32 ± 0.07	0.33 ± 0.07	0.33 ± 0.07	0.32 ± 0.07
5.	521 ± 6	517 ± 6	521 ± 6	519 ± 6	0.35 ± 0.07	0.34 ± 0.07	0.35 ± 0.07	0.35 ± 0.07
6.	531 ± 6	526 ± 6	534 ± 6	531 ± 6	0.93 ± 0.04	0.92 ± 0.04	0.92 ± 0.04	0.93 ± 0.04
7.	30 ± 0.4	31 ± 0.4	30 ± 0.4	31 ± 0.4	0.46 ± 0.09	0.46 ± 0.09	0.46 ± 0.09	0.45 ± 0.09
8.	1,781 ± 16	1,776 ± 17	1,787 ± 16	1,787 ± 16	0.14 ± 0.04	0.15 ± 0.04	0.14 ± 0.03	0.15 ± 0.04
9.	NA	NA	NA	NA	NA	NA	NA	NA
10	NA	NA	NA	NA	NA	NA	NA	NA
11	NA	NA	NA	NA	NA	NA	NA	NA
12.	NA	NA	NA	NA	NA	NA	NA	NA
13.	69 ± 0.8	68 ± 0.8	68 ± 0.8	68.0 ± 0.8	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
14.	416 ± 5	418 ± 5	416 ± 5	416 ± 5	0.34 ± 0.07	0.33 ± 0.07	0.33 ± 0.07	0.33 ± 0.07
15.	NA	NA	NA	NA	NA	NA	NA	NA
16.	NA	NA	NA	NA	NA	NA	NA	NA
X.	4,630 ± 37	4,627 ± 37	4,624 ± 37	4,625 ± 37	0.98 ± 0.04	1.00 ± 0.04	0.98 ± 0.04	0.98 ± 0.04
Y.	2,963 ± 24	3,008 ± 24	2,968 ± 24	2,972 ± 24	2.50 ± 0.11 ,	2.51 ± 0.11	2.49 ± 0.11	2.49 ± 0.11

NA = Not Applicable

The detection limit for Arsenic in sediment using NAA = 0.3ppm

The detection limit of gold in sediment by NAA is 0.08 ppm

TABLE 4.5: THE POTASSIUM, PHOSPHORUS AND SODIUM CONCENTRATION IN THE SEDIMENT SAMPLES.

SITE	POTASSIUM (ppm)				PHOSPHORUS (ppm)				SODIUM (ppm)			
	Nov. '95	Jul. '96	Nov. '96	Mean σ cv (%)	Nov. '95	Jul. '96	Nov. '96	Mean σ cv (%)	Nov. '95	Jul. '96	Nov. '96	Mean σ cv (%)
1.	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA
2.	1.61	1.55	1.50	1.55 0.04 3	2.47	2.33	2.51	2.44 0.08 3	0.23	0.21	0.20	0.21 0.01 6
3.	4.62	4.35	4.53	4.50 0.11 2	2.55	2.30	2.45	2.44 0.09 4	0.53	0.54	0.50	0.52 0.02 3
4.	4.55	4.63	4.60	4.59 0.03 1	3.25	3.15	3.33	3.24 0.07 2	0.45	0.42	0.43	0.43 0.01 3
5.	5.80	5.75	5.90	5.82 0.06 1	3.75	3.70	3.63	3.69 0.05 1	0.60	0.62	0.60	0.61 0.01 2
6.	9.51	8.93	9.30	9.22 0.29 3	4.32	4.13	4.25	4.23 0.08 2	0.39	0.41	0.38	0.39 0.01 3
7.	4.92	5.05	4.86	4.94 0.08 2	3.10	2.96	3.15	3.07 0.08 3	0.41	0.42	0.40	0.41 0.01 2
8.	4.10	4.35	4.30	4.25 0.11 3	3.65	3.53	3.33	3.50 0.13 4	1.55	1.50	1.53	1.53 0.02 1
9.	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA
10.	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA
11.	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA
12.	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA
13.	2.50	2.65	2.60	2.58 0.06 2	0.80	1.86	1.79	1.82 0.03 2	0.41	0.38	0.43	0.41 0.02 5
14.	4.65	4.70	4.60	4.65 0.04 1	2.96	3.00	2.85	2.94 0.06 2	0.83	0.81	0.78	0.81 0.02 3
15.	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA
16.	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA	NA	NA	NA	NA NA NA
X.	6.50	6.25	6.55	6.43 0.13 2	2.67	2.50	2.65	2.77 0.18 6	0.85	0.82	0.83	0.83 0.01 1
Y.	3.50	3.20	3.33	3.34 0.13 4	1.55	1.64	1.60	1.60 0.04 2	0.60	0.62	0.59	0.60 0.01 2

σ = Standard deviation
cv = Coefficient of variation
NA = Not Applicable

**TABLE 4.6: THE NAA MEASUREMENT OF ARSENIC AND OTHER METALS IN THE
CLARIAS ARIIDAE, FRESH WATER CAT FISH**

SITE	ARSENIC (ppm)	SODIUM (ppm)	BROMINE (ppm)	CERIUM (ppm)	POTASSIUM (ppm)
1.	NA	NA	NA	NA	NA
2.	1.72 ± 0.33	734 ± 9.5	11.60 ± 63	747.1 ± 9.2	3,920 ± 90
3.	NA	NA	NA	NA	NA
4.	ND	569.30 ± 8.5	6.30 ± 0.4	143.9 ± 3.4	3,470 ± 83
5.	NA	NA	NA	NA	NA
6.	NA	NA	NA	NA	NA
7.	0.96 ± 0.19	3,422 ± 34.2	40.10 ± 1.2	769.2 ± 9.5	18,880 ± 226
8.	NA	NA	NA	NA	NA
9.	NA	NA	NA	NA	NA
10.	NA	NA	NA	NA	NA
11.	NA	NA	NA	NA	NA
12.	NA	NA	NA	NA	NA
13.	NA	NA	NA	NA	NA
14.	1.00 ± 0.20	742 ± 8.9	6.70 ± 0.5	1,197 ± 10.6	2,273 ± 59
15.	NA	NA	NA	NA	NA
16.	NA	NA	NA	NA	NA

ND = Not Detected

NA = Not Applicable

TABLE 4.7: AVERAGE MEASUREMENT OF ARSENIC FOR THE VARIOUS PARTS OF SITE 2 CLARIAS ARIIDAE, FRESH WATER CAT FISH BY NAA

PART OF FISH	ARSENIC LEVEL (ppm)
Gill	3.58 ± 0.55
Muscle	2.02 ± 0.36
Skin	6.07 ± 0.36
Bone	ND
Composite ^a	1.72 ± 0.33

a = Mixture of all parts of the fish

ND = Not detected

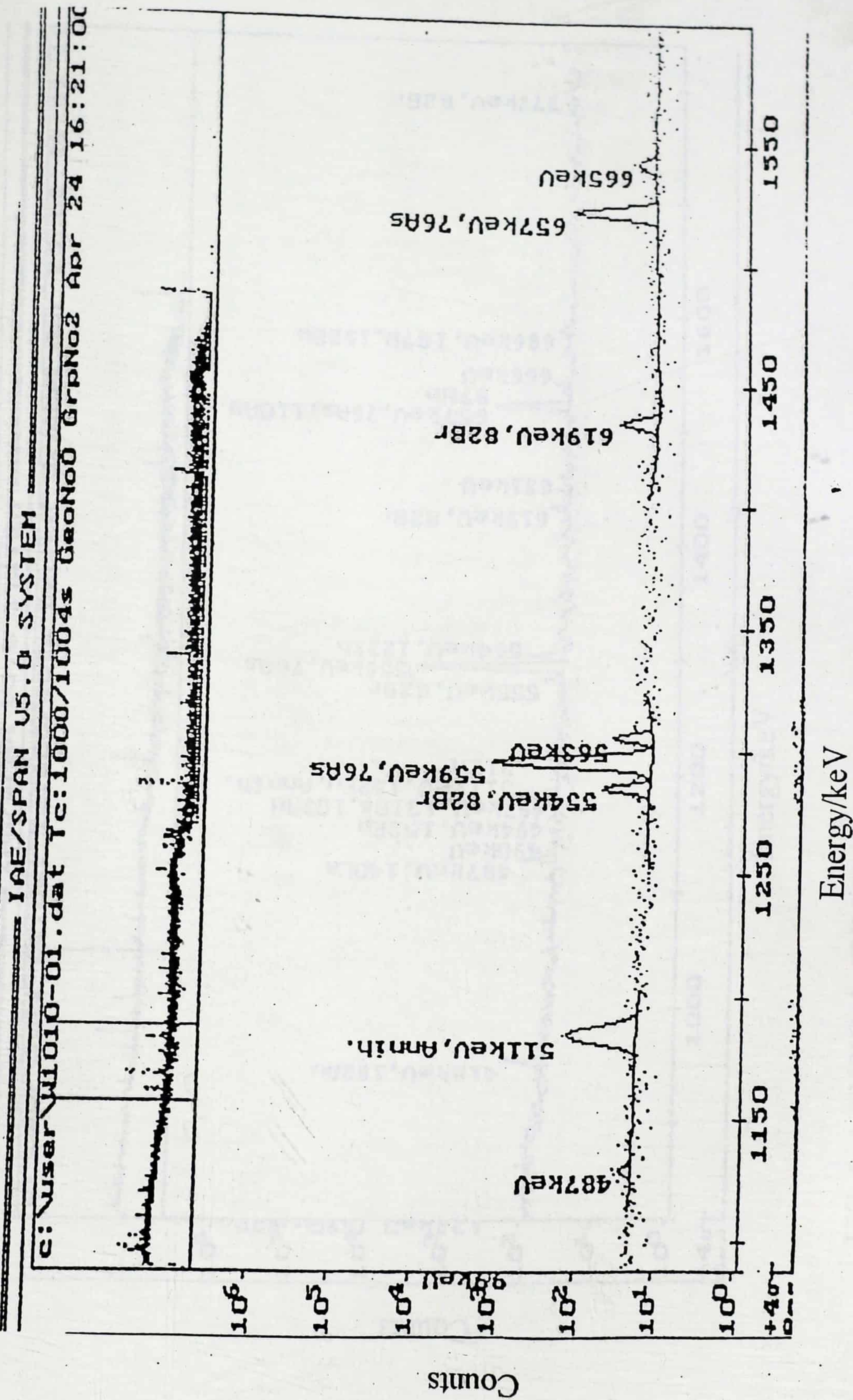


FIG. 5: A TYPICAL SPECTRUM FOR WATER SAMPLE FROM SITE 1 SHOWING THE ARSENIC-76 PEAKS

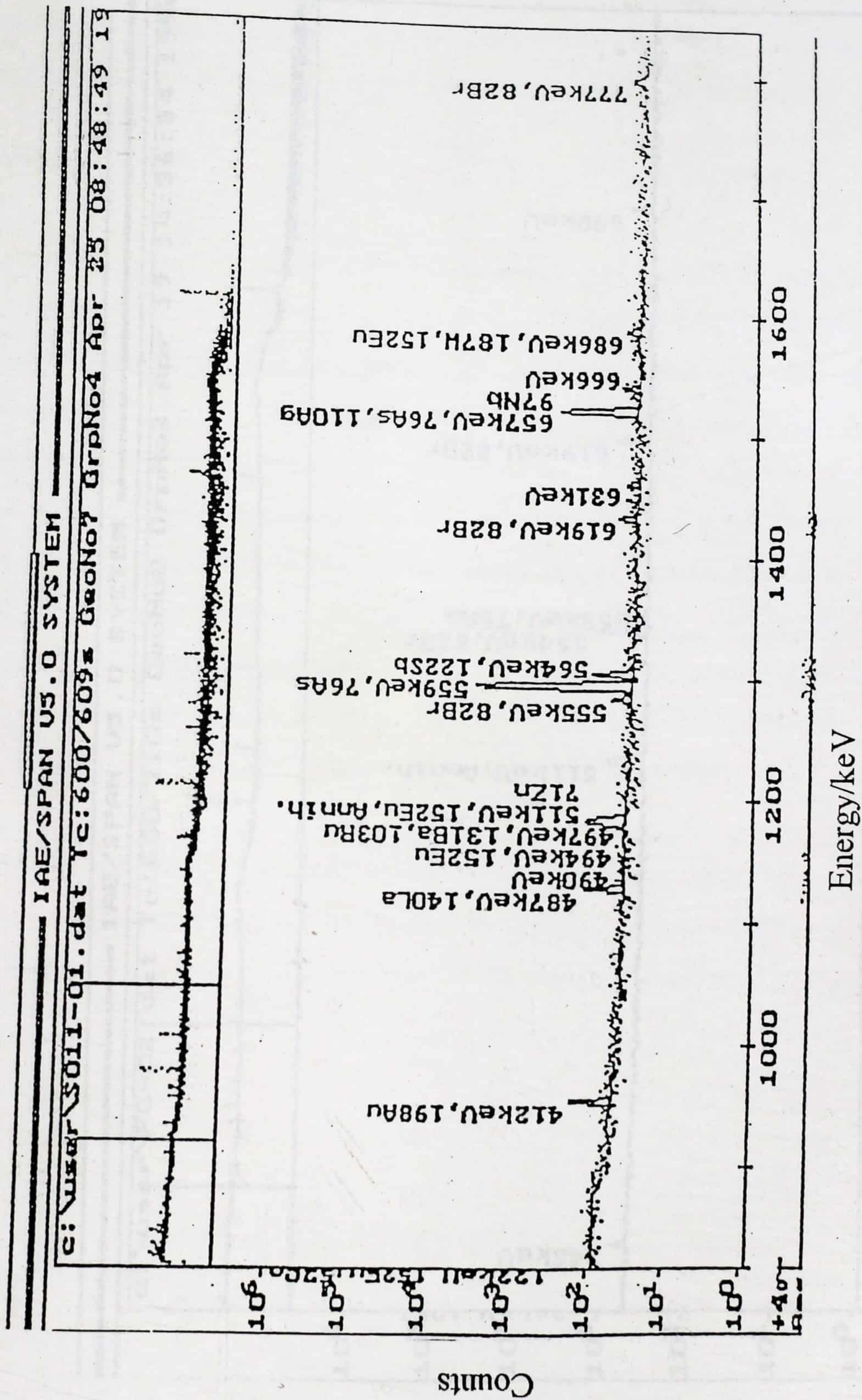


FIG. 6: A TYPICAL SPECTRUM FOR SEDIMENT SAMPLE FROM
SITE 8 SHOWING THE ARSENIC-76 PEAKS

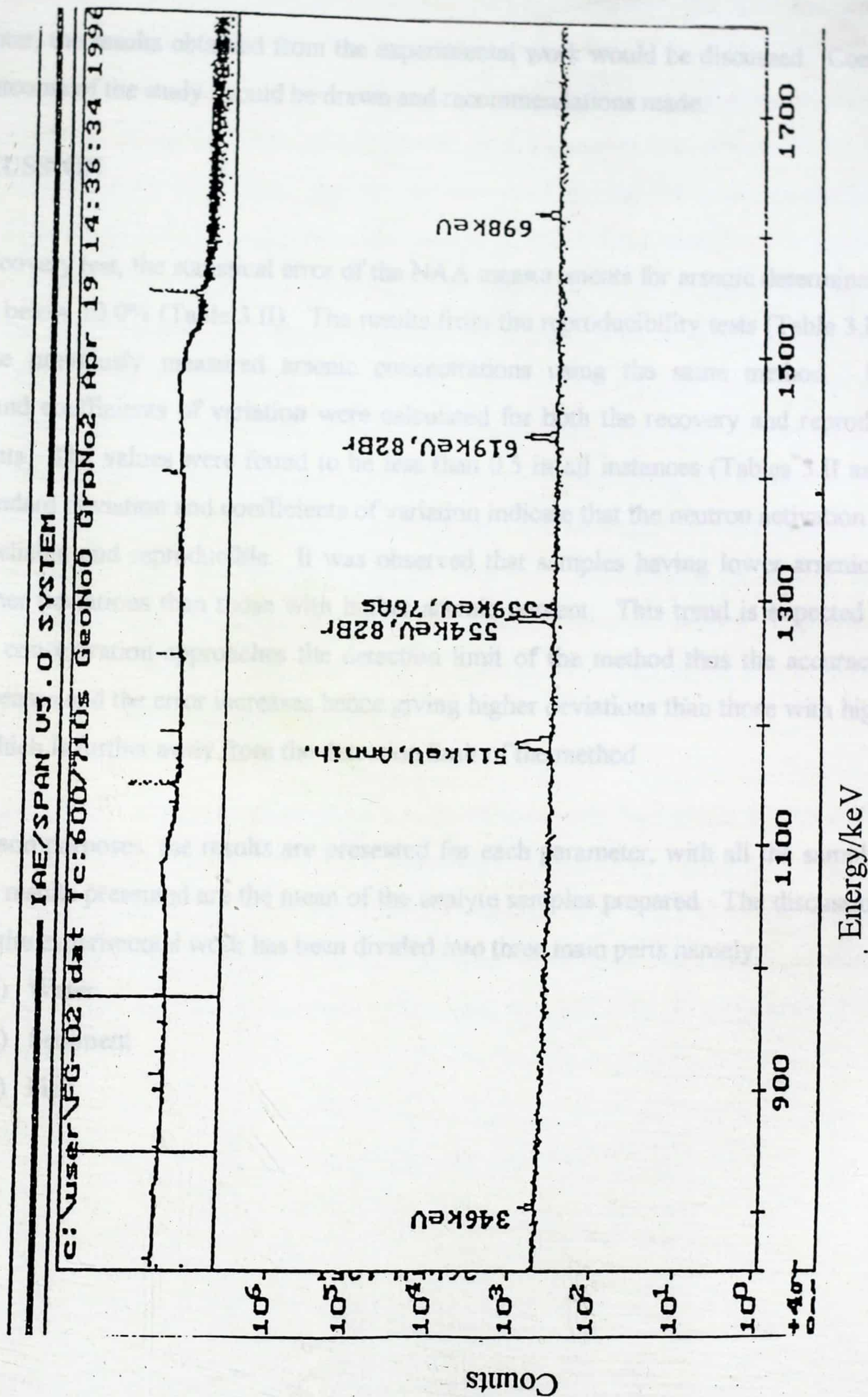


FIG. 7: A TYPICAL SPECTRUM FOR FISH SAMPLE FROM SITE 2
SHOWING THE ARSENIC-76 PEAKS

DISCUSSION, CONCLUSION AND RECOMMENDATION

In this chapter, the results obtained from the experimental work would be discussed. Conclusions from the outcome of the study would be drawn and recommendations made.

5.1 DISCUSSION

From the recovery test, the statistical error of the NAA measurements for arsenic determination was found to be below 10.0% (Table 3.II). The results from the reproducibility tests (Table 3.III) were close to the previously measured arsenic concentrations using the same method. Standard deviations and coefficients of variation were calculated for both the recovery and reproducibility measurements. The values were found to be less than 0.5 in all instances (Tables 3.II and 3.III). The low standard deviation and coefficients of variation indicate that the neutron activation analysis method is reliable and reproducible. It was observed that samples having lower arsenic content showed higher deviations than those with higher arsenic content. This trend is expected because low arsenic concentration approaches the detection limit of the method thus the accuracy of the method decreases and the error increases hence giving higher deviations than those with high levels of arsenic which is further away from the detection limit of the method.

For comparison purposes, the results are presented for each parameter, with all the sampling sites shown. The results presented are the mean of the analyte samples prepared. The discussion of the results from the experimental work has been divided into three main parts namely:

- 1) Water
- 2) Sediment
- 3) Fish

5.1.1 Water Samples

The drinking water samples were represented by sampling Sites 6,11,12,13,15 and 16. The results of the water samples are shown in Tables 4.1 to 4.3. Some of the sampling sites were found to contain some level of arsenic (Table 4.2). The levels found range from 0.04 to 12.2 ppm of arsenic. River Awirekye i.e. Site 7 which is the main source of drinking water for some of the cocoa farmers whose cocoa farms are along the banks of the river showed the presence of arsenic with a level of 0.04 ppm. This value however is lower than the WHO's recommended maximum acceptable value of 0.05 ppm (Table 4.0). This river receives the run-off of waste from abandoned heaps from the old mine. River Owerri, i.e. Sites 2 to 5 and 14 whose tributaries could be found in almost every town within the sampling area, was found to contain quite high levels of arsenic. The level was found to range from a minimum of 0.13 ppm to 0.43 ppm. It was realized that the river receives run-offs from abandoned heaps from the old mine. Fortunately, this river does not serve as drinking water for the inhabitants in the area except for Patriensa, a village along the Konongo-Odumase road but with the introduction of boreholes in the area, the river no longer serves that purpose. The level of arsenic at Site 13 (0.21-0.23ppm) is higher than that recommended for arsenic by WHO (0.05ppm). The water (Site 13) comes through a rock from an unknown source. This water is the main source of drinking water for the inhabitants of Obenemase. Part of the concessions of the Obenemase Gold Mine is close to this water body.

The tailing dams of the Obenemase Gold Mine was found to contain high levels 6.1-6.8 ppm (Table 4.2) of arsenic. This was not surprising since it was realized that the ore contain very high levels of arsenic. The tailings dams do not serve any domestic purpose. The water body that contained the highest level of arsenic was found to be an underground water from the abandoned shaft of the former Konongo Gold mine (old mine shaft). The level was found to be between 11.7 and 12.2 ppm (Table 4.2).

For both total alkalinity and total hardness (Table 4.1), all the sampling sites gave values far below the recommended value by the WHO. Site 1 however, gave a total hardness value of 489.2 mgCaCO₃/L which is close to the recommended value of 500 mgCaCO₃/L. The total alkalinity and total hardness measurements showed some correlation with the arsenic content. It was observed that the sites with the high arsenic content also gave high values of both total alkalinity and total hardness. However sites with low arsenic content did not show low values for total alkalinity and total hardness (Table 4.1).

Due to the multi-elemental nature of NAA technique, some other heavy metals were also identified in the water samples. They were Lanthanum (La) and Cerium (Ce). The concentrations measured were given in Table 4.3. For Ce, the range was 105.5 - 251.8 ppm while that of La was from 0.12 - 10.63 ppm. Both cerium and lanthanum are not of particular interest from dietary point of view (Reilly, 1980). The results for both the lanthanum and cerium measured did not show any clear relationship between their concentrations and arsenic content.

5.1.2 Sediment

Arsenic was found to be present in all the sediment samples collected (Table 4.4). Because of depth it was impossible to collect sediment samples from sites 1, 9-12, 15, 16. These sites (1, 9-12, 15, 16) corresponds to the old mine shaft, tailing seepage and processed dams, pipe borne water, Basel well and bore holes. The level ranged from 31 to 4626 ppm of arsenic. The lowest level of arsenic was found at Site 7 and the largest at Site X, which were respectively the sediment of river Awirekye and untreated ore from the surface of the trench in which the ore was mined. The untreated ore from the surface and bottom of the trench also gave a high arsenic level. It was observed that the surface ore samples contained higher arsenic content than the bottom sample. Serfor-Armah in 1994 found similar results for sediments in Obuasi gold mine. The level of arsenic in sediments found in this work are comparable to that reported on other mining environs in Ghana. Some of the findings obtained by earlier workers are presented below:

- (i) Work carried out by Acheampong in 1993 on the mining environs of Obuasi showed arsenic content in sediment with a range of 2.1-265 ppm. The highest arsenic contents were found in streams in the immediate periphery of the treatment plant of the Obuasi Gold mine.
- (ii) In his work on food items, water, vegetation, soil, and mine materials of the Obuasi Goldmine, Amasa in 1975 found high levels of arsenic in those objects close to the treatment plant of the mine. The vegetation in the immediate periphery of the mine showed arsenic levels as high as 4700 ± 110 ppm. The hair samples of workers at the roaster and chemical processing section or the treatment plant showed arsenic level ranging from 196 ± 7 to 1940 ± 62 ppm. The arsenic content of the hair of the shaft workers ranged from 7.7 ± 0.9 to 78.0 ± 3.2 ppm. The arsenic content of these samples are far above the level found in an uncontaminated hair reported by Leniham and Smith (1958) which had a range of 0 to 2.5 ppm.
- (iii) In their work on arsenic determination of As^{3+} and As^{5+} in some Ghanaian gold tailings by distillation, Ahmed and Carbo (1997) found gold tailings from Obuasi to contain $3,795 \pm 394$ ppm of arsenic by Atomic Absorption Spectrophotometry (AAS) and $8,305 \pm 75$ ppm of arsenic by Neutron Activation Analysis.

These works and others reported elsewhere show high levels of arsenic in and around mining areas. Generally sediments are found to contain high levels of arsenic. The results obtained for this work thus compare favourably with those conducted in other mining areas in the country. Uncontaminated soils however have been recommended to contain arsenic with a range of 2 ppm to 5 ppm (Dickerson, 1980).

The arsenic level found for this work with an average range of 31- 4626 ppm appears to be very high compared to an earlier work done by Ntow in 1993 in the same sampling area using AAS in

is continued, there won't be an environmental pollution except leaching into water tables. However, when the sulphide ore is to be mined and processed, then the necessary inputs must be put in place to safeguard the health of the inhabitants of the area as well as the mining workers from arsenic poisoning.

It has been asserted that the goldfields found at Konongo and Tarkwa are the free-milling gold type that are usually finely dispersed in quartz vein or lodes. An environmental impact assessment of the Gold Mining Industry in Ghana carried out by Akoto Bamford et al at the Prestea and Tarkwa mining areas using X-ray fluorescence (XRF) analysis and AAS showed the absence of arsenic in the gold tailings (Akoto-Bamford, 1989). Ntow also did environmental assessment of Konongo and its environs for arsenic using AAS and concluded that there was no arsenic present in the area sampled. The present work using NAA has shown that arsenic is present in the ore at Konongo with levels that cannot be ignored. With this observation, it can be concluded that in addition to the free-milling ore type found at Konongo fields, there might be some arsenopyrites ores. This assertion could be supported by the high iron and arsenic contents observed in the sediments.

5.1.3 Fish

The fish samples were from sampling Sites 2, 4, 7 and 14. Sampling Sites, 2, 4 and 14 represent the same river, Owerri, while Site 7 represent river Awirekye. Results from the fish analysis are shown Table 4.6 and 4.7. Arsenic was present in three of the four samples analyzed with a range of 0.96 - 1.72 ppm. In all the cases, the level of arsenic found in the fish were higher than the level found in corresponding water sample. This is in agreement with the accumulative effect of arsenic in certain fish organs (EHC, page 1981).

The different parts of the fish, fresh water catfish, Clarias ariidae, (Beadle, 1974), from Site 2 as well as the composite of all the parts of the same fish including the fish bone were analyzed separately for arsenic, see Table 4.7. The level of arsenic found in the different parts of the fish gave the following order: skin > gill > muscle > composite > bone. The bone showed zero

level of arsenic and might not be the usual organ for storage of arsenic in fish. This is not conclusive. A lot of work would have to be carried out first. It came out clear that the 'skin' of the fish had the highest level of arsenic followed by the gills and muscle respectively while the composite of all the parts gave the least amount of arsenic. The above trend was expected as the 'skin' has the greatest contact with the water and might slowly but constantly absorb the metal. The high levels in gills also might be due to the absorption or adsorption of the metal constantly through filtration during respiration and will transfer or eliminate it faster into other parts of the fish.

The levels of arsenic found in the fish samples were very low compared to that found in the corresponding sediment samples, they are higher than the levels of arsenic found in the corresponding water samples.

5.2 CONCLUSION

From the experimental work, the following conclusion could be drawn:

Some of the water bodies found at Konongo and its surrounding towns and villages were contaminated with arsenic with levels which ranged from 0.03 to 12.2 ppm. The fish in the rivers were also polluted with arsenic. The concentration of arsenic found in the fish from the study area ranged from 0.96 to 1.72 ppm. The sediments contained high levels of arsenic. Arsenic concentration in the sediment ranged from 31 to 4626 ppm. The trend of arsenic concentration in the three samples was:

sediments > fish > water

The arsenic levels found in the untreated ore was on the high side indicating that there may be some arsenopyrite ore present in the concession of Gold mine. If the ore should be processed for gold extraction, arsenic is likely to be released into the atmosphere and may have negative effects on the inhabitants of Konongo and its surrounding towns and villages unless an effort is made to prevent entry into the environment.

The results obtained point out that arsenic is present in some parts of the Konongo gold fields at quite significant levels. However, since the drinking water bodies are quite some distance from the mining areas, the inhabitants of Konongo and surrounding towns would not be in danger of arsenic poisoning if care is taken to prevent the release of the element into the environs.

Neutron Activation Analysis has a good detection method for arsenic. The work load is very minimal and so is the handling time. Thus contamination due to handling of sample is negligible. The analysis time for arsenic using NAA, is fast. The only set back to NAA is the location of the facility. Currently, the facility could be found only at the Ghana Atomic Energy Commission, Accra (G.A.E.C.). Thus if transportation is not a problem, then samples could be taken to GAEC and the analysis carried out almost immediately.

3. Water, bottom and core samplers and winch.
4. Life jackets.
5. Fishing nets and hooks.
6. Fishermen.
7. Swimming pools for researchers to learn how to swim.
8. Tents and camping facilities.
9. Higher night allowances for field work.

b. Methyl Orange Indicator

0.5g of methyl orange indicator was dissolved in 100cm³ doubly-distilled water.

1.2 PROCEDURE

APPENDIX

1. Total alkalinity

1.1 REAGENTS

a Hydrochloric Acid (0.02M)

1.66cm³ of concentrated hydrochloric acid (HCl) was diluted to 1 litre with doubly-distilled water. The solution was standardized with a standard sodium carbonate solution.

b Methyl Orange Indicator

0.5g of methyl orange indicator was dissolved in 100cm³ doubly-distilled water.

1.2 PROCEDURE

100cm³ of water sample were transferred into a 250cm³ conical flask and 2 drops of methyl orange indicator added to form a yellow solution. The yellow solution was titrated against the standard hydrochloric acid solution to a pink colour.

1.3 CALCULATION

$$\text{Total Alkalinity} = \frac{\text{Vol. of HCl}}{\text{Vol. of sample used}} \times 1000. \text{CaCO}_3 \text{ L} \dots\dots\dots(25)$$

2. Total hardness

2.1 REAGENTS

a Buffer solution (aqueous ammonia)

16.9g of ammonium chloride (NH₄Cl) was dissolved in 143cm³ of concentrated ammonium hydroxide (NH₄OH). 1.179g of disodium salt of ethylenediaminetetraacetate (EDTA) and 780mg magnesium sulphate were dissolved in 50cm³ distilled water and added to the ammonium solution. The solution was diluted to 250cm³ with distilled water and stored in a plastic container for no longer than 1 month.

b Standard EDTA titrant, (0.01M)

3.723g of disodium ethylenediaminetetraacetate dihydrate was dissolved in distilled water and diluted to 1 litre.

c Total hardness indicator powder (Eriochrome black T)

2.2 PROCEDURE

50cm³ of sample was transferred into 250cm³ conical flask. 2cm³ of the buffer solution was added. About 0.5g of the Eriochrome black T indicator powder was added. A wine colour was formed. The solution was titrated slowly with the EDTA solution while stirring continuously to a clear blue solution.

2.3 CALCULATION

$$\text{Total hardness} = \frac{\text{Titre Vol.}}{\text{Sample Vol.}} \times 1000 \text{mgCaCO}_3 \dots\dots\dots (26)$$

3. Available phosphorus and potassium in sediment samples

3.1 PRINCIPLE

Available phosphorus and potassium in soil are determined by the elements in aqueous extracts. K is determined by flame photometry while P is determined colorimetrically by the ammonium molybdate method with ascorbic acid as a reducing agent (CSIR, ;ISRIC, 1992).

a Extracting Solutions

There are four common extracting solutions.

- 1) North Carolina Extraction Solution (0.05N HCl + 0.025N H₂SO₄)
- 2) Olsen Extraction Solution (0.5N NaHCO₃ of pH 8.5)

3.2 REAGENTS

- 3) Truog Extraction Solution (0.002N H₂SO₄ buffered with (NH₄)₂SO₄ to pH 3.0)

4) Bray No.1 Extraction Solution (0.03N ammonium fluoride + 0.025N HCl)

Any of these extracting solution yields good results with a soil to extracting solution ratio of between 1:5 and 1:10. For this work, Bray No.1 Extraction Solution was employed.

b Bray No.1 Extraction Solution

- i) 0.03N ammonium fluoride (NH_4F) : 37g of NH_4F was dissolved in distilled water and diluted to 1 litre. The solution was stored in polyethylene bottle.
- ii) 0.025N HCl: 21.5cm³ of concentrated HCl was diluted to a volume of 500cm³ with distilled water.

30cm³ of i) and 50cm³ of ii) were taken added to 920cm³ of distilled water to obtain 1 litre of the Bray No.1 Extraction Solution.

Procedure for Extracting P and K

10g of the homogenized sediment sample was weighed into a polyethylene shaking bottle. 50cm³ of the extracting solution was added. The resulting mixture was shaken for 10 minutes on an orbital shaker. The mixture was then filtered through a Whatman No.41 filter paper.

Colour Developing Reagent (Concentrated molybdate solution)

2g of Bismuth subcarbonate ($\text{Bi}_2\text{O}_2\text{CO}_3$) was placed in a litre pyrex graduated flask and 250cm³ distilled water added. 150cm³ of concentrated H_2SO_4 was rapidly added and the solution swirled to dissolve the bismuth subcarbonate. The solution was allowed to cool. After cooling, 20g ammonium molybdate in 200cm³ distilled water was added. The solution was diluted to the 1 litre mark with distilled water. The solution was stored in a cool place in a dark container. 200cm³ of this solution was taken and diluted to 1 litre with distilled water to obtain the working solution.

c Standard phosphorus solution (1000ppm)

0.2194g of dry potassium dihydrogen phosphate was accurately weighed and placed in a litre graduated flask and made up to the mark with the extraction solution. From the standard phosphorus solution were prepared 1, 2, 3, 4, 5 and 6ppm dilute phosphorus solutions.

d Standard potassium solution (1000ppm)

0.4769g of potassium chloride was accurately weighed and dissolved in the extraction solution and made up to 500cm³. From this standard solution were prepared 5, 10, 20, 30, 40 and 50ppm dilute potassium solution.

3.3 PROCEDURE FOR ESTIMATING PHOSPHORUS

5cm³ of each of the standard P solution was put into a test tube. 10cm³ of the colour reagent was added and mixed well. A small amount of L-ascorbic acid was added to each of the solutions and left to stand for 30 minutes for colour to develop. The solution now blue in colour were read on a colorimeter at 600nm to determine their absorbance. A calibration curve for P standard of concentrations 0 (blank solution), 1ppm, 2ppm, 3ppm, 4ppm, 5ppm and 6ppm was prepared. 5cm³ aliquot of each of the soil extracts were taken and treated as the standard. The absorbance for each sample was measured and the corresponding concentration read from the graph. All measurements were done in triplicate.

CALCULATION

Concentration of P in soil = Extract concentration x 5 (5 = Dilution factor)

3.4 PROCEDURE FOR ESTIMATING POTASSIUM

500ppm potassium solution was drawn into the flame and atomized. The reading was adjusted to 100 with sensitivity control. Similarly blank solution was drawn and the reading adjusted to zero. The operation was repeated. The standard K solutions of concentrations 0 (blank solution), 10ppm, 20ppm, 30ppm, 40ppm and 50ppm were drawn into the flame and the meter readings (%) noted. A calibration curve was drawn with concentration of K against

meter reading (%). The extracts of the samples were drawn into the flame and the % recorded. The K in the extracts were estimated from the calibration curve.

CALCULATION

Concentration of K in soil = Extract Concentration $\times$ 5 (5 = dilution factor)

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