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EFFECTIVE UTILIZATION OF RAW MATERIALS: A CATALYST FOR INDUSTRIALIZATION IN NIGERIA.

INAUGURAL LECTURE SERIES 66

Delivered by

OLUBODE OLUMUYIWA AJAYI
BSc. (Ibadan), MSc. (Zaria) PhD (Strathclyde)
Professor of Chemistry

On

Tuesday June 24, 2014.

Ogunsuyi, H. O., Ajayi, O. O., Ipinmoroti, K. O. and Oladipo, M. O. A. (2012). 'Neutron activation analysis of some Nigerian Bitumen samples and their components.' *Oriental Journal of Chemistry, 28(1), 333 – 342.*

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EFFECTIVE UTILIZATION OF RAW MATERIALS: A CATALYST FOR INDUSTRIALIZATION IN NIGERIA.

The Vice-Chancellor,

Deputy Vice-Chancellor (Academic)

Deputy Vice-Chancellor (Development)

The Registrar,

Other Principal Officers of the University,

Deans, Directors and Heads of Department,

Fellow Academics and Non-Academic Colleagues,

My Lord Spiritual and Temporal,

Distinguished Guests and Friends of the University,

Ladies and Gentlemen of the Press,

Distinguished Ladies and Gentlemen,

Great FUTARIANS.

PREAMBLE

I wish to thank the Almighty God for making it possible for me to deliver this 66th Inaugural Lecture of this Great University of Technology. This is the 5th Inaugural Lecture series coming from Chemistry Department; the last being the one delivered by Professor L. Lajide in 2002, closely following those of Professor A. V. Popoola, late Professor K. O. Ipinmoroti and Professor A. A. Oshodi in that order. I have chosen this day to speak on the 'effective utilization of raw materials; a catalyst for industrialization in Nigeria'. The title was borne out of my experience in Leather Research Institute of Nigeria, Zaria and later the National Research Institute for Chemical Technology, Zaria where I served for 17 years before I joined the services of this great University in the year 2000. My initial work was on the evaluation of raw materials for leather production and later the utilization of raw materials for production of industrial chemicals. While in this university I continued to look into agricultural wastes as raw materials for environmental cleansing as well as bitumen and some other minerals. Before I go on, it is pertinent to define raw material; its importance in the economic development of the nation and the utilization.

Raw Materials

Raw material or chemical feedstock is defined as something that is acted upon or used by human labour or industry (Austen, 1984).This term is also used to denote materials that came from nature and is in an unprocessed or minimally processed state (Austen, 1984). Non-human related raw materials would include twigs and objects found by birds to make nest and the fibrous metabolites produced and used by spider to make webs. In Marxian Economics and some industries, the term is used in a more distinct sense; raw material is a 'subject of human labour', something that will be worked or acted upon by labour or that has already undergone some alteration by labourers.

Simply put, a raw material is anything that has undergone a regime of physico-chemical processes to produce a desired good or service. In essence, almost everything that occurs in nature is a raw material for production of a characteristic product or service. For example, the air we breathe contains many raw materials for many natural processes.

Nitrogen, a component of air that makes up 78% of it is a raw material for 'Nitrogen fixation' in plants as encountered in 'Nitrogen cycle'. For the production of inorganic fertilizer, nitrogen is converted to ammonia in an industrial process called 'Haber Process' in which nitrogen and hydrogen are chemically combined.

$3H_2 + N_2 \leftrightarrow 2NH_3$--------------------------------1.

Oxygen, another component of air is an essential raw material for life processes such as respiration and other metabolic processes in living organism. It is also essential for combustion of various fuels that are used to produce energy. In critical clinical condition, pure oxygen is desirable particularly for patients in state of coma and pre-matured babies. Those patients have to be put in oxygen tents to keep them alive during the period of their comatose or incubation in the case of the pre-matured babies. A typical example is the case of the former Prime Minister of Israel, General Ariel Sharon who was in coma for almost eight years and had to be supported on oxygen in a life supporting machine.

Carbon dioxide, CO_2, is a natural raw material for photosynthesis in plant. Carbon dioxide and water are the primary raw materials for this process that is essential for plant as a primary producer of food.

Carbon dioxide water *Glucose* *oxygen*

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$------------------2.

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My sabbatical leave at Afe Babalola University, Ado-Ekiti made a lasting impression on my service delivery. For this I cannot forget to appreciate the Founder and Chancellor of this University, Aare Afe Babalola SAN, CFR for the opportunity. I appreciate the Acting Vice-Chancellor (ABUAD), Professor Michael O. Ajisafe, who not only taught me in Christ's School, Ado-Ekiti, but also facilitated my sabbatical leave in this university.

I wish to acknowledge the services and contribution of my immediate family; my wife, Mrs. Oladunni Ajayi for her devotion and love particularly for the good care she is taking of our autistic daughter, my sons; David Oluwole and Victor Abayomi and my daughter, Monica Toluope Ajayi.

Once more, I say Thank you all.

This self-same carbon dioxide is also used to carbonate soft drinks, as fire extinguisher and in rain seeding.

Helium is used for filling balloon. Even air in its hot form is used to fill balloons for flight. Argon another component of air is used as a raw material for scientific instrument like inductively coupled plasma emission spectrometer for metal analysis. Water as a universal solvent is a raw material for almost all industrial processes. Man from time immemorial has been ingenious in using anything that is found in his environment to produce one good or service or the other. A mineral is any naturally occurring element or compound. The earth crust has minerals in abundance with about 3000 mineral species in existence. All the rocks forming the earth crust consist to varying degrees of minerals. For instance, the clay derived from the earth crust has been used to mould blocks, pots, ceramics and other ear then wares. Gold was one of the earliest metals used by man. Gold existing [illegible] uncombined state as a mineral is used as ornament, jewels, in electronic industries and in coinage either as pure gold or as alloy. The processing of other minerals to produce gold was the foundation of Alchemy which is the precursor of the modern day Chemistry and Metallurgy. The processing of iron from various ores started ages ago when man discovered the use of fire to produce metals from ores. The term 'Iron Age' refers to the period when man started to exploit iron minerals to make metal implements and tools. These minerals are raw materials that man has also been exploiting in making goods and services for his use. Raw materials play an important role in the economic life of a nation. The economy of Nigeria is mostly dependent upon the exploitation and exportation of major raw materials particularly; crude oil. The availability and quality of raw material for any product dictates the price, ease of production, labour cost and the price of the product.

Raw material and national development

Raw material exploitation is essential to the economic development of any nation. For instance, the vast resources of oil and gas in Russia make the nation the major energy supplier in Eastern Europe. This nation now holds the monopoly of energy in that part of the world. The economy of Nigeria is about 90% dependent on the sale of crude oil.

The acquisition of raw materials acquisitions was responsible for the spate of colonization encountered in the past. In fact, the need for cheap sources of raw materials for the emerging industries in Europe following the Industrial

Revolution of the 18th Century was responsible for the colonization of Asia, Americas and Africa by the major European Powers. These industrial developments gave the colonial powers the impetusto acquire the much-needed resources to manage their economies. In West Africa, the raw materials derived from the colonies dictated the initial names given to them. For instance, the present-day Ghana was called Gold Coast due to the fact that gold was one of the major resources; Cote d'Ivoire, or Ivory Coast due to ivory and 'Slave Coast' was the name of Nigeria and Benin Republic as a result of supply of slave labour to the Americas in 17th to 19th Century. It is gratifying to know that some agricultural productsthat are major foreign exchange earners todaywere introduced to Nigeria from elsewhere; and these eventually formed the basis of colonial economy. For instance, crops like cocoa (*Theobroma cacao*), cashew (*Anacardium occidentale*), cassava (*Manihot esculenta*), Para rubber (*Hevea brasiliensis*)were introduced from Brazil. Maize (*Zea mays*), turkey bird (*Meleagris ocellata*), tobacco (*Nicotiana tabacum*) and even the pest, cockroach (*Periplenata americana*) was from North America. In fact, cocoa bean was the medium of exchange in the Aztec Empire of Mexico prior to the Spanish Conquest (Wallace, 1962). The North American colonies of Britain (U. S. A. and Canada) were the sources of cotton, sugar cane, tobacco, gold, furs and some other minerals. The development of railway transport in Nigeria in the early 20th Century was principally to transport raw materials from various part of Nigeria to the ports of Lagos and Port Harcourt. For instance, groundnut, hides and skins, millet and sorghum from the North East made Nguru and Maiduguri important railway termini. Jos was the collection centre for tin and columbite; while Port Harcourt served as the collection port for timber, palm and kernel oils, coal and cocoa from the South East. Cocoa, coffee, palm oil, palm kernel oil, rubber and gold derived from the southwestern part of Nigeria were usually exported through the Lagos Port.

Raw materials are important for siting of industries. The development during the colonial era was that the economy of the nation was derived from the sale of the available raw materials and surplus was used to feed the existing industries established by the multi-national companies. For instance Blue-Band Margarine, a product of Lever Brothers Limited, was produced from palm oil and palm kernel oil. In building, bricks were made from local clays and these were used to build the strong colonial edifices that adorned the Provincial and District Offices nationwide. Raw materials; if processed into essential goods and services attract better market values; hence the need to establish cottage, small

necessary stimulus for growth.

7. Massive investment in university education should be pursued.
8. The problem of insecurity is a major hindrance to industrialization. Armed insurgency, kidnapping, armed robbery and other anti-social behaviours are paramount and these discourage industrialization and foreign investment. This problem needs to be effectively tackled.
9. Smuggling and unbridled taste for imported materials are poisonous to our industrial drive. The need to curb smuggling to the barest minimum may give potential investors breathing space to industrialize.
10. The students are facing many distractions that impact negatively on their academic pursuit. As future leaders the need to be adequately trained and equipped for future is very paramount.

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I wish to thank the Lord Almighty for my creation and wellbeing and for making this day a reality. May God's name be praised. Amen.
My father, Mr. Oluwatoyin Owolabi Ajayi, deserves much gratitude for the sacrifices made to train me through all levels of education. I am equally grateful to my mother, Mama Mary Ige and my stepmother, Mrs. Elizabeth Ajayi for their contributions. I thank God for my father-in-law, Chief Akin Oluyemi for being there for me every time. I will like to express my gratitude to my deceased relatives and mentors whose contributions cannot be forgotten; my sister Mrs. Olufunke Fasanmade, my aunt, Mrs. Susan Olofin, my grandmother, Mrs. Elizabeth Sanya, my uncles; Mr. Simeon Sanya, Mr. Jacob Sanya, Chief James Aroboto, Mr. Jerry Balogun and Mr. Sunday Balogun, my mentors; Professor Kolade Ipinmoroti, Dr. Adebisi Adeloye, my supervisor, Professor John Michael Ottaway, my bosses at Leather Research Institute, Zaria; Dr. Ariel Simkat Mshelbwala and Dr. Raphael O. Adewoye. May their gentle souls rest in peace for the lasting imprint they made in my life. Amen. I wish to thank my uncle; Chief S. O. Agbaje, my cousins; Arc. Bolaji Balogun, Director of Physical Planning at NUC, Colonel Victor Fagoyinbo (retired) and Pastor Gbenga Oladimeji. I appreciate my supervisor, Professor David Littlejohn for not only seeing me through my PhD; but also co-authoring my first set of publications. I appreciate the Vice-Chancellors under whom I served; they are Professor Lawrence B. Kolawole,

A similar study on Ikere-Ekiti was reported by Ogunmodede *et al.* (2014) in which bacteria like *Staphylococcus, Pseodomonas, Escherichia and Salmonella/Shingellas* species were reportedly present.

CONCLUSIONS

These are few of the raw materials available in the country. The evaluation of the materials showed that they were of appreciable quality for the consumption of industries. The exploitation of these raw materials is skeletal and this was due to the reliance on crude oil for foreign exchange earnings. Exploitation of minerals like bitumen holds promise for the nation. Maybe this mineral is being strategically reserved for the future.

The need to preserve our environment for posterity is equally paramount and hence the need to pursue industrialization for sustainable environment. Industrial policy should explicitly place emphasis on environmental impact assessment.

RECOMMENDATIONS

Nigeria has just celebrated the Centenary of her existence as a sovereign nation. The need to look into future development is paramount. As the nation has an ambitious programme of Vision 20-20-20; a lot needs to be done to emerge as a member of 20 global economies. The following suggestions are made:

1. The nation sadly is yet to attain a truly nation-state that is synonymous with development. It behoves on us to evolve a truly nation-state where justice, equity and fair play is paramount. It is when such a nation is evolved that the necessary patriotism that engenders meaningful development can emerge.
2. Infrastructural development should be vigorously pursued to enhance economic development. These infrastructures include good network of roads and rails, available energy supply, potable water and good education and health institutions.
3. Mandatory budgetary 26% allocation should be made available to resuscitate our educational system. This will address the problems plaguing this sector.
4. Our value system of unbridled materialism must change.
5. Comprehensive economic planning and execution must be put in place to foster development
6. Agricultural and solid mineral sectors must be revived to provide the

and large-scale industries that will consume them as feedstocks. For a raw material to be economically viable, it must be available in sustainable quantity and quality. The quality of any raw material depends on its chemical composition. For instance, crude oil is a viscous, slick liquid that burns; but the characterization of this mixture of hydrocarbons revealed the composition and the usefulness of the components as chemical feedstock or raw materials for petrochemical and allied industries today. The chemical composition can only be assessed by various techniques of chemistry; hence the need to discuss what is chemistry and its importance in our daily life.

CHEMISTRY

Chemistry is defined as the study of nature and the changes or transformation it undergoes (Chang, 2002, Brown *et al.*, 2009, Microsoft Encarta, 2009a). Chemistry is often called the 'Central Science' because a basic knowledge of chemistry is essential to geology, biochemistry, physics, biology, ecology and many other subjects. Indeed, Chemistry has been found to be essential to life in that a living organism is a complex chemical factory in which precisely regulated reactions occur among thousands of substances. The raw materials for this life process are derived from food, water, air and other substances taken in by the living organism. The life's chemical process is called metabolism in Biochemistry and the reactions taking place in cells are catalyzed by enzymes, regulated by hormones and coordinated by nerve cells. The living cell of every living organism can be regarded as a chemical reactor vessel. Chemistry has been found to be central to our ways of life without which, we could have been having shorter life span in what we consider primitive devoid of automobiles, electricity, medicine, CD computer and many other conveniences (Chang, 2002; *Brown et al.*, 2009, Microsoft Encarta, 2009). The production of goods and services from basic raw materials emanated from their transformation; which is essentially chemistry.

Chemistry is an ancient science, but its modern foundation was laid in the 19th Century when intellectual and technological advances enabled scientists to break down substances even to smaller components and consequently to explain many of their physical and chemical characteristics (Chang, 2002, Brown *et al.*, 2009). The ability to break down and assemble a substance makes Chemistry to ***recreate nature***. The origin of Chemistry can be traced to the Greek Philosophers who first defined atom as the smallest component of matter and latter to the Alchemists in 100 A. D. whose work formed the precursor of the modern-day chemistry and metallurgy (Microsoft Encarta, 2009). The quest of alchemists was to convert every metal to gold. They were looking for the 'mythical philosopher's stone'. The conversion of metal to gold was only achieved in 20th Century through the bombardment of bismuth by Carl Seaborg (Brown *et al.* 2009). The foundation of modern chemistry was laid by Lavoisier in 18th Century when he propounded the Law of Mass Conservation. Others through experimentation formulated laws and hypotheses that brought chemistry to the level it is today.

Chemistry has played an important role in health and medicine, energy and environment, materials and technology, food and agriculture. In health and medicine; four major advances have been made in prevention and treatment of diseases. These are the establishment of sanitation systems, surgery with anesthesia, production of potent drugs, vaccines and antibiotics and gene therapy (Chang, 2002, Brown *et al.*, 2009). Energy is a bye-product of many chemical processes. The demand for energy continues to soar with ever increasing population of the world. With fossil fuels contributing majorly as energy source and the fact that this source can only last for 50 to 100 years at most, necessitate the need to look for alternative source. The recent advances in solar, fuel cells and nuclear energy make these sources alternative sources to fossil fuel with its attendant problem of contributing to global warming. Material science and technology has improved the quality of life tremendously. Typical advances have made polymer and plastics, ceramics, liquid crystals, adhesives and coating, computers, semiconductors and superconductors available. The development of fertilizers, pesticides and high-yielding crops as well as farm inputs has made food available despite the presence of mounting challenges of food insecurity (Brown *et al.* 2009). Genetic engineering which is as a result of alteration of the chemical makeup of genomes has been of tremendous help in agriculture and medicine. Gene therapy is a recent development in medicine. The technology of stem cell is an emerging area of research. Defence industry has benefited tremendously from application of chemistry. Chemical weapons, nuclear and atomic bombs, firearms, depleted uranium bomb and other weaponry are derived from chemical research. Radioactivity has advanced the course of medicine through radiotherapy, production of nuclear energy and atomic and nuclear weaponry.

Chemistry is made up of many areas of specialization including biochemistry, physical, organic, inorganic, analytical and environmental chemistry. Chemical engineering is a branch of engineering that incorporates

In another study, Abata *et al.* (2013) evaluated the level of heavy metals like Cd, Cr, Cu, Fe, Ni, Pb and Zn in the sediments of Ala River that runs through Akure Metropolis in the raining season of 2012. The indices of pollution such index of geo-accumulation (I_{geo}), contamination factor (C_f) and degree of contamination (C_d) indicated that this river was appreciably polluted.On the basis of enrichment factor measured by I_{geo}, sediments were enriched in this order; Pb>Cd>Cr>Cu>Zn>Ni>Fe. On the other hand contamination factor (C_f), this same trend was followed. Pearson Correlation indicated that Zn, Fe and Ni, Cr were highly significant ($p<0.01$), suggesting the anthropogenic sources of these metals in the sediment under study.

In a related study, Ogunmodede *et al.* (2013) investigated the heavy metal and microbial loads of some dumpsites' soil in Ado-Ekiti and Ijero-Ekiti. Other characteristics examined included the soil type and organic matter. The bacteria identified in both sites included *Bacillus megatarium, Chromatium violasceus, Bacillus subtilis, Klobsiella rhinosederomalis, Kurtia zopfi, Clostridium spirogenes, Bacillus lichenifermis, Xanthomas fraganie and Bacillus cereus*. The ranges of metals detected in measurable quantities in the two locations are as shown in Table 23.

The soil in both locations was found to be sand + silt. Comparable concentrations of the metals were recorded for both locations except that chromium, nickel, iron, manganese and zinc were higher in Ado-Ekiti than Ijero-Ekiti. Only lead, cadmium and copper recorded higher concentration at Ijero-Ekiti.

Table 23: Ranges of metals detected in the soil of dumpsites in Ado-Ekiti and Ijero-Ekiti.

	Concentration in mg/kg	
Element	Ado-Ekiti	Ijero-Ekiti
Cr	2.00 – 13.00	1.10 – 10.20
Ni	1.00 – 11.00	1.00 – 16.80
Fe	8.20 – 24.70	9.20 – 26.40
Mn	1.20 – 60.80	1.12 – 50.00
Zn	2.40 – 72.00	3.40 – 70.00
Cu	2.36 – 86.40	3.30 – 94.00
Pb	7.28 – 72.50	7.40 – 88.82
Cd	1.42 – 3.62	1.66 – 3.74

Source: Ogunmodede *et al.* (2013).

Rio de Janeiro in 1992 as well as well as in Kyoto in 1997. The Rain Forest Regions of the world used to serve as carbon pool that takes in most of the carbon dioxide. During the period of Ottoman Empire, the Sultan used to tax the people including imposing tax on every standing tree. The Bedouins of the Middle East resorted to cutting down all the trees in order to evade taxation leading to desertification of the Area (Michener, 1981). On the emergence of Israel as a nation, the trees had to be replanted. Israel has an aggressive Afforestation Programme in that whenever a child is born, a tree is planted.On the other hand when a child is born in Nigeria, many trees have to be felled to prepare native concoction and as fuel for naming ceremony. In fact, the desert belt is reputed to be shifting southward by a kilometer yearly. The need to evaluate our environment is very paramount so as to save this land for posterity. Oil prospecting activity is taking place in the Niger Delta Region of Nigeria. Studies carried out in 26 locations on the coastal region of Warri in Delta State showed a buildup of heavy metal (Olowoyo *et al*, 2010). The result of the heavy metal analysis of sediments in seven selected locations is illustrated on Table 22.

Olowoyo *et al*. (2010) observed that the concentration of some metals like Ni, Cr, Cd and Zn in many locations were higher during the wet season than the dry season. Iron (Fe) was expectedly high in this area due to the proximity of Delta Steel Company. The high value of Ni, Fe, Cd, Mn and Cr in the sediment indicated that oil operational activities contributed significantly to the concentration levels of these metals (Olowoyo *et al*., 2010).

Table 22: Average Concentration of metals of sediments in seven locations in Warri area.

	Concentration µg/g								
Location	Pb	Ni	Fe	Cu	Zn	Cd	Mn	Cr	Co
Koko	10.76	0.68	178.3	1.04	1.00	8.08	6.63	0.119	0.267
Oghara	0.001	1.80	89.88	0.001	0.815	1.06	0.923	0.003	0.001
Sapele	0.739	2.50	135.43	0.105	1.104	0.383	1.128	0.001	1.62
Abigborodo	3.62	9.94	914.73	1.00	1.54	1.25	1.187	8.45	1.252
Okogho	1.102	9.87	546.62	0.38	1.45	4.21	2.75	0.034	2.66
Ajasiolo	16.55	15.07	7065.0	1.73	2.16	248.0	20.315	482.27	2.21
Gboritseduwa	5.98	0.70	39.65	0.347	0.67	0.772	3.98	0.023	1.074

Source: Olowoyo *et al*. (2010).

chemical principles into industrial production. Chemical engineering came into existence in 1914 as a separate discipline that offered sound approaches to chemical plants design (Austen, 1984).This discipline is characterized by physical operation necessary for manufacturing chemicals as 'unit operation' (heat transfer, fluid flow distillation, filteration etc.) (Austen, 1984).

Analytical Chemistry

Analytical Chemistry provides the methods and tools needed for insight into our material world....for answering four basic questions about our material world such as; 'what?', 'where?', 'how much?' and 'what arrangement, structure or form? (Christian, 2007).

In medicine, analytical chemistry is basic for clinical laboratory tests that help physicians to diagnose diseases and chart progress in recovery. For example, in typhoid fever test, the blood of the patient is titrated with Widal reagent in Widal Test. The titre value of the Widal reagent will dictate the regime of antibiotics to be prescribed for the treatment of this ailment.

In industry, the means of testing raw materials and assure the quality of finished goods is through chemical analysis. Environmental quality is evaluated by testing. The chemical composition of food is also critical to analytical chemistry. Analytical chemistry makes important contribution to diverse fields such as forensic, geology, archeology and space science (Christian, 2007).

Record of Analytical Chemistry, being a basic tool for chemical measurement, dated back to the earliest recorded history (Christian, 2007). For instance, the fire assay of gold was referred to in the Bible (Zechariah 13^9). The alchemists accumulated chemical knowledge that formed the basis of quantitative analysis today (Christian, 2007). Lavoisier was considered the 'father of Analytical Chemistry' because of the quantitative experiments that he performed with analytical balance that led him to propound the Law of Mass Conservation (Christian, 2007; Microsoft Encarta, 2009). Analytical chemistry grew rapidly in 20th Century with evolution of instrumental techniques like electroanalysis, conductometric titration, automatic titration and colorimetry. Today, the progress has led to the development of sophisticated and powerful computer-based instruments with ability to perform highly complex analysis and measurement at extremely low concentration (Christian, 2007). In fact, analytical tools capable of detecting potentially dangerous weapons have been employed for security purposes in the banks, airports and other places to detect metals. This reminds us of the legend of Chinese Pineiho Jade. Pineiho found an uncut jade and presented it to Emperor Wu as a loyal subject. However, following the pronouncement of the royal jeweler denouncing it as an ordinary stone; the emperor in a rage cut off one of Pineiho's feet. Following the death of Emperor Wu, and his succession by Emperor Wen, he represented this same jade to him. He also ordered that his second foot be cut off following denunciation by royal jeweler again. Under the third emperor, the jade was polished and found to be precious. This jade is now in one of the Chinese Museums today (Wurmbrand, 1990). If analytical chemistry had developed to the extent it is today; it would have been needless for Pineiho to have undergone this treatment because x-ray microprobe and other instrumental techniques might have been used to reveal its authenticity.

INDUSTRY

The term 'industry' refers to a group of enterprises (private businesses or government operation and corporations) that produces a specific type of good or service (Heintz and Saez, 2009). The term industry was derived from the Latin word '*Industria*' which means 'diligence' that reflects the highly disciplined way the human energy, natural resources (raw materials) and technology are combined to produce goods and services in a modern economy (Guest, 1983, Heintz and Saez, 2009). Hence, industry is simply the production of goods and services in an economy (Heintz and Saez, 2009). The Industrial Revolution of the 18th Century in Britain emerged following the mechanization of industrial production. Larger scale production driven by machinery makes use of advanced technology and employs sizeable work force (Guest, 1983, Heintz and Saez, 2009). Industry has been classified as primary, secondary and tertiary.

Primary industries use raw natural resources as major inputs. These include agriculture, fishing, mining and forest industries. These respectively use farmland, rivers, lakes and ocean, mineral deposits and forest as their major inputs or raw materials (Heintz and Saez, 2009).

Secondary industries use producer goods to assemble their products. For example, construction industry produces house, other buildings and roads. Its input include lumber produced by forest industry, quarried stones and asphalt from mining industry and steel structure produced from iron ores. Manufacturing industries such as food processing, petroleum refineries, motor assembly, textile industry and other manufacturing outfits form the

shell relative to 0.931 for snail shell powder (Ajayi *et al.* 2005). In view of this, cow hoof powder was used to adsorb many metal ions. The thermodynamic and kinetic data of this process has been reported for zinc ions (Osasona *et al.*, 2013a), chromium (VI) ions (Osasona *et al.* 2013b) and for lead (II) ions (Osasona *et al.* 2013c). Table 21 provides summary of this study.

Table 21 : Thermodynamic parameters of biosorption Pb(II), Zn(II) and Cr (VI) ions on cow hoof adsorbent.

Ion	pH	T(K)	$\Delta G(kJ/mol)$	ΔH (kJ/mol)	$\Delta S\ (\frac{kJ}{mol})$
Zn (II)	4.0	298	-11.14	42.792	177.61
Pb (II)	2.0	298	-10.28	-33.27	-0.77
Cr (VI)	2.0	298	-1.707	33.357	0.118

Source: Osasona et al. (2013a, b, c)

This adsorbent being a keratinous protein was effective in adsorbing Zn ions at pH 2.0, Pb (II) ions at pH 4.0 and Cr (VI) ions at pH 2.0. The thermodynamic data showed that the reactions were spontaneous. The adsorption conformed to both Langmuir and Freundlich isotherm models.

Environmental studies

The environment in which we live is constantly under threat as the various components that make it are changing as a result of natural disasters and anthropogenic activities of man. Man generates a huge volume of wastes that are discharged or disposed on soil, water and air. Deforestation, mining, unbridled dumping of refuse, crude oil spillage, acid rain, natural disasters and sewages are the principal agents of environmental degradation. The greatest scourges facing humanity are the depletion of ozone layer, acid rain, global warming, flooding and attendant emergence of drug-resistant diseases. All these can be attributed to human activities that are imparting negatively on the environment. The recent epidemic of lead poisoning in Zamfara State, Nigeria, is sad enough. This incidence in which over 400 children died was attributed to the activities of illegal gold miners that released lead ions into the environment. The declining forest reserves worldwide is responsible for global warming is a matter of concern. In fact, the World leaders gathered in

Table 20: Concentration of elements in the produce water of borehole and near surface bitumen.

Element	Borehole bitumen (mg/L)	Near-Surface (mg/L)	FEPA(1991) Limit (mg/L)
Hg	1.13 ± 0.03	0.98 ± 0.05	0.05
Fe	15.5 ± 4.60	11.0 ± 5.40	20
Zn	1.38 ± 0.80	1.79 ± 0.23	<1.0
Pb	BDL	BDL	<1.0
Cd	1.59 ± 0.37	BDL	<1.0
Co	0.05 ± 0.03	0.04 ± 0.03	NR
Ni	2.50 ± 0.4	1.00 ± 0.00	<1.0
As	BDL	BDL	0.1
Mg	0.84 ± 0.04	0.20 ± 0.00	200
Ca	0.34 ± 0.05	0.04 ± 0.02	200
Cu	1.56 ± ±0.19	BDL	<1.0

Key:
NR: Not Reported
BDL: Below Detection Limit.
Source: Ogunsuyi *et al.* (2008).

mercury poisoning in Japan. The water also absorbs a number of elements from the environment. One of the ways of removing these metals from water is by the process called Adsorption. Adsorption is simply a process of concentration chemical species on the surface of solids. Adsorption is both chemical and physical process. The chemical adsorption known as Chemisorption has been very important in catalysis. The use of agricultural wastes to adsorb metals from aqueous solution is the subject of this discourse. Following the report of Ogunsuyi *et al* (2006) on the adsorption of copper by powdered activated carbon, corn cob, coconut shell powder and oyster shell powder; with oyster shell powder having adsorption coefficient of 0.537, relative to 0.012 to 0.282 of others, the potentiality of oyster shell for adsorption of lead (II) ions was evaluated. Oyster shell powder along with snail shell powder was evaluated for their adsorption capacity for Pb (II) ions in aqueous solution. The two adsorbents of chitin origin were found to be comparable. The adsorption coefficient that defines the ratio of lead ions in adsorbent to that in equilibrium solution was comparable at 0.944 for oyster

largest group of secondary industries (Heintz and Saez, 2009).

Tertiary industries are majorly service outfits that provide services. Example include banks and other financial institutions, insurance, universities and other schools, hotels, hospitals, radio and television stations, travel agencies and print media outfits to mention a few. All forms of government activities ranging from local waste disposal to armed forces are also classified as tertiary industries (Heintz and Saez, 2009).

The economy of a nation depends on the industries that drive it. A robust economy is reflective of manufacturing outputs, science and technology, capital inflow and good governance. In Nigeria, the economy is mainly driven by the primary industry outfits. Hence, there is a need to enhance the manufacturing sector so as to effectively drive the economy.

MY CONTRIBUTIONS

My research contributions include the followings:

1. Leather research.
2. Instrument development in Atomic absorption spectroscopy.
3. Industrial chemicals and tobacco.
4. Hydrometallurgy.
5. Bitumen.
6. Use of agricultural wastes in removal of heavy metals.
7. Environmental monitoring.

Research in Leather

Leather is defined as an animal skin that has been chemically modified to produce a strong flexible material that resists decay (Microsoft Encarta, 2009b). Unprocessed skin easily degrades unless consumed as a menu called '*Ponmo*' in Yoruba language. Most of the World's output of leather is produced from cowhides and calfskins, goat skins and kid skins, sheep skins and lamb skins. Other sources include skins of horse, pigs, kangaroos, camels, llamas, seal and walrus (Microsoft Encarta, 2009b). Hides are used to denote the flayed skins of big animals like cow, buffalo, llamas, horse and camel. Skins of smaller animals used in leather processing are simply called animal skins. Uses of leather include soft leather for clothing, upholstery and bags while hard leather finds its use for shoes. Hides and skins are the major raw materials for leather processing. Other raw materials include lime (calcium hydroxide, sulphuric acid, vegetable oils, vegetable and mineral tannins, bates, sodium sulphites and dyes.

Leather processing starts from the flaying and curing of hides and skin, followed by soaking and unhairing, liming, deliming and bating, tanning, lubricating, dyeing and finishing.

The raw material of concern in this research was vegetable tannins that are used to form cross-linking with the collagen fibres of the processed hides and skins. Mineral tannage involve the use of chromium salts and sometimes those of aluminium. In the Northern parts of Nigeria, tannins derived from Bagaruwa barks (*Acacia nilotica*) is a popular tanning agent. However, the initial trial with powdered fruit husk of locust bean (*Pakia clyperoniana now Pakia biglobosa*) gave some promising results of this source as a potential raw material for leather industry (Adewoye and Idris, 1982). This necessitated the research into the chemical constituents of this source. The tannins were of condensed type. Various extracts of this fruit husks were chromatographed and co-chromatographed to determine the glycosides and aglycones of the tannins. Tannins are polyphenolic compounds that are natural products of plants (Harbourne, 1984). These compounds like others such as glycosides, alkaloids, terpenes and others are usually found in plant's parts like barks, leaves, fruit husks and sometimes in tubers. Locust bean, *Pakia biglobosa*, is widely grown in Nigeria. The bean or seed is usually fermented to produce soup flavouring agent, the fluffy part of the fruit is consumed while the husk is usually discarded. The husk was found to contain about 45% Tannins (Adewoye and Ajayi, 1988a). The tannins are of the condensed type like flavonols. Characterization of the tannins was accomplished with paper chromatography of the extracts.

Aqueous acetone extract of the powdered fruit husks was successively extracted with diethyl ether and ethyl acetate. The resulting extract was concentrated and spotted along with authentic samples of the compounds on Chromatographic paper for separation using solvent systems tertiary/secondary-butanol: acetic acid: water (14:1:5) and 6%(v/v) acetic acid. The separation showed the presence of elagic acid, (+)-catechin, rutin (quercetin-3-rutinoside), gallic acid and an unconfirmed compound (Table 1) (Adewoye and Ajayi, 1988a).

On the other hand, solvent extraction of bitumen by soxhlet and Dean and Stack procedures was undertaken using toluene and chloroform as extracting solvents (Ogunsuyi *et al.*, 2008). The yield from this process varied with solvent and the procedure employed. From soxhlet process that had the optimum yield of 46.75%, 88.50% and 92.50% respectively for tar sand, near surface and bore hole samples. Correspondingly lower yield of 43.0%, 87.13 and 87.56% were obtained from tar sand, near surface and borehole samples respectively. Dean Stack method on the other hand yielded 44.38%, 85.13% and 90.25% respectively for tar sand, near surface and borehole samples with toluene. The yield from chloroform using this procedure amounted to 40.62%, 78.75% and 82.25% respectively for tar sand, near surface and borehole samples. No produce water was however produced form soxhlet process. The produce water or co-extracted water of 4.83% to 4.94% was obtained from tar sand, relative to 25.21 to 26.79% from near surface sample and 24.14% to 24.32% from borehole sample. Soxhlet process was the best procedure and optimum yield being from toluene. On the other hand, extraction using Dean and Stack Process afforded the access to co-extracted water which was hitherto not possible with soxhlet process. Analysis of the produce water revealed the presence of eleven trace elements as shown in Table 20. Eleven elements were detected in measurable quantities in the two samples. The highest concentration of each element was recorded for the borehole sample. Lead and arsenic were found to occur below the detection limit of the instrument in both samples. The presence of these elements in the produce water might not bode well for the refining process as they can pollute the environment during mining and poison the catalysts employed in the refining process. The bitumen exploitation is on a minor scale restricted to the artisanal miners at present. The potential economic benefit of this mineral is immense. This mineral is best put on strategic reserve if not to be exploited presently.

Application of agricultural wastes in adsorption of metals in aqueous solution

Wastes are usually generated from anthropogenic activities of man. Metals particularly the heavy metals have been found to be injurious to the environment and its components including man. The cleaning of the environment to rid it of accumulated pollutants has been agitating the minds of scientists globally. Reported hazards emanating from metal poisoning include itai-itai and Minamata diseases due respectively to cadmium and

Table 19: Elemental composition of tar sand.

	Concentration (μg/g)			
Element	Crude sample	Maltene	Asphaltene	Sand residue
Al	2624±0.20	117.50±0.05	387±0.35	15460±12.6
Ti	856.38±0.23	280.56±0.08	134.5±0.26	1324.2±0.96
V	142.6±0.02	27.09±0.28	4.26±0.09	28.55±0.03
Mn	57.75±0.03	3.37±0.17	14.50±0.50	23.08±0.36
Na	321.8±1.8	81.31±0.15	455.26±0.66	73.86±0.60
K	4623.4±9.93	75.90±0.43	BDL<1183	1822.60±0.09
Br	7.59±0.04	1.29±0.08	8.01±0.01	1.10±0.03
La	3.30±0.04	BDL<0.17	2.97±0.06	14.05±0.65
Sc	1.54±0.03	BDL<0.25	1.38±0.03	3.80±0.05
Cr	14.82±0.12	BDL<6.05	BDL<7.62	20.90±0.50
Fe	25370±17.6	12808±0.85	22139±10.68	11550±0.95
Co	8.03±0.01	2.31±0.02	7.39±0.06	1.86±0.03
Sm	1.10±0.03	BDL<0.02	0.97±0.01	2.66±0.03
Cs	BDL<0.83	BDL<1.19	BDL<0.81	BDL<0.81
Ce	BDL<7.10	BDL<6.49	BDL<5.01	27.64±0.06
Yb	BDL<0.83	BDL<0.49	BDL<0.83	1.02±0.03
Lu	0.40±0.01	BDL<0.05	BDL<0.04	0.12±0.03
Hf	0.99±0.05	BDL<0.05	BDL<0.97	2.15±0.30
Th	1.28±0.09	BDL<0.58	1.38±0.1	3.25±0.05
Rb	28.64±0.12	27.69±0.22	BDL<16.25	BDL<25.42
Ni	49.42±0.30	35.56±0.55	BDL<0.30	BDL<0.60

Source: Ogunsuyi *et al.* (2012).

Table 1: Phenolic constituents of *Pakia biglobosa*(formerly *Pakia clypertoniana*) fruit husk.

Phenolic compound	R_f values		Colour		UV (EtOH)
	1	2	UV	UV +NH_3	λmax (nm)
Elagic acid	0.4	0.04	light blue	yellowish blue	256, 367
(+)-Catechin	0.72	0.55	Absorption	light blue	-
Unconfirmed	0.57	0.25	Blue	violet	-
Rutin	0.55	0.49	brown	yellow	260
Gallic acid	0.71	0.46	violet	deep violet	234

1 = See butanol: acetic acid: water (4:1:5)
2 = 6% Acetic acid
Source: Adewoye and Ajayi (1988a)

On the other hand, two methods were employed in detection of flavones, flavonols and tannins of *Pakia biglobosa* fruit husk; and this involved (a) the hydrolysis of husk powder with 2M HCl followed by extraction with ethyl acetate and (b) mixing powdered husk with acid washed sand and making slurry that was allowed to stand for 3 days. The resulting aqueous extract from "b"above was concentrated before successively extracting with ethyl acetate. The resulting extracts from both processes were examined by 2-dimensional paper chromatography with BAW (Butanol: Acetone: Water) (4:1:5), Forrestal and 2% acetic acid solution. Ethyl acetate extract from (a) yielded 5 flavonol aglycones; myricetin, azaleatin, quercetin, kaempferol and morin. On the other hand, ethyl acetate extracts from (b) yielded the above-mentioned aglycones except azaleatin with additional two compounds like fisetin and tricin (Table 2). (Adewoye and Ajayi, 1988b).

Table 2: Chromatographic properties of flavonols and flavones of *Pakia biglobosa* (formerly *Pakia clypertoniana*) fruit husks.

Flavonol	R_f values			Colour	
	1	2	3	UV	UV +NH_3
Myricetin	0.44	0.35	0.07	Bright yellow	Yellowish green
Azaleatin	0.49	0.51	0.26	Fluorescent yellow	Fluorescent yellow
Quercetin	0.65	0.61	0.32	Bright yellow	Purplish yellow
Morin	0.74	0.61	0.34	V. bright yellow	Fluorescent yellow
Kaempferol	0.87	0.67	0.43	Bright yellow	Bright yellow
Fisetin	0.72	0.62	0.04	Fluorescent yellow	Fluorescent yellow
Tricin	0.76	0.76	0.42	Fluorescent yellow	Fluorescent yellow

1 = Butanol: Acetic acid: Water (4:1:5) 2 = Forrestal 3 = 2 %(v/v) Acetic acid.

Source: Adewoye and Ajayi (1988b).

Extraction of the powdered husk with amyl alcohol of aqueous fraction of acid hydrolyzed powder on chromatographic examination yielded 5 anthocyanidins such as petunidin, pelargonidin, malvidin, delphinidin and cyaniding (Table 3) (Adeoye and Ajayi, 1989).

Table 3: Characteristics of Anthocyanidins of *Pakia biglobosa* (formerly *Pakia clypertoniana*) fruit husks.

Anthocyanidin	Rf values			UV spectra
	1	2	3	(λmax nm)
Petunidin	0.22	0.49	0.47	(279), 546
Pelargonidin	0.53	0.82	0.70	(276), 525
Malvidin	0.27	0.62	0.56	(272), 538
Delphinidin	0.05	0.40	0.30	(287), 559
Cyanidin	0.49	0.66	0.55	(271), 528

1 = 2% (v/v) Acetic acid, 2= Butanol: Acetic acid: water (4:1:5) 3 = Forrestal

Source: Adewoye and Ajayi, (1989).

(25.4%) followed by Al and Ti in this sample. The high concentration of Fe and Ti suggested the possible occurrence of ilmenite ($FeTiO_3$) within the tar sand (Ogunsuyi *et al.*, 2012). In the three samples about 23 elements were detected in measurable quantities. Other elements such as Ca, Dy, Zn, Sb, Ba, Ta, Mg and Cl occurred below the detection limit of the instrument. The distribution of elements in the various components of tar sand (Table 19) presented a similarly interesting picture. Twenty-one elements were detected in measurable quantities in the various components of this mineral. The unextracted and crude tar sand had the highest concentration of most of these elements. For the refining of the bitumen due to the presence of these elements in their various matrices, demetalization process needs to be employed.

Table 18: Comparison of elemental composition of bitumen and tar sand samples.

Element	Concentration (µg/g)		
	Borehole	Near-surface	Tar sand
Al	722.55±0.13	527.60±0.03	2623±0.21
Ti	285.33±0.34	BDL<57.85	856.38±9.23
V	92.84±0.02	101.20±0.02	142.60±0.02
Mn	6.56±0.07	7.80±0.06	57.75±0.03
Na	178.80±0.02	161.23±0.09	321.8±1.8
K	1893.0±0.07	3525.0±0.05	4623.4±9.93
Br	4.74±0.09	1.65±0.09	7.59±0.04
La	20.90±0.01	40.47±0.06	3.30±0.04
Sc	7.50±0.04	16.51±0.06	1.54±0.03
Cr	51.58±0.04	90.74±0.33	14.82±0.12
Fe	19230±0.02	33450±0.12	25370±17.6
Co	3.40±0.98	8.62±0.07	8.03±0.01
Cs	1.44±0.39	2.23±0.98	1.10±0.03
Sm	4.59±0.02	12.35±0.02	BDL<0.83
Ce	44.12±0.04	BDL<1.93	BDL<7.10
Yb	1.80±0.15	4.61±0.10	BDL<0.83
Lu	24.27±0.07	0.58±0.05	0.40±0.01
Hf	5.13±0.05	11.07±0.05	0.99±0.05
Th	5.81±0.03	9.18±0.02	1.28±0.09
Rb	29.97±0.02	37.73±0.33	28.64±0.12
Ni	59.54±0.15	69.12±0.31	49.42
Eu	BDL<1.48	3.11±0.09	BDL<1.20

Source: Ogunsuyi *et al.(2012)*

Bitumen

Bitumen is an energy raw material that has promise for the future in view of depleting crude oil reserves. Athabasca Tar Sand Company has developed a technology for extraction petrochemicals from this source. Bitumen is a mixture of organic liquids that are viscous, black, sticky and soluble in organic solvents. The composition of bitumen has been variously reported to consist of highly condensed polycyclic aromatic hydrocarbons (PAH), heterocyclic compounds and heavy metals such as nickel, vanadium, lead, chromium, mercury, selenium, arsenic, manganese and other toxic elements (Ipinmoroti and Aiyesanmi, 2001). The use of bitumen predates the modern age. Romans and Mesopotamians used bitumen as binders. During the period of the Roman Empire, bitumen from the Dead Sea in the present-day Israel was very much in vogue. The Dead Sea was named '*Mare Asphaltis*' meaning '*Sea of Asphalt*'(Guest, 1983). Nigeria has a vast reserve of bitumen and tar sand that is estimated to be about 150 billion barrels equivalent of crude oil (Ogunsuyi et al. 2008). The coastal plain of Ondo State is reputed to be rich in tar sand and bitumen. This area in question is dotted with bitumen deposit from Agbabu to Ilaje, EseOdo and Okitipupa Local Government areas by the sea-shore (Ogunsuyi *et al.*, 2012).The locality is within the belt of bitumen impregnated sandstone that runs east-west within Benin Basin. The Benin Basin runs parallel to the coastal margin of the Gulf of Guinea covering the Southwestern Nigeria and Republic of Benin (Ogunsuyi *et al.*. 2012). This research was on three deposits of bitumen in Odigbo Local Government area of Ondo State. Neutron activation analysis technique was used to characterize the borehole, near-surface and tar sand samples in both raw and processed forms (Asphaltene and Maltene). Soxhlet extraction of the sample was variously accomplished using chloroform and toluene as solvents. The extract was separated into asphaltene and maltene components by dissolving 10.0 g of extract in 100 ml of pentane. The asphaltene containing saturated hydrocarbon was precipitated out by this treatment. The maltene was soluble in pentane. The separation was accomplished by decantation of asphaltene from the mixture. The products from this process were subjected to neutron activation analysis. The sand residue obtained from the soxhlet was also subjected to neutron activation analysis using the CERT Facility of Ahmadu Bello University, Zaria. The result of the analysis is as shown in Tables 18 and 19.

As shown in Table 18, the highest concentration of metals like Al, Ti, V, Mn, K, Fe and Na were recorded for the tar sand sample. The highest concentration of Fe

Instrument development in Atomic absorption spectroscopy.

The quality of raw materials and products are usually evaluated with analytical techniques. Atomic absorption spectrometry is one of the instrumental techniques widely used in this analysis. My PhD programme at the University of Strathclyde, Glasgow, U. K. was on the development of instrumentation of atomic absorption spectrometry.

Atomic absorption spectrometry (Figure 1) using flame cell came into being in 1955 following the independent reports of Sir Allan Walsh in New Zealand and Alkemade in Netherland (Price, 1983). The instrument consisted of hollow cathode lamp source of the element, flame/nebulizer cell, monochromator, detector and read-out system (Price, 1983). The principle is based on the absorption of resonance line of an element from its hollow cathode lamp source by vapourized element generated in flame or graphite furnace cell. The flame employed in the flame atomic absorption spectrometry is usually from acetylene/air or acetylene/nitrogen dioxide. The flame normally breaks down salt into its constituent atoms and atomic vapour so generated absorbs characteristic radiation from source and the amount absorbed is proportional to the concentration of the atoms in the vapour following Beer-Lambert Law. The application of this technique is a monumental success in that this instrument is now used routinely in many laboratories worldwide to determine metallic elements in varieties of samples.

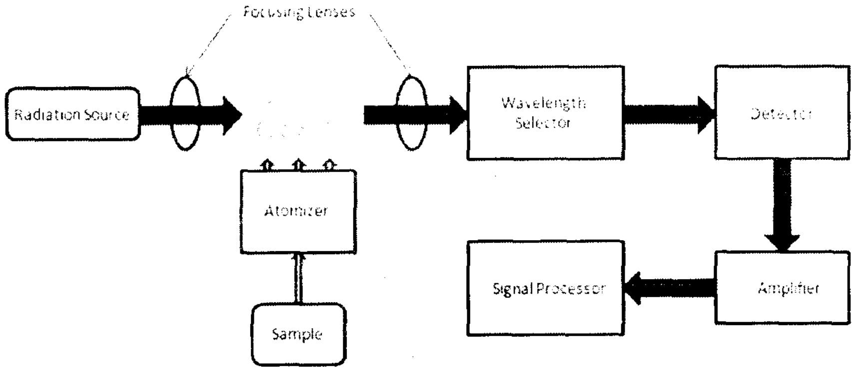

Figure 1: Schematic diagram of an atomic absorption spectrometer.

However, the need for a new atomizer cell arose from some limitations of the combustion flame atomizers. The limitations include incomplete dissociation of some molecules, insufficient flame temperature, vaporization of some reactive species, influence of physico-chemical properties of the solution, poor sensitivity for some elements and certain hazards in practical use.

In 1961, L'vov described the design of an electrically heated carbon tube which overcame many of the limitations of the flame atomizer cell. In this system a relatively small volume of sample was placed on a carbon 'plug' which was inserted into a resistively heated graphite tube. The furnace was a graphite cylinder of about 30 mm to 50 mm long and 2.5 to 5.0mm internal diameter. This tube had a hole underside through which a sample-bearing electrode or plug was inserted. The sample was usually dried by passing current through the sample electrode before being inserted into the isothermally-heated graphite furnace tube (Price, 1983). The main advantage of this system included volatilization of atoms into an isothermally heated furnace, improved detection limits and sensitivities for many elements, reduced chemical interferences and possibility of operating in vacuum UV region to determine elements like Se, P and As (Figure2). The main disadvantage of L'vov design was bulkiness and complexity of atomizer for commercial exploitation.

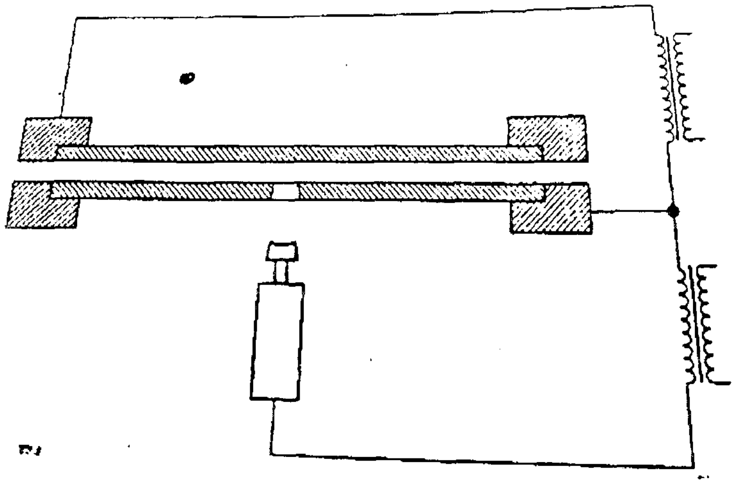

Figure 2: Schematic representation of Lvov's furnace.

Table 17 : Bioremediation Factor (BF), Transfer Factor (TF) and Remediation Ratio of heavy metals in *Jathropha gossypifolia*.

		BF		TF		RR	
Element	Location	Exp	Con	Exp	Con	Exp	Con
Cd	Aba-Igbira	1.1	0.5	5.9	4.2	1.2	0.5
	Atinkankan	1.2	0.4	5.9	4.3	1.3	0.5
	Igbehin	1.1	0.4	5.8	3.9	1.6	0.6
	Moshood	1.2	0.3	5.7	4.4	1.2	0.4
Fe	Aba-Igbira	0.05	0.02	4.2	4.6	0.06	0.03
	Atinkankan	0.05	0.02	4.1	4.7	0.05	0.02
	Igbehin	0.05	0.02	4.4	3.9	0.05	0.02
	Moshood	0.05	0.02	4.4	5.3	0.06	0.04
Pb	Aba-Igbira	1.6	1.0	5.3	4.4	1.6	1.0
	Atinkankan	1.5	1.0	5.0	5.0	1.5	1.1
	Igbehin	1.5	1.0	5.3	5.0	1.5	1.0
	Moshood	1.2	0.9	5.0	5.0	1.3	1.0
Cr	Aba-Igbira	0.4	0.01	3.7	5.6	0.3	0.1
	Atinkankan	0.3	0.1	4.0	5.6	0.4	0.1
	Igbehin	0.3	0.1	3.4	6.4	0.3	0.2
	Moshood	0.4	0.1	3.6	6.4	0.4	0.1

Note: Aba -Igbira, Atinkankan and Igbehin are locations in Ado -Ekiti while Moshood Road is major dumpsite in Ikere-Ekiti.

Source: Awokunmi *et al.* (2012).

Bioaccumulation factor (BF), defined as the ratio of chemical concentration in plant to soil and is used to measure the effectiveness of plant in concentrating pollutant into its aerial parts (Bolan et al., 2006, Awokunmi et al. 2012). Translocation factor (TF), on the other hand is the quotient of contaminant concentration in root to shoot; and it is used to measure the effectiveness of plant in transferring a chemical from roots to shoots (Awokunmi et al. 2012). All these parameters are illustrated in Table 16. The BFs, TFs and RR values were found to be greater than unity for Pb and Cd when 1g/kg EDTA was added to enhance phytoremediation potential of the plant (Awokunmi *et al.* 2012). Noticeably high transfer factor of greater than unity was also observed for chromium and iron for both control and experimental samples. This plant was found to be a hyper-accumulator of both lead and cadmium ions in the soil as shown from the phytoremediation efficiency indices in Table 16.

Table 16: Concentration of heavy metals in the tissue of *Jathropha gossypifolia* grown on soil.

Concentration in mg/kg.

		Root		Stem		Leaf		Fruit	
Element	Location	Exp	Con	Exp	Con	Exp	Con	Exp	Con
Cd	Aba-Igbira	70.3	40.0	48.1	16.6	279.6	112.0	89.7	37.7
	Atinkankan	70.0	38.2	46.2	18.2	276.0	110.0	96.0	36.0
	Igbehin	68.6	38.0	45.0	17.6	258.0	98.0	96.0	32.2
	Moshood	66.2	32.0	40.3	16.2	242.0	96.0	95.2	30.0
Cr	Aba-Igbira	16.2	6.8	18.0	11.2	26.0	16.2	18.6	10.8
	Atinkankan	15.2	6.7	17.0	11.0	25.6	16.0	18.4	10.8
	Igbehin	15.9	5.6	16.2	10.6	22.0	15.7	16.2	9.6
	Moshood	14.8	5.3	16.0	10.2	20.2	15.3	16.8	8.6
Fe	Aba-Igbira	8.5	3.2	12.5	6.2	17.1	6.4	5.6	2.1
	Atinkankan	8.2	3.0	12.2	6.2	16.2	6.0	4.8	1.1
	Igbehin	7.0	3.0	17.2	5.8	16.0	5.8	4.1	1.9
	Moshood	6.8	2.9	10.7	5.8	14.8	5.6	4.1	1.7
Pb	Aba-Igbira	72.0	42.0	84.0	40.2	180.0	96.0	112.0	48.0
	Atinkankan	70.0	40.0	84.2	42.0	156.0	92.0	110.0	46.8
	Igbehin	68.2	36.6	80.2	36.0	160.0	86.2	115.0	47.0
	Moshood	66.0	32.0	80.0	33.0	136.0	84.0	112.0	42.0

Note: Aba-Igbira, Atinkankan and Igbehin are locations in Ado-Ekiti while Moshood Road is major dumpsite in Ikere-Ekiti. Source: Awokunmi *et al.* (2012).

The Massmann's furnace is incorporated into most atomic absorption spectrometer using electrothermal means of atomization (Price, 1983). The tube dimensions are approximately 5.0 cm or 50 mm in length and 5.0 to 6.5 mm internal diameter with 2.0 mm hole in the middle of the tube for introduction of 2.0 to 200 µl volume of liquid sample. The tube is supported by water-cooled steel end-cones which make the electrical connections to a low voltage supply(Figure 3) (Price, 1983). The whole device is held within a metal casing containing an inert gas atmosphere. The operation cycle of this system consist of four principal steps of drying at 100 °C, ashing or pyrolysis at 400 to 500 °C, atomization of the mineralized residue at 600 to 2500 °C and cleaning/purging at temperature above the atomization temperature (Price, 1983). There are three types of graphite tubes; uncoated, pyrolytically coated and totally pyrolytic graphite tubes. The operation results in transient signal of the analyte and both peak height and area are used for calculation. The mechanism of atom formation was postulated to be via dissociation of oxides or chloride for Al, Cd, Ca, Fe, Mg, Mn, Sb, Si and Zn (Ottaway, 1976). On other hand, atoms could be formed by the dissociation of carbides in case of refractory elements like Al, Ca, Mo, Cr and V. The advantages of this process include the economy of samples in which 5 to 10 µl of sample can be introduced to the furnace, better detection limit and sensitivity in parts per billion, transient signals and reproducibility.

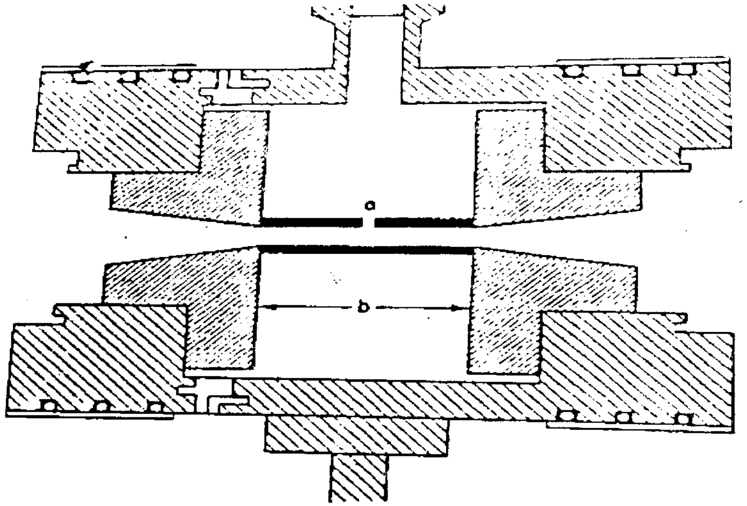

Figure 3: Schematic diagram of Massmann Furnace.

In operation; physical, spectral and chemical interferences are encountered. Physical interferences tend to alter the shape and reproducibility of the absorption signal. The causes are spreading of the droplets due to the viscosity and surface tension of the liquid, occlusion, incomplete drying, atomization and cleaning of the sample and accumulation of carbonaceous residue. This can be tackled by repeated firing of the furnace after operation. The spectral interferences are due to the absorption of the hollow cathode lamp radiation by particles of matrix salt, scattering by salt particles and absorption by undissociated molecules. All these lead to background absorption problem. The spectral interference has been effectively curbed by various background correction devices incorporated into the system. The chemical interferences are condensed and vapour phases interferences. The condensed phase is due mainly to the formation of carbides with some elements particularly the refractory elements. This has been effectively tackled by use of pyrolytically coated tubes. Vapour phase interference results from the reaction between vaporized components and analyte atoms thereby reducing the concentration of free atoms produced. This is particularly encountered when chloride-rich samples are analyzed. This is due to the release of hydrogen chloride gas produced from the hydrolysis of $MgCl_2.6H_2O$ (Ottaway, 1976).

$MgCl_2.6H_2O_{(s)} \leftrightarrow MgO_{(s)} + 5H_2O_{(g)} + 2HCl_{(g)}$-------------------(3)

$M(g) + HCl(g) \leftrightarrow MCl(g) + \frac{1}{2}H_2\,(g)$-------------------------------(4)

The extent of interference is subject to the temperature of furnace and the extent of overlap of overlap of analyte and matrix species in the furnace. Various approaches have been made to minimize this and these included matrix modification to alter the chemical environment of the analyte, delayed atomization through the use of platform means of sample introduction.

Two approaches were proposed to combat this problem and these are; modification of graphite tubes to enhance vapour temperature and probe means of sample introduction.

A. Modification of graphite tubes to enhance vapour temperature.

In the conventional tubewall process, the atoms were found to be vaporizing into a rather cool environment with insufficient vapour temperature. Evaluation of graphite tube design (Fig. 3) was undertaken. The vapour temperature was measured using the lead 2-line methods while the tube temperature was measured at the centre and the ends of the tube using optical

has engaged the attention of concerned government, scientists and individual worldwide. The use of living plant to absorb these metals in ionic form has been the basis of phytoremediation. Bioremediation is an allied technique using microorganisms in this instance to absorb the pollutants. Plants that have been identified as phytoremediators include water hyacinth (*Eichhornia crassipes*), duckweed (*Lemna minor*) and jathropha (*Jathropha gossypifolia and Jathropha curcas*) to mention a few. Soil from solid waste dumpsites in Ado-Ekiti and Ikere-Ekiti vicinities were collected and used in a greenhouse experiment to provide nourishment for Jathropha plant in the university environment (UNAD). The growth patterns observed and the concentration of a number of heavy metals like lead, chromium, copper, iron, manganese, cadmium, zinc, nickel cobalt and tin was determined in the leaves, stem, root and fruits of this plant. The phytoremediation potentials were determined using factors such as bioaccumulation factor (BF), translocation factor (TF) and remediation ratio (RR) to determine the efficiency. The result is promising for a number of elements. In this instance, the discussion will be limited to response to cadmium, lead, chromium, iron and zinc. The effect of EDTA solution on this process was also evaluated.

The plant growth index used was the height at pre-flowering, flowering and matured stages. With application of EDTA on the dumpsite soils, the plants attained at maturity between 105and 188 cm height. On the other, the control plant attained a height of more than 120 cm. Noticeable yellowing of leaves was noticed at the pre-flowering stage of the plant (Awokunmi et al. 2012). The amount of lead, cadmium, iron and chromium determined for the various part of this plant is illustrated in Table 16.

From Table 16, it was obvious that the various parts of this plant bioaccumulated the metals in question. The highest concentration of each metal at every location was found in the leaf for both control and experimental sample. The concentration of each of the metal at every part of the plant was more in the experimental sample due to influence of EDTA that facilitated more accumulation. In fact, the concentration of metal accumulated by the experimental sample was one and a half to three times of what obtained for the control sample in each part for each element. The concentration of the heavy metal s were found to increase in the order of leaf> stem>root>fruit. The sample Jathropha gossypifolia was found to have accumulated considerably high contents of Cd and Pb in their harvestable sections (Awokunmi et al., 2012).

On the other hand the phytoremediation efficiency of the plant was measured by bioaccumulation factor (BF), translocation factor and remediation ratio.

Acidified hydrogen peroxide (H_2O_2) was used to selectively leach out copper from this complex ore, chalcopyrite. The conditions, mechanism of the process and thermodynamic data were recorded (Adebayo *et al.,* 2003, 2006a). Optimum leaching of copper was achieved with 20% (v/v) H_2O_2, 6.0M H_2SO_4, minimum stirring at 353 K. Shrinking Core model was proposed for this leaching, while the Activation Energy of 39.0 kJ/mol was recorded with electrochemistry being at the heart of the leaching (Adebayo et al, 2006a). This process was particularly important based on the level of potential gangle-forming component of this ore. Similar feat was accomplished with the leaching of sphalerite ZnS with hydrogen peroxide in nitric acid solutions (Adebayo *et al.* 2006b).

Another approach to hydrometallurgy is the use of solvents to selectively extract metals form solution. This approach has been reported by Obaseki *et al.* (2006) in the extraction of copper and zinc ions from aqueous acid sulphate solution using Tri-N-butyl phosphate (TBP). Copper ions were effectively extracted at pH 5.0 in presence of zinc ions in acidic sulphate solution using TBP. Increasing the pH to 7.0 there was effective in removing zinc ions. Temperature of 32 °C was the ambient temperature of this exercise (Obaseki *et al.* 2008).

Ojo and Ajayi (2013) reported the extraction of Mo (IV) ions in dilute HCl and HNO_3 solutions with di(2-ethylhexyl)phosphoric acid (D2EHPA) dissolved in n-hexane. The mechanism of extraction by both acids at pH 1.0 – 6.0 was found to be majorly by cation exchange of MoO_2^{2+} for H^+ of the extractant (H_2R_2). At lower pH value, formation of neutral, unstable isopoly acid, $H_4Mo_8O_{26}$ or $nMoO_3.2H_2O$ and MoO_2^{3+} predominated. Solvent extraction at pH 1.0 – 6.0 was found to be best for this ion. The efficiency of extraction from HCl was better than from HNO_3, making HCl a better process acid.

Phytoremediation

This is a green technology of removing heavy metals from the polluted soil, air and water by use of a living plant that grows on the medium. Man through his various activities has generated wastes which are usually deposited on the immediate environment. Heavy metals like mercury, cadmium, lead, iron, copper etc. have been deposited on water and soil, and the presence of these has altered the physical and chemical properties of the environments. Heavy metals emanate from solid and liquid wastes, effluents, runoff, agriculture, mining and domestic activities. Effort to clean such environment

pyrometer. The changes in the vapourtemperature and surface temperature were monitored using a software programme called 'Temp calc'. Philip's SP-9 electrographite tube coated with pyrolytic graphite was modified by reducing the tube wall thickness at different sections along the length of the tube (Figure 4) (Ajayi *et al.*, 1988 and Ajayi *et al.*, 1989).

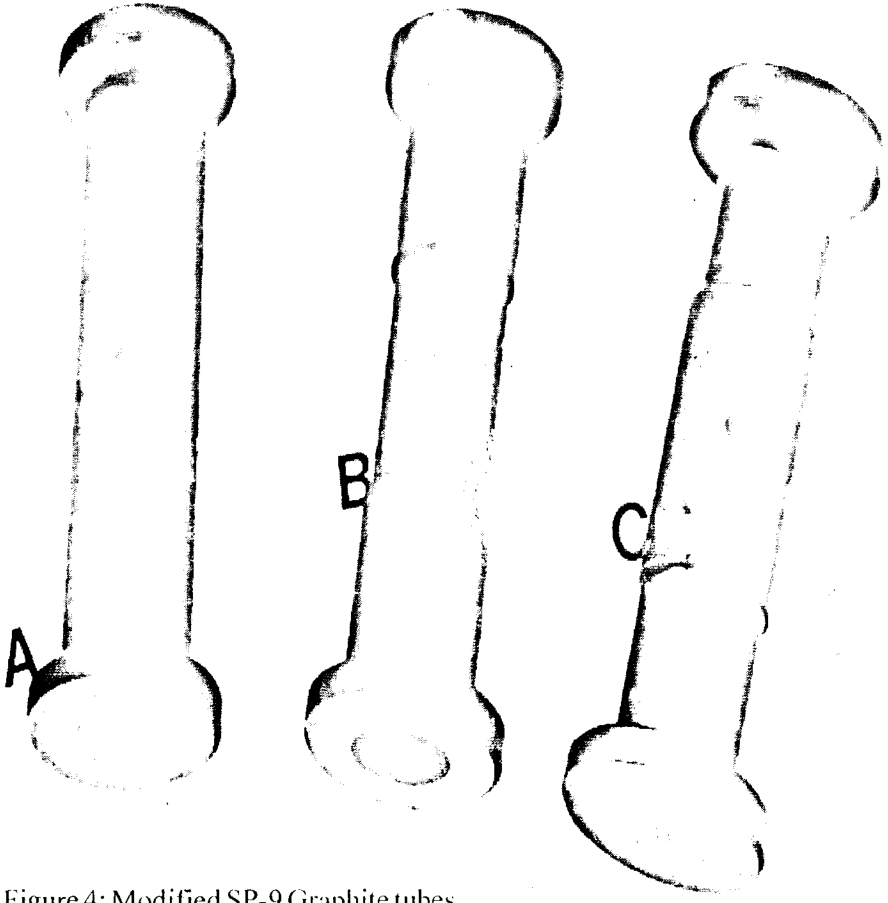

Figure 4: Modified SP-9 Graphite tubes.

Modified tube I (B) was created by shaving off 0.5mm thick layer of graphite from 10-12mm mid-portion of the tube. This was intended to increase the temperature gradient from the hottest section of the injection hole towards the cool end of the tube. The second design, Modified Tube II (C) was prepared by removing 0.5 mm thick layer of graphite from 5 – 6 mm section starting from 3 or 4mm from the end of the tube. This was to reverse the temperature gradient in the initial few seconds of heating. The temperatures of the tube centre and tube end were measured by focusing optical pyrometers on these points. Interferences of 0.1% to 0.5% (w/v) of $MgCl_2$ and 0.2% NaCl 5µl of 50 µg/l Pb, 2 µg/l Cd and 10 µg/l Mn were undertaken at the respective atomization temperatures of the elements. The surface and vapour temperature profiles of the three tube (unmodified and modified) are shown in Figures 3 – 5. From the Figures. It was evident that both the surface and vapour temperatures experienced by Modified Tube II were higher than what obtained for the other tube. Table 4shows the depression of analytes signals by these chloride salts.

Table 4: Depression of Cd, Pb and Mn signals of AAS in the presence of NaCl and $MgCl_2$.

	Depression (%)							
	Cd 20pg		Pb 0.5 ng		Mn 0.1 ng			
	$MgCl_2$ 50μg		$MgCl_2$ 50 μg		NaCl 20 μg		$MgCl_2$ 10 μg	
SP-9 Tube	height	area	Height	Area	Height	Area	Height	Area
Unmodified	50	46	48	54	39	41	48	61
Modified I	78	56	89	92	59	69	46	62
Modified II	34	35	44	34	24	21	36	33

Source: Ajayi *et al.*, (1989)

The depression was relatively least for Modified Tube II for each of the analytes. Modified tube II was apparently the best design, but might not be profitable in terms of lifespan and production cost (Ajayi et al., 1988 and Ajayi et al. 1989). The next approach was to introduce samples into isothermally heated furnace by means of graphite probe as obtained for the L'vov's furnace. This forms the basis of the next discourse.

Hydrometallurgy is an economic and efficient, cost effective procedure of extracting metals from their ores using solvents. This procedure is particularly useful for the extraction of lean and complex ores. With the dwindling of high grade ores globally, and the attendant cost of pyrometallurgical processes, it is desirable to apply hydrometallurgical processes. For this process, high level of extraction has been achieved and reported (Gosh and Ray, 1991; Adebayo *et al.*, 2006a). The observed limitations of pyrometallurgy include being energy and cost-intensive process, formation and disposal of slags, release of gaseous pollutants to the environment and formation of thermodynamically stable matters that limit metal extraction (Gosh and Ray, 1991; Adebayo *et al,*2003, 2006a). High oxidation potential is desirable for successful hydrometallurgical processes. Chalcopyrite, $CuFeS_2$, is a complex ore with some gangles. Since hydrometallurgy is a process of leaching lean ores and having been found to overcome some shortcomings of pyrometallurgy; was a process of choice for the extraction of chalcopyrite. The ore was chemically characterized by various analytical techniques. The findings are as shown in Table 15.

Table 15: Composition of a Nigerian Chalcopyrite sample.

Element/oxide	Composition (% w/w)
Cu	32.49
Fe	17.04
SiO_2	13.97
S	11.91
Al_2O_3	5.98
MgO	0.78
CaO	0.90

Source: Adebayo *et al.* (2006a)

Table 14: Comparison of element concentration ranges in Nigerian tobacco and cigarettes and Egyptian cigarettes.

	Concentration in ?g g^{-1}			
Element	Nigerian tobacco	Nigerian cigarette	Egyptian tobacco	ICP-MS detection limit (?g/l)
Al	139 – 524	216 – 528	504	0.04
Sc	0.73 – 1.29	ND – 2.79	ND	0.01
V	0.04 – 8.60	0.06 – 1.66	1.10	0.009
Cr	0.92 –16.4	1.28 – 3.86	4.11	0.008
Mn	53.3 – 150	113 – 144	110	0.009
Fe	191 – 2240	257 – 744	787	0.3
Co	0.53 – 1.91	0.69 – 1.68	0.87	0.005
Ni	1.08 – 4.17	2.04 – 6.32	6.12	0.009
Cu	3.59 – 22.8	7.32 – 26.4	12.6	0.008
Zn	18.9 – 43.2	21.6 – 34.2	31.2	0.01
Ga	2.11 –13.7	2.74 – 4.98	2.4	0.01
As	0.02 – 0.04	ND – 0.14	0.18	0.1
Rb	28.7 – 136	20.1 – 51.7	19.7	0.009
Sr	37.3 – 170	97.3 – 123	100	0.008
Y	0.12 – 2.83	0.41 – 0.81	0.57	0.008
Mo	0.57 – 51.1	0.92 – 49.7	ND	0.01
Ag	2.06 – 7.03	ND – ND	ND	0.01
Cd	0.08 – 0.95	0.29 –0.91	1.61	0.009
Cs	0.007 – 0.29	0.06 – 0.15	0.22	0.003
Ba	45.2 – 385	81.3 – 144	69.4	0.008
La	0.49 – 8.25	1.61 – 28.3	1.58	0.002
Ce	0.89 – 13.4	1.04 – 2.64	2.32	0.002
Nd	0.24 – 5.35	0.60 – 1.29	0.88	0.008
Sm	0.07 – 0.92	0.11 – 0.25	0.15	0.006
Eu	0.01 – 0.14	0.02 – 0.07	0.03	0.003

ND = not detected or determined or below the detection limit.

Source: Oladipo *et al.* (1993).

B. Evaluation of automatic probe device for electrothermal atomic absorption spectrometry.

The probe device consists of a graphite strip containing the sample being inserted into the pre-heated furnace for atomization. This was intended to mimic the L'vov's furnace that effectively minimized vapour-phase interference. In this system, a 6.0mm internal dimension tube preferably a totally pyrolytic graphite tube usually designed to have slot under the injection hole to accommodate this strip of graphite known as probe. The temperature programme is such that drying and charring of the sample takes place inside the tube. The probe is removes before pre-heating of the furnace to the desired atomization temperature. As soon as the temperature is attained, the probe is re-inserted to the furnace to atomize the sample. The pioneering work was done by Giri *et al.* (1983). The exercise involved the determination of a number of elements in certified reference samples. The results as shown in Tables 5 and 6.

Table 5: Determination of elements in Seronorm and Lanonorm reference urine by probe ETAAS.

			Probe ETAAS	
Sample	Element	Dilution factor	Concentration µg/dm^3	Assigned concentration µg/dm^3
Seronorm	Cd	5	5.5±0.9	5.7
	Cr	2	21±2	21.6
	Co	2	11±4	10.6
	Mn	2	20±1.5	20.0
	Ni	2	36±6	36.0
	Pb	5	102±29	102.0
Lanonorm 2	Cd	10	95±7	94.0
	Co	2	43±8	40.9
	Ni	Neat	29±3	31
	Pb	2	121±9	126
Lanornom 3	Cd	10	37±6	38
	Co	2	133±25	147
	Ni	2	72±11	71
	Pb	10	552±66	548

Values based on integrated absorbance; ± one standard deviation.
N = 10 for Pb and Cd: n = 8 for other elements.
Source: Ajayi et al., (1992)

Table 6: Determination of Cd and Pb in Kontrolblut-1 by probe ETAAS.

	Concentration in µg/dm3		
	Probe ETAAS	Assigned concentration	
Element	Concentration	RSD(%)	
Cd	29±7	24.1	30
Pb	415±40	9.6	412

Source: Ajayi *et al.* (1992)

The probe system of atomization due to appreciable vapour temperature experienced by the atoms was able to minimize vapour phase interference. This is evident in the analysis of the three certified reference samples the indication of its analytical figures merit as close to the assigned values were determined for the elements (Ajayi *et al.*, 1992)

Chemical Technology Research.

In 1987, the erstwhile Leather Research Institute was renamed the National Research Institute for Chemical Technology with expanded mandate for research into chemical technology with leather inclusive. The researches undertaken included the production of hydrated lime and some other derivatives from limestone, production of alum from kaolin, evaluation of gypsum and a look into Nigerian Tobacco and cigarette products.

In order to produce hydrated lime from limestone, there was a need to build a calcination kiln. To accomplish this, refractory bricks had to be produced. The refractory brick was produced from kaolin and sawdust and the moulded blocks had to be calcined at high temperature. The pictures of the kiln along with the bricks and their raw materials and products are shown Plates 1 – 3.

Formerly, the Company was known as Nigeria Tobacco Company up to year 2000. The raw material was sourced locally throughout Nigeria. There used to be tobacco plantations located in Soba, Guma and other places nationwide where the raw materials were procured. Tobacco (*Nicotiana tabacum*) is an important raw material for the production of smoke-able cigarette and tobacco snuff. It was introduced from North America and has become a household plant. The leaves when harvested and cured are used in Tobacco Industries. The cultivation is nationwide and raw materials are obtained from plantations and local farming communities nationwide. The dried leaves were collected and analyzed along with the cigarette products both in Nigeria and overseas. The intention of this exercise was to evaluate the effect of fertilizer application on the raw material as well as the product. Inductively coupled plasma-mass spectrometer, a multi-element technique was employed in this exercise (Table 14).

ND = not detected or determined or below the detection limit.

Source: Oladipo *et al.* (1993)

From the Table 14 below, thirty elements were detected in measurable concentration in all these samples. The detection limit of the elements as measured in this instrument was very good in order of part per billion (p.p.b) or

It was observed that the concentration range of tobacco leaves was wider µg/ than that of the cigarette for each element. This could be attributed to the soil conditions; soil geology, fertilizer and pesticides applications. The difference between Nigerian cigarette and Egyptian product was not much in terms of metal contents except that the concentration of each metal was slightly higher than what obtained for the Egyptian's (Oladipo *et al.* 1993 and Ajayi, 2001). Other comparisons were made as reported by Oladipo *et al.* (1993).

Hydrometallurgy

Traditionally, metal smelting used to be through carbon reduction in smelting furnaces. However, with dwindling mineral resources, lean minerals from worked-out mines, rising energy cost and accompanying environmental problems from dusts and flue; the need to extract minerals through an economical process arose and hydrometallurgy came into the fore.

Table 13: XRF analysis of some limestone samples used in operation of WAPCO.

Parameter	LOC 1	LOC 2	LOC 3	LOC 4	LOC 5
Na_2O (%)	-	-	-	-	-
MgO (%)	0.46	0.50	-	1.47	0.74
Al_3O_3 (%)	0.69	0.78	0.61	1.30	0.74
SiO_2 (%)	3.15	9.44	5.38	6.21	6.24
SO_3 (%)	-	-	-	-	-
K_2O (%)	0.10	0.05	-	-	0.05
CaO (%)	51.02	47.91	53.42	50.93	50.04
Fe_2O_3 (%)	1.23	0.96	1.02	1.02	1.02
Purity (%)	91.20	85.55	95.39	90.94	89.36

Source: Ajayi and Dugbe (2004).

The purity of the limestone samples determined ranged between 85.55% and 95.39% for the assembly line stocks for the factory operation. Some of these stocks were obtained from the company's quarry while some came from other quarry such as Mfamosin in Akwa Ibom State. The recycled dust used as certified reference samples; DRPA, DRPB, DRPC and DRPD were being used during the period of gypsum importation ban of 1994 to 1999. The cost of transporting gypsum from Yobe, Gombe and Bauchi States was a hindrance to WAPCO operations during the period in questions hence the use of recycled dust.

Analysis of tobacco and cigarette

There are two Tobacco Processing Industries in Nigeria presently namely Nigeria-American Tobacco Company located in Ibadan and Zaria.

Plate 1: Calcination kiln with raw materials; sawdust and kaolin beside it.

Plate 2: Refractory bricks; fresh bricks (white), burn bricks (brown) along with raw materials; kaolin and sawdust.

Plate 3: Calcination kiln in operation at the National Research Institute for Chemical Technology, Zaria.

The calcination kiln using kerosene burner was able to attain a temperature up to 1200 °C that was sufficient to break down limestone to its desired product of quick lime and carbon dioxide. In 1998, when Numan Sugar Industry was about to be resuscitated, the industry approached the Institute (NARICT) to build a similar kiln in Numan to facilitate the production of hydrated lime in-house for its operation.

The production of hydrated lime involved the hydration of calcium oxide (CaO). Calcium oxide or quicklime is a product of calcination of limestone $CaCO_3$at high temperature and this was why a calcination kin was built using kaolin and sawdust as raw materials for production of refractory bricks. The reaction is highly exothermic and this was why the CaO is called quicklime.

$CaCO_3..CaO+CO_2$ ---5

$CaO+H_2O \rightarrow Ca(OH)_2$---------------------------------------6

Kaolin for making the bricks was obtained from Kankara in Katsina State. There was a need to know the chemical composition of this kaolin sources. Hence, the chemical analysis of the kaolin and its potential application as a raw material for alum production. This forms basis of the next discourse.

Analysis and potential application of kaolin as a raw material for alum production.

Kaolin is a silicate mineral of clay with chemical formula $Al_2(OH)_4[Si_2O_5]$. It is a white solid and this is formed by the decomposition of granite (Lee, 2008). It is a raw material for paper manufacturing as paper filler and as refractory.In 1992, about 22.5 million tonnes was produced annually worldwide with U. S. A. being responsible for 41% of production (Lee, 2008). Kaolin occurs nationwide with reported deposits in Katsina, Sokoto, Zamfara, Ondo and Ekiti States. In this exercise, Katsina deposits of Kankara, Batsari and two others were used. The kaolin samples were examined using a sample-nondestructive technique of x-ray fluorescence facility of the Centre for Energy Research and Training (CERT) of Ahmadu Bello University, Zaria. The samples were evaluated along with the certified reference material; Obsidian Rock 278. The results of the analysis are as shown in the Tables below.

The Reference samples used were gypsum dust being used for the quality assurance of the X-ray Analyzer Model QX XRF. The gypsum reference samples; DRPA, DRPB, DRPC and DRPD, had purity ranging between75.6% and 88.06% (Table 11). These samples were basically gypsum dust and were being used to complement the local gypsum during the period of ban on importation (1994 to 1999).

Table 11: Analysis of Recycled Dust Standard Reference Samples.

Parameter	DRPA	DRPB	DRPC	DRPD
Na_2O (%)	0.02	0.03	0.03	0.02
MgO (%)	0.68	0.68	0.68	0.54
Al_3O_3 (%)	2.30	2.35	2.30	1.15
SiO_2 (%)	9.95	10.0	9.90	3.85
SO_3 (%)	32.5	35.1	35.3	40.9
K_2O (%)	0.23	0.23	0.23	0.10
CaO (%)	31.2	31.1	31.1	31.3
Fe_2O_3 (%)	1.4	1.4	1.4	0.6
Purity (%)	75.7	75.6	76.0	88.06

Source: Ajayi and Dugbe (2004).

Table 12: Analysis of Gypsum samples.

Parameter	Bajoga	Gombe	Sokoto	Imported Gypsum	Thailand
Na_2O (%)	0.02	0.00	0.1	0.00	0.01
MgO (%)	0.54	0.56	0.54	0.57	0.60
Al_3O_3 (%)	1.55	1.56	1.19	0.14	0.81
SiO_2 (%)	3.85	5.08	4.00	0.37	2.68
SO_3 (%)	40.96	40.15	40.00	44.73	38.66
K_2O (%)	0.10	0.13	0.15	0.01	0.40
CaO (%)	31.30	29.45	30.20	32.36	33.61
Fe_2O_3 (%)	0.60	0.59	0.49	0.01	0.30
Purity (%)	88.08	86.32	86.0	96.17	83.12

Source: Ajayi and Dugbe (2004).

It was evident that the performances of the alum samples were at par with the commercial samples in the treatment of highly turbid tannery effluent.

Gypsum and limestone

Portland cement is one of the building materials used in construction industries. The raw materials for production of cement include limestone, calcite, marble, gypsum as clinker and clay to mention a few. The use of cement in the building industry dated back to the Roman Era when concrete consisting of broken stone with burnt limestone as binding medium (Kirk-Orthmer Enclyclopaedia, 1992, Microsoft Encarta, 2003). This form of construction material was called '*Opus Caementum*'. Later on, a term '*Cementum*' was used to denote that admixture of lime, brick dust and volcanic stuff (Austen, 1984, Stocchi, 1990, Kirk-Orthmer Encyclopedia., 1992). Evidences of cement usage can be found in various Roman architectures like 'The Pantheon'; a circular temple in Rome built in 120 A. D. (Stocchi, 1990,Kirk-Orthmer Encyclopedia., 1992, Microsoft Encarta, 2003). The development of cement over the ages was a continuous process until the present 'State-of-Art' product available today was accomplished. There are many patents of Portland Cement, a typical example being the German Standard DIN 1164 which defined cement as a finely ground hydraulic binding medium for mortar and concrete (Microsoft Encarta, 2003). This patent prescribed the constituents as compound of CaO and Fe_2O_3 formed by sintering or fusion (Microsoft Encarta, 2003). These components are usually derived from limestone, clay and gypsum. In this treatise, the analysis of limestone and gypsum is discussed. Limestone is chemically $CaCO_3$, occurring globally. Gypsum, $CaSO_4.2H_2O$ occur widely in Nigeria, particularly in Goronyo in Sokoto State, Ashaka, Bajoga and the environments in Gombe State and in Fika, Yobe State. Gypsum is used as clinker in cement industry. In 1994, the Federal Government of Nigeria banned the importation of gypsum as raw material in cement industries. This resulted in the use of local supply. Some of the local samples used formed the basis of this discourse. Analysis of gypsum samples from Gombe, Thailand, Goronyo, Bajoga, imported stock (IG) and Bauchi were analyzed using x-ray fluorescence facility of WAPCO Cement Industry, Shagamu (Table 12). Similarly, the limestone stock of this industry was also subjected to analysis. The concentrations of the detected elements certified reference samples as well as the real samples of gypsum and limestone were calculated as their respective oxides.

Table7: Result of X-Ray Fluorescence analysis of certified Reference Material Obsidian Rock 278.

Element	Certified value	This work	This work/Certified value
Si (%)	34.0	33.6	0.99
K (%)	3.44	3.98	1.16
Ca (%)	0.70	0.77	1.03
Ti (%)	0.15	0.17	1.13
V	15.0	14.9	0.99
Fe (%)	1.05	1.25	1.19
Co	1.50	1.68	1.22
Zn	55.0	73.4	1.33
Rb	127	123	0.97
Sr	63.5	62.2	0.95
Y	41.0	41.8	1.02
Zr	295	296	1.01

Concentration in $\mu g\ g^{-1}$ (ppm) unless otherwise stated

Source: Adesina *et al.* (2003).

The result shown for the analysis of this certified reference material (Obsidian Rock 278) showed good agreement between the certified values and what was obtained from this analysis. From this result, it is evident that the result obtained can be relied upon for accuracy, reproducibility and to some extent, precision.

Analysis of kaolin from these Katsina State deposits was similarly undertaken with XRF and the result is as shown in Table 8.

Table 8: Result of XRF analysis of Katsina Kaolin.

Element	Kaolin S1	Kaolin S2	Kaolin S3	Kaolin S4
K (%)	7.49	6.62	7.45	8.0
Ti (%)	<0.33	<0.34	<0.31	<0.38
V	54.7	64.0	45.5	61.0
Ca(%)	0.33	0.33	0.39	0.42
Fe(%)	0.10	0.19	0.14	0.14
Zn	95.50	90.10	89.30	90.0
Pb	84.50	70.0	139.0	174.0
Y	31.20	40.60	46.7	22.20
Rb	31.3	32.10	53.30	38.60
Zr	108.0	137.0	131.0	133.0
Sr	<15.7	93.50	40.0	37.30
Si(%)	14.70	17.30	15.30	14.90

Concentration in µg g^{-1} (ppm) unless otherwise stated

Source: Adesina *et al.* (2003).

The major components were silicon, potassium, iron and calcium. However, aluminium, a major element was not determined because the system was not calibrated for this element. The kaolin was eventually used in production of alum in the form of a double salt, $KAl(SO_4)_2.12H_2O$. Four approaches used were the preparation from kaolin, aluminium scraps, blend of kaolin with alumina and a blend of kaolin with aluminium scraps. The products obtained were analyzed for purity using classical methods and the result is as shown in

Table 9.

Table 9: XRF Analysis of alum products

Alum product	K (%)	Ca(%)	Si(%)	Sr	Zr
Kaolin	27.84	0.24	<11.65	-	-
Alumina: Kaolin (20:10)	14.96	-	<18.6	-	-
Scrap	8.28	0.44	<1.6	-	-
Kaolin: scraps(30:4)	12.50	0.049	<15.8	-	-
Commercial 1	-	-	-	-	-
Commercial 2	-	-	-	78.6	72.3

Concentration ~~in~~ µg/g (ppm) unless otherwise stated.

Source: Adesina *et al* (2002).

The in-house produced alums were basically double salt with potassium, silica and calcium as detectable elements, while the commercial product is aluminium sulphate with traces of strontium and zirconium. The best samples were obtained from blend of kaolin with either alumina or with scraps at ratio of 30:20 and 30:4 respectively. However, the use of kaolin should be restricted to its traditional application in paper and refractory industries.

When these products were used to treat high turbidity tannery effluent, the following parameters were compared; turbidity, alkalinity, pH and electrical conductivity. The results for 30 mg/l solution on 10 litres effluents are as shown in Table 10.

Table 10: Performance of alum preparation on treatment of highly turbid tannery effluent.

Sample	Turbidity	pH	Alkalinity (mg/l)	Conductivity (10^3 µmoh/cm^3)
Raw Effluent	468	3.15	300	4.5
Kaolin alum	461.01±0.3	3.63	206±3.9	2.3±0.2
Kaolin:alumina	460.4±0.35	3.58	246±6.0	2.3±0.3
Kaolin:scrap	463.3±0.33	3.55	188.6±7.4	2.33±0.2
Scrap alum	467.8±0.3	3.65	221±4.4	2.20±0.1
Commercial 1	551±0.54	3.59	212.2±4.4	2.61±0.3
Commercial 2	550±0.31	3.55	209.4±4.1	2.70±0.3

Source: Adesina et al. (2003b).