THE DEVELOPMENT AND EVALUATION OF ANALYTICAL PROCEDURES FOR THE DETERMINATION OF HEAVY METALS IN INDUSTRIAL EFFLUENTS

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CERTIFICATION

This is to certify that the research work for this thesis and the subsequent preparation of this thesis by AZEB THEOPHILUS LAGI (PGNS/UJ/10895/99) were carried out under our supervision.

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DECLARATION

I hereby declare that this work is the product of my own research efforts; undertaken under the supervisions of Prof. J. N. Egila and Prof. M. M. Ekwenchi and has not been presented elsewhere for the award a degree or certificate. All sources have been duly distinguished an appropriately acknowledged.

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ABSTRACT

This project is concerned with the development and evaluation of an atom-trapping technique for determination of heavy metals in environmental samples. Modified atom-trapping technique using fabricated nickel tube/sample holder (crucible) was employed to increase the sensitivity of a flame atomic absorption spectrometry. Basic performance data for different parameters, such as burner height and the height of the support, were studied. Different designs and ways of placing the atom trap over the burner were evaluated to optimize the experimental conditions. The height of the tube's support was varied, as well as, its design. The optimal position, for maximum light path through the tube, was obtained experimentally. Results of this attempt using nickel atom trap method on a number of standards of lead, cadmium, copper, zinc, cobalt, manganese and nickel concentrations, showed high sensitivity for the technique (1.2 - 4.1 fold) when compared to the conventional flame atomic absorption spectrometry. The improvement factors on the absorbance signals for the various metals were as follows: Cd =3.8 - 4.1; Pb = 1.8 - 2.2; Cu = 1.9 - 2.3; Mn = 1.2 - 1.7; Zn 2.3 - 2.5; Co = 1.2 - 1.8 and Ni = 1.6 - 2.1. These data indicated that a significant improvement in sensitivity has been achieved, using the nickel tube atom trap method. The results from this study suggested that the method, as an analytical procedure, is more sensitive than the conventional method for the determination of heavy metals in environmental samples. Thus a study was carried out to analyse effluents discharged from small and medium scale industries. These are

Naraguta leather tanning effluents, Jos; Majema leather tanning effluents, Kano; a small-scale industry located at Sharada Industrial Estate Phase III leather tanning effluents, Kano; NASCO Group of Companies, Jos and Jos International Brewery (JIB), Jos. The results showed some pollution in these effluents for the various elements above the Interim Effluent Limitation Guidelines in Nigeria for all Categories of Industries. The Naraguta leather tanning had high value of zinc. The Majema leather tanning effluent is polluted with lead, copper, and zinc, while the Sharada leather tanning effluent had high zinc, with a very close value to the limit of copper. NASCO is polluted with copper, and zinc, as well as, Jos International Brewery (JIB).An attempt was made to increase sample volume from 0.2 ml to 2 ml by redesigning the nickel tube, accommodating more analyte reaching the flame. Analytical performance, such as sensitivity, precision, detection limit, and accuracy of the method, was carried out and the results compared with those from literature. One advantage of the developed nickel tube atom trap method is the very small sample solution requirement for analysis. Further more; its simplicity and low cost would be an advantage to many laboratories with limited resources. The interference study of NaCl on the absorbance of lead was carried out. The result showed that NaCl exhibited a significant level of suppression at 5mg/L of Pb (i.e. 1.17% at 10% NaCl to 1.28% at 30% NaCl reduction in absorbance signal).

CHAPTER ONE

INTRODUCTION

1.1. BACKGROUND TO THE STUDY

Pollution is contamination by a chemical or any agent that renders part of the environment unfit for man or other living organisms. Pollution damages the land, water and air. It results in contamination of the earth's environment with materials that interfere with human health, the quality of life and the natural functioning of ecosystems. Pollution is usually caused by human actions but can also be the consequence of natural disasters (Rao, 2006). A pollutant is defined as a substance that occurs in the environment as a result of human activities and which has a deleterious effect on the environment (Moriarity, 1990). Domestic, industrial and agricultural processes and other sources produce large quantities of waste products that cause rapid changes to the environment. Exposure to the pollutant at sufficiently high concentrations can cause a variety of health effects (Dara, 2002).

1.1.1 Environmental Pollution

There has been increasing concern chemicals in the environment. Such concern has arisen in response to the widespread distribution of chemicals stemming from human activities and the potentially harmful effects of those chemicals on humans or on the ecological systems. As nations develop their industrial activities, the production and use of chemicals rise in parallel to the standard of living and the consequent increase in the life expectancy (Adepetu & Eziashi, 1998). Technology has made it possible for people to live longer in comfort and with greater leisure. Environmental deterioration threatens our well being when air, water or food become contaminated (Eisenbud, 1979).

United Nations Conference on Environment and Development (1992) has identified the following adverse global environmental impacts, which have caused

deterioration of the planet earth due to developmental processes: eutrophication, acid precipitation, ozone layer depletion, deforestation, soil erosion, global warming, climate change, air, water and land pollution, from toxic and hazardous industrial wastes, depletion of natural resources, land degradation, ill health and death (human), loss of biodiversity and loss in beauty and aesthetic value of the physical environment. At its ninth session in 1981, the Governing Council of the United Nations Environment Program (UNEP) recognized that the list of selected environmental dangerous chemical substances harmful at the global level should be prepared (Andersen & Sarma, 2002). Harmful chemicals are defined as those, which enter the environment as product, or by-product of human activities, threat man's health, the environment and which can be eliminated with difficulty from the environment (Redwood & Dixon, 1992).

The causes of most environmental problems have their origins in the development process or in its failures and inadequacies. Technological advancement and increasing industrial which is satisfying human needs and comforts, and to improve on civilization and human life styles, have created unexpected adverse effects. Man and nature have been at odds since the industrial revolution, and especially in this century (Odiette, 1993).

Environmental and toxicological concern over heavy metals, such as cadmium, lead, copper, and zinc etc, has been documented in recent years in the large volume of analytical literature presenting methods for their determination (Taylor, Branch, Halls, Owen & White, 1998). Environmental degradation and pollution threaten not only the development process, but the safety of man and other organisms. Heavy metal contamination of soil, water, and food are causes of concern because of the toxicological effects of such metals on humans and other living systems (Matin, 1995).

As urban areas increase, there is increase of wastes such as water and solid wastes, and other demands. Urban and industrial areas are polluted by the increasing number of motor vehicles, the expansion of existing industrial areas and the aging in old factories (Pham, Dang & Nguyen, 1995). Increasing industrialization and globalization have spawned the unprecedented generation of environmental toxic and hazardous wastes (Pandey & Carney, 1989). Hazardous waste management is now a major and urgent global concern because hazardous substances significantly contribute to destruction of life. Far more controversial is the issue about the quantities of wastes from the developed nations shipped to developing countries in Asia, Africa and other parts of the world. The existence of known hazardous waste such as toxic spills and river pollution put pressure on each national government to take an extensive role in hazardous waste control (Kellog, 1977).

Bartley and Gardiner (1977) described the level of heavy metals in a water body as a pointer to the cause. These are natural sources based on the geochemical nature of the soil and the rock beds within the water basin including the presence of mineral deposits, and the discharge of untreated industrial wastes. Both tend to cause the enrichment in metals depending on the nature and scope of the industry or geology of the area.

Water pollution is a problem in the wake of rising population, rapid urbanization, and industrialization. The urban growth has increased domestic wastes, while new industries have augmented industrial wastes. The discharge of these chemicals into water courses have resulted in hazard of water pollution (Itanna, 1998). Undesirable results from the discharge of inorganic materials include changes in the pH and toxicity by heavy metals or other toxic materials.

Industrial emissions are potential sources of environmental contamination. Major industries including fertilizer, pulp and paper mills, dyeing, printing, textile, tanneries, cement and pesticides, plastic, food processing, distilleries etc. generate wastes with varying pollution burdens. Monitoring these emissions helps to improve industrial processes, and consequently, to protect the environment (Maier, 1996).

1.1.2 Sources of Pollution

The advanced technology as well as the rapid urbanization in recent years has affected the quality of the ecosystem. Due to human activities the chemical compositions of soil, water and air have been altered. Pollution can also be as the consequence of a natural disaster (Duggal, 1988).

1.1.2.1 Land Pollution

Environmental problems associated with the land degradation are caused by mining activity. Exploration affects landscape specifically aesthetic deterioration of the landscape, path-construction and trampling in wilderness areas. The land degradation and ecosystem destabilization caused by mineral extraction has specific impacts, such as land surface devastation (including erosion), disruption of drainage system, deforestation, and contamination of the water table. Processing, transportation, storage and consumption of mining activities are also of concern, because oil spills and land pollution (acidification of soil) are pronounced in mining regions. Environmental problems connected with petroleum exploitation is oil spillage, both on-shore and offshore. The rate of the spill has been with the increasing tempo of petroleum production (Igbozurike, 1978).

Mining and smelting wastes contain heavy metals such as cadmium, copper, lead and zinc. Shaheen (1995) observed that mining wastes can pollute streams and ground water, harm wildlife, fishing and agriculture in areas influenced by mining activity.

Erosion is the detachment and transportation of soil particles by running water, wind and waves. Wind erosion affects northwest Sokoto, northern Kano and Borno. Coastal erosion affects Lagos (especially Bar Beach at Victoria Island), Ogun, Ondo, Rivers, Akwa Ibom, and Cross River States. Bigger sizes of gully erosion are mainly to be found in Imo and Anambra states, where a combination of weak, sandy soils, widespread deforestation, and high rainfall has promoted accelerated erosion (Adefolalu, Ade-Odutola, Afolayan, Agunbiade & Aina, 1991).

1.1.2.2 Water Pollution

Water pollution could be from plant nutrient used to fertilize farmlands, ashes, and detergents. When these plant nutrients are washed into water bodies, they encourage growth of algae, and phytoplankton. The unregulated use of fertilizers, pesticides, and herbicides to increase crop production has led to environmental pollution. Medical wastes generated in the diagnosis, treatment, and immunization of human or animals pose a great danger to the environment (Okoronkwo, 1998). Also, industries discharge of their effluents without prior treatment, into rivers, estuaries or lagoons. Solid wastes such as metal (scraps), plastics and other objects pollute water bodies. The ever increasing solid wastes being generated are disposed indiscriminately, and managed poorly by the relevant government authority (Umeh & Uchegbu, 1997).

1.1.2.3 Air Pollution

Air pollution involving the release of chemicals and particulates into the atmosphere, in sufficient concentrations endanger human health. The increasing skin cancer, cataracts, weakening human immune systems, and damaging crops and natural ecosystem) or produce other physical effects on living matter, and other materials (Britton & Greeson, 1994). The sources contributing to the pollution of the atmospheric air are:

a) Smoke due to incomplete combustion of coal in industrial plants, furnaces and hearths.

b) Finely divided dust particles, salt particles from oceans, pollens, spores etc, remain suspended in air.

c) Gaseous impurities from chemical manufacturing industries and including sulphur dioxide, benzene, carbon monoxide, acid vapours, fumes etc.

d) Automobile exhaust gases, in particular, exhaust from trucks and buses. These contain products of incomplete combustion, carbon monoxide, hydrogen, methane, unburnt carbon, and partially burnt hydrocarbons; oxides of sulphur, and nitrogen contribute significantly to air pollution (Raina & Aggrawal, 2004). Motor vehicles have been regarded as the primary source of air pollution in the urban areas, and accounts for 60- 70% of the pollution found in the urban environment (Singh et al., 1995).

The atmosphere, a relatively thin layer of gas enveloping our globe, is basically of constant composition, temperature, and pressure (Duggal, 1988). The minor changes that do occur, however, have an enormous influence on man’s life.

1.1.2.4 Noise Pollution

Another source of environmental pollution is noise. Noise pollution affects the physical and mental health of man and, reduces working efficiency (Maruthi, Rao & Ravindra, 2004). The rapid urbanization and the increased transportation in the recent years have helped the people to develop but on the other hand left impacts that have affected the human environment (Arutchelvan, Venkatash, Damodharan & Elangovan, 2004). The growing needs of human life in this fast track society and the increased automobiles have contributed to increase in noise pollution.

1.1.3 Heavy Metals in Environmental Pollution

Heavy metals are not biodegradable, but persist in the environment for a long time. They are known to be causative for many diseases including cancer, immune diseases, allergies, and asthma. Toxic effects of heavy metals on biological systems are very variable, and are related to their chemical form. Certain heavy metals forms, such as bio-available forms, are potentially toxic, and hazardous to the biota of receiving water. However, recent studies have shown that the free ions, and weakly complexed forms as being the bio-available, and more toxic forms of metal (Mendoza, Cories & Munoz, 1996). The metals, with the highest impact on organisms are copper, chromium, cadmium, tin, lead, vanadium, molybdenum, cobalt, and nickel. From an environmental point of view, all these elements are important because they cannot be biodegraded in water, soils and sediments (Carson & Munford, 1994).

The heavy metals are given consideration in monitoring activity to prevent acute toxicity and destruction to ecosystems. Though there are some natural sources of heavy metal contamination, the greatest to the quality of the environment is posed by human activity. Some chemicals even in trace quantities are carcinogenic, mutagenic, teratogenic and toxic to man and other biological substances of economic importance (Moriarity, 1990).

Itanna (1998) described contamination by heavy metals as contributors of toxic substances, is not restricted to the soil alone. The effect goes beyond that, affecting every component in the food chain, namely; plants, grazing animals and ultimately man. Air and aquatic environments including the sea foods of both plant and animal origin like fish are subject to this hazard.

Many heavy metals affect the vegetation in terresterial habitat (Pahlsson, 1989). The uptake of heavy metals by plants from contaminated soils is of interest because an excess dietry intake of some of these metals could be deleterious to the health of a consumer (Davies, 1992).

The problem of heavy metal contamination in water bodies is widespread threatening an ever-increasing portion of the global population. The presence of toxic heavy metals in water resources poses unacceptable chronic and acute health risks (Roy, Greenlaw & Shane, 1993).Heavy metals are known to be essential for living organisms. They are used in respiratory pigments – (iron, copper, and vanadium), enzyme – zinc, vitamins – cobalt and other metabolic processes. It is only when normal concentrations are exceeded, that they become potentially toxic (Kielly, 1988).

Excess of dietary intake of these heavy metals might be deleterious to the man (Dudka, Piotrowska & Chlopecka, 1994). It is therefore considered that removals as well as recovery of toxic metals are the desirable approach to control pollution and safeguard the environment and health (Wasay et al., 1994). The maximum tolerable levels of trace elements set by the World Health Organisation are as shown in Table 1.

According to Koul, Zutsch and Dubey (1988), studies pertaining to the toxicity of trace metals follow the general trend that an undersupply leads to deficiency, sufficient supply results in optimum conditions but an oversupply leads to toxic effects, and ultimately death.

1.1.4. Effects of Heavy Metals on Man

Heavy metals are known to be toxic to man, as their concentrations in the environment has been progressively increasing, and might cause severe health hazard to man. Lead and cadmium are trace metals with no known beneficial physiological effect, but they are toxic to plants and animals if their concentrations exceed certain values (Adriano, 1986).

Table 1. The Maximum Tolerable Levels for Trace Elements Proposed by World Health Organization (1984)

Element	Concentration (mg/L)
Copper	1.0
Lead	0.05
Zinc	5
Cadmium	0.005
Manganese	0.1
Nickel	0.5
Cobalt	0.05

* Source: Recommendations, World Health Organization.

A study by Abdel-Saheb, Schwab, Banks and Hetrick (1994) indicated that people exposed to lead and cadmium from contaminated drinking water and surface soils suffer from increased chronic kidney disease and anaemia.

There are many ways in which human are exposed to lead through air, drinking water, food, contaminated soil, deteriorating paint, and dust. Lead is an important pollutant in emissions from industries, and automobiles. Much of the stable lead pollution is of atmospheric origin. Drinking water can become contaminated with significant amounts of lead in its distribution system as a result of corrosion, and leaching from lead pipes, and lead/tin soldered joints associated with the copper service lines used in household plumbing (Subramanian & Connor, 1991). Lead is responsible for serious damage to the health of human, and birds. Lead affects all systems within the body. It is bio-accumulative and 30 – 50% of inhaled lead lodges in the respiratory system with the remainder absorbed into the body.

Elevated lead levels in blood could lead to hematological problems, particularly at blood levels in excess of 0.2μg/ml (O'Halloran, Myers & Duggan, 1988). Lead at high levels (80 μg/dl of blood) can cause convulsions, coma, and even death. Lower levels of lead can cause adverse health effects on the central nervous system, kidney, and blood cells. A study carried out by Needleman, Schell, Bellinger, Levinton and Allred (1990) has shown that exposure of children to lead is extensive, and ingrained public health problem. The effects of lead exposure on fetuses and young children can be severe. Fetuses, infants and children are more vulnerable to lead exposure than adults. Since lead is easily absorbed into growing bodies, tissues of small children are more sensitive to its damaging effects. At low levels, it poses a public health hazard (Subramanian, 1988). Wolverton and Mcdonald (1978) reported that excess levels of lead can cause anaemia, kidney, liver disease, paralysis, brain damage, convulsions, and death. Low levels of this metal may contribute to hyperactivity, learning disabilities, night blindness, and suppression of the body's immune response.

Cadmium is probably the heavy metal of most environmental concern due to its high toxicity, relative high mobility in the terrestrial environment, and its occurrence in the human diet at the highest percentage of the provisional tolerable intake (De Haan, Van Der Zee & Giraldez, 1989). A recent study by Cvetković, Arpadjan, karadjova and Stafilov (2006) described that the sources of cadmium pollution being the non- ferrous metal production, waste incineration, phosphate fertilizer manufacture, wood, coal, oil and gasoline combustion, iron and steel production and industrial cadmium application. These authors indicated that in industrialized areas cadmium in air varies from 1 to 50 ng/m^3, while in rural air is 0.1 to 6 ng/m^3. Cadmium affects the agricultural soil via air deposition (41%), phosphate fertilizers (54%) and sludge application (5%), also in unusual conditions via liquid effluents and solid wastes from cadmium processing plants. The authors reported that cadmium enters the human body via plants and animal food products and is readily absorbed by plants than lead. Cadmium is widely distributed in soil and water and is a by-product of many industrial processes (Pahlsson, 1989).

Food and cigarette smoke are contributors to non-occupational cadmium exposure. It is considered non-essential, and highly toxic element, with a serious cumulative effect (Berman, 1980). Cadmium toxicity is comparable to that of arsenic and mercury, but its lethal potential is higher than that of any other metallic element. Interests in its potential link with carcinogenicity have drawn attention to its concentration in body fluids, tissues, and foods. Although reports of its carcinogenic activity are inconclusive, measurement of cadmium in body fluids is still used for exposure monitoring, because of its very toxic effects. Besides this, the analyses of different kinds of samples are important in order to know other sources of its contamination (Yaman, 1999). Although Friberg, Piscator and Norberg (1992) earlier reported that cadmium toxicity is associated with hypertension, emphysema, renal tubular damage, liver dysfunction, and cancer. After the World War II in Japan, Itai-Itai disease, a severe bone disease related in part to cadmium exposure, was diagnosed in postmenopausal women who lived in Toyama prefecture downstream from a lead/zinc mine. People in this area were exposed to cadmium from the river water, which was used for drinking and rice paddy irrigation (Bhattacharyya, 1991).

There are many known sources of contamination by cadmium, owing to the large number of its inorganic salts used in catalytic and synthetic reactions, in Ni-Cd battery manufacturing, stabilizers for plastics, and pigments and still many unknown sources (Tsalev & Zaprianov, 1985). Spehar, Anderson and Finnat, (1978) reported that cadmium can cause permanent damage to the kidney, and give rise to nephril protenium. The accumulation of cadmium in the body gives cause for concern because of its long biological half life and the damage that high levels can do to the kidney. Although high levels of cadmium can occur from natural causes but may be elevated by localized pollution (Dellar, 1989).

Copper is biologically essential, a balance between absorption and excretion has to be maintained, otherwise retention in the body may cause diseases of liver and central nervous system. Hepatic diseases are known to arise from exposure to copper (Duffus, 1980). Theophanides and Anastassopoulou (2002) reported that copper is a trace element essential for the activity of such mammalian metalloenzymes as ceniloplasmin cytochrome C oxidase, dopamine and tyrosinate. They reported that copper helps to form haemoglobin in the blood, facilitating the absorption and use of iron so that red blood cells can transport oxygen to tissues. Copper assists in regulating blood pressure and heart rate. Although copper is an essential element for human and animals, a high concentration of copper could induce growth proliferation, and cancer by damaging deoxyribonucleic acid with toxic-free hydroxyl radicals. Massive accumulation of copper occurs in the liver, and brain in patients with Wilson's disease due to the genetically determined metabolic defect in copper metabolism. A normal individual absorbs sufficient amount of copper to meet the body's needs, and excess copper is readily eliminated (Parker, Weil &Richman, 1987). Gupta, Sinha and Chandra, (1994) reported that excess copper causes alteration in plant metabolism, and poses health hazards.

Nickel is an essential element and anaemia, prenatal mortality, growth retardation, acute stroke in rats, and primates have been attributed to its deficiency. Nickel is a co-factor of jackbean urease, glycoprotein and albumin. Accumulation results in damage of alveoli of the lungs (Birch & Saddler, 1979). High levels of nickel elevated red blood cells, haemoglobin content and packed cell volume can cause leucopoenia and lymphopenia. Ghazaly (1992) reported that the presence of nickel results in its accumulation in the blood, kidney, liver and muscle. Nickel markedly elevates the blood zinc content of the other tissues. Sen and Bhattacharyya (1994) reported that nickel causes dermatitis, dizziness, headache, nausea, and carcinogenesis.

Halls and Fell (1980) in occupational health have focused on the relationship between manganese exposure and early signs and symptoms of health effect in active working populations. Accumulation of manganese resulting from prolonged industrial exposure has been implicated in the incidence of hepatitis, liver and necrotic cirrhosis. In general, occupational and animal studies have identified three major types of effect: respiratory, reproductive and neurotoxic disorders. Exposure to manganese has been associated particularly with extra pyramidal signs and symptoms and with the development of Parkinson's disease (Loranger, Zayed & Forget, 1994).

Cobalt is unique in that, only one combined form cyanocobalamin or vitamin B_{12}, is physiologically active in man. This vitamin is essential to deoxyribonucleic acid synthesis and propionate metabolism to the avoidance, and control of pernicious anaemia. In cases of iron deficiency anaemia, inorganic cobalt may be added to the diet to increase the rate of haemoglobin synthesis. However, cobalt in doses of about 5mg per day can be toxic to man and may in the long term, cause heart disease. Cobalt can cause allergic and non-allergic asthma (Barfoot and Pritchard, 1980). Cherian and Gupta (1991) reported that a deficiency of zinc uptake, in food, leads to dwarfism, hypogonadism, and sickle cell anemia. High levels of zinc salts are corrosive and irritating to the gastrointestinal tract and ingestion may lead to vomiting and fever.

Chromium (III) is an essential micronutrient for both humans and experimental animals. This element was once considered to potentiate the action of insulin by forming a ternary complex with it at the membrane receptor. In essence, this element is a co-factor for insulin. The side effects of chromium deficiency include renal opacity in primated and impaired glucose tolerance in human beings leading to diabetes (Ottaway, 1981). Birch and Saddler (1979) described the toxic nature of chromium (VI) arising from industrial exposure to dichromates or chromic acid as evident in skin diseases, and increased incidents of various forms of cancer experienced by chrome industrial workers.

Mise and Shanta (1993) attributed the over exposure to chromium dust and mist as causes of irritation, lung carcinoma, corrosion of skin and respiratory tract. High concentrations of chromium (VI) present in water bodies were lethal to various fishes. In a biological system chromium undergoes the process of bioaccumulation resulting in chromium laden biological sludges, which cause most concern.

1.1.5. Industrial Effluent Discharges

Industries are the major sources of environmental contamination arising primarily from the discharge of untreated industrial effluents into the environment. These sources from the industries are the use of herbicides and insecticides, agricultural chemicals, industrial effluents, metal processing factories, dust emissions from metallurgical industries, cement, coal grinding, asbestos, and related industries are contributors of metal pollution (Albasel, 1985).

Industries contribute to environmental pollution by discharging toxic chemicals as effluents in to the environment. Hutzinger, Van Lelywed and Zoeteman, (1978) reported the polluting ability of these compounds depends on their intrinsic properties determined by their structure and non- chemical factors like production and pattern of use. Contamination may have just occurred or may already have been caused centuries ago. Maier (1996) described all types of industrial activities as sources of contamination whether by organic or inorganic chemicals, natural or artificial compounds. They may be produced by small or medium sized enterprises or large production plants.

Jyoti, Pandey and Singh, (1994) reported that the industrial effluents discharged directly into the streams and rivers are frequently used for drinking, cooking or dry season farming of vegetables. As such there is the tendency that the heavy metals will pass through this drinking or eating of the food prepared using such water. With the increase in industrial activities, release of heavy metals in the environment cannot be prevented. The industrial wastewater is specific and particular to the industries, each having its own undesirable waste constituents and their negative effect (Eckenfelder, 1989).

Increased industrial activities have led to urbanization and pollution stress on the environment both from industrial and domestic sources. Ajayi and Osibanjo (1981) indicated that the major streams in the industrial estates of cities like Lagos, Kano and Kaduna were already polluted by wastes from industrial sources and all the streams flowing through the densely populated city of Ibadan were polluted by wastes from domestic wastes.

1.1.6 Regulations and Monitoring Of Pollutants

Water quality monitoring has focused upon surface water heavy metal concentrations to safeguard drinking water supplies and to characterize the state of the aquatic environment (Bubb and Lester, 1994).

The World Health Organization Expert Committee on Environmental Pollution Control (WHO, 1983) in relation to development, reported amongst many sections, the health hazards related to development with special reference to chemical pollution in developing countries. Many of the recommendations involved policy issues, which were to be decided by each government (Andersen, 1985). The global approach to monitor the world environment in order to protect human health and preserve essential natural resources has become important. Thus, the United Nation Environmental Programme in 1979 established the Global Environment Monitoring system in view of monitoring the air and water quality as well as food contamination (Walters, 1987).

Human interactions and over-exploitation of resources are increasingly degrading the potential land, water, and air resources, due to the use of metal contaminated sewage sludge, as toxic metals may accumulate in some soils, and foods. Like many developing nations, Nigeria has had to face new problems of chemical pollution, beside traditional ones such as poor sanitation, poor quality drinking water, and deforestation. Adequate legislation, guidance, and monitoring for generation of toxicity data are important

(Dung-Gwom, 1999). The control option requires emissions suppression from the point of generation until the affected process wastewater streams are properly treated or reduced.

Nigeria has laudable legislative and policy initiatives in environmental management, which led to the creation of Federal Ministry of Environment (Formerly Federal Environmental Protection Agency in 1988), charged with the responsibility for the protection, and development of the Nigerian environment including policy initiation in relation to environmental research and technology (Aina, 1991). The agency has come up with the interim national water quality guidelines and standards (Table 2).

Nigeria has taken active part in all major international initiative aimed at alleviating global environmental problems, and is a signatory to a number of international treaties, protocols, and conventions. A number of programs and projects have been funded through utilization of official development assistance, financial, and technical aids, which supplement internal resources gaps following the downturn in the economy, and the rising external debts. One of the on-going bilateral assistance activities include, the Environmental Management Project being sponsored by the World Bank in Nigeria through an IDA loan, of which a major component is the State Environmental Action Plans (SEAP) (Onwuka, 1995).

There are many individual sources of water pollution. The major sources in Nigeria are soil erosion, urban wastes, industrial wastes, and oil spillages. Waste loads from urban areas tend to increase owing to growing populations and greater per capita water usage. Wastewaters from industries are also expanding due to increasing water-using factories and industries. Accidental spillage of oil and hazardous substances into

Table 2. Interim Guidelines and Standards for Water Quality

Parameter	Drinking water (mg/L)
Cd	0.01
Co	0.05
Cu	0.1
Pb	0.05
Mn	0.05
Ni	0.05
Zn	5.0

* Source: Federal Environment Protection Agency, 1991.

watercourses is a fairly recent interest. These pollutants can cause devastating and extensive damage to the aqueous environment. In 1988, accidental discharge of water containing high ammonia level into Okrika river from the National Fertilizer Company of Nigeria (NAFCON), a fertilizer company near Port Harcourt, Rivers State caused massive fish kill, and socio-economic problems for the artisan fishery industry in the surrounding village (Umeh & Uchegbu, 1997).

Odiette (1993) observed that the deplorable state of solid waste disposal in cities in Nigeria demands the urgent actions by the various states of the Waste Disposal Board. It has become a concern because of the accumulation of refuse on all the cities threaten health. Epidemic diseases like malaria fever have been associated with the indiscriminate dumping of refuse, and with the added problem of high temperatures, which encourage the spread of many infections. Also the several forms of enteric infections like cholera, typhoid fever, and schistosomiasis are linked to the exposure of the sufferers to garbage.

According to Odubela, Adeleke-Adedoyin, Ene-Ita and Baiyeroh (1990), much of the drinking water in Nigeria is supplied without effective treatment; the primary concern in relation to pollution is with the dangers arising from the entry of pathogenic microorganisms to the environment, and the consequent hazards of water related diseases. Thus a rational pollution control measures are vital factors in improving the health of the Nation. The degree of water quality could only be ascertained through periodical physical, bacteriological, and chemical monitoring.

1.1.7 Atomic Absorption Spectrometry

The flame atomic absorption spectrometry is the technique for the determination of trace elements in a variety of samples (Brown, Roberts & Kahokola, 1987). This technique is used for the analysis of a variety of materials containing trace elements (parts per million concentrations) to (> 1%) inorganic constituents, such as agricultural, biological, geological, petroleum products, glass and its raw materials, cement, ferrous metals and alloys, water effluents, and air (Bauer, Christian and O'Reilly, 1985). This technique became a reality when Walsh (1955) succeeded in making radiation sources with narrow bandwidths, whose wavelengths matched the absorption wavelengths of different analytes (Hargis, 1988).Walsh (1955) recognized the importance of a high-intensity, narrow line-width source for sensitivity, and suggested the use of hollow cathode discharge lamps as meeting these requirements. A flame was used to produce neutral atoms, through which the energy emitted by the hollow cathode could be passed to produce the absorption signal. The theoretical factors governing the relationship between atomic absorption and atomic concentration, also the potential and practical realization of atomic absorption spectrometry as a method of analysis appeared in 1955.

Alkemade and Milatz (1983) independently proposed an atomic absorption system utilizing a flame as radiation source and a second flame as the sample cell. The analyte concentration is related to the difference in radiation between two intensities. They indicated the potential of atomic absorption spectral techniques to the field of analytical chemistry. The atomic absorption technique extended the range of flame methods to elements with best lines in the deep ultraviolet region. This enhanced the detection of additional elements, and made the method less susceptible to interferences than emission methods. The absorption methods gave precision equal to the best flame emission methods (1-2%), and the instrumentation could be inexpensive (Koirtyohann, 1980).

In general, the flame atomic absorption spectrometry is used to determine elements with sensitivity down to parts per million, and measurement precision of one percent (Wassall, 1986). The advantages of the technique are specificity, low detection limit, many elements can be determined in one solution, there is rarely any lapsed time requirement (as in colour development, drying of precipitates, etc) in sample preparation, and data output in a directly readable form. These advantages include versatility with regard to both types of samples, and concentration ranges. Among the attractive features of flame atomization are its comparatively low capital and operation costs besides its ease of operation (Alvarado & Jaffe, 1988).

The technique provides fast, accurate, and reliable method for determining the concentrations of metals. Flame atomic absorption spectrometry (FAAS) is used for the determination of metals, showing good selectivity but low detectability, which may be improved by a preconcentration step. Several methods for the separation and preconcentration of metals have been developed, enhancing the detection, and the versatility of the techniques (Bortoleto, Macarovscha & Cadore, 2004). For many elements, detection limits for their atomic absorption with flame atomization lie in the range of 1 to 20 ng/ml or 0.001 to 0.020 ppm. Under the usual conditions, the relative error associated with a flame absorption analysis is of the order of 1% to 2% (Skoog, 1998).

The proportion of ground state to excited state atoms, suggests that absorption are direct measurement of the number of ground state atoms. Analytical methods based on atomic absorption are specific because atomic absorption lines are narrow (0.002 to 0.005 nm) and electronic transition energies are unique for each element.

The basic instrumental components needed to make absorption measurements are the source of radiation, flame (atomizer or sample holder), monochromator (a wavelength selector), detector, and readout system (Fig. 1).

Double-beam instruments are required for background correction using deuterium continuum lamps. For broadband absorption a background correction can be made in the ultraviolet region of the spectrum (where most elements absorb and background absorption is serious) with a hydrogen or deuterium continuum source. In the visible region, a tungsten continuum source may be used. Sharp line absorption of the continuum source by the test element is assumed negligible, compared to that by the broad background over the bandwidth of the monochromator, so the absorbance of the continuum source can be subtracted from the absorbance of the resonance line from the hollow cathode lamp (Christian, 2004).

The source beam is sent through the flame and around the flame by the chopper. The detector measures these alternately and the logarithm of the ratio of the incident radiation versus the transmitted radiation (I_0/I) is displayed. The detector amplifier is tuned to receive only radiation modulated at the frequency of the chopper, and so direct current radiation emitted by the flame is discriminated against (Robinson, 1996).

This is the basis of a Philips Pye –Unicam SP9 Atomic Absorption Spectrometer used in the atomic absorption investigations in this Thesis, as well as for those commercially available automatic background correctors. A mirror alternately passes the hollow cathode radiation and the continuum radiation, the absorption of each is measured, and the continuum source absorbance is automatically subtracted from the absorbance to obtain the net sharp line absorbance by the test element. So only a single measurement is required (Christian & Feldman, 1970).

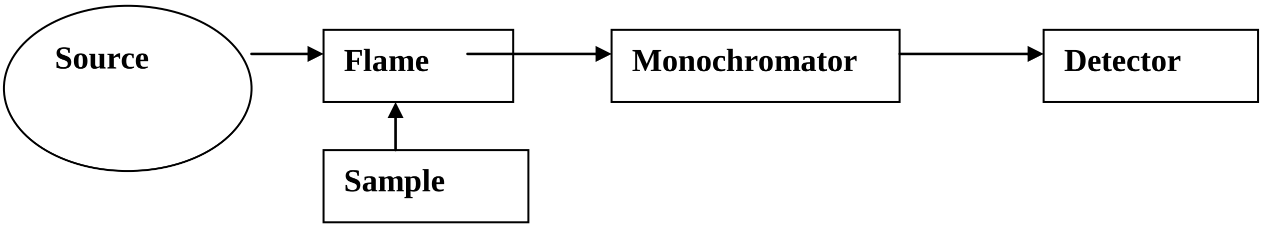


Fig. 1. Block Diagram of Atomic Absorption Spectrometer

The common source for atomic absorption measurements is the hollow cathode lamp, which consists of a cylindrical metallic cathode, and tungsten anode sealed in a glass tube containing neon or argon at a pressure of about 1 to 5 torr. When a high voltage is applied between the anode and cathode, the filler gas becomes ionized, and positive ions are accelerated toward the cathode. They strike the cathode with enough energy to “sputter” metal atoms from the cathode into the gas phase. Many of the sputtered atoms are in excited states; they emit photons, and then return to the ground state. This atomic radiation is of the same frequency as that absorbed by the atoms of the analyte. The line width is sufficiently narrow, with respect to that of the high temperature analyte, to be nearly `monochromatic’ (Harris, 1987).

Light, from the lamp generating a sharp line spectrum characteristic of the desired element, passes through the flame, into which the sample solution is sprayed as a fine mist (Hargis, 1988). In a flame atomizer, a sample solution is aspirated by a flow of gaseous oxidant mixed with a gaseous fuel; the heat of the flame first causes the solvent to evaporate producing a finely divided solid molecular aerosol. The micro crystals remaining are partially or wholly dissociated into elements in the gaseous form or atomic gas (Christian & O’Reilly, 1986).

The dissociated atoms can react with other atoms or molecules in the flame to produce molecular species and/or radicals. These in turn may give rise to molecular spectra. Also for elements of low ionization energy, ions and electrons may be produced. The ions may be excited and emission lines of the excited ions are produced. Such lines are not useful analytically, but in certain cases can cause interference with the desired process (Schrenk, 1975).

The flame converts the sample, introduced into it as an aerosol. This aerosol generated using a pneumatic nebulizer connected to the flame burner by a spray chamber (Fritz & Schenk, 1979). The ground state atoms must be obtained from the sample in a reproducible manner if quantitative data are to be obtained. The atomic vapour forms a cloud of atoms; only atoms of one particular element will absorb the radiant energy of a characteristic wavelength, and become excited to a higher electronic state leading to a decrease in the radiant power transmitted.

The neutral atom distribution is variable in the flames. Therefore the maximum absorption signal from a flame cell will only be obtained if the optical path traverses the flame through the region of maximum neutral atom population. The optimum path through the flame is different for different elements, varies with the fuel-oxidant combination used and the fuel to oxidant ratio. Flame temperatures and fuel – to – oxidant ratios are two important parameters to consider, when using a flame as an atomic absorption sample cell (Svehla, 1975).

The region of the spectrum in the immediate neighborhood of the resonance line to be measured is selected by the monochromator, the functions of which is to isolate the resonance line from non-absorbing lines close to the source spectrum. Such line may originate from the cathode metal or the lamp fill gas. A further function of the monochromator is to isolate the measured resonance line from molecular emission, and other background which originate in the flame (Ebdon, 1998).

The isolated resonance line falls onto the detector, a photomultiplier, the output of which consists of a pulse of electrons, for each photon that reaches the detector surface. A single photon that strikes the cathode of a photomultiplier ultimately leads to a cascade of 10^6 to 10^7 electrons, which produce a pulse of current that can be amplified, and drives a readout device (e.g. meter, strip- chart recorder, to a digital display unit, printer). Most modern spectrometers now provide effective microprocessor – based measurements of the signals (Price, 1983).

The intensity of the resonance line is measured with and without the sample passing into the flame. The log ratio of these readings is a measure of the absorbance, and therefore proportional to the amount of the element being determined. It is more suitable for routine analysis that has higher sample quantity reaching the flame, of simpler operation, and the instrumentation has a lower total cost than electrothermal atomization-atomic absorption spectrometry.

In spite of the present state of electrothermal atomization, the most convenient, stable source of atomic vapor remains the combustion flame. The important parameters in the production of free atoms from a given element are the flame temperature, the chemical effects of radicals, and other substances present in the flame. The dissociation equilibrium of a molecule MA containing the analyte element, M

$$MA \rightleftharpoons M + A$$

is characterized by a temperature – dependent equilibrium constant K_D, where

$$K_D = \frac{[M][A]}{[MA]}$$

The atoms of the analyte element, M, may be bound as molecules with one of the bulk constituents of the flame gases (e.g. O or OH) or with one of the atoms introduced into the flame in the sample nebulized (e.g. Cl or F).

The widely used of fuel/oxidant mixtures is air-acetylene, as it enables (about 30) of the common metals to be determined. These are elements that do not form refractory oxides. Calcium, iron, cobalt, nickel, magnesium, molybdenum, strontium and the noble metals are among the elements normally determined with this flame.

Both the gas flow rates and thermal expansion of the flame gases after combustion contribute to the dilution of the absorbing species and to the length of time of the absorbing atom in the radiation beam. The best sensitivity at any given temperature is by flame having the smallest combustion gas / sample volume ratio (Price, 1983).

The flame is a convenient and reproducible source of heat, but is less ideal as a sampling device for atomic absorption in that the two endothermic processes, (solvent evaporation followed by atomization), must take place within short time interval for a particle to shoot through the flame. In addition, the flame introduces significant random fluctuations in the effective optical path length, because of turbulence, and this causes excessive noise in the signal (Ewing, 1975).

The precision and accuracy of atomic absorption spectrometric method is critically dependent upon the atomization step and the method of introduction of the sample to the atomization region (Skoog, 1998). Innovation in atomic absorption spectrometry sample introduction ways have been employed in order to solve challenging analytical problems in science and technology (Bings, Bogaerts & Broekaert, 2004).

Magda, Khayyal and Farrag (1985) reported new approaches for the application of atomic absorption spectrometry in drug analysis. The technique was based on the measurements of the metal content of the precipitated complex after treatment with the complexing agent. Holen, Bye and Lund (1981) determined selenium in technical sulphuric acid by electrochemical preconcentration on a platinum filament followed by atomization in an argon-hydrogen flame with simultaneous electrothermal heating of the filament.

Multiple pass devices have been constructed, so that effective optical path length through the flame could be increased, which increased the sensitivity of the method. Various attempts have been made to use simple cell other than flame to produce the atomic vapor in the optical path of the spectrometer.

The graphite furnace devised (L’vov, 1961) is electrically heated tube furnace as an atomizer for atomic absorption, the carbon rod analyzers; this device can be used to convert a powdered sample into atomic vapour. An electric current is applied to a very thin, heated carbon rod that contains the solid sample in order to vaporise it (West & Williams, 1969). The tantalum boat devices enabled the introduction of the entire sample into the flame without nebulization (Hwang, Ullucci & Smith, 1971). High intensity sources other than hollow cathode tubes have been investigated like the electrodless discharge lamps (Barnett, Voller & De Nuzzo, 1976). Also new and better atomic absorption systems have been developed to readout the data.

The limitations of flame atomic absorption spectrometry are the low efficiency of the nebulizer system. That is, not all the samples reach the atomizer and hence, sample volume requirements are greater with the technique (Milner & Whiteside, 1984). In a typical nebulizer, liquid droplets will be produced with particle sizes ranging from a few micrometers. The droplets have a diameter of 5 to 10 μm, but the sample volume is contained in droplets of 20μm in diameter. In a premix burner the larger droplets never reach the flame at all. Particles larger than 10 to 20μm are used inefficiently in the flame or are deposited on the premix chamber walls to flow out the drain tube. From 85-90% of the sample literally goes down the drain (Bauer, Christian & O’Reilly, 1985).

The sample is drawn into the nebulizer by the low pressure created around the end of the capillary by the flow of the carrier or oxidant gas. The resulting droplets are ejected with the carrier gas into the spray chamber. The design of the chamber is such that droplets with a diameter greater than 5 μm fallout onto the sides of the chamber and flow to waste.

Another way of improving a flame atomic absorption spectrometry is to increase the efficiency of the nebulizer system (Nygren, Nilsson & Gustavsson, 1988). These authors developed an improved system for the determination of lead in blood by flame atomic absorption spectrometry. The system was based on flow injection, a nebulizer interface, and a computer signal evaluation system. The system improved the detection limit 12-fold compared with that obtained by unmodified instrumentation.

To improve the nebulization efficiency various ways and means of altering the normal droplet size distribution have been employed (Rawson, 1966);

i. The application of heat – either to the sample and gases before they enter the spray chamber or in the spray chamber itself.

ii. Impact beads are placed close to the orifice of the nebulizer. The droplets, whose speed at this point is near sonic, are fragmented by the impact and the mass of material vaporized in the flame is increased by 50 – 100%.

iii. Counter flow nebulizers – the oxidant/sample aerosol and fuel nozzles are placed opposite each other within the spray chamber. It results in a high-speed turbulence, which produces larger proportion of the small size droplets. Increases in sensitivity of two or three times have been obtained with this system.

The maximum useful population of droplet sizes constitutes about 10% of the total mass of sample nebulized and an absorbing atom remains in the radiation beam usually no more that 10^{-4} sec. These limitations of atomic absorption spectrometry with insufficient sensitivity could be overcome if the atomic vapour are constrained to remain longer in the resonance beam, and if the sample could be introduced without inefficient nebulization process, or indeed without any pretreatment involving dilution at all.

Ideal liquid sample introduction implies reproducible transfer of the total sample solution into the atomization cell. The elements with sensitivity improvements are the volatile elements, which decompose thermally in the primary reaction zone of an air–acetylene flame. The sensitivity improvement is due to the increased residence time of analyte atoms in the light path of the atomic absorption spectrophotometer (Brown & Milner, 1985).

1.1.7.1 Problems Encountered in the Conventional Flame Atomic Absorption Spectrometry

The conventional flame atomic absorption method is a versatile analytical technique like other techniques. It is not an absolute method, as it is plagued with the low efficiency of the nebulizer system. The nebulization process is of importance, as it is meant to convert the sample solution into aerosol with 100% efficiency. The sensitivity of the analysis depends upon its correct function and efficiency. The sample introduction step limits the accuracy, the precision, and the detection limits of atomic absorption spectrometric measurements (Browner & Boorn, 1990).

The droplet diameters should be less than 10μm, and preferably approaching 1 to 2μm. However, most nebulizers are only about 3 to 15% efficient which means that 85 to 90% of the sample goes down the drain. This remains an unsolved problem for flame atomic absorption spectrometry. The absorbing atom remains in the radiation beam for not more that 10^{-4} seconds, even though gas flow rates and thermal expansion of the flame gases after combustion both contribute to the total dilution of the absorbing species in the flame and to the length of time (Price, 1983).

1.1.7.2 Methods for Improving the Sensitivity of Flame Atomic Absorption Spectrometry

An analytical chemist is often required to quantify an element in a sample, and is always seeking new and improved analytical methods. The sensitivity of the atomization of some elements is insufficient for many sample materials, so that some degree of enrichment is needed (Daniel, Mats & Stig, 1981). Suvardahan, Suresh Kumar, Reddy and Chiranjeevi (2003) observed that the drawback can be overcome by a combination of preconcentration techniques with subsequent atomic absorption spectrometry determination.

When lower concentrations are sought, the sensitivity of flame Atomic Absorption Spectrometry could be increased if more of the sample is introduced into the flame, or if the analyte could be constrained longer in the light path. The sensitivity of flame atomic absorption spectrometry is limited by several factors. The analyte atoms generated in the flame pass rapidly and comtinously through the measurement zone during sample aspiration. A further limitation is the poor efficiency of the nebulizer/burner system.

There has been increasing focus on the development of a number of devices to increase the sensitivity of flame Atomic Absorption Spectrometry (Rawson, 1966, Kahn, 1968, Delves, 1970, Brown, 1984, Alvarado, 1998). Advances in Atomic Absorption Spectrometry have continued to improve the nebulization, process and are exemplified by the introduction of a circular flame atomizer, the use of radiofrequency, the effect of long chains surfactants, and discrete sample nebulization (Jackson & Qiao, 1992). The atom – trapping technique used to increase the sensitivity of Flame Atomic Absorption Spectrometry could be described as the slotted quartz tube and the water – cooled silica tube (Brown, Roberts & Kahokola, 1987).

The slotted quartz tube is used to increase the sensitivity of the volatile elements that decompose thermally in the primary reaction zone of an air-acetylene flame (Plate i). The sensitivity improvement is due to an increased residence time of analyte atoms in the light path of the atomic absorption spectrometer and the reduction of potential interferences. It is inexpensive and the required quartz tube is easily manufactured (Brown & Taylor, 1984). In the water – cooled silica tube technique atoms are trapped on a water – cooled silica tube. After a fixed collection time, the tube rapidly heats up releasing the trapped metals species, resulting in an increase in sensitivity (Brown & Milner, 1985).

1.2. CONCEPT

Atomic absorption spectrometry is considered a versatile laboratory technique. The method renders itself for improved instrumentation, more reliable source of resonance radiation, hotter flames and non flame atomizers. A key disadvantage of the method is the inefficient use of sample by the nebulizer spray chamber burner system. Thus considerable effort has been directed toward sample introduction step by many researchers. The atom trap technique is used to increase the sensitivity of the conventional flame method by constraining the analyte atoms to remain longer in the measurement zone. As a consequence, low concentrations in parts per billion are determined.

1.3. AIMS/OBJECTIVES OF THE STUDY

This thesis would be devoted to the design and the development of atom – trapping collecting tubes as a method for analysis in the determination of trace elements in environmental samples, and where appropriate comparisons would be made with the conventional flame atomic absorption spectrometry. Various sizes of the developed atom trap would be checked. The method developed would be compared with the existing conventional flame atomic absorption spectrometry.

Detailed interference study, which describes the effect of NaCl on lead and cadmium atomic absorption signals with the developed atom – trapping technique would be carried out. Standard reference materials with known concentrations would be analysed to ascertain the validity of the developed procedure. Precision, detection limit and sensitivity check would be performed to assess the developed method.

The method would be used to analyse heavy metals from industrial wastes namely from Naraguta village (local leather processing outfit), effluents discharged from NASCO group of companies and Jos International Breweries all located in Jos, Plateau State. Also effluents discharged from leather tanneries located in Kano state, Majema area of Kofar Wambai, and Sharada Industrial Estate Phase III would be analysed.

1.4. SCOPE AND LIMITATIONS OF THE STUDY

The research covers the designing of nickel tube atom trap for the determination of low concentrations of heavy metals in industrial effluents. The developed method provides increased sensitivity particularly at parts per billion (ppb) level, which otherwise could have been undetected by the conventional flame atomic absorption spectrometry. The sensitivity increase achieved is due to the analyte atoms being constrained in the light path for longer period. The developed method is used to assess the environmental exposure of heavy metals in effluents obtained from various sources. As in every method development analytical performance data such as precision, accuracy, detection limit and sensitivity would be checked.

The developed method is limited to the study of elements that are decomposed in air acetylene flame. One of the drawbacks of the developed method is manually reproducing the exact position of the atom trap tube with respect to the source radiation. This lowers the reproducibility of the method.

1.5. SIGNIFICANCE OF THE STUDY

The developed nickel tube would provide a direct measurement of trace heavy metals at very low concentrations without preconcentration. When these samples are analysed the time consuming preconcentration step is avoided. Sample volume requirement is small when compared to the conventional flame atomic absorption spectrometry method. The nickel tube can be fabricated locally and easily fitted to the equipment. The nickel tube atom trap method is characterized by simplicity, efficiency and low cost. It is an added advantage to many laboratories such as industries, research institutes and universities with limited resources.

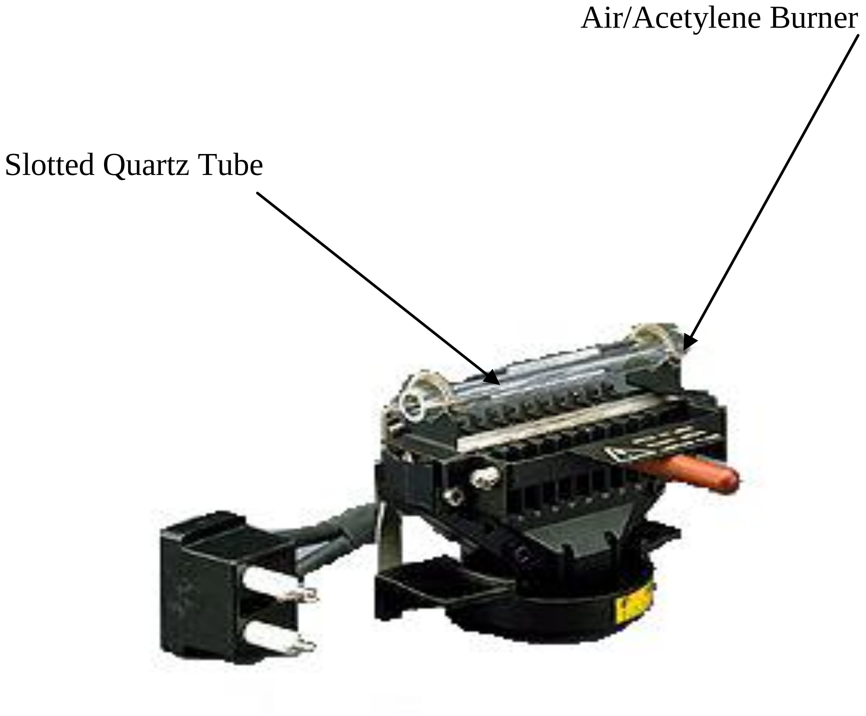


Plate i. The Slotted Quartz Tube Atom Trap

CHAPTER TWO

LITERATURE REVIEW

2.1.APPROACHES FOR THE IMPROVEMENT OF SENSITIVITY OF FLAME ATOMIC ABSORPTION SPECTROMETRY

The virtues of the nebulizer/spray chamber are stability and in conjunction with the appropriate gas mixture and burner, very high reproducibility, and atomization efficiency. In a conventional burner, however, any one atom remains in the light path for a very short period of time.

Several studies have shown on devices that improve the sensitivity of flame atomic absorption spectrometry (Jackson & Qiao, 1992). Suvardhan, Suresh Kumar, Reddy and Chiranjeevi, (2003) reported that the atomic absorption spectrometry technique, which offers fast multielemental analysis in a sample solution suffers from poor sensitivity in the determination of elements in environmental samples.

To provide increased sensitivity in atomic absorption spectrometry several authors have described burner systems in which the flame gases are directed along the optical path, when a total consumption nebulizer-burner was employed. The success of such device depended upon the mean lifetime of free atoms. This in turn varied with the element, the temperature, and composition of the flame gases. Robinson (1962) passed the flame into a T-piece adaptor, which directed the flame horizontally to produce a long absorption cell.

Fuwa and Vallee (1963) reported high sensitivity for cadmium, zinc, magnesium, copper, and nickel using a long horizontal ceramic tube 90 cm x 1 cm and pointed an air-hydrogen flame from an inclined total consumption nebulizer-burner into the tube. The sensitivity was not proportional to the tube length for most elements, as their transmission times exceeded the lifetimes of the free atoms. Koirtyohan and Feldman (1964) utilized similar techniques and extended the range of application of these systems to other elements. The commonly used flames were the unpremixed hydrogen-air and hydrogen – oxygen. Rubeska and Moldan (1968) described a tube device which consisted of an alumina tube 45 cm long with one end cut at a slight angle, so that the flame could enter when the burner was tilted. The burner was a total consumption type from a spray chamber system. Better results were obtained with an air-hydrogen flame.

The best sensitivities for all possible elements were achieved under fuel-rich conditions. When the burner was positioned and the flow rates of hydrogen and air are adjusted the primary and secondary reaction zones were at the entrance and exit to the tube respectively leaving the inter-conal zone to occupy the tube. Improvements in sensitivity by a factor of approximately 50 over standard flames were reported for some elements. The operation and results given by this system are described in more detail by Rubeska and Moldan (1968) who reported that some elements which formed stable oxides gave improved sensitivity in the tube.

Complete protection from atmospheric oxygen was obtained by the use of a long absorption tube with separated flames (Hingle, Kirkbright & West, 1968). A long side arm was provided on the flame separator, along which the partly combusted gases were drawn. An optical window was provided at each end and a furnace which maintained its temperature at 1100°C, surrounded a tube. Combustion gases were air-acetylene with auxiliary hydrogen. Sensitivities using this separated flame system were at least comparable with the other long tube systems but there was less background less noise and less deposition of material in the tube. The long tubes design suffered from the disadvantage that they could not be accommodated in the burner position of a standard atomic absorption spectrometry.

The micro-sampling technique used by Kahn, Peterson and Schallis (1968), introduced dried samples into the flame in a tantalum-boat and recorded the transient absorption signals. With this technique, they resolved the absorption signals for the direct determination of lead in urine. The authors reported that though the method was accurate the procedure required attention and was time consuming. Wide variations in sensitivity were observed not only between different boats but also with different sample positioning within a given boat. The later effect was caused by the variation in the cross-section of the radiation from the hollow-cathode lamp, as it traversed the flame above the boat.

White (1968) introduced a flame adaptor, which consisted of a nickel tube about 10 – 12 cm long and 1 cm diameter supported in the optical axis with the burner positioned about 2 cm below. A hole 5 mm diameter was made midway along the wall of the tube nearest the burner. He described the set up as follows; the flame was lit, heating the tube, and the sample is introduced on a platinum wire loop between the flame and the hole. The sample became partially atomized, and the atoms were retained in the optical path by the tube for longer time than with a conventional burner. The author reported that only comparatively cool flames such as air-propane or the lean air-acetylene flame could be used with the device. This limited its use to elements, atomized at low temperatures such as lead, cadmium, and thallium. He further reported that good sensitivity for lead, for example, less than 10 µg/100 ml (0.1 ppm) of whole blood, but since reproducibility’s were not usually of the highest order, its common use was applied as a screening method.

Delves (1970) used a combination of flame adaptor and the micro-sampling technique, which provided a simple accurate method for the determination of lead in blood. The blood was placed in a nickel cup, dried and oxidized. The sample was then volatilized, into a nickel absorption tube, mounted parallel to, and just above the air-acetylene flame. The sample size commonly used was 50micro-litre. The nickel – absorption tube was 100 mm long with a 12.5 mm inner diameter. The tantalum boat was replaced by a micro-crucible, which eliminated the intra-boat sensitivity variation. The use of an absorption tube with such crucible eliminated variations of observation height in the flame as samples were oxidized in the crucible. The nickel tube can be considered as a flame heated tube furnace in which a gaseous sample is introduced. The sensitivity of the method reported was 1 x 10^{-10}g of lead per 1 percent and the standard deviation was ± 4 percent, at the 3ng level.

Application of the Delves cup technique to other metals in aqueous solutions were also investigated by Kerber and Fernandez (1971), who reported the method useful particularly for metal of relatively high volatility, such as silver, arsenic, bismuth, cadmium, mercury, lead, selenium, tellurium, thallium, and zinc.

Kirkbright (1982) described the Delves cup technique as boat-in-flame, which permits high sensitivity using only small samples (10- 100 µl) by increased sample transfer efficiency to the flame compared with pneumatic nebulization. The author emphasized that the Delves cup method provided greater residence time of the analyte atoms in the cylindrical cell, which yielded additional signal enhancement. Though, the entire sample atomization process is usually complete within few seconds after insertion of the boat into the flame and the amplification and recorder system employed in the atomic absorption system must, therefore have a fast response time (<1 sec).

Cernik (1973) adapted the Delves' cup technique after pretreatment of the sample by heating to 425^0C on a hot plate, with limited success. This was due to the difficulty of eliminating the non-atomic signal reduction, when the sample is subsequently analysed by atomic absorption spectroscopy.

Tetsuo and Chuzo (1975) used a long absorption tube with the hydrogen- air flame and ring burner. They studied the various effects, such as the external heating of the tube, rate of exhaust of the burnt sample, preheating of the aspirating air on the sensitivity, detection limit, and memory effect of 24 elements, and reported, that the external heating of the tube had more than 40% enhancement in sensitivity for manganese, copper etc.

Jackson, Ebdon, Webb and Cox (1981) described a simple, reagent-free solid sampling method for determining lead in vegetation. The dry sample was ground to a powder and 0.5 g was suspended in 10 ml of deionized water. Aliquots (20 µl microlitre) were pipetted into nickel microsampling cups, which were dried at 110^0C and inserted into an air-acetylene flame. The resulting atomic absorption signal was time-resolved, from any non-specific absorption, making further sample pretreatment unnecessary. Suitable dilutions of the suspension provided a linear range of 0.072- 240 µg (micro gram) Pb/g of dry vegetation. They reported that the method was simple, accurate, faster than competitive methods, and provided adequate precision (typically 4- 9% RSD) for this application.

Alvarado and Jaffe (1998) described a method, which used graphite tube in an air – acetylene flame. Tubes of different sizes, and made of different types of graphite were compared regarding detection limit, reproducibility, and useful life- time. The authors reported that using the system, the extended residence time of the atoms in the absorption volume allowed lead to be determined with an detection limit about fifty times lower than that obtained using conventional atomization. Reproducibility of the measurements expressed as percentage relative standard deviation, at the 5ng Pb level was reported to be 3.9%.

2.2. SLOTTED TUBE ATOM TRAP

The method of atom- trapping as proposed by Watling (1977), made use of a silica tube suspended in the air-acetylene flame. This increased the residence time of the analyte atoms within the tube, and therefore within the measurement system. This device is a heated quartz tube, which can be placed in a conventional flame. Guihua and González (2002) attributed the increase in sensitivity of the instrument as a result of the dissociated ground state atoms pass into the tube, then the analytes are delayed, and stay longer in the optical path.

The main advantages of the slotted tube atom trap compared to the conventional flame method lie in the increased sensitivity, and reduction of potential interferences, as the technique allows greater dilution of the sample. The sensitivity improvement is attributed to the increased residence time of the analyte atoms in the light path, as well as, to a longer optical path. The partial exclusion of entrained, air created more stable chemical environment, which enhance the concentration of neutral atoms.

In the slotted tube atom- trap system, a double slotted quartz tube is installed above the burner. The length of the upper slot of the tube is shorter than the lower slot. This is placed into the flame gases and analyte atoms using a pneumatic nebulizer system. Watling (1980) determined arsenic, antimony and selenium in water using a simple preconcentration procedure and modified flame atom-trap.

Further studies were also carried out by Taylor, Branch, Halls, Owen and White (1983), to determine cadmium and lead in waters. Milner (1983) used the slotted tube atom-trap as a flame atomic absorption spectrometry accessory, and recorded greater sensitivity in the detection of lead, arsenic, cadmium, selenium, copper, tin, and zinc. The atom-trap consisted of a fire-glazed silica tube – 8 mm id, with two lateral slots at 180 degree. The tube was aligned with the optical path of the spectrophotometer, and the tube slots were aligned with the burner slot.

The slotted quartz tube was used to determine copper and zinc in blood serum and urine, following 21- fold dilution with water (Brown & Taylor, 1984). The study revealed that the determination of copper in urine showed that a urine matrix caused a significant (30%) signal depression with the use of the slotted quartz tube.

Brown and Taylor (1985) determined cadmium, lead, copper and zinc in environmental and clinical samples using commercially available slotted quartz tube and reported an increased sensitivity of the flame atomic absorption spectrometry. The advantages included the small amounts of sample required to perform the analysis, and also the increased sample throughput, when compared with the graphite furnace atomic absorption spectrometry.

Brown and Milner (1985) used the slotted quartz tube as atom-trapping technique to determine calcium and lead in waters, whole blood, and urine. Lee (1985) analyzed lead in beer, and reported improvements (2 to 5 fold) in the sensitivity of the slotted quartz tube as atom-trapping technique over the conventional flame atomic absorption spectrometric method.

Ebdon, Steve and Jones (1985) speciated tin in natural waters using coupled high performance liquid chromatography with flame atomic absorption spectroscopy, by using the slotted tube atom-trap method. The tube was modified in design, so that, the slots were at 180^o to each other. This modification was found to give improved detection limits for some elements. The authors also reported that sample introduction was facilitated using discrete volume nebulisation (i.e. allowing the nebuliser to draw air between aliquots of sample). Their study indicated that the use of the slotted tube atom trap lowered the detection limit by a factor of four.

Ivanova, Vracheva, Khavezor and Iordanov (1986) determined micro-trace amounts of bismuth, lead, and tellurium in Selenium of 99.9% purity after pre-concentration, and used a slotted silica tube atom-trap, which was attached to the burner to improve sensitivity.

Burns, Atkinson, Chimpalee and Harriott (1988) carried out a study on a series of quartz slotted tube atom-traps, designed to increase the sensitivity of flame atomic absorption spectrometry for the determination of lead. The slotted tube atom-traps were made of either translucent or transparent quartz. Precision reported by using a slotted tube atom-trap was better than that obtained with a conventional flame system.

Chimpalee, Harriott and Burns (1989) examined various designs of slotted tube atom-trap, the lanthanum oxide coated transparent silica 14 cm x 1.3 cm id with an 11.5 cm x 3 mm width entrance slot, and a row of six 6 mm diameter holes set apart with 9 mm held aligned along the optical path directly above the burner head slot. Result for bismuth in bismuth carbonate and subgallate pharmaceuticals agreed with those obtained by a Spectrophotometric method. The precision of the proposed method was superior to that of conventional flame atomic absorption spectrometry.

Roberts (1989) reviewed developments in atomic absorption spectrometry with improved sensitivity and ease of operation and particular attention was paid to the slotted tube atom trap and the water cooled atom trap for sample introduction. Thomerson (1990) described the slotted tube atom trap as one of the methods used for increasing the sensitivity of flame atomic absorption spectrometry. Trace metals were determined and results compared with those obtained by conventional flame atomic absorption spectrometry.

Harriot, Burns and Chimpallee (1991) dissolved a sample containing about 0.1 mg of antimony and determined antimony in copper-based alloys after hydride generation. The set up included for the spectrometer to be equipped with a slotted quartz tube atom-trap, with arrow of six holes, through which the flame passed to increase sensitivity. The tube was aligned, directly above the burner head slot along the optical path of the spectrometer. The coefficient of variation reported was 1.3% with the use of the slotted tube atom trap method.

Matusiewicz, Sturgeon, Luong and Moffatt (1991) determined copper, iron, manganese and zinc in river and estuarine water using the double slotted quartz tube mounted in an air-acetylene flame. The results reported were superior to those obtained by conventional flame techniques.

Li, Lian and Du (1991) studied the slotted tube atom-trap, and determined cadmium, copper, lead, zinc in tap water and beer by atomic absorption spectrometry, with the use of slotted quartz tubes. Burns, Chimpalee and Harriott (1992) described an improved system for the determination of tin in zircalloys by flame atomic absorption spectrometry. Sensitivity and precision reported compared with conventional flame atomic absorption spectrometry improved by a factor of 2 to 3 by using a slotted quartz atom- trap.

Tsalev et al (1993) reported an analytical scheme for the determination of cadmium and lead in human toenails and hair with the use of the slotted tube atom-trap. The authors reported that the method provided accurate and precise data, and is suitable for monitoring occupational exposure to these elements.

Burns, Chimpalee and Harriott (1994a) used a 14 cm long slotted quartz tube atom-trap having a central longitudinal base slot 10 x 3 mm and six 6 mm diameter holes 15 mm apart centrally drilled above the base slot, and analysed tin in copper-based alloys. The slotted tube atom-trap was placed with an 8 mm gap between the burner head and its base. The detection limit reported was 0.22μg/l of tin compared with 1.46μg/ml for conventional flame atomic absorption spectrometry.

Burns, Chimpalee and Harriott (1994b) determined antimony in copper-based alloys by atomic absorption spectrometry in an air-acetylene flame equipped with a slotted quartz atom-trap. The use of a slotted tube atom-trap improved precision, and characteristic concentration by factors of 3 and 1.6 respectively, compared to the use of conventional flame absorption spectrometry. They also, reported that the results for 8 standard reference materials were in excellent agreement with certified values.

Burns, Chimpalee and Harriott (1994c) used a slotted tube atom-trap for the determination of tin in copper-based alloys after hydride generation. The slope enhancement factor compared to that of a flame alone was reported to be 1.95. The use of the atom-trap together with hydride generation improved sensitivity by a factor of 200, compared to the conventional flame atomic absorption spectrometry. The results for four standard reference alloys were in agreement with certified values.

Thorburn-Burns, Chimpalee and Harriott (1995) described an improved system for the determination of up to 0.1 % bismuth in copper-based alloys by atomic absorption spectrometry using a slotted quartz tube atom-trap. Detection limits reported for bismuth were 0.6µg/ml without slotted tube atom-trap in position, and 0.3µg/ml with slotted tube atom-trap.

Huang, Mu and Zhong (1996) employed a homemade slotted tube atom-trap setup in the trapping of volatile elements including copper, silver, gold, zinc, cadmium, lead, antimony, and bismuth in air acetylene flame atomic absorption spectrometry. Compared to the conventional set-up, sensitivities were reported enhanced by 3 to 5 fold. The method was applied to the determination of lead and calcium in standard materials, with detection limits of 5 and 0.5ng/ml respectively.

Xu and Chen (1997) dissolved 10g of cooking salt in 100 ml of 1% hydrochloric acid. Following dilution, 150µl was injected into a flow injection system in a water carrier before nebulization into the slotted tube atom trap for flame atomic absorption determination of silver, gold, cadmium, cobalt, copper, iron, manganese, nickel, lead, palladium, antimony, and zinc. The authors reported that the system was optimized with polytetrafluor ethylene (PTFE) tubing (17cm x 0.5mm id) for linking the sampling valve and nebulizer, and the distance between the slotted tube and 5cm burner was 3mm. They reported enhancement in sensitivity by 1.2 to 3.3 fold when the slotted tube atom-trap was used in the determination of silver, gold, cadmium, cobalt, copper, iron, manganese, nickel, lead, palladium, antimony, and zinc in cooking salt. The method was applied to tap water, boiler water, industrial wastewater, and industrial grade $ZnSO_4$ as well. The recoveries reported for copper, cadmium, manganese, and lead were 90-110% by standard addition method.

Liang and Lee (1998) used a slotted quartz tube to increase the sensitivity for the determination of lead in herbal medicine by flame atomic absorption spectrometry. Pre-sputtering the tube with a solution of vanadate produced an orange-red coating and prevented the deposition of sodium salts and carbon on the surface of the tube, thus prolonging its lifetime.

Yaman (1999) determined cadmium and lead in human urine, by slotted tube atom-trap in an air- acetylene flame, after enrichment on activated carbon. Detection limits reported were 0.27 and 0.03 μg/l for lead and cadmium respectively based on the preconcentration of a 210 ml urine sample to a final volume of 1.5 ml. Yaman, Silgin and Guccer (2000) determined lead concentrations in fruit samples by using slotted tube atom-trap enrichment flame. Acceptable agreement was reported between the results of slotted tube atom-trap enrichment flame atomic absorption spectrometry and graphite furnace atomic absorption spectrometry.

Yaman (2001) determined toxic metals such as cadmium, lead, nickel and aluminium in drinking, dam lake stream, and lake water by use of flame atomic absorption spectrophotometer (FAAS) after enrichment. In the enrichment procedure, their chelates with cupferron were preconcentrated on activated carbon. For increasing the sensitivity of cadmium and lead, the slotted tube atom trap (STAT) was used as accessory in the flame atomic absorption spectrometry determination.

Sun, Gao, Yuan, Zhang Y. and Zhang (2002) described a simple and sensitive method for the determination of trace lead in Chinese herbs by derivative atom-trapping flame atomic absorption spectrometry with a modified water-cooled quartz atom-trapping tube. The effects that influenced the sensitivity of the derivative method, such as the trap position, the flame conditions, and the collection time were studied. The characteristics of the derivative atom trapping atomic absorption signal, and the linear nature of the working curve were studied. The authors reported that the sensitivity of the derivative method as 2 or 3 orders of magnitude higher than that of FAAS, and the detection limit improved by 1 or 2 orders of magnitude. Recoveries of 93.0-108.0% for lead were obtained by determining several Chinese herbs with a relative standard deviation range of 2.9 to 4.2%.

Yang et al (2002) determined cadmium in Chinese herbs by atomic absorption spectrometry using atom-trapping technique. The experimental conditions included the flame, the trap position, the coolant water flow rate, and the collection time, which affected the absorbance were studied. The optimum experimental conditions obtained were the acetylene flow rate of 90 L/h, the distance of the tube from the burner of 5mm, the distance of the tube from the light path of 2mm, and the coolant water flow rate of 1.5L/min. The results reported that the absorbance was linearly dependent on the collection time in the range of 0-6min for cadmium solution of 50ng/ml. For 2 min collection time, the characteristic concentration, and the detection limit for cadmium were 1.8ng/ml and 0.42ng/ml, which were 16 and 5 times better than the conventional flame atomic absorption spectrometry respectively. The relative standard deviation (RSD) was 1.8% and the proposed method was successfully applied to the determination of cadmium in Chinese herbs with a recovery range of 89.5%-104%.

Yaman and Akdeniz (2004) examined various designs of quartz tube in a slotted tube atom trap for improving the sensitivity of flame atomic absorption spectrometry. A 3.5 fold enhancement in the sensitivity was obtained by using the optimized method. The method was applied to determination of copper and zinc in cancerous and non-cancerous human thyroid tissues.

Manufacturers such as Philips Pye-Unicam offer the slotted quartz tube atom-trap as an accessory to the range of methods used to increase the sensitivity of the conventional flame atomic absorption spectrometry (Milner & Whiteside, 1981). The disadvantage of the slotted quartz tube is its limitation to few elements. Even with a Lanthanum oxide coating the tube life-time was substantially reduced by samples containing high concentrations of alkali metals (Brown, Roberts & Kahokola, 1987). Another limitation is that the slotted quartz tubes breakdown, when initially heating up after insertion into the flame or when cooling down after an analysis.

2.3. WATER-COOLED SILICA TUBE

Lau, Held and Stephens (1976) increased the sensitivity of flame atomic absorption spectrometry, by placing a water-cooled silica tube in an air-acetylene flame. The sample was nebulised for a preset time (typically 1-10mins). When the collection was completed, the water was ejected from the silica tube. The tube then rapidly heated up and released the collected analyte into the light beam above the tube. The transient signal observed using the method was greater than that observed using conventional flame atomic absorption spectrometry for a number of volatile elements.

The technique above is a method of preconcentrating the analyte atoms in a flame using a water-cooled silica tube, mounted above a conventional spray chamber-burner assembly and serves as atom collector. After a fixed collection time of the sample, the water is blown out of the silica tube, which then rapidly heats up causing atomization of the trapped analyte. Sensitivity enhancement depended upon the collection time, and on the analyte element.

The atom-trapping technique worked well for volatile elements, such as lead, cadmium, zinc and copper; however, matrix occlusion interferences limited this technique to samples with a low dissolved solid content. The-water cooled silica tube method reported first by Lau, Held and Stephens (1976) was subsequently investigated by Khalighie, Ure and West in 1979, 1981 and 1982. They extended the use of the atom-trapping technique to a number of relatively volatile elements such as silver, arsenic, gold, bismuth, cadmium, copper, manganese, lead, antimony, selenium, titanium, and zinc with increased sensitivity for a 2 min collection time of between 8 and 40 times over conventional flame atomic absorption spectrometry. Coating the silica tube with aluminium oxide and or iron (III) oxide minimised inter-element effects. These coatings prevent direct interaction of the alkali and alkaline earth metals with the silica surface of the tube, at the same time greatly increased the effective surface area for the trapping of both determined and concomitant species.

Khalighle, Ure and West (1981) applied the atom-trapping atomic absorption spectrometry in determination of cadmium, lead, selenium, and zinc in an air-acetylene flame and arsenic in an air-propane flame, and reported an improved sensitivity. An improvement in sensitivity was observed for the determination of cadmium by replacing the aluminium oxide coating with vanadium (III) oxide by these authors. Khalighle, Ure and West (1982) determined cadmium, selenium, lead and zinc by the use of water-cooled metal collector tubes.

Lau, Ure and West (1982) described the use of a double-tube arrangement in an attempt to minimise matrix interference effects in the determination of selenium. The double-tube arrangement consisted of two 4 mm outer diameter tubes mounted vertically in the flame. The lower tube was maintained cold throughout the determination, to trap interfering species condensed on the upper-cooled tube. The sensitivity, precision and criterion of detection were reported to have all improved two fold.

Hallam and Thompson (1985) developed a method for the determination of cadmium and lead in potable waters using a dual silica tube system devise which utilised two 3 mm outer diameter silica tubes pre-coated with Al_2O_3 or La_2O_3, mounted horizontally in the flame. The rapid rise in temperature of the tubes resulted in volatilization and atomization of the analyte. The coolant water was returned through the system after complete release of the analyte. The optimum distance between the tubes was 1 mm. Detection limits reported were low, with good recoveries. They also applied the method to other elements. Sensitivity, precision and criterion of detection reported were all improved approximately two-fold. Also aluminum oxide coated silica tubes were found to be satisfactory for lead to both sensitivity and inter-element effects.

Sun, Kang, Yang, Li and Shao (1985) described a method that uses water-cooled stainless steel atom-trap (55 cm x 5 mm outer diameter). The sample was fed at 1.5L/min for 4 min through the tube. Residual water in the trap is removed with air, and the atomic absorption signal was recorded with the spectrometer. Sensitivity for silver was increased a 100-fold relative to conventional flame atomic absorption spectrometry.

A method was described for the determination of cadmium in 0.05M calcium chloride extracts of soils by atom-trapping atomic absorption spectrometry. Fraser, Ure, Mitchell and West (1986) reported that the water –cooled silica method showed a 30-fold sensitivity enhancement for cadmium compared with the conventional flame atomic absorption spectrometry.

Brown, Roberts and Kahokola (1987) described various designs of water-cooled silica tube atom-traps, and evaluated for thier analytical performance in flame atomic absorption spectrometry. Different designs of water-cooled atom-trap tubes were studied, but the dual silica atom-trap tube improved sensitivity 1.8 to 2.0 fold compared with the single tube. Sensitivities reported were increased to about 20 – 30 times for the determination of lead and cadmium in waters, with the use of the water-cooled silica tube atom-trap with 2 min collection time.

Bradshaw, Gascoigne, Headridge and Moffett (1987) determined copper in natural waters by atom trapping atomic absorption spectrometry after liquid-liquid extraction. After the extraction, the organic layer was nebulized, and collected on an atom-trap for 3 min. The results agreed with those obtained by graphite furnace atomic absorption spectrometry.

Roberts and Kahokola (1989) reviewed developments in atomic absorption spectrometry with improved sensitivity and ease of operation and particular attention was paid to the slotted tube atom trap for sample introduction. They described the operation of a water-cooled dual silica tube atom-trap for flame atomic absorption spectrometry, and also showed the circuit diagram for its automation. They studied the sensitivities for 12 elements by coating the outside of the silica tube with Al_2O_3, Fe_3O_4, La $(OH)_3$ or V_2O_3 and applied the system for the determination of cadmium, lead, copper and manganese in river water.

Matusuewicz, Sturgeon, Luong and Moffatt (1991) determined copper, manganese and zinc in river and estuarine water, by using a 2 min in-situ pre-concentration time with water-cooled dual silica tubes. Detection limits recorded were 0.9, 1.5 and 0.3ng/ml for copper, manganese and zinc respectively. Water-cooled silica tube, as a method for improving the sensitivity of flame atomic absorption spectrometry was reviewed by Granzhan and Charykov (1992) who reported significant enhancement of sensitivities of many trace elements with wide range of matrices.

Turner and Roberts (1995) redesigned the dual-tube water-cooled atom-trap in order to increase sensitivity and precision. Operating parameters were optimized, such as the cooling water pressure through the tubes, the position of the tubes with respect to the flame and the light beam. Sensitivities reported were 0.3579 and 2.994 ng/ml for cadmium and lead respectively.

Ellis and Roberts (1996) aspirated analyte solutions through dual 'bent' silica tube coated with appropriated material. Water flowed through the tubes cooling the surface, and allowing the analyte to be trapped on the surface. After 2 min, argon was used to expel the water, the tube was then heated in the flame of the absorption spectrometry, and the trapped ions were volatilized from the surface of the tube generating a transient atomic absorption signal. High sensitivity was reported for arsenic, antimony, copper, and manganese (8.6, 8, 0.93 and 0.38ng/ml respectively) using a high fuel flow, high percentage obscuration, and low tube height.

Turner and Roberts (1996) described a hybrid atom-trap for use in atomic absorption spectrometry, which consisted of a single silica tube water-cooled atom-trap, and a quartz slotted tube atom-trap clamped onto a modified 5 cm burner head, so that the analytical section of the single silica tube was held inside the slotted tube cylinder. The trap was used for the determination of cadmium and lead in river water and the results obtained were compared to those obtained using a single silica tube, water-cooled atom-trap, and a ‘bent’ dual water-cooled atom-trap. The new trap showed high sensitivity, and good precision.

Ellis and Roberts (1996) determined mercury in sediment, by a method in which the external surface of the silica ‘dual’ bent tube used was coated with gold by spraying the outside with 0.1% $HAuCl_4$ for 30 seconds. The sample solution was atomised directly on to
the outside surface of the trap held in the flame, while the trap was cooled with an internal flow. After concentration for a suitable time, the water was expelled, and the tube temperature rose, rapidly expelling the mercury from the amalgam for measurements. The results reported agreed well with those obtained by cold vapour atomic absorption spectrometry.

Matusiewicz and Kopras (1997) described the design and construction of an atom-trapping device, that combined the advantages of the slotted tube atom-trap and the water-cooled atom-trap. The performance of the combined device was compared with those of atom-traps based on the individual atom-trapping techniques in the determination of silver, cadmium, copper, iron, indium, manganese, lead, tellurium, and zinc in beer, by atomic absorption spectrometry in an air-acetylene flame. Best detection limits were obtained with the use of the combined atom-trap device and with collection for 2 min, these were in the range of 0.1 – 10 ng/ml.

The optimization of the slotted tube has been attempted using various designs and parameters such as exit holes, tube length, and tube material (Matusiewicz, 1997). The author indicated various procedures based either on Delve’s micro-sampling cup technique or atom trap system, and the possible limit of detection for a wide range of analytes. The procedures reported were simple, and in many cases enhanced the signal.

Zhang, Li, Yang and Sun (1998) reported a method for the determination of cadmium by derivative flame atomic absorption spectrometry with a modified water-cooled stainless-steel atom trapping tube in an air- acetylene flame. The laboratory-made derivative measurement system, and atom trapping equipment gave a detection limit and sensitivity improvement two or three orders of magnitude over the conventional flame atomic absorption spectrometry. The limit of detection (3σ) for cadmium was reported to be 0.2 µg/l, with a recovery range of 85.9 - 114%. The authors applied the method to the measurement of cadmium in vegetable samples.

The detection limit of flame atomic absorption spectrometry can be improved by increasing the efficiency of aerosol generation/transport, and prolonging the residence time of the free analyte atoms in the absorption volume. Thus Gaspar and Berndt (1999), described a new flame method of atomic absorption spectrometry. In the paper the analyte was transported as a high-speed liquid jet into a heated tube that was positioned in an air/acetylene flame. The authors reported, that both the complete introduction of the entire sample, and the extended residence time inside the absorption volume resulted in an improvement in limit of detection from 6-to 202-fold for 17 elements (silver, arsenic, gold, bismuth, cadmium, copper, mercury ,indium, potassium, lead, palladium, antimony, rubidium ,selenium ,tellurium, thallium, and zinc). Also reported was a standard deviation of1.7-4.0% (n=12, 50µl).

Sun, Gao, Yuan, Zhang Y. and Zhang D. (2002) used a derivative atom trapping flame atomic absorption spectrometry with a modified water cooled quartz atom trapping tube, and obtained a relative standard deviation of 2.9-4.2% determining lead in several Chinese herbs.

Sun and Li (2005) applied the derivative signal processing technique (rate of signal intensity with time dI/dt) to improve the signals 50 times higher than the conventional flame atomic absorption spectrometry. The combination of the derivative signal processing technique with atom trapping method, resulted in 1000 fold improvement in sensitivity over the conventional flame atomic absorption spectrometry.

CHAPTER THREE

MATERIALS AND METHODS

3.1. MATERIALS

3.1.1 Atomic Absorption Spectrometer

The Atomic Absorption investigations in this work involved the use of the SP9 Pye-Unicam Spectrometer.

3.1.2 SP9 Pye- Unicam Model Atomic Absorption Spectrometer

The spectrometer consists of a four- lamp turret, a deuterium hollow cathode lamp for background correction, an optical system incorporating a chopper, mirrors, lenses, monochromator, and photomultiplier detector.

The basic components of the SP9 Pye- Unicam model atomic absorption is a radiation source; atomizer cell (contains the gaseous atomized sample), a wavelength selector, a detector, and a signal processor and readout (Plate ii).

The schematic diagram of the instrument (SP9 Pye- Unicam model atomic absorption spectrometer) and that of its optical diagram (SP9 Pye-Unicam atomic absorption spectrometer) are shown in Figures 2 and 3 respectively.

The monochromator is of the Ebert type of geometry. Its wavelength is selectable between, 190 to 853 nm via a micrometer screw drive connected to an arm adjusted to a linear relation between wavelength and rotation of the control knob. The slit width may be varied in discrete steps by means of the “band pass” control knob, which can be selected to give a band pass of 0.2, 0.5, 1.0, 5.0 and 10.0 nm.

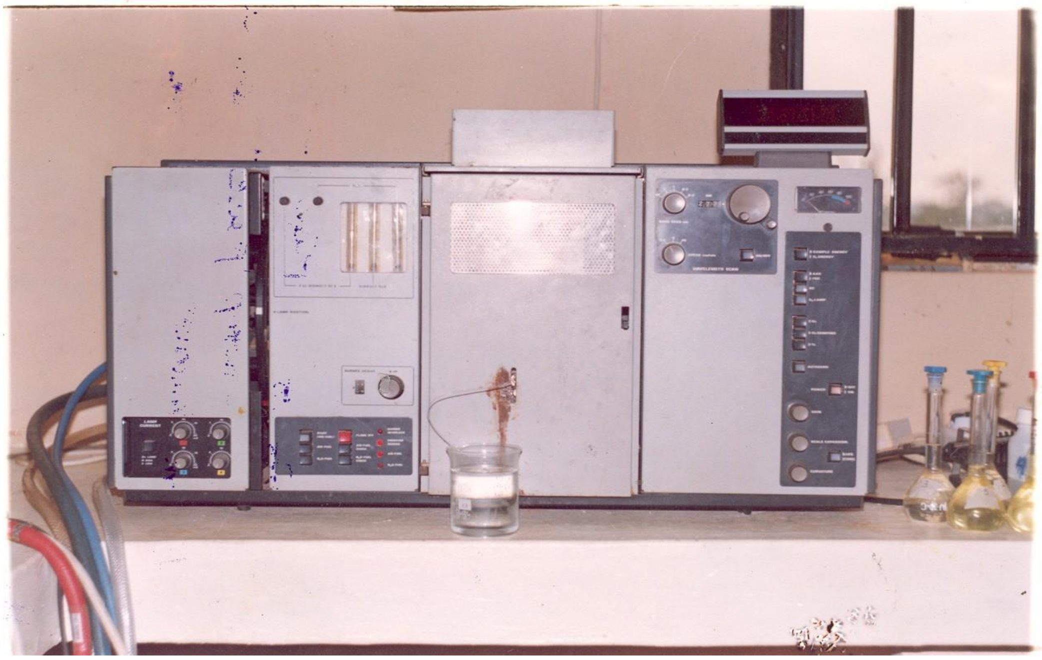


Plate ii. A Philips Pye-Unicam SP9 Atomic Absorption Spectrometer

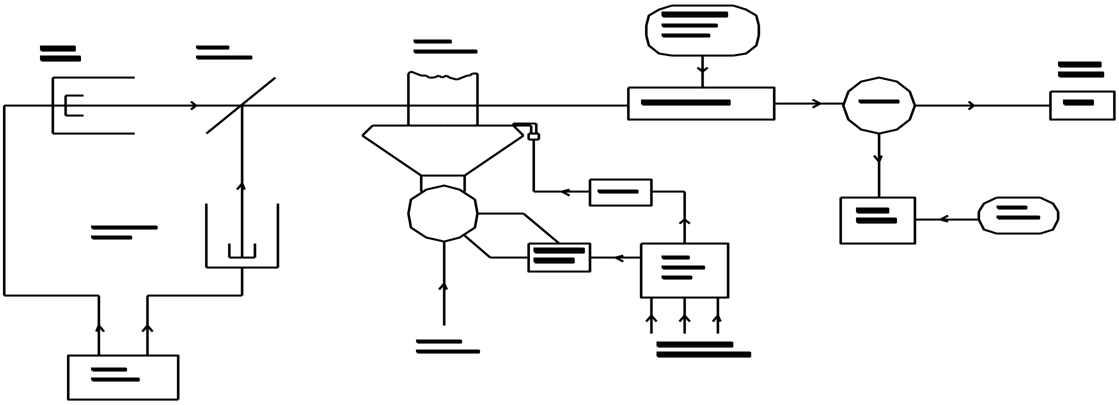


Fig. 2. The Schematic Diagram of Pye-Unicam SP9 Atomic Absorption Spectrometer

Where, E.T.A .= Electrothermal atomizer

P.M.T. = Photomultiplier tube

E.H.T = Extra high tension

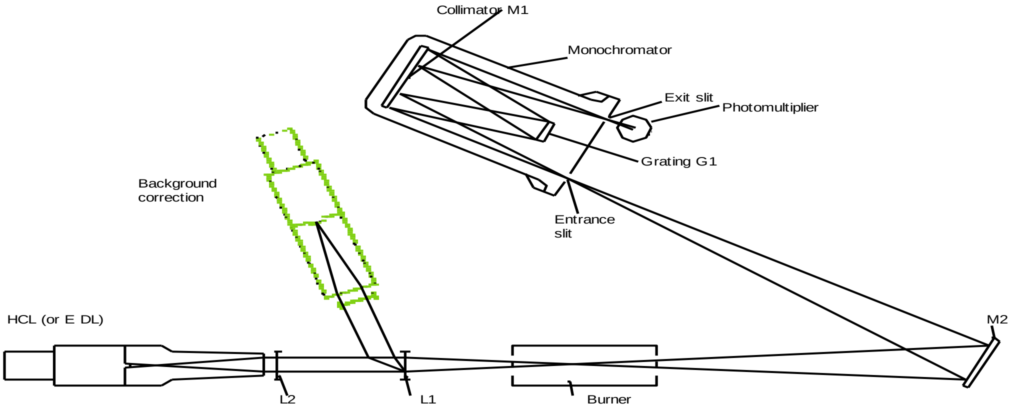


Fig. 3 . Optical Diagram of SP9 Spectrometer

Where,	H.C.L	= Hollow cathode lamp
	E.D.L	= Electrodeless discharge lamp
	L_1 & L_2	= Lenses
	M_1 & M_2	= Mirrors

The photomultiplier or optical detector comprises an evacuated tube containing a photosensitive cathode and series of dynodes, which increase the initial electrical signal by many orders of magnitude. The photo-cathode is sensitive to radiation over the working range of the instrument (i.e. 190- 853 nm) and releases electrons in proportion to the amount of radiation incident upon it (Price, 1983).

These electrons are accelerated in the electric field present in the photomultiplier and strike the first dynode. Each electron striking the dynode causes more to be released and is in turn accelerated to the second dynode. This process continues until the last dynode by which time a current amplification of some 10^6 times is possible. This resulting signal is then presented as a digital display, which can also be processed by a data handling system. A schematic diagram of the SP9 electronic system is shown in Figure 4. The lamp current can be adjusted to give the required output. The flame is controlled and ignited by the gas control logic, which operates various solenoid valves to select the required gases and flow rates (Milner & Whiteside, 1984).

The photomultiplier detects the radiation and converts it to an electrical signal. Adjusting the voltage output of the extra high-tension power supply controls the photomultiplier gain. The energy meter indicates the light energy throughput of the system, which is useful when optimizing the lamp position or monochromator setting for maximum intensity.

In order to convert intensity to absorbance, it is necessary to use a logarithmic amplifier. This is under the control of the auto zero function which enables an absorbance reading of zero to be selected for any particular light level, subsequent changes of which are then registered relative to the artificial ‘zero’ light level.

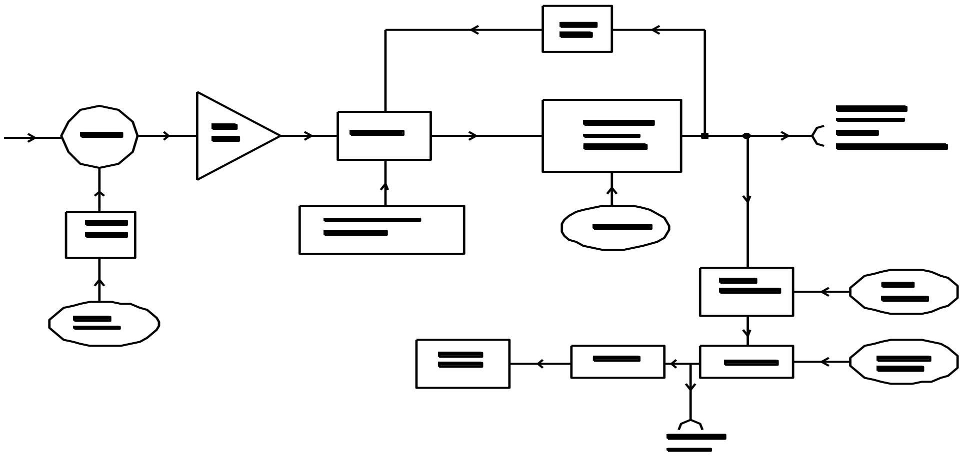


Fig.4. A Schematic Diagram of SP9 Electronic System.

Where, E.H.T = Extra high tension

S.E. = Scale expansion

F.E.S = Flame emission signal

A.D.C. = Analogue to digital conversion circuit

P.M.T. = Photomultiplier tube

3.1.3 Hollow Cathode Lamp Sources

Seven hollow cathode lamps were used in the atomic absorption investigations and manufactured by Philips Pye- Unicam Limited, England. The lamps maximum operating currents and wavelengths of the absorbing lines used for this study are given in Table 3.

The lamp current setting has a significant effect on the sensitivity, thus lamp current setting of 75% of the maximum was used.

The instrumental operating conditions for the elements are listed in Table 4.

Table 3. List of Hollow Cathode Lamps and their Operating Currents (for SP9 Pye Unicam Spectrometer)

Hollow Cathode Lamp	Maximum Operating Current (mA)	Resonance line (nm)
Pb	6	217.0
Cd	6	228.8
Cu	5	324.8
Ni	15	232.0
Co	15	240.7
Mn	12	279.5
Zn	10	213.9

Table 4. Operating Conditions of the SP9 Pye-Unicam AAS with 10 cm Burner

Element	Pb	Cd	Cu	Ni	Co	Mn	Zn
Mode of operation	Absorption	Absorption	Absorption	Absorption	Absorption	Absorption	Absorption
Wavelength (nm)	217.0	228.8	324.8	232.0	240.7	279.5	213.9
Bandpass (nm)	0.5	0.5	0.2	0.2	0.2	0.5	0.5
Flame (air-acetylene)	Stoichiometric	Stoichiometric	Fuel- lean	Fuel-lean	Stoichiometric	Stoichiometric	Stoichiometric
Lamp current (mA)	5	4	4	11	12	9	8
Height of the burner (mm) Conventional	12	12	12	12	12	12	12
Height of the burner (mm) Atom trap	20.5	20.5	20.5	20.5	20.5	20.5	20.5
Air flow rate (1/min)	4.5-5.5	4.5-5.5	4.5-5.5	4.5-5.5	4.5-5.5	4.5-5.5	4.5-5.5
Solution aspiration (1/min) rate	4 – 6	4 – 6	4 – 6	4 - 6	4 - 6	4 - 6	4 – 6

3.1.4 Reagents and Stock Solutions

All chemicals used in the preparation of the stock solutions of elements and compounds were of analytical reagent grade. Unless otherwise stated, stock solutions were prepared in dilute nitric acid, with a final concentration of 0.1%.

Deionized water was used throughout. Working solutions were freshly prepared from these stock solutions as required by dilution with deionized water. Stock solutions of the elements were supplied by VHG laboratories Inc (Spectrochemical Solution Standard, USA).

3.1.5 Sampling Site and Sample Collection

Leather tanning is one of the sources of the heavy metals, such as lead, copper, cadmium, zinc and nickel. Stakeholders were approached in the designated areas and their permission sought to collect samples from the leather processing pots as well from the surroundings.

Environmental samples from a local leather-processing site were obtained from various points of the Naraguta village, Jos North LGA of Plateau State. They were numbered in the order of decreasing discharge flow so that site 1 is located at the point of discharge, while site 13 is far away. Within the site, samples were taken at three spots that were spaced approximately 1m intervals; and were then mixed to give a composite sample of 300ml. Duplicate samples were collected from each site and were kept in polyethylene containers.

Also investigated were effluents discharged near and around a leather tannery located in Kano State, Majema area of Kofar Wambai, Kano. For processing of the leather locally, pipe-borne water is used as the source of water supply. The leather is processed, using local materials such as katsi i.e. locally made paste like substance (made of ash soaked in water for some days, then dried, burnt again and ground), sodium sulphide, kanwa – an impure form of potassium carbonate (K_2CO_3) and Acacia arabica (Egyptian Mimosa) pods.

The manufacturing of leather consists of drying and soaking the leather in different basins with different materials and chemicals. The effluent generated at the leather-tanning site is discharged into low-lying gutter without treatment and subsequently into rivers.

The samples which are labeled as follow: - at site A1, A2 and A3 (animal skin), at site B1, B2, and B3 (snake and crocodile skins), while at site C1, C2 and C3 (animal skin) are presented in Plates iii, iv, v, vi, vii, viii, ix and x respectively. The processed leather and animals grazing at the sampling site are shown in Plates xi and x. Consumption of these animals from the sampling site could lead to a variety of health problems. Similarly ten samples from a leather (tanning small-scale) factory located at Sharada Industrial Estate, Phase III, Kano were collected and investigated for their heavy metal contents. Also, seven environmental samples discharged from Nasco Group of Companies and five sample effluents from Jos International Brewery (JIB) were collected for analysis.

3.2. METHODS

3.2.1 Sample Handling

The environmental samples collected from the various points of the study area were kept in polyethylene containers. The effluents collected were not subjected to further treatment except for appropriate acidification at the sampling spot using (1:1) nitric acid (Greenberg, Clesceri and Eaton, 1992). Acidification of the sample at the sampling site helps in preserving the sample by minimizing adsorption of the trace heavy metals onto the container walls (Bartley & Gardiner, 1977).

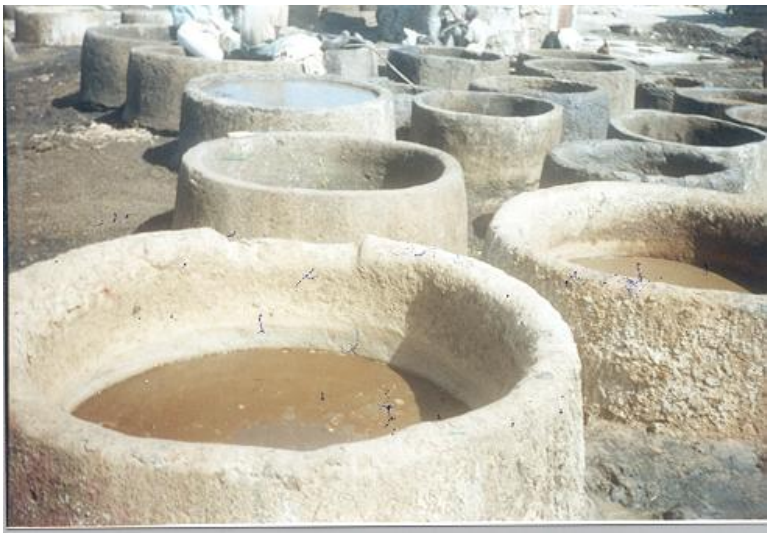


Plate iii. Sample A, Animal Skin Being Processed in Basins

Plate iv. Sample B1, Treatment of Snake and Crocodile Skins

Plate v. Sample B2, Snakes and Crocodile Skins

Plate vi. Sample B3, Skin Soaked in a Basin

Plate vii. Sample C1, Animal Skin Being Processed

Plate viii. Sample C2, Point of Discharge 1

Plate ix. Sample C3, at the Point of Discharge

Plate x. Sample C4, Collected at the Discharge Point 3

Plate xi. The Processed Leather

Plate xii. Animals Grazing at the Sampling Site

3.2.2 Evaluation of Techniques

The performance characteristics of the developed method with the use of atomic absorption spectrometer were assessed using quantitative performance criteria; such as sensitivity, detection limit, precision and accuracy.

3.2.3 Sensitivity

Sensitivity is defined as that concentration of the element in part per million (or μg/ml or mg/l) in aqueous solution, which gives an absorbance of 0.0044, equal to a 1% of the transmitted radiation. Sensitivities are checked by aspirating a freshly prepared aqueous solution of the element, to give an absorbance reading of about 0.1A. Instrumental parameters are then adjusted for optimum sensitivity of the element in mg/L.

3.2.4 Detection Limits

Detection limit is a statistical function which takes into account blank levels, sensitivity and signal to noise ratios. It is defined as that concentration of an element in mg/L, which gives a reading equal to three times the standard deviation of a signal measured close to the blank level. The standard deviation is calculated using at least 10 sequential readings (Svehla, 1975). The detection limits depend on the signal to noise ratio and are therefore a function of the performance of the various instrument components.

3.2.5 Precision and Accuracy

A measure of the precision is obtained with a reproducibility test in which the standard deviation or coefficient of variation is calculated from at least ten and preferably twenty replicate results. It is usually expressed as percentage relative standard deviation (%RSD).

$$\%RSD = \frac{100\delta}{\bar{X}}$$

_Where δ is the standard deviation

$\bar{X}$ is the mean absorbance or concentration

Accuracy is a measure of agreement between a measured value and the value accepted as "true". In this work, the accuracy of the procedure developed was demonstrated by analyzing reference standard materials, which had been analyzed by other procedures, and comparing the result, obtained with certified ones.

3.2.6 The Development of Modified Atom-trapping Collecting Tubes

The nickel tube met the requirements of the material as having good stability and chemical resistance to the corrosive conditions of an air/acetylene flame. Thus a tube made of nickel, 128mm long, has 7.2mm inner diameter and a hole at the center of 5mm inner diameter width was fabricated at the Mechanical Production/Fabrication Workshop, Engineering Services Department, National Metallurgical Development Centre, Jos. Also a sample holder (or a tiny crucible) made of nickel, of 8mm inner diameter and 6mm depth was used (Fig. 5).

In the tiny crucible, 0.2ml of sample solution was placed and the solvent evaporated at 105^{o}C for about 10 minutes to avoid spraying or boiling of the sample if inserted directly before drying. The micro-crucible is then held in the flame at a position exactly under the centre hole of the tube, through which the vapour enters into the nickel tube and a signal is measured.

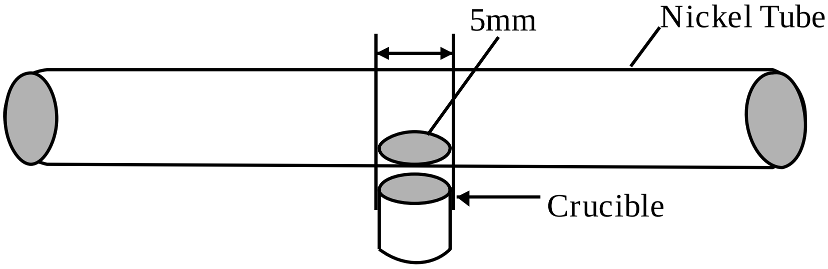


Fig. 5. Schematic Representation of the Tube and Crucible(Detachable

This gave a good but not reproducible result due to the considerable time wasted in positioning the cup, thereby leading to loss of sample into the flame. An atom – trap a nickel tube, with a hole at the centre of 5mm inner diameter width and a crucible attached at the centre hole of the tube is shown in Fig. 6. A 0.2ml sample solution is placed using a micropipette through a tiny hole, which is located at the center of the tube.

3.2.7 Optimization of Experimental Conditions

Different designs and ways of placing atom-trap over the burner were evaluated. The height of tubes support was varied as well as its design. As the sensitivity of the method depends on the positioning of the tube with respect to source radiation, the optimal position ensuring maximized light path through the tube was obtained experimentally.

Though a very good flame was observed using the 21.8mm steel support , however repeated removal of the tube in the course of analysis affected the proper positioning of the tube, and hence the absorbance.

The other variant used was to place a hanger through the exhaust as shown in Plate xiii; the tube was placed on the hanger about 2cm above the 10cm air-acetylene burner. However, when sample was introduced into the crucible, it was observed that manually retaining the same position of the crucible beneath the tube was not feasible. As a result the tube and the crucible were joined to minimize the problem of retaining the tube in position. The signals obtained in the later configuration were reproducible.

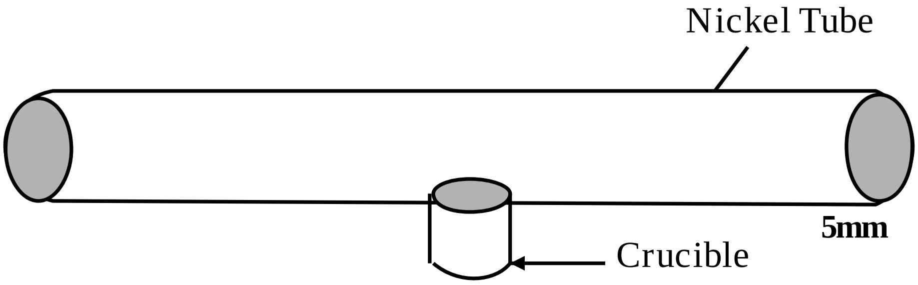


Fig. 6. Schematic Representation of the Tube and Crucible (Joined

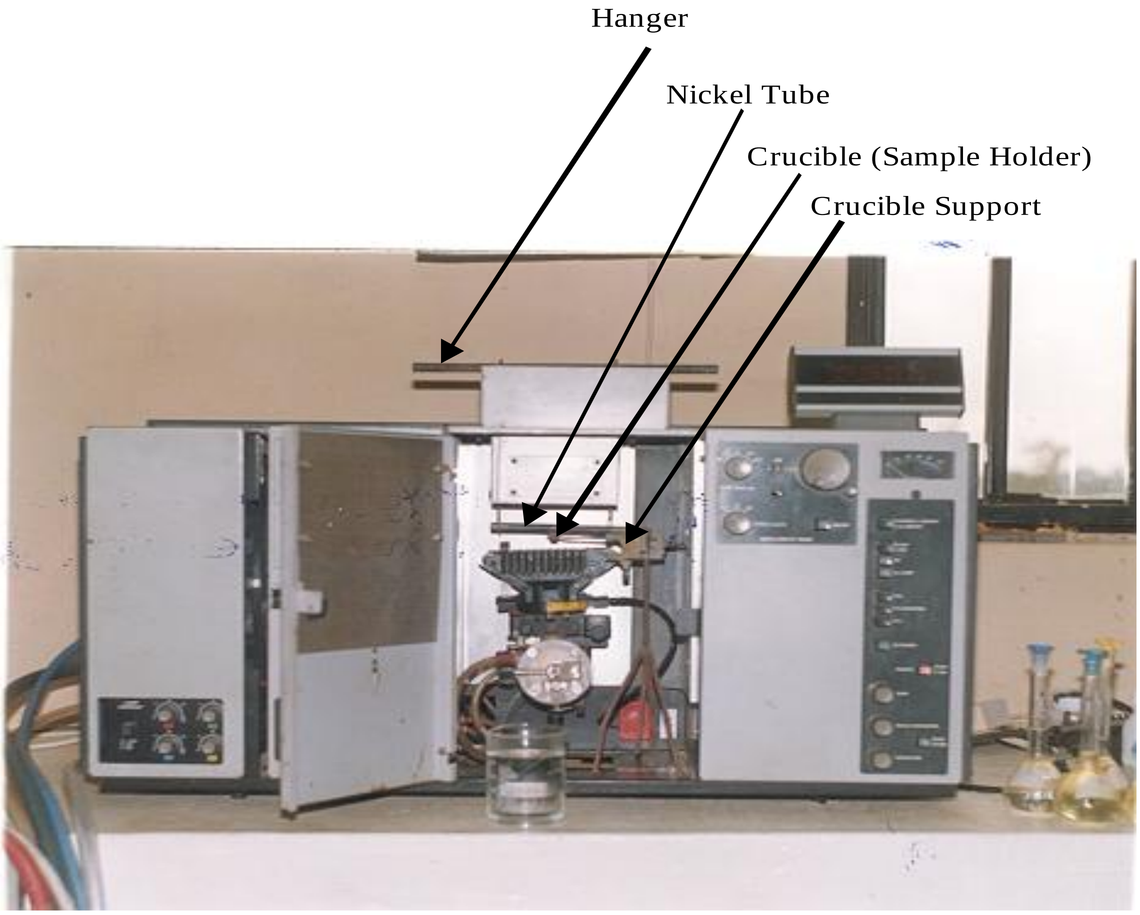


Plate xiii. The Atom Trap Placed on a Hanger.

The arrangement shown in Fig. 6 in which the tube could easily be fixed and removed from the burner while the support stayed firm gave the best signals. The height of the burner was adjusted to 20.5 mm throughout the measurements. The nickel tube atom trap placed on a 10cm burner head is shown in Plates xiv and the same burner head but at a close view is shown in Plate xv. The initial nickel tube design was altered and made to contain 2ml (Plate xvi).

3.2.8 Procedure

Standard solutions of the elements (copper, lead, zinc, cadmium, manganese, nickel and cobalt) in Table 1 of various concentrations were prepared and aspirated using the conventional flame atomic absorption spectrometric method.

The same standards were analysed using the developed modified atom- trap method, in which 0.2 ml of the standard solution was evaporated for about 10 minutes at 105ºC. The tube was then inserted into the flame and the signal measured. All environmental samples were analysed in the same manner.

Plate xiv. The Atom Trap Placed on a 10 cm Burner

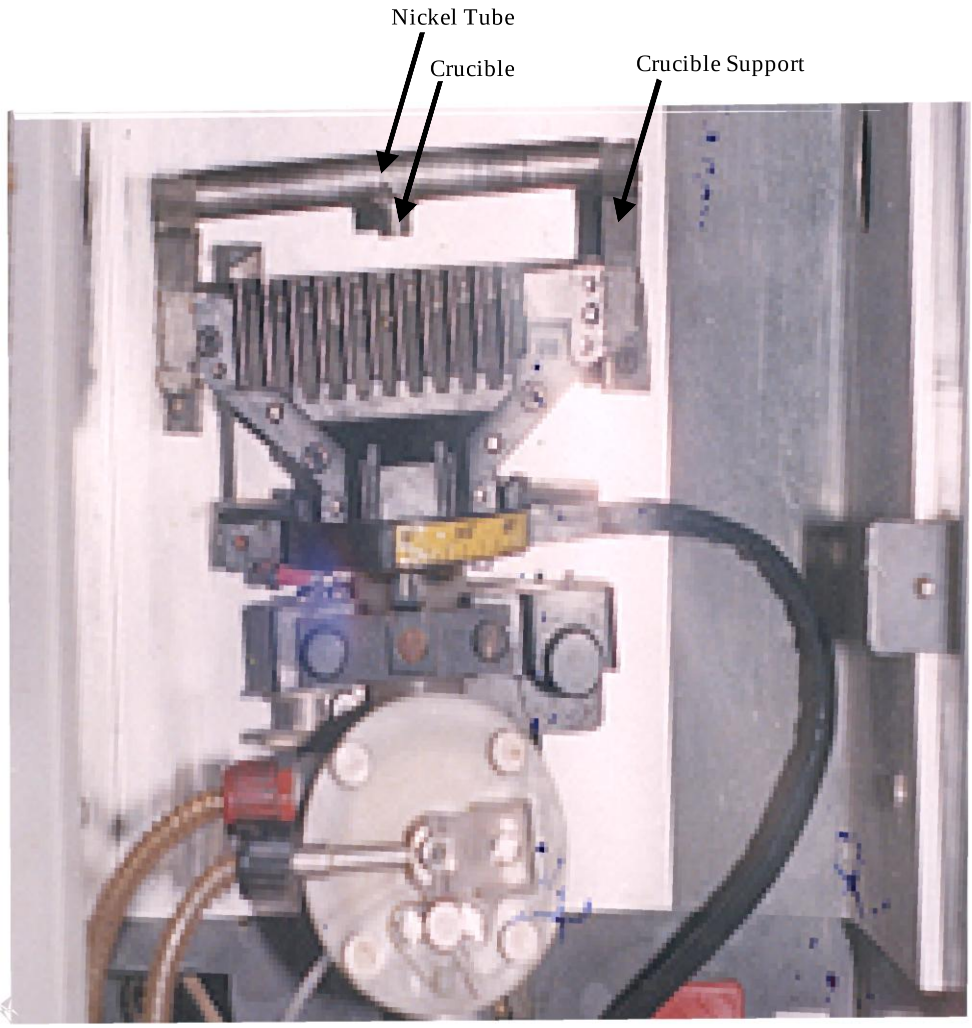
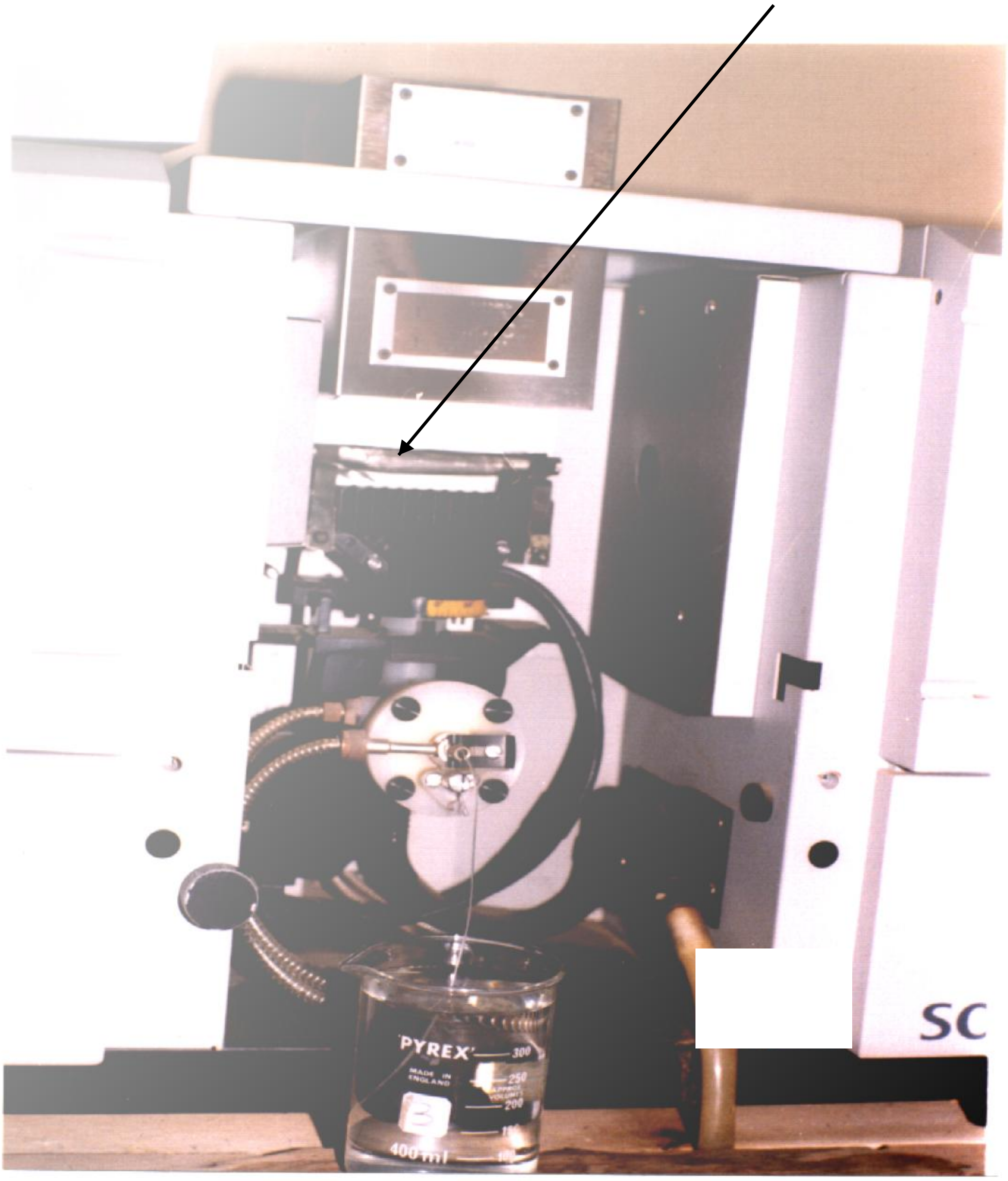


Plate xv. A Close View of the Atom Trap Placed on a 10 cm Burner



The 2 ml Nickel Tube

Plate xvi. The 2ml Nickel Tube Placed on a 5 cm Burner

CHAPTER FOUR

RESULTS

4.1. INITIAL EVALUATION OF TUBE DESIGNS.

The first experiments were carried out using the quartz tube, but its use was discontinued because divitrification of the quartz tube was unavoidable as earlier reported (Taylor et al., 1985). Other factors against its use include breakage due to temperature changes (Brown et al, 1987), and its scarcity.

Non-Magnetic stainless tube/crucible was fabricated at the Mechanical Production/Fabrication Workshop of Engineering Service Department, National Metallurgical Development Centre, Jos, with the specifications given in Table 5. The use of this tube was discontinued because the sample solution and the flame readily attack the walls of the tube, thereby destroying it and hence its shorter lifetime.

The nickel tubes, fabricated at the Mechanical Production/Fabrication Workshop of Engineering Services Department, National Metallurgical Development Center, Jos, for improving sensitivity are of different sizes. Thus nickel tube 1, nickel tube 2 and nickel tube 3 with their various specifications are shown in Table 6. Of the three nickel tubes, the first one gave the best results, and was used in carrying out the analysis reported in this research work. Its suitability could be ascribed to its larger diameter, and shorter length that allowed radiation from the hollow cathode lamp to pass through the tube, and subsequently to the detector. This could possibly explain the higher sensitivity obtained using this tube.

Table 5. Stainless (Non-Magnetic) Atom Trap Tube Specifications.

Parameters	Tube	Crucible
Length (mm)	120	9
Internal diameter (mm)	10	_
Outer diameter (mm)	12	10
Thickness (mm)	1	_
Depth (mm)	_	8

Table 6. Nickel Tube/Crucible Joined

Parameters	Nickel tube 1	Nickel tube 2	Nickel tube 3	Crucible
Length (mm)	128	130	135	_
Inner diameter (mm)	7.2	6.7	6.5	8.1
Centre hole (mm)	5	5.2	5.1	_
Depth (mm)	_	_	_	6.0

4.2. OPTIMIZATION STUDY

The height of the nickel tube above the burner head was varied from 2 - 28 mm in 2 mm increments. The results obtained are shown in Fig 7. In general, the signal increased with the height increase. The optimum height was about 20.5 mm. The flame became unstable, when the tube was below 18 mm. At the height of 23 mm, the radiation beam was no longer passing through the tube.

4.3. THE NICKELTUBE AND ITS ASSEMBLIES

To allow for free insertion and withdrawal of the tube, in and from the flame, a small metal tong was used. The tube was placed approximately 2 cm above the burner, as such the maximum radiation from the hollow cathode lamp passed through the tube (See Plate xiv). Once the flame was on, the instrument was zeroed as the first step before any measurement.

The samples or standards were easily injected manually through the centre hole of the tube. This tiny hole is large enough to introduce the sample in a micropipette yet small enough to keep the sample vapour in the tube. In the course of the analysis it was assumed, that no flame gases are entering the tube, thus preventing interference effects from the flame gases. The tube was then placed on a hot plate. This step promoted the evaporation process, which minimized the possible losses of the analyte due to mechanical expulsion, resulting from violent evaporation of the solvent. Atomization was then achieved by introducing the tube inside the flame.

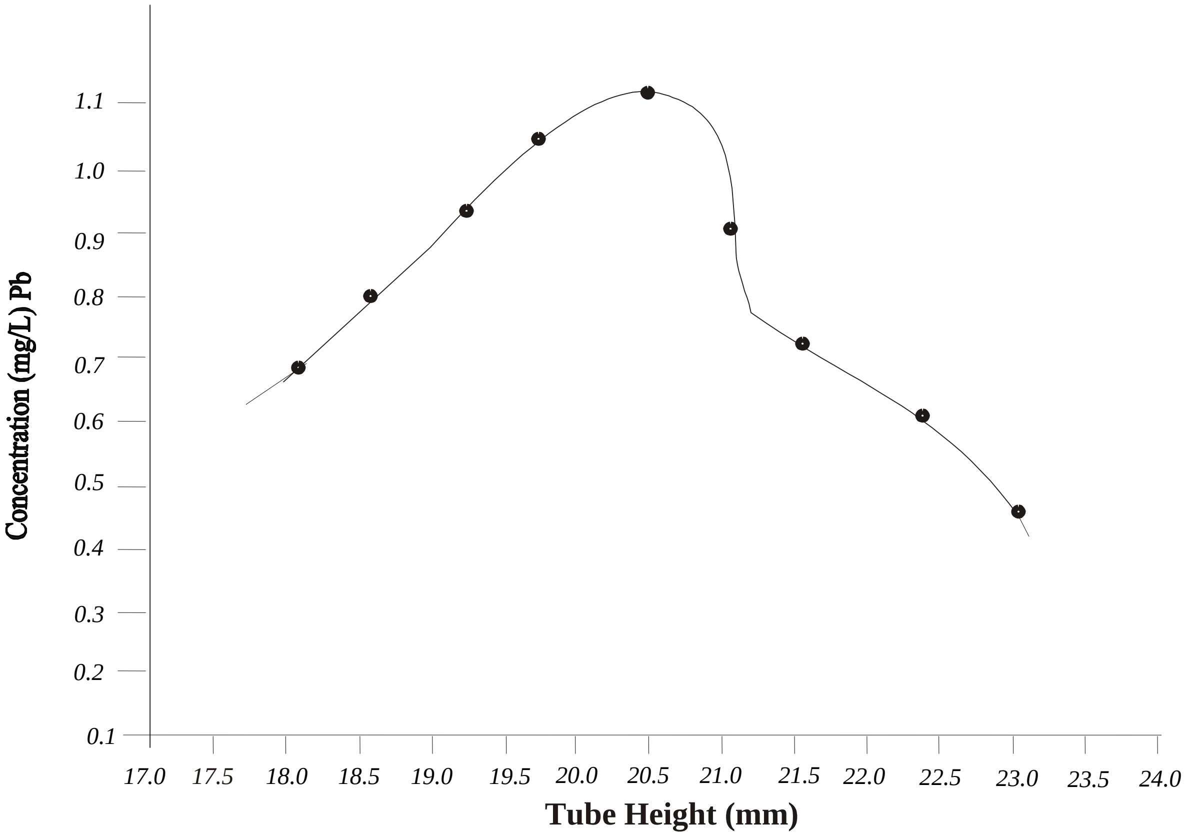


Fig. 7. Variation of Concentration with Tube Height

4.4. COMPARISONS OF LEAD AND CADMIUM SIGNALS OBTAINED WITH THE USE OF CONVENTIONAL FLAME AAS AND THE DEVELOPED ATOM-TRAP METHOD.

A number of standard lead concentrations were analyzed using the conventional flame atomic absorption spectrometry and the developed atom-trap method. The resulting absorbance signal for each concentration at the lead wavelength of 217.0nm was measured as shown in Fig 8. Likewise, the various standard concentrations of cadmium were measured at 228.8 nm wavelength, and the resulting signals are shown in Fig. 9.

From the calibration curves for these elements i.e lead and cadmium, the atom-trap method showed higher sensitivity with various degrees of absorbance signals.

The increase in sensitivity achieved with the use of modified nickel atom-trapping tube could be attributed to the element trapped and concentrated for a longer period of time. The residence time of the atoms in the light path is increased, hence the signal is enhanced. This is in line with the report by Brown et al (1984), as well as, by Alvarado et al (1998).

In the course of analyzing standard solutions, using the nickel-tube atom-trap procedure, two difficulties were encountered:

1. Prior to the commencement of the production of lead and cadmium atoms, the standard solutions diffused out of the nickel-tube resulting in low absorbance signals.
2. Also, due to the difficulty of manually reproducing the exact position of the tube, with respect to the hollow cathode lamp light beam, signals were affected by a high dispersion.

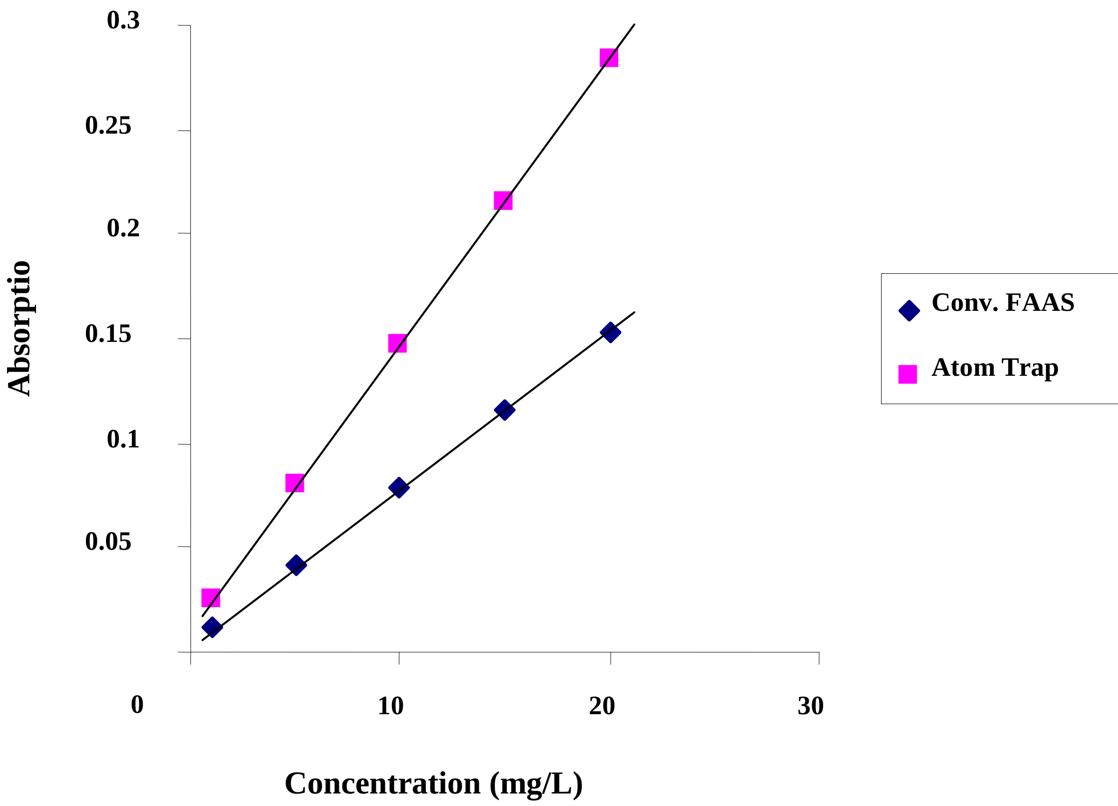


Fig. 8. Calibration Graph for Lead

Y = 0.0075X + 0.0037; r = 1 Conv. FAAS
Y = 0.0136X + 0.017; r = 0.99 Atom Trap

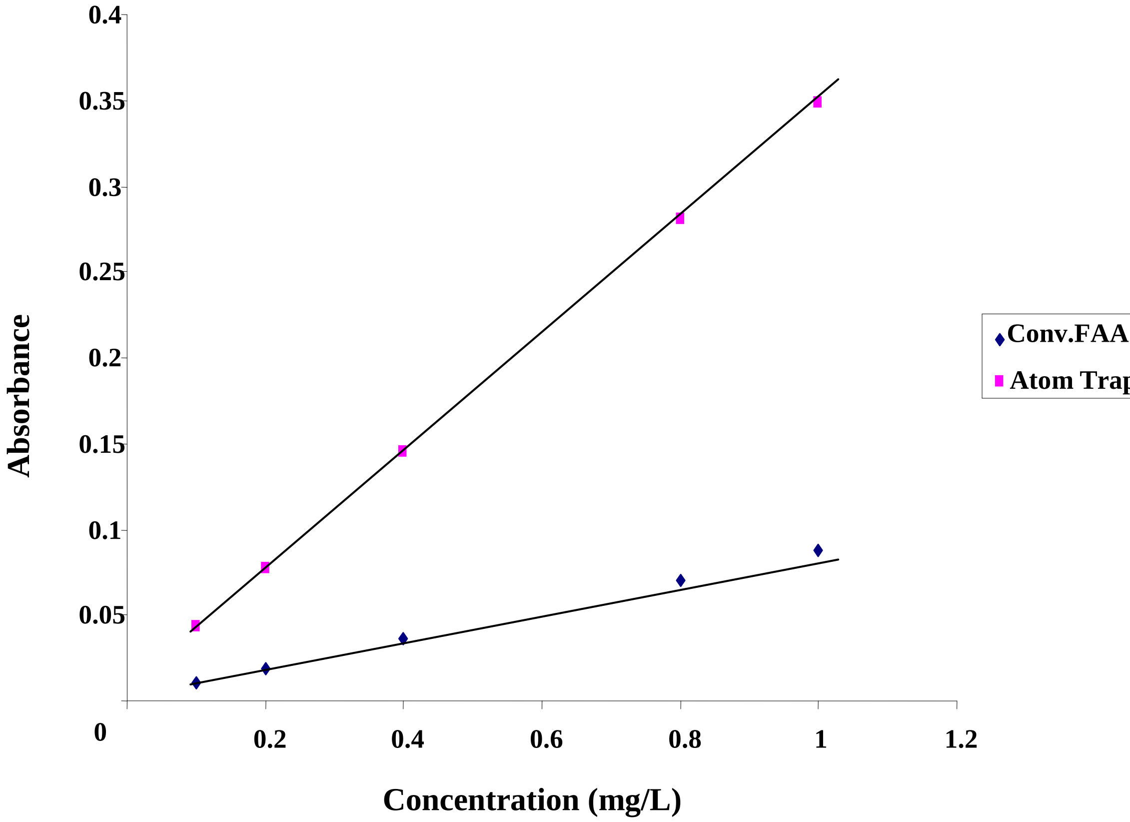


Fig. 9. Calibration Graph for Cadmium

Y = 0.0857X + 0.0018; r = 1 Conv. FAAS

Y = 0.339X + 0.0091; r = 1 Atom Trap

With the precautions (i.e. 1 and 2) attempts were made to analyze real samples from leather tanning effluents from various points of the Naraguta Village, Jos North Local Government Area of Plateau State, Nigeria.

A comparison of absorbance signals obtained using atom trap technique for lead and cadmium in leather tanning effluents versus using the conventional flame atomic absorption spectrometry is shown in Tables 7 and 8, respectively.

Known concentrations of lead in standard reference materials BCS by Bureau of Analyzed samples limited (with BCS No 392) were determined, as guide for acceptability or otherwise of the atom-trap method. From the result in Table 7, wide variations in the absorbance signals were observed due to variation in the cross-section of the radiation from the source, as it traversed through the tube. This reaffirmed that the position of the tube with respect to the flame is an important parameter in atom-trap flame atomic absorption spectrometry.

From the results (Figures 8, and 9, Tables 7 and 8), i.e. the determination of lead and cadmium in standard solutions, as well as, in the real samples, the atom-trap method showed higher sensitivity over the conventional flame atomic absorption spectrometry.

Table 7. Absorbance Signals Obtained Using the Conventional Flame AAS and Atom Trap Method for Lead in Leather Tanning Effluents (Naraguta, Jos)

Sample no	Absorbance Conv. FAAS	Absorbance atom trap	Fractional Increase in signal	Concentration (mg/L)
1	0.005	0.008	1.6	0.611
2	0.004	0.007	1.8	0.485
3	0.003	0.005	1.7	0.433
4	0.005	0.007	1.4	0.551
5	0.004	0.007	1.8	0.477
6	0.006	0.011	1.8	0.692
7	0.007	0.013	1.9	0.778
8	0.006	0.009	1.5	0.671
9	0.006	0.011	1.8	0.691
10	0.002	0.003	1.5	0.260
11	0.001	0.002	2.0	0.188
12	0.001	0.002	2.0	0.184
13	0.001	0.002	2.0	0.129
Ref. material Bcs no 392	0.001	0.002	2.0	0.190

* Average of five absorbance readings.

Table 8. Absorbance Signals Obtained Using the Conventional Flame AAS and Atom Trap Method for Cadmium in Leather Tanning Effluents (Naraguta, Jos)

Sample no	Absorbance Conv. FAAS	Absorbance atom trap	Fractional Increase in signal	Concentration (mg/L)
1	0.007	0.028	4.0	0.121
2	0.007	0.027	3.9	0.127
3	0.008	0.030	3.8	0.134
4	0.007	0.027	3.8	0.123
5	0.008	0.031	3.9	0.136
6	0.009	0.037	4.1	0.161
7	0.010	0.038	3.8	0.173
8	0.011	0.043	3.9	0.194
9	0.010	0.036	3.6	0.174
10	0.006	0.022	3.7	0.102
11	0.006	0.023	3.8	0.103
12	0.006	0.025	4.2	0.108
13	0.005	0.019	3.8	0.092

* Average of five absorbance readings.

4.5. DETERMINATION OF THE EASILY VOLATILE ELEMENTS IN EFFLUENTS

Attempts to analyze volatile elements in effluents, using the developed atom-trap method were made. Khalighie et al (1982); Brown et al (1985), analyzed volatile elements, and showed improved sensitivity with the method.

The method was extended to determination of copper, manganese, zinc, cobalt, nickel, and iron in the environmental samples. The environmental samples considered were effluents generated at a leather tanning site of Majema area, Kofar Wambai, Kano, Nigeria, and a leather factory at Sharada Industrial Estate, phase III, Kano State. Effluents discharged from NASCO Group of companies, and Jos International Breweries both located in Jos, Plateau State, Nigeria. The calibration curves obtained for each metal is as shown in Figs 10 -14.

From the calibration curves presented, it was apparent that the developed method enhanced the sensitivity of flame atomic absorption spectrometry with various degrees of increase for various elements.

A 1.9 to2.3 fold increase in absorbance signal was recorded for copper, by using the nickel tube to trap the analyte in the flame for a longer period of time, a 1.2 to 1.7 fold increase in absorbance signals were recorded for manganese, while zinc had 2.3 to 2.5 fold increases in absorbance signals. Cobalt had 1.2 to1.8 fold increase in absorbance signal, while nickel had a 1.6 to 2.1 increase in absorbance signal in the concentrations of the standard solutions of the elements.

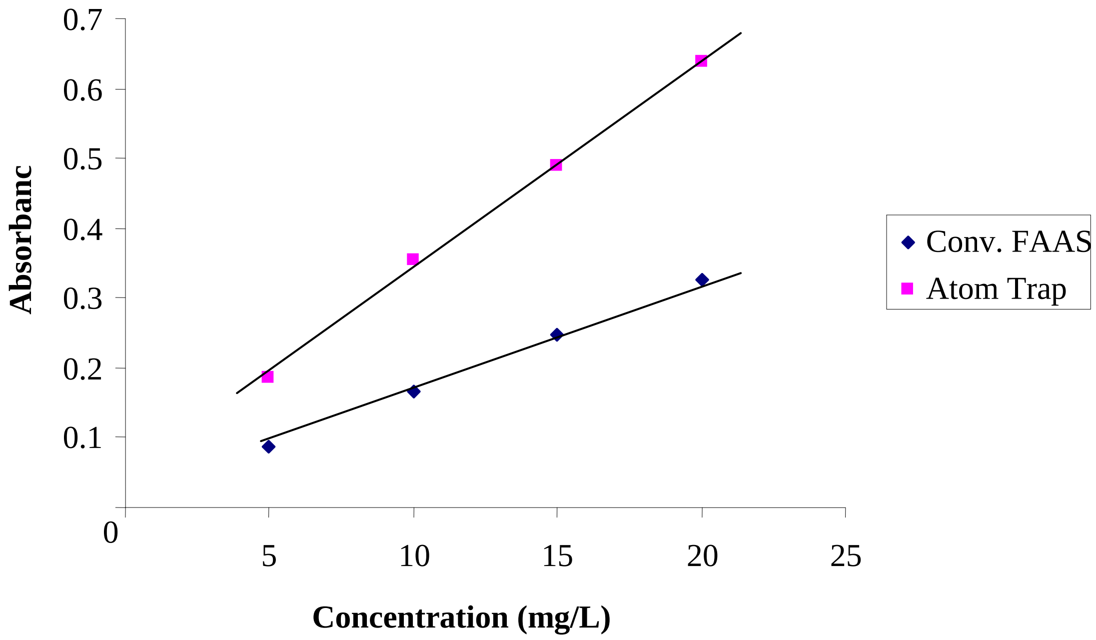


Fig. 10. Calibration Graph for Copper

Y = 0.016X + 0.0072; r = 1 Conv. FAAS
Y = 0.0302X + 0.0352; r = 0.99 Atom Trap

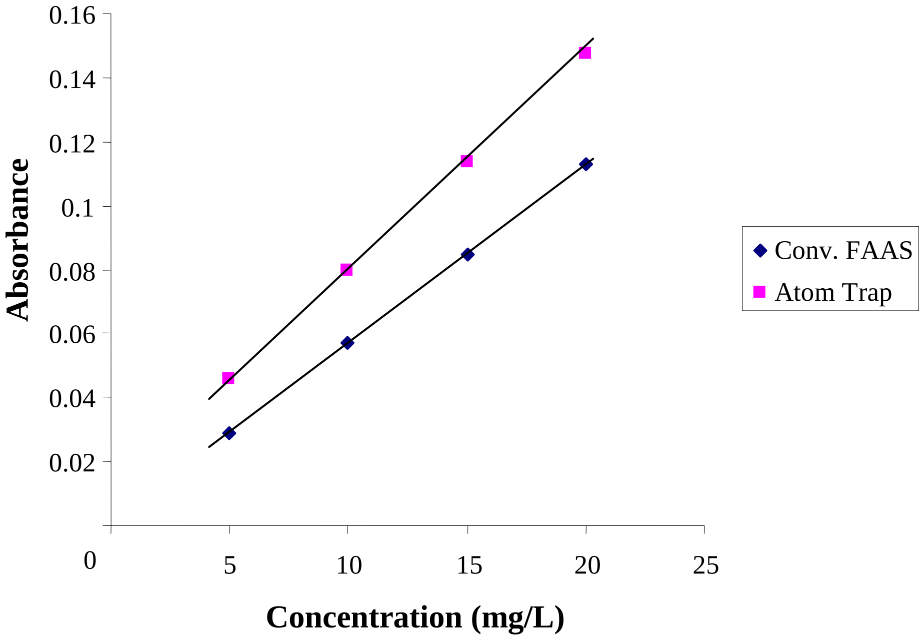


Fig. 11. Calibration Graph for Manganese

Y = 0.0056X + 0.0008; r = 1 Conv. FAAS
Y = 0.0068X + 0.0116; r = 0.97 Atom Trap

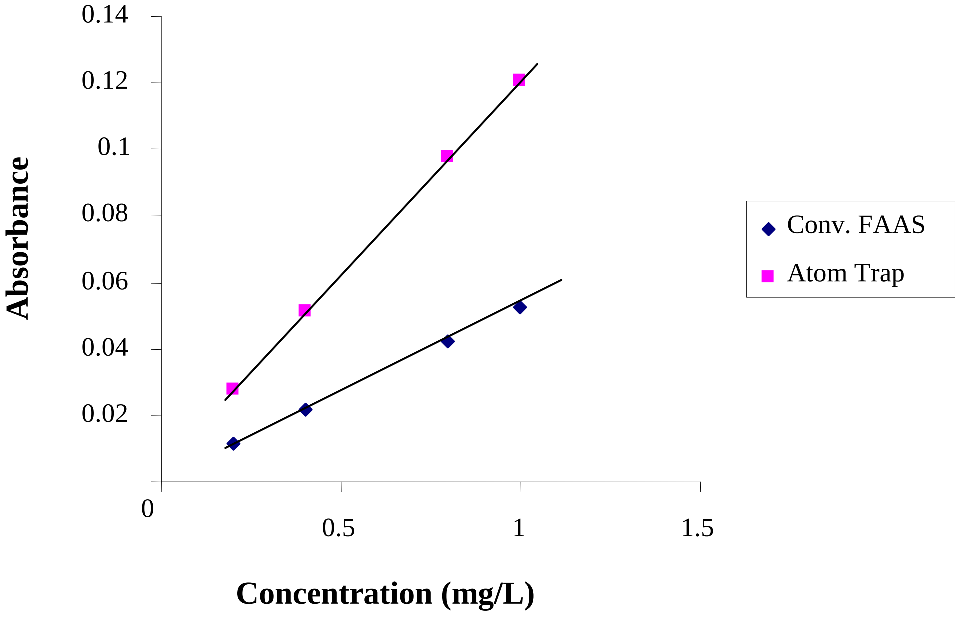


Fig. 12. Calibration Graph for Zinc

Y = 0.051X + 0.0013;	r = 1	Conv. FAAS
Y = 0.116X + 0.0047;	r = 0.99	Atom Trap

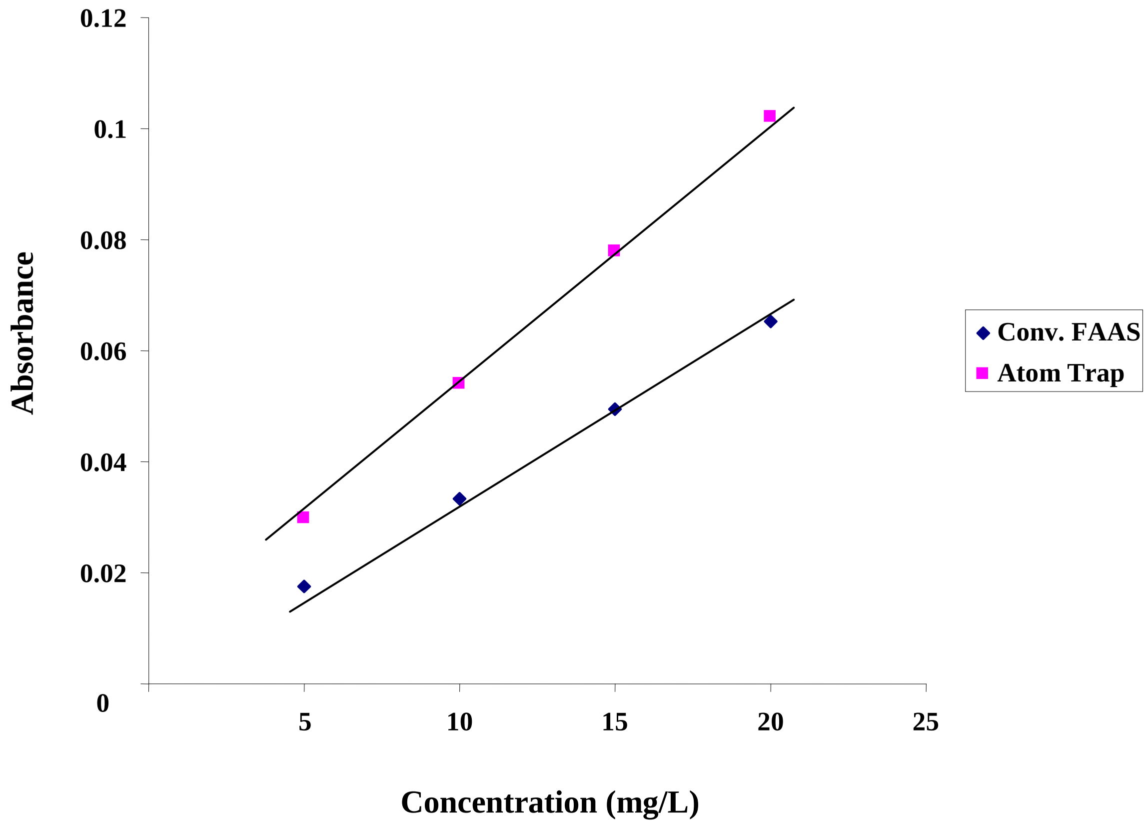


Fig. 13. Calibration Graph for Cobalt

Y = 0.0032X + 0.0014;	r = 1	Conv. FAAS
Y = 0.0048X + 0.006;	r = 0.98	Atom Trap

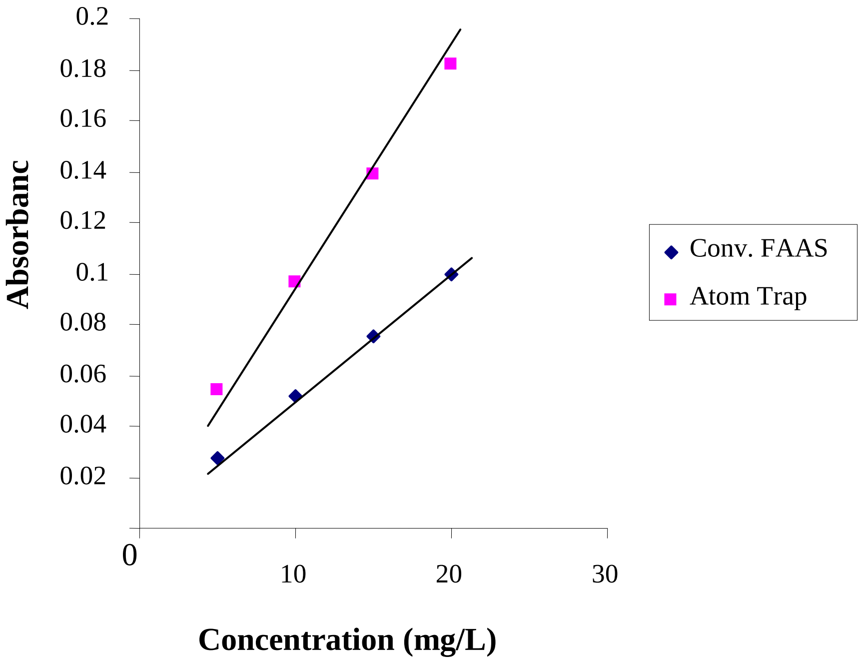


Fig. 14. Calibration Graph for Nickel

Y = 0.0048X + 0.0034;	r = 1	Conv. FAAS
Y = 0.0085X + 0.0116;	r = 0.98	Atom Trap

Table 9. Absorbance Signals of the Easily Volatile Elements Using the Conventional Flame AAS and the Developed Nickel Atom Trap Method in Leather Tanning Effluents (Majema Area, Kano).

Sample	Cu		Mn		Zn		Co		Ni		Pb		Cd	
	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap
A1	0.015	0.032	0.006	0.008	0.145	0.196	0.004	0.006	0.005	0.009	0.013	0.021	0.008	0.031
A2	0.020	0.038	0.001	0.002	0.013	0.017	0.004	0.005	0.004	0.008	0.012	0.022	0.006	0.023
A3	0.022	0.046	0.004	0.006	0.046	0.052	0.004	0.006	0.004	0.007	0.018	0.027	0.006	0.025
B1	0.016	0.034	0.006	0.009	0.147	0.188	0.004	0.005	0.005	0.009	0.021	0.029	0.005	0.021
B2	0.018	0.028	0.002	0.005	0.037	0.040	0.005	0.007	0.005	0.008	0.021	0.038	0.006	0.025
B3	0.018	0.032	0.003	0.005	0.022	0.028	0.005	0.007	0.004	0.007	0.012	0.019	0.007	0.028
C1	0.018	0.029	0.002	0.004	0.034	0.038	0.005	0.006	0.004	0.009	0.021	0.034	0.008	0.029
C2	0.021	0.038	0.006	0.007	0.096	0.101	0.006	0.008	0.005	0.009	0.021	0.032	0.009	0.032
C3	0.022	0.040	0.004	0.006	0.035	0.039	0.006	0.007	0.005	0.011	0.011	0.017	0.005	0.021

Where:

A1 - Animal skin effluent (basin)

A2 - Animal skin effluent (1)

A3 - Animal skin effluent (2)

B1 - Snake and crocodile skin effluent (1)

B2 - Snake and crocodile skin effluent (basin)

B3 - Snake and crocodile skin effluent (3).

C1 - Animal skin processed effluent at a different point from A1, A2 and A3

C2 - Animal skin processed effluent (at the point of discharge)

C3 - Animal skin processed effluent (at the discharge point 2)

*** Average of five absorbance readings.**

Table 10.Concentrations (mg/L) of the Easily Volatile Elements in Leather Tanning Effluents (Majema Area, Kano).

Sample	Cu	Mn	Zn	Co	Ni	Pb	Cd
A1	0.780±0.008	1.10±0.01	2.20±0.03	0.340±0.004	0.220±0.002	0.940±0.007	0.080±0.001
A2	1.02±0.01	0.170±0.002	0.230±0.007	0.310±0.002	0.210±0.003	0.900±0.004	0.060±0.003
A3	1.13±0.02	0.70±0.02	0.730±0.003	0.340±0.002	0.180±0.002	0.902±0.005	0.070±0.002
B1	0.850±0.006	1.10±0.03	2.20±0.04	0.340±0.002	0.240±0.003	0.920±0.002	0.060±0.001
B2	0.91±0.02	0.360±0.005	0.590±0.004	0.380±0.003	0.230±0.002	0.890±0.002	0.060±0.001
B3	0.940±0.007	0.530±0.004	0.370±0.002	0.390±0.003	0.200±0.001	0.900±0.003	0.070±0.001
C1	0.910±0.004	0.350±0.003	0.54±0.01	0.380±0.003	0.190±0.001	1.20±0.01	0.070±0.001
C2	1.10±0.01	1.10±0.01	1.50±0.02	0.430±0.003	0.230±0.002	1.10±0.02	0.080±0.001
C3	1.10±0.02	0.71±0.02	0.60±0.01	0.420±0.002	0.240±0.003	0.870±0.004	0.050±0.001

Table 11. Absorbance Signals of the Easily Volatile Elements Using the Conventional Flame AAS and the Developed Nickel Atom Trap Method in Leather Tanning Effluents (Leather Processing Factory, Kano)

Sample	Pb		Cu		Ni		Co		Cd		Zn		Mn	
	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv.F AAS	Atom trap	Conv. FAAS	Atom trap	Conv FAAs	Atom trap	Conv. FAAS	Atom trap
1	0.004	0.006	0.014	0.021	0.014	0.025	0.005	0.006	0.006	0.019	0.026	0.033	0.153	0.245
2	0.004	0.006	0.012	0.017	0.015	0.024	0.005	0.007	0.005	0.022	0.038	0.045	0.032	0.038
3	0.006	0.010	0.012	0.016	0.014	0.028	0.005	0.006	0.006	0.020	0.062	0.074	0.022	0.031
4	0.003	0.005	0.014	0.021	0.014	0.027	0.006	0.007	0.006	0.023	0.230	0.253	0.021	0.025
5	0.004	0.006	0.011	0.018	0.014	0.025	0.005	0.006	0.005	0.016	0.060	0.072	0.012	0.017
6	0.006	0.008	0.011	0.015	0.014	0.025	0.006	0.008	0.005	0.016	0.048	0.056	0.134	0.161
7	0.005	0.006	0.011	0.019	0.014	0.022	0.006	0.007	0.004	0.013	0.060	0.068	0.027	0.043
8	0.005	0.006	0.011	0.020	0.014	0.020	0.006	0.008	0.004	0.012	0.050	0.055	0.015	0.023
9	0.007	0.011	0.010	0.014	0.013	0.017	0.004	0.005	0.003	0.009	0.014	0.017	0.010	0.012
10	0.007	0.011	0.009	0.012	0.014	0.017	0.004	0.005	0.004	0.013	0.023	0.025	0.010	0.011

- **Average of five absorbance readings.**

Table12. Concentration (mg/L) Values for the Easily Volatile Elements in Leather Effluent Samples (Leather Processing Factory, Kano)

Sample	Pb	Ni	Cu	Co	Mn	Cd	Zn	Cr
1	0.450±0.003	0.170±0.002	0.900±0.002	0.430±0.004	2.30±0.01	0.080±0.003	0.461±0.007	7.80±0.01
2	0.520±0.004	0.170±0.001	0.740±0.008	0.441±0.004	0.490±0.009	0.063±0.001	0.669±0.004	7.90±0.02
3	0.660±0.002	0.170±0.002	0.78±0.01	0.453±0.001	0.333±0.004	0.070±0.001	1.10±0.01	7.90±0.01
4	0.370±0.003	0.170±0.003	0.910±0.007	0.490±0.003	0.330±0.005	0.068±0.001	4.00±0.04	7.00±0.01
5	0.450±0.001	0.160±0.002	0.700±0.007	0.461±0.003	0.183±0.001	0.063±0.001	1.40±0.02	9.60±0.02
6	0.730±0.003	0.170±0.001	0.710±0.004	0.491±0.003	2.170±0.008	0.060±0.001	0.839±0.003	7.70±0.01
7	0.570±0.004	0.170±0.004	0.700±0.003	0.504±0.002	0.358±0.004	0.052±0.003	1.10±0.01	5.890±0.009
8	0.610±0.002	0.160±0.003	0.720±0.002	0.540±0.001	0.210±0.003	0.042±0.001	0.880±0.005	7.680±0.006
9	0.810±0.004	0.160±0.001	0.620±0.002	0.370±0.002	0.162±0.003	0.054±0.002	0.258±0.002	9.340±0.005
10	0.840±0.003	0.170±0.001	0.590±0.002	0.360±0.002	0.171±0.005	0.056±0.001	0.410±0.002	5.00±0.01

Table 13. Absorbance Signals of the Easily Volatile Elements Using the Conventional Flame AAS and the Developed Nickel Atom Trap Method in NASCO and JIB Effluents

	Pb		Cu		Mn		Cd		Zn		Co		Ni	
Sample	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv. FAAS	Atom trap	Conv FAAs	Atom trap	Conv. FAAS	Atom trap
Soap eff.	0.004	0.006	0.009	0.012	0.003	0.005	0.012	0.032	0.045	0.056	0.003	0.004	0.012	0.022
Stor.tank A1	0.005	0.006	0.009	0.011	0.002	0.003	0.011	0.028	0.071	0.085	0.004	0.006	0.014	0.025
Stor.tank B1	0.006	0.008	0.008	0.010	0.009	0.011	0.011	0.026	0.016	0.021	0.003	0.004	0.016	0.026
Eff.outlet	0.006	0.009	0.009	0.011	0.008	0.010	0.011	0.027	0.018	0.023	0.002	0.003	0.017	0.028
Det.eff. outlet	0.006	0.008	0.009	0.011	0.011	0.019	0.010	0.024	0.011	0.015	0.002	0.003	0.018	0.026
Mixed (soap+dete.)	0.007	0.011	0.010	0.014	0.011	0.019	0.012	0.029	0.026	0.036	0.003	0.004	0.020	0.032
Eff.+stream	0.006	0.010	0.009	0.012	0.008	0.010	0.006	0.019	0.014	0.017	0.002	0.003	0.018	0.029
JIB eff. 1	0.007	0.011	0.010	0.014	0.008	0.009	0.006	0.019	0.026	0.032	0.002	0.003	0.015	0.026
JIB eff. 2	0.007	0.012	0.009	0.013	0.007	0.009	0.005	0.016	0.027	0.034	0.002	0.003	0.015	0.027
JIB eff. 3	0.005	0.006	0.012	0.016	0.007	0.010	0.005	0.017	0.028	0.039	0.002	0.003	0.015	0.025
JIB eff. 4	0.005	0.007	0.012	0.017	0.007	0.010	0.004	0.012	0.033	0.046	0.002	0.003	0.015	0.028
JIB eff. 5	0.004	0.006	0.022	0.030	0.009	0.012	0.004	0.013	0.020	0.029	0.002	0.003	0.015	0.027
JIB eff.+sream	0.004	0.006	0.031	0.048	0.009	0.013	0.003	0.010	0.019	0.025	0.002	0.003	0.015	0.025
Clean stream	0.003	0.005	0.010	0.014	0.011	0.018	0.001	0.003	0.013	0.017	0.001	0.002	0.014	0.020

*** Average of five absorbance readings**

Table 14. Concentration in mg/L (atom trap) Values for the Easily Volatile Elements in NASCO and JIB Effluent Samples (Jos)

Sample	Pb	Cu	Mn	Cd	Zn	Co	Ni
Soap Effluent	0.423±0.001	0.571±0.008	0.150±0.001	0.135±0.008	0.793±0.009	0.307±0.003	0.145±0.003
Storage Tank A1	0.689±0.001	0.542±0.002	0.140±0.002	0.129±0.004	1.300±0.001	0.328±0.004	0.162±0.002
Storage Tank B1	0.670±0.001	0.515±0.003	0.77±0.02	0.127±0.001	0.277±0.008	0.242±0.007	0.198±0.003
Effluent Outlet	0.734±0.008	0.535±0.003	0.668±0.002	0.125±0.003	0.315±0.009	0.219±0.006	0.207±0.003
Detergent Effluent Outlet	0.745±0.008	0.560±0.004	0.87±0.02	0.115±0.003	0.204±0.002	0.192±0.005	0.219±0.005
Mixed (Soap+ Detergent)	0.838±0.004	0.607±0.006	0.887±0.008	0.138±0.002	0.463±0.003	0.258±0.002	0.234±0.004
Effluent +Stream	0.687±0.007	0.580±0.009	0.667±0.004	0.076±0.004	0.256±0.005	0.130±0.002	0.218±0.002
JIB Effluent 1	0.858±0.001	0.62±0.01	0.640±0.004	0.068±0.004	0.461±0.007	0.209±0.004	0.180±0.004
JIB Effluent 2	0.807±0.002	0.59±0.02	0.543±0.009	0.063±0.008	0.472±0.005	0.196±0.004	0.191±0.004
JIB Effluent 3	0.643±0.002	0.73±0.01	0.55±0.02	0.059±0.006	0.488±0.003	0.152±0.005	0.180±0.003
JIB Effluent 4	0.649±0.009	0.73±0.02	0.57±0.01	0.056±0.009	0.575±0.006	0.156±0.005	0.183±0.005
JIB Effluent 5	0.536±0.001	1.410±0.008	0.717±0.009	0.046±0.009	0.355±0.003	0.235±0.003	0.182±0.006
JIB Effluent Stream	0.516±0.002	2.00±0.01	0.715±0.008	0.042±0.009	0.336±0.010	0.198±0.002	0.177±0.002
Clean Stream	0.402±0.002	0.65±0.01	0.885±0.009	0.022±0.001	0.224±0.003	0.085±0.002	0.171±0.002

Table 15. Interim Effluent Limitation Guidelines in Nigeria for all Categories of Industries

Parameters	Limit of Discharge into Surface Water in mg/L
Manganese, Mn	5
Cadmium, Cd	< 1
Copper, Cu	< 1
Lead, Pb	< 1
Nickel, Ni	< 1
Zinc, Zn	< 1
Cobalt, Co	< 1

*** Source: Federal Environmental Protection Agency, 1991.**

4.6. EFFECT OF THE NICKEL TUBE ON THE ABSORBANCE SIGNALS OF THE EASILY VOLATILE ELEMENTS IN ENVIRONMENTAL SAMPLES

4.6.1 Lead

The developed nickel tube atom-trap method for lead increased the absorbance signals from1.4 to 2.0 fold over the conventional flame atomic absorption spectrometry method as shown in Table 7. Also the absorbance signals for the determination of lead in the Majema leather-tanning effluents increased from 1.4 to 1.8 fold with the atom-trap method over the conventional flame atomic absorption spectrometry (Table 9).

Similarly, in the determination of lead in effluents obtained from leather factory in Kano 1.2 to 1.7 fold increase, as well as, effluents obtained from NASCO and JIB Jos, a 1.2 to 2.4 fold, and 1.2 to 1.7 fold respectively were recorded for atom-trap when compared with the conventional flame atomic absorption spectrometry (Tables 11 and 13). However, improvement factor for lead with the use of the slotted quartz tube over the conventional flame atomic absorption spectrometry was reported to be 3.3 (Brown et al, 1985), which is higher than values obtained with the developed nickel tube method.

4.6.2 Cadmium

The developed nickel tube atom-trap method for cadmium determination in leather tanning effluents (Naraguta, Jos) had an increase in the absorbance signals of 3.6 to 4.2 fold over the conventional flame method, as shown in Table 8.

An increased absorbance signals observed for cadmium in the leather tanning effluents from Majema area, Kano, using the nickel tube atom-trap method. The result showed a 3.6 to 4.2 fold increase over the conventional method (Table 9). Also, a 3.0 to 4.4 fold increase in absorbance signals over the conventional flame AAS for the determination of cadmium in leather tanning effluents (Kano), using the developed nickel tube method was observed (Table 11). Similarly, the absorbance signals of cadmium in effluents from NASCO and JIB with the nickel tube atom-trap method was 2.4 to 3.4 fold increase over the conventional flame atomic absorption spectrometry (Table 13). However, with the use of the water-cooled Silica tube atom-trap (2 min collection time) cadmium sensitivity was 30 times over the conventional flame atomic absorption spectrometry (Brown et al., 1987).

4.6.3 Copper

The absorbance signals of copper in the leather tanning effluents (Majema area, Kano), with the use of nickel tube method increased by an improvement factor of 1.6 to 2.1 fold as shown in Table 9.

The absorbance signal for the determination of copper in the leather tanning effluents obtained from leather factory (Kano), as well as, NASCO and JIB (Jos), a 1.3 to 1.8 fold and 1.2 to 1.6 fold increase in absorbance signals were recorded for atom-trap, when compared with the conventional flame atomic absorption spectrometry (Tables 11 and 13). An improvement factor of 2.3 was achieved by use of a slotted quartz tube for copper (Brown et al, 1985), a value comparable with the results obtained with the developed atom- trap technique in this work.

4.6.4 Zinc

The developed nickel tube atom-trap method for zinc had an increase in the absorbance signals of 1.1 to 1.4 fold over the conventional flame AAS method as shown in Table 9. Similarly, in the determination of zinc in the leather tanning effluents obtained from leather factory in Kano, as well as, effluents obtained from NASCO and JIB (Jos), a 1.1. to 1.3 fold, and 1.2 to 1.5 fold increase in signals respectively were recorded for atom-trap, when compared with the conventional flame AAS (Tables 11 and 13).

Brown et al (1985) reported an increase in the sensitivity of zinc by an improvement factor of 2.5 by use of a commercially available slotted quartz tube, the later factor doubled in improvement over the developed method.

4.6.5 Manganese, Cobalt and Nickel

As can be observed in Tables 9, 11 and 13, the measured absorbance values for manganese, cobalt and nickel with the use of the modified nickel tube atom-trap method were greater than those obtained with the conventional flame atomic absorption spectrometry at the same sample concentrations.

As shown in Table 9, a 1.2 to 2.5 fold increase for manganese, a 1.2 to 1.5 fold increase for cobalt, and a 1.6 to 2.3 fold for nickel increase in absorbance signals were recorded. In Table 11, a 1.1 to 1.6 fold increase for manganese, a 1.2 to 1.4 fold increase for cobalt and a 1.2 to 2.0 fold increase for nickel in absorbance signals were observed. In Table 13, a 1.1 to 1.7 fold increase for manganese, a 1.3 to 2.0 fold increase for cobalt and a 1.4 to 1.9 fold increase for nickel in absorbance signals were recorded with the use of the nickel tube atom-trap method.

4.7. ENVIRONMENTAL ASSESSMENT

4.7.1 Lead

The level of lead (Table 7), in Naraguta leather tanning effluents was low. All sample concentrations were lower than the interim effluent limitations guidelines in Nigeria.

The results in Table 10 showed, that two of the samples namely sample C1 and sample C2 had concentrations (i.e. 1.183 mg/L and 1.083 mg/L for sample C1 and sample C2 respectively) above the maximum tolerable limit given by

Federal Environmental Protection Agency. Although the rest of the sample concentrations did not exceed the interim guidelines for effluents in Nigeria, they were close to the maximum tolerable limit for comfort.

All lead concentrations in Kano leather factory effluent (Table 12) were lower than the maximum tolerable limit for effluent discharge into surface water. Sample C2 with concentration value of 0.807 mg/L and Sample C3 with concentration value of 0.838 mg/L were close to the maximum tolerable limit of 1 mg/L. The possible reasons for these higher values of lead in the effluents could be attributed to the use of chemicals in the processing of the leather (Wilson & Newall, 1974).

The concentrations of lead in NASCO effluents (namely soap and detergent), as well as, JIB effluents (Table 14), were lower than the maximum tolerable limit. The mixed effluents (soap and detergent) and JIB outlet 1 effluents had the highest concentrations, with values of 0.838 mg/L and 0.858 mg/L respectively. Again, these values were close to the maximum tolerable limit.

4.7.2 Copper

The concentrations of copper (Table 10) in Majema area of Kano leather effluents showed that the concentrations exceeded the maximum tolerable limit for discharge into surface water. Samples A2, A3, C2 and C3 recorded copper concentrations of 1.019, 1.127, 1.103 and 1.110 mg/L respectively. Sample effluents, B2, B3 and C1 had copper concentrations of 0.905, 0.936 and 0.914 mg/L respectively which were close to the maximum tolerable limit of 1 mg/L. The concentrations of copper (Table 12) in effluent samples from a leather factory, Kano was lower than the maximum tolerable limit. The highest concentrations recorded was that of sample No 4 with concentration of 0.907 mg/L, followed by sample

No 1 with concentration of 0.899 mg/L.

Samples from JIB effluent mixed with the stream water had the highest values of 1.410 and 1.998 mg/L (see Table 14), which exceeded the maximum tolerable limit by Federal Environmental Protection Agency. However, the concentration of copper in the rest of the samples in Table 14 met the requirements by the interim guidelines for discharge into surface water.

4.7.3 Manganese

The results in Table 10 showed that concentrations of manganese in all the effluent collected from Majema area of Kano were lower than the maximum tolerable limit of 5 mg/L. The highest concentration of manganese was found in sample A1 with concentration of 1.071 mg/L, followed by sample C2 with concentration of 1.068 mg/L and sample B1 with concentration of 1.052 mg/L.

All the investigated effluents from leather factory, Kano (Table12) contained lower concentration of manganese than the maximum tolerable limit of 5 mg/L. The concentrations in soap, detergent, and JIB effluents (Table 14) of manganese were all lower than the maximum tolerable limit of 5 mg/L.

4.7.4 Cadmium

The concentrations of cadmium in Naraguta leather effluents, Jos (Table 8) were lower than the maximum tolerable limit by Federal Environmental Protection Agency. Cadmium concentrations in all the leather effluents from Majema area of Kano (Table 10) were far below the maximum tolerable limit of 1 mg/L.

The same was observed for effluents from the leather factory, Kano (Table 12). Also, sample effluents from NASCO and JIB (Table 14) were all lower than the maximum tolerable limit for the interim effluent limitation guidelines in Nigeria.

4.7.5 Zinc

The concentrations of zinc in samples A1, B1 and C2 (Table 10) were the highest that exceeded the maximum tolerable limit of the interim effluent limitation guidelines in Nigeria with concentrations of 2.189, 2.217 and 1.469 mg/L respectively.

Zinc concentrations in environmental samples from a leather processing factory, Kano (Table 12) were the highest in sample no 4 with concentrations of 4.041 mg/L followed by sample no 5 with concentration of 1.408 mg/L. Sample No 3 had concentration value of 1.084 mg/L while sample No 7 had concentration value of 1.061 mg/L. In Table14, except the storage tank effluent B1 (1.250 mg/L) that had exceeded the effluent limitation guidelines, all the rest had lower concentrations than the maximum tolerable limit of 1 mg/L. The low values for Zinc in NASCO and JIB could be due to the effluents being organic waste.

4.7.6 Cobalt

The concentrations of cobalt in all the environmental samples (Tables 10, 12 and 14) were found to be lower than the maximum tolerable limit of 1 mg/L. The concentration of cobalt was low, implying that its contamination has been mild.

4.7.8 Nickel

The concentrations of nickel in all the environmental samples (Tables 10, 12 and 14) were lower than the maximum tolerable limit of 1 mg/L. The reasons for the low concentrations of Ni in all the samples could be attributed to its scarcity in the environment.

4.7.9 Chromium

The concentrations of chromium in effluents of leather factory (Table 12) were high, exceeding the maximum tolerable limit for discharge by Federal Environmental Protection Agency, 1 mg/L. The high levels of chromium in these leather effluents could be attributed to increased use of chromium salts in leather processing.

4.8. INTERFERENCE EFFECTS

The interference study of the effects of sodium and magnesium chloride on the absorbance signals of lead was carried out.

In Figures 15 and 16, possible interference effects from the various concentrations of NaCl and $MgCl_2$ added to the standard concentrations of lead were observed.

The result showed that NaCl exhibited a significant level of suppression in absorbance signals at 5 mg/L of Pb i.e. 1.17% at 10% NaCl to 1.28% at 30% NaCl.

The interference of NaCl and $MgCl_2$ with the lead atomic absorption signal is to be attributed to the formation of lead chloride particles during the aerosol generation. The vaporization of these particles is not completed in the analytical zone of an air acetylene flame, resulting in signal depression (Bruno, 1980).

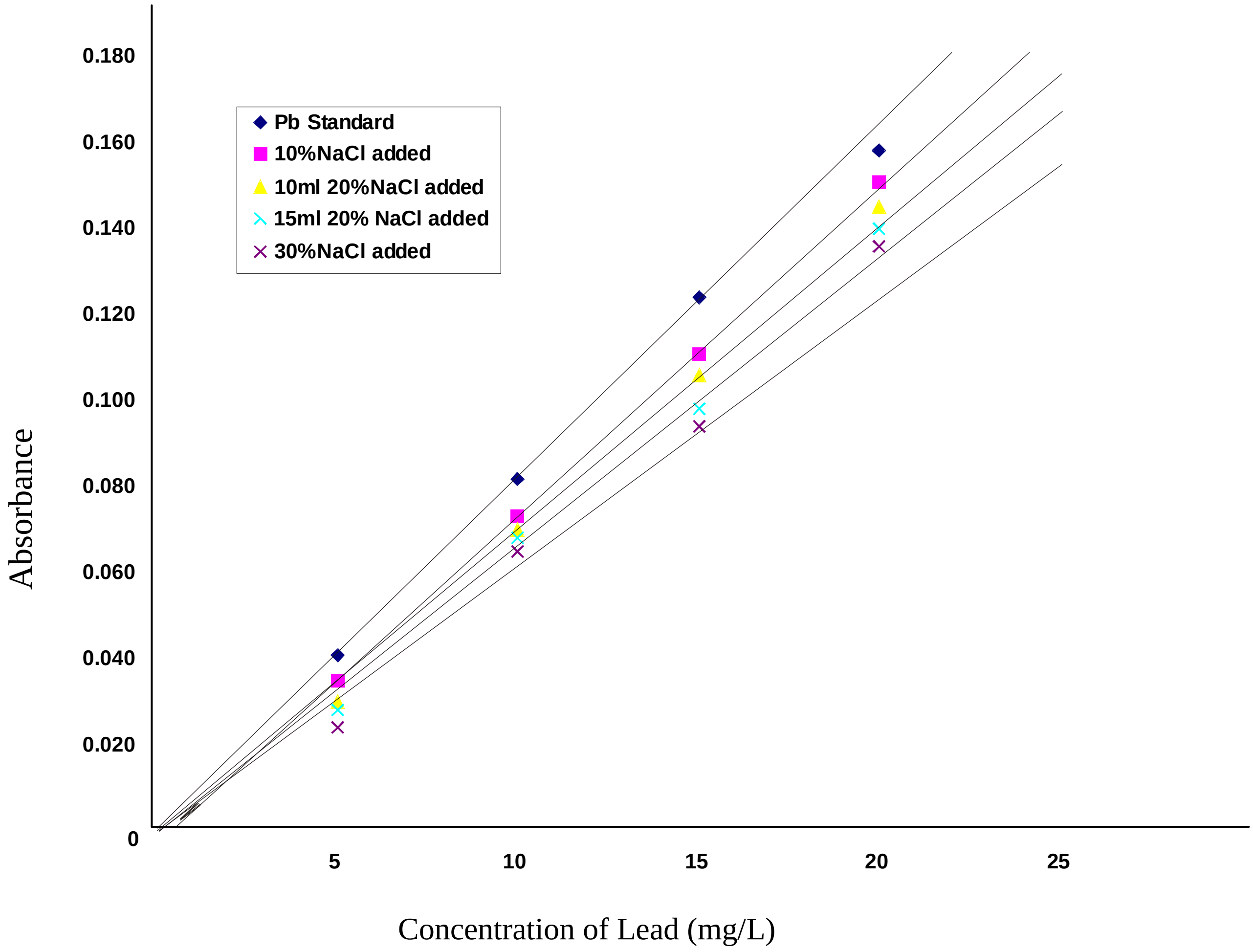


Fig 15. The Interference Effects of NaCl on Lead Absorbance Signals

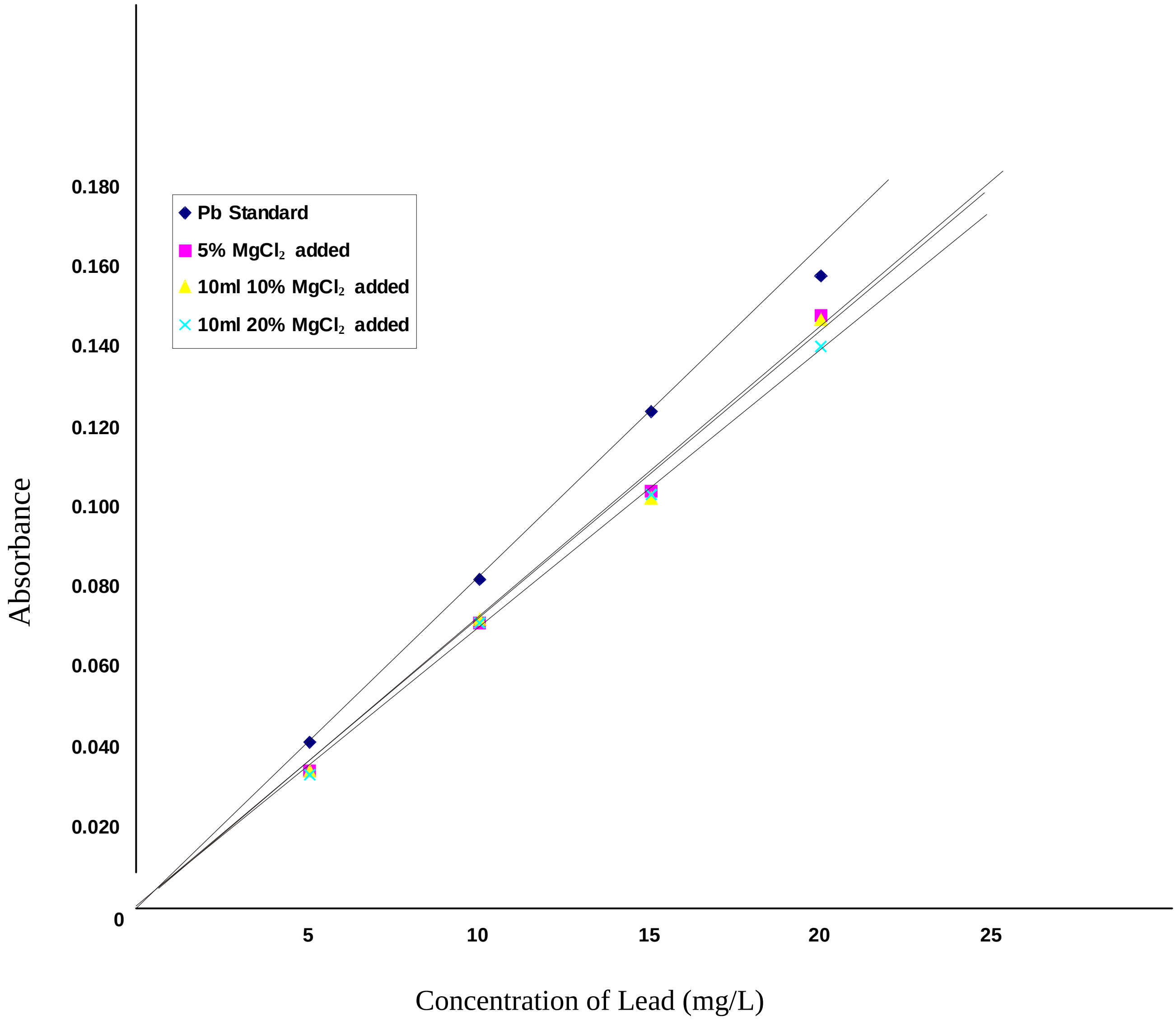


Fig 16.The interference Effects of $MgCl_2$ on Lead Absorbance Signals