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ADVENTURES IN THE WORLD OF TRACE ELEMENTS

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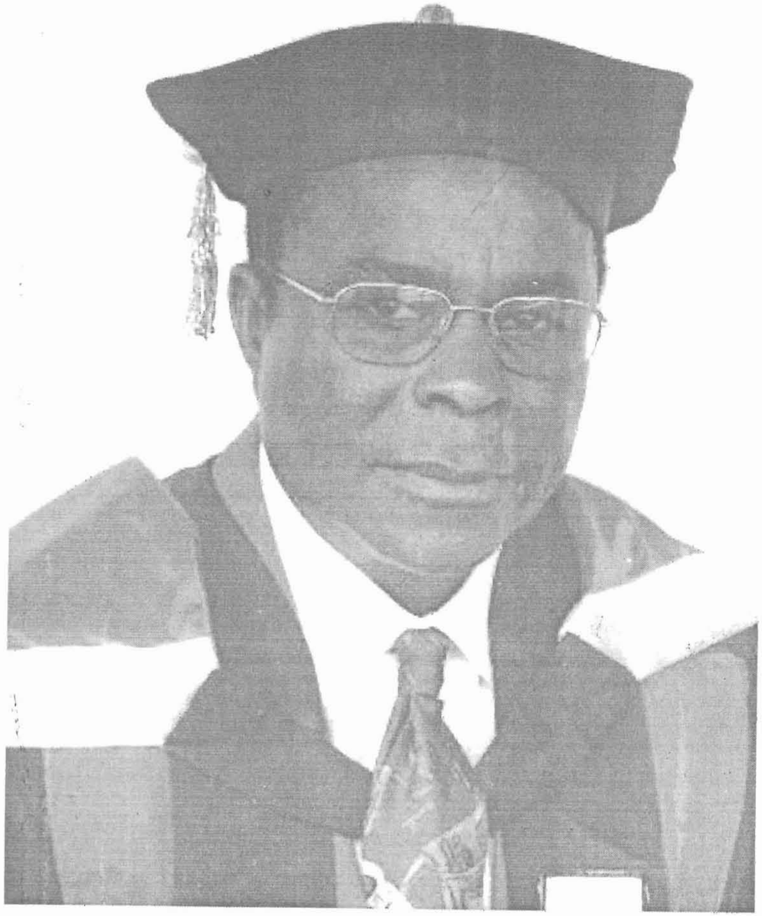

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1.0 INTRODUCTION

Mr. Vice Chancellor Sir, my fascination with chemistry started very early in my educational career – indeed in my third year in the secondary school when it was first introduced as a subject.

Two colourless liquids were mixed in a beaker, and a purple colour was produced instantly. To a young boy who had sometimes gone to the market place to watch "magicians" perform, this was another form of magic. The only difference was that, whereas the market place magician wanted me convinced of his magical powers, the chemistry teacher took great pains to explain that what he had just done was to produce a new substance, whose colour and other physical properties were quite different from the original two substances. My curiosity subsequently grew in this subject which appeared capable of unraveling what otherwise would be regarded as mysteries.

Basic chemistry teaches us that elements are the basic building blocks of matter. What distinguishes one substance from another are the nature and proportions of elements making up each of them. Thus while common table salt is composed of the elements Sodium and Chlorine in a 1:1 ratio, water is made up of the elements Hydrogen and Oxygen in a 2:1 atomic ratio.

The difference (s) between 2 substances could be even more subtle; a sample of water could be contaminated by some minute amounts of "foreign" substances (with their own different chemical compositions) which could make it unsafe for drinking. In the same fashion, while some countries like ours allow the use of gasoline to which some quantity of lead (in form of tetraethyl lead) has been added, other countries (e.g. the U.S.A.) do not allow the use of leaded gasoline, and this makes a lot of difference in the effects of the usage of the 2 gasoline types. From the above examples, it is evident that, in a lot of cases, it is really not the major components of materials that are crucial for our intended use(as these are usually well – known) but those elements which are present in minute quantities in the materials of interest, i.e trace elements. Incidentally, most of the 105 elements so far known, occur in trace quantities and hence are "trace elements".

I have spent the greater part of my research career investigating the nature, concentrations and implications of the occurrence of these trace elements in different parts of the Nigerian environment, including even parts of the human body. However, before presenting the results of my works, it would help to discuss the origin of elements in general, including their relative abundances in the universe.

1.1 Origin of the Elements

A discussion of the origin of the elements transcends conventional pure chemistry – it dovetails into the fields of cosmology and astrophysics. In actual fact, probing the origin of chemical elements is indeed probing into the origin of the universe itself.

According to the hot big bang theory (Lemeitre, 1927; Gamov 1946), the universe (including the sun and other planets) began in a state of unimaginably high density and temperature about 6 billion years ago. Under these conditions, the average kinetic energy of particles was so high that no other elements besides the lightest two- Hydrogen and Helium, could exist without dissociating immediately. Thus only Hydrogen and Helium were formed initially.

One second after the beginning, the temperature had cooled to about 10 billion degrees Centigrade at which point, some heavier elements could be stable. As the universe cooled, a point was reached, about 1-1.5 million years from the beginning, when the temperature was now low enough (a few thousand degrees Centigrade) for electrons and nuclei to combine to form neutral atoms of elements. Subsequently, heavier elements were formed through a series of fusion reactions starting with Hydrogen.

$${}^{1}_{1}H + {}^{1}_{0}n \longrightarrow {}^{2}_{1}H + {}^{0}_{0}\gamma$$

$${}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{3}_{1}H + {}^{1}_{1}H$$

$${}^{3}_{1}H + {}^{1}_{1}H \longrightarrow {}^{4}_{2}He + {}^{0}_{0}\gamma$$

$$3\,{}^{4}_{2}He \longrightarrow {}^{12}_{6}C$$

$${}^{12}_{6}C + {}^{4}_{2}He \longrightarrow {}^{16}_{8}C + {}^{0}_{0}\gamma$$

$${}^{12}_{6}C + {}^{16}_{8}C \longrightarrow {}^{28}_{14}Si + {}^{0}_{0}\gamma$$

e.t.c

As the various elements were formed, they combined in varying proportions to form different materials e.g sand, a combination of Silicon and Oxygen; table salt, a combination of Sodium and Chlorine; water, a combination of Hydrogen and Oxygen.

When the earth was first formed, its atmosphere was mainly Hydrogen with little quantities of Oxygen, Carbon and Nitrogen. Hydrogen then combined with Oxygen, Carbon and Nitrogen to form Water, Methane and Ammonia respectively. From these were simple organic molecules formed with the influence of ultraviolet radiation from the sun and electrical energy. 3.5 billion years ago these simple organic molecules started forming more complicated ones like amino acids, Ribonucleic acid (RNA) and Deoxyribonucleic acid (DNA) which constitute the molecular basis of life.

Ninety chemical elements have since been discovered in the substances that make up the crust and atmosphere of the earth. Fifteen more have been synthesized artificially by man. From these fundamental elements, all the compounds and mixtures that make up man's environment and indeed man himself were obtained by appropriate combinations.

1.2 Trace Elements – Essentiality and Toxicity

As the name implies, a trace element is one whose natural abundance in terrestrial samples is usually less than 0.01% or 100ppm. (Bowen, 1966; Laul 1979). Besides the major elements, viz C, H, N, O and some others classified as minor elements, viz:- Ca, Cl, K, Mg, P, and Na, all other elements are trace elements. With the exception of a few elements like F and Be, most trace elements are metals of high atomic weights (Atomic number > 23), hence they are usually referred to as "heavy metals". Thus

the 2 terms are usually used interchangeably and would be thus used in this lecture. However, it should be borne in mind that not all trace elements are heavy metals but most are.

In addition to the 3 essential macro elements Ca, P and Mg, some trace elements are essential for human and animal life. There are 14 such trace elements, viz:- Fe, I, Cu, Zn, Mn, Co, Se, Cr, Ni, Sn, Si, F, and V (WHO 1973). For example, Fe is needed for transporting Oxygen in blood, with its deficiency causing anaemia; I is a constituent of thyroid hormones and its deficiency in diet is responsible for goiter, while F deficiency leads to incidence of dental carries. All the other essential trace elements – as constituents of enzymes , hormones, vitamins, and other biological molecules, play one role or another in human and animal health at moderate concentrations. However, most of these trace elements become toxic at higher concentrations (albeit still in the ppm range). Some of them are toxic because of their interaction with Sulphur – containing biochemicals such as enzymes and proteins. For example, while Fe is needed in small amounts for Glutathione peroxidase, with its deficiency leading to endemic cardiomyopathy, it can cause damage to the nervous system at higher concentrations. Similarly, while small amounts of Ni are needed to produce red blood cells, long – term exposure to it causes decreased body weight, heart and liver damage and skin irritation. Thus it is evident that the margin between "essential" and 'toxic" could be very small (Underwood 1971; Miettinen, 1973). Nevertheless, there are a few elements which are generally considered toxic and not much is known about their essentiality. Key examples of these are Pb and Hg. Even moderate exposure to Pb adversely affects neuropsychological developments in children leading to decrease in Intelligence Quotient (Baghurst *et al,* 1992, 1995). High levels of exposure affect haemoglobin synthesis, cause kidney problems and chronic damage to the nervous system among other health problems, even in adults. Mercury has no known function in human biochemistry but causes damage to the brain and the central nervous system.

From the foregoing, the need to obtain reliable data on the levels of trace elements in different parts of the environment is apparent. I have thus devoted most of my research career to investigating trace element concentrations in different matrices from different parts of Nigeria, using state – of-the –art chemical analytical techniques.

2.0 My Own Works

2.1 Trace Elements in Geochemistry

As discussed earlier, the types of elements and their individual abundances in any sample provide a lot of information about the materials. In the case of rocks, Rare Earth Element (REE) abundance data are very useful indicators of their origin and mode of formation, in addition to aiding in mineral prospecting. This is because this group of elements are geochemically coherent and generally resistant to postmagmatic alterations (Haskin and Paster, 1979), Consequently, REE patterns can be used to distinguish one type of rock from another. However, in spite of this general resistance to the various rock alteration processes, REE abundances in rocks do show some dependence on their environment, and in some instances, they have been shown to be mobile (Humphris and Thompson, 1978). Thus, REE patterns of one type of rock in one area are not necessarily the same as in another area. In a nutshell, REE patterns of rocks are very useful

in characterizing rock types as well as providing information on whatever metamorphism may have taken place leading to any modifications in the original mineralogy of the rocks. This was the basis of my collaboration with some geology colleagues in embarking on a systematic study of Rare Earth and other trace element abundances and their patterns in different rocks types from different parts of Nigeria (Rahaman *et al*, 1983; Ajayi & Asubiojo, 1983; Asubiojo, Ajayi & Guinn 1984; Asubiojo, deLancey & Guinn 1985; Ajayi *et al*, 1989; Ige and Asubiojo, 1991; Asubiojo and Ige, 1992.)

For most of the rock types – amphibolites, gneisses, sandstones and limestones, the chondrite- normalized concentrations decrease progressively from Light Rare Earth Elements (LREE) to Heavy Rare Earth Elements (HREE). This progressive decrease from LREE to HREE is consistent with the geochemical coherence of REE. Conversely, the chondrite – normalized concentrations of the pegmatites and ultramafic rocks increase from LREE to MREE, and later decrease towards the HREE.

The 2 types of amphibolites have distinctly different REE patterns, with the Foliated Leucocratic Amphibolites (FLA) being very rich in LREE and low in HREE, resulting in high fractionation (La/Yb = 297), whereas the Massive Melanocratic Amphibolites (MMA) exhibit low fractionation (La/Yb = 5.6). The REE pattern of the FLA is characteristic of Island arc calc – alkaline rocks and the rather flat pattern for the MMA is characteristic of tholeiitic basalts (Cox *et al*, 1979; Shimokawa and Masuda, 1972).

The 2 types of gneisses (banded and granite) and the sedimentary sandstones have similar REE patterns with negative Eu anomalies. The banded gneisses have lower LREE and higher HREE concentrations than the granite gneisses resulting in a smaller La/Yb ratio for the former. This feature could thus serve as a fingerprint for distinguishing between the 2 types of gneisses.

From these features and others for the various rock types, we were able to provide valuable information on their origins and mode of formation. In addition, our works in this area provide the much – needed baseline data for REE patterns of Nigerian rocks for which there was virtually no previous data.

Our attention subsequently shifted to Nigerian crude oils whose sales account for over 80% of Nigeria's foreign exchange earnings. The study of trace element contents of crude oils, while providing information on the origin of the oils, is also very important from environmental, refining, and exploration considerations (Ball *et al.* 1951; Hitchon and Filby, 1984).

At one stage or another of the various processes of petroleum exploration, refining and marketing, parts of it are released into the environment in gaseous or liquid forms whose trace element contents could be toxic. Thus in order to make a meaningful assessment of the impact of these processes on the environment, it is important to know the trace element composition of the oils. In addition, some trace elements like Cu, As and Ni cause corrosion of the turbines and refining columns and also poison the catalysts used for cracking during petroleum refining. Information on the levels of these trace elements in the oils is thus important for incorporating removal procedures before the refining stage, if necessary. Finally, because trace elements are incorporated into oils in form of porphyrin complexes at the early stages of oil formation, absolute or relative values of these

elements in the oils provide very useful information on their origin. (Ball *et al*; Hitchon & Filby, 1984).

In view of the above, 40 crude oil samples from 10 different Nigerian Oil fields were analyzed for 39 elements and the results were subjected to statistical treatment to decipher the source of the oils (Oluwole *et al*; 1993; Nwachukwu *et al*, 1995).

From previous geochemical studies, there were 3 shades of opinion on the source of the Niger Delta oils. Two groups favoured one source rock but disagreed on which source – the Akata (Weber, 1987) or Agbada formation (Reed 1969; Lambert – Aikhionbare & Ibe, 1984). The third group favoured a combination of the Akata and Agbada source rocks (Ekweozor and Daukoru, 1984; Nwachukwu and Chukwuwa, 1986).

The results of our trace element studies show clearly that the oils belong to 2 major groups, with the 2 groups being fairly well correlated with each other, which tend to support the joint Akata and Agbada formation theory for the Niger Delta oils.

From refining and environmental impact considerations, the elements of interest are S, Ni, As and Sb. All of these elements were found to occur at very low concentrations in the oils confirming their environmental friendliness, which is why Nigerian Crude Oil is one of the most prefered crude oils in the world.

In addition to the crude oil and natural gas reserves of the Niger Delta, Nigeria is also endowed with huge reserves of about 30 – 40 billion barrels of bitumen in the southwestern part of Nigeria – the second largest deposit in the world. This important resource is under – exploited. However, it is a viable source of energy if properly refined. In recent times, elemental characterization of these bituminous sands and their associated fractions has also engaged our attention prior to full – scale exploitation (Adebiyi, Asubiojo & Ajayi; 2005; Adebiyi *et al*, 2005).

Unlike the crude oils, the Nigerian bituminous sands contain high concentrations of some elements of environmental pollution concern such as Vanadium, Chromium, Nickel, Copper, Zinc, Arsenic and Lead which would require careful monitoring during exploitation. However, cluster analysis of the elemental concentration data showed that, just like the crude oils, these bituminous reserves also originate from 2 closely related sources. In addition, the host soils, air, water and vegetation of the bituminous sands areas are currently being analyzed to provide baseline data preparatory to full exploitation of the bituminous deposits.

2.2 Environmental Pollution and Impact Assessment

Environmental protection has been one of the major global topical issues of our time. By 1972 when the United Nations organized its first International Conference in Stockholm, only about 10 countries, mostly in Europe and North America had specific agencies or government departments dealing with environmental matters. By 1992 when the second United Nations Conference on the Environment and Development (the Earth Summit) was held in Rio de Janeiro, more than 100 countries had established their own environmental agencies or ministries.

Nigeria is not left behind in this wind of environmental consciousness blowing across the globe, and a lot of my research efforts in the last 15 years have been devoted to addressing some

environmental problems in the country, using trace element data as tools.

Trace elements are of tremendous importance from environmental pollution considerations because, unlike their major and minor elements and their organic counterparts most of them (the heavy metals) are non – biodegradable, and hence persistent in the environment.

2.2.1 Air Pollution and Impact Assessment

The most obvious air pollution problem in Nigeria is atmospheric dust, so its baseline studies have received wider attention than other types of air pollutants.

There have been some reports of measured suspended particulate concentrations in some parts of the Nigerian environment (Beavington & Cawse, 1978; Simoneit *et al.,* 1988; Oluwande, 1977; Akeredolu, 1989). In the course of these studies, there had been some concern about the possibility of certain elements existing in toxic chemical forms in these particulates, and their eventual deposition in the lung could cause a variety of health problems. Hence we have carried out some detailed studies of the elemental concentrations and distribution patterns in atmospheric dust from both ambient and industrial settings in Nigeria.

Our first port of call was Harmattan dust which is prevalent in Nigeria between the December and February months. Atmospheric deposition samples collected over 3 harmattan seasons in Ile – Ife were analyzed for 29 major\ minor and trace elements (Asubiojo *et al* 1986, Adepetu *et al*, 1988). All the elements were found to follow the normal concentration patterns of regular soils.

Later, size – segregated suspended particulate samples of Harmattan dust were collected from lle-lfe and Kano. These were analyzed for 29 elements for comparison of their chemistry (Asubiojo *et al*, 1993). The total suspended particulate (TSP) concentration of the harmattan dust was much higher at Kano (1033mg/m^3) than lle-lfe (329mg/m^3) which explains the much poorer visibility at Kano during the period. The higher dust concentration at Kano leads to a corresponding increase in elemental concentrations(ng/m3 of air) at Kano than Ife. The weight/volume concentrations of most elements are also about 3 to 4 times higher than the corresponding ones in Ife, an indication that the chemical compositions of these dusts are similar. In fact, the calculated weight/weight elemental concentrations (in ug/g of dust), which are independent of the quantity of suspended particulates per unit volume of air, are virtually the same for Ife and Kano, confirming that there is not much difference (in terms of the chemistry) between harmattan dust at Kano and lle-lfe. Statistical analysis of the elemental concentrations showed strong correlation between the 2 sites. Thus, even though the 2 sites are about 2000km apart, harmattan dust at both sites have the same origin, confirming chemically what had been conjectured earlier that all harmattan dusts originate from the Faya Largeau area of the Chad basin (McTainsh, 1980). The higher concentration of the atmospheric dust at Kano is simply due to its closer proximity to the source of the dust.

Particle size studies of the dusts also show that the Kano dust is mainly coarse while that of Ife is mainly fine, the finer particles traveling farther from the source. However, the fact that more of the Ife dust is in the respirable fraction makes it potentially more dangerous from the health point of view.

My attention subsequently shifted to Lagos, the commercial and industrial capital of Nigeria. Suspended particulate matter is the most conspicuous form of air pollution in the city and it is desirable to develop effective control measures for its emissions. However, an important step in an air pollution control programme is the correct identification of the pollutants, the contributing sources, and the relative contribution of each source. Receptor modeling is very useful in this regard, and it was applied in our air pollution studies of the Lagos environment

The basic proposition of receptor models is that the properties of the airborne particulate matter can be used to infer their origins. These properties incl;ude particle size, shape and elemental distribution (Hopke, 1985; Albert & Hopke, 1980; Watson 1984; Gordon 1980, 1985). With this model, elemental concentrations at a receptor site are apportioned to different sources which contribute to the mass of total suspended particulates at the receptor site.

Size – segregated suspended particulate samples were collected daily for 3 regular (non – harmattan) months at 3 different sites, viz:- Ikeja, Yaba and Ikoyi in the Lagos metropolis (Oluyemi *et al*; 1994; Oluyemi & Asubiojo, 2001). The samples were analyzed for trace and some major/ minor elements.

There were no major differences in elemental composition of suspended particulate matter (SPM) at the 3 sites, apparently due to efficient mixing of SPM at the sampling levels (9m). These measurements of air particulate concentrations at heights of about 9 metre and above at any location in the metropolis is fairly representative of the airshed in the whole metropolis. Concentrations of Na, Al, Si, Cl, Ca, Ti and Fe are higher in the coarse fraction (1.5 - 10mm) while Mg, S, K, V, Mn, Co, Cu, Zn, Br and Pb are more concentrated in the fine, respirable fraction (<1.5mm). The elements in the former group except Cl, are usually associated with crustal sources while most of the elements in the latter group are usually associated with anthropogenic sources. This is reinforced by the results of the enrichment factors of the individual elements whereby V, Na, Cr, Zn, Cr, S, Cu, Br, Pb and Cl have high enrichment factors (E.F >10). Incidentally, with the exception of Na and Cl, these are the same elements which are more concentrated in the fine fraction, and which are associated with anthropogenic sources. The enrichment of Na and Cl is mainly due to sea – salt contributions because of the proximity of Lagos to the sea, a conjecture which is reinforced by the Na/Cl ratio which is almost 1 from each of the fractions.

From the receptor modelling of the elemental concentration data, 4 major sources were found to be contributors to the coarse fraction of the suspended particulates at all the sites. These are entrained soil (with Si, Al and Fe as the main components), Marine (with Na and Cl as the main components) vehicular exhaust (Pb and Br as the main components) and Traffic (Zn as the main component). For the fine fraction, there were 5 contributing sources, viz:- Soil (mainly, Si, Al and Fe), Marine (Na and Cl), oil combustion (mainly S), Incineration (S and K), Vehicular exhaust (mainly Pb and Br) and Traffic(solely Zn). Thus entrained soil, marine, vehicular exhaust and other traffic sources are common to both the fine and coarse fractions of the suspended particulates while incineration is peculiar to the fine fraction.

Silicon, Aluminium and Iron are understandably the major components of the entrained soil source as soil dust is mainly

made up of the oxides of these elements. Sodium and Chlorine are the elements making up sea – salt, hence they are the marker elements for marine contribution to the suspended particulates. Lead and Bromine are source signatures for vehicular exhaust because of the addition of tetraethyl lead as an anti – knock additive to gasoline in use in Nigeria. This, in combination with dibromoethylene in the additive, forms Lead Bromide which is emitted during gasoline combustion.

Atmospheric dust pollution in Lagos and Ile- Ife was investigated further from the stand point of vehicular traffic. As discussed above, Nigerian gasoline contains as much as 0.74g/litre of Lead, which is added as an antiknock additive. Combustion of such gasoline leads to emission of Lead into the atmosphere. This could have deleterious effects on the health of roadside workers such as traffic wardens, traders, street beggars, e.t.c.

As part of efforts to combat this problem, the concentrations of Lead, Bromine, Zinc and some other vehicle traffic – related elements in roadside air particulates, soil and human blood were determined in Lagos and Ile- Ife (Ogunsola *et al,* 1993 a,b,c). Lead, Bromine and Zinc were highly enriched in ambient air and roadside dust in both cities, with the enrichments being higher in Lagos, and the elemental concentrations being positively correlated with traffic density. Concentrations of the traffic related trace elements also decreased with soil depth. In addition, the mean concentration of Lead was significantly higher in the blood of Lagos traffic wardens (18.1± 6.4mg/dl) than Ile-Ife traffic wardens (10.2± 2.7mg/dl), in correspondence with the traffic densities in the 2 areas. There was no significant difference in the blood Lead levels of Ile- Ife traffic wardens and control subjects. However, the results for the Lagos traffic wardens give cause for concern because of the toxicity of Lead. Infact, studies have shown that there may be a loss of up to 2 Intelligence Quotient (IQ) points for a rise in blood level of 10-20mg/dl in young children (Baghurst *et al* 1992 a, b).

This work was recently extended to vegetation by determining Lead, Copper and Zinc levels in moss samples, *Barbula lambarenensis* along major and minor roads in Ile – Ife (Ogunfowokan *et al*, 2004). The concentrations of Lead (from gasoline additive) and Zinc (from tyre wear) were generally higher in the moss samples in high traffic than low traffic areas.

Beside vehicular traffic, another very important source of atmospheric pollution is the industrial sector. This sector also engaged our attention.

The most notorious industry from dust pollution considerations is the cement industry. In order to assess the level of pollution emanating from Nigerian cement factories, elemental characterization of suspended and settleable dust as well as actual soils within and in the neighbourhood of major cement factories in Nigeria were carried out (Asubiojo *et al*, 1991; Adejumo *et al* ,1994; Oluwole *et al*; 1994). As expected, cement – related elements such as Calcium (from the raw materials – limestone $CaCO_3$ and gypsum $CaSO_4$) were found to be highly enriched in the air particulate and settleable dust as well as in soils within and in the neighbourhoood of these factories. Infact, Calcium levels in particulate dust within and in the immediate neighbourhood of the factories were as much as a factor of 100 – 1000 higher than WHO, USEPA and Nigerian FMEnV limits, while the concentrations of some other elements were higher than standard

limits by as much as a factor of 20. The elemental concentrations also decrease sharply with depth from soil surface and taper off rapidly with distance from the factories. On the basis of these studies, recommendations for better dust control measures have been made to the managements of these factories.

Similar studies were also carried out in the neighbourhood of Lead – processing factories, as well as other industrial establishments in Lagos, Kaduna and Port Harcourt. The concentrations of Lead and some other associated elements in airborne particulates exceeded the USEPA and FMEnV permissible limits in the smelting areas of the factories thus exposing the workers to considerable health hazards such as nervous system disorder, kidney and gastro – intestinal problems. Significantly elevated levels of Lead were also found in the soils (365 – 10,300 mg/g) and vegetation (600- 1200mg/g) around the Lead smelting factories, compared to the WHO standards of 50mg/g and 0.3mg/g respectively.

2.2.2 Soil Pollution

The trace element status of soils in a particular area is very important from geochemical, micronutrient supply and environmental pollution considerations. Anomalous concentrations of some of them could constitute an expression of mineralization, inadequate amounts could result in micronutrient deficiency in the resident plants while excessive concentrations of others could be indicative of environmental pollution.

Our trace elements studies of soils have been mainly from the last perspective. Trace element pollution is more long – lasting in soils than air or water due to the relatively strong adsorption of many elements onto the humic and clay colloids in soils. The duration of contamination may be for hundreds and thousands of years in many cases, depending on the soil types and their physico – chemical properties (Alloway and Ayres. 1993). Unlike organic pollutants which will ultimately be decomposed. metals will remain metal atoms, although their speciation may change with time as the organic molecules binding them decompose or soil conditions change.

In order to make meaningful interpretations of anthropogenic contributions to trace element values, there is a need to establish their background concentrations locally, regionally and nationally. Background levels of trace elements of soils in parts of Europe, America and Asia abound in the literature (Adriano, 1992) but such data for African, nay Nigerian soils are very scanty. Thus we carried out a detailed trace element (and some major and minor element) characterization of 9 different soil types in the Ife – Ijesa area of southwestern Nigeria (Asubiojo and Okoya, 2005).

The concentrations of most of the trace elements in this area fall within the normal range for soils, with very few exceptions of Lead enrichment which was attributed to the use of leaded gasoline. Overall, soils in the area are still relatively free of any major contamination (at least from trace element perspectives) and the concentrations obtained can serve as reference levels for future soil studies in the area and elsewhere in the country.

In another vein, trace element studies of major cocoa – producing soils of Ondo state were also carried out (Akinnifesi, Asubiojo, Amusan, 2005). This was primarily to assess the effects of the application of Copper fungicides in Cocoa plantations on the soils of the area. As expected, Copper concentrations were found to be

much higher in the areas of fungicides application, although the levels were not in ranges which are considered toxic to plants. On the other hand, there were no clear-cut differences in the concentrations of the other trace elements in soils of the fungicide – treated and control areas. However, the organic matter contents of the soils of the fungicide treated areas increased, which is good for the health of the cocoa plantations. Earlier studies have shown that organically complexed Copper (Cu^{2+}) is bound very tightly, leading to low lability with consequent limited bioavailability (McBride, 1994). This is responsible for the relatively low negative impact of the application of the high Copper-containing fungicide on the cocoa plantations. On the negative side, the Copper fungicide residues caused a lowering of the Nitrogen (N) Phosphorous (P) and Potassium (K) concentrations of the soils, which might imply the need to apply N, P, K fertilizers to replenish the soils of these important soil nutrients.

2.2.3 Water Pollution and Impact Assessment Studies

Water is very essential for human existence — in fact not only human existence, but also for all animals and even plants. However, in spite of its importance, it still remains one of the cheapest commodities available, next only to air.

Perhaps because water is so cheap, occupying two – thirds of the earth's surface, it receives enormous environmental insults. All kinds of imaginable pollutants are washed down into water – the ultimate environmental sink, from a variety of sources such as industrial effluents, agricultural activities, domestic waste, leachates from solid waste dumps, e.t.c. Some of these discharges manifest in excessive levels of some trace elements which are injurious to health., With the importance of water to life and the role of trace elements earlier highlighted, I have spent considerable time investigating the concentrations and distributions of trace elements in Nigerian waters, including drinking waters, river waters, industrial and domestic wastewaters.

2.2.3.1 Drinking Waters

Apart from air and dietary intake, drinking water plays an important role in the bodily intake of trace elements. Drinking water supplies contain variable amounts of trace elements arising from the source, water treatment chemicals and corrosion of piping and solder.

Prior to our works, there was very little available information on the levels of toxic trace elements in drinking waters in Nigeria. The only recorded work was that of Kapu *et al* (1989) who determined Lead concentrations in tap water and well water in Zaria as 2.0mg/l and 0.9mg/l respectively.

With the recognition of the need for accurate data on trace element concentrations in drinking waters for proper assessment of the hazards associated with their intake, we sampled and analyzed drinking water samples from groundwater supplies (boreholes and shallow well), water treatment plants and public taps from over 300 stations distributed over major cities and towns in the southern part of Nigeria (Asubiojo *et al*, 1997; Nkono and Asubiojo 1998).

On the average, the levels of trace elements in the tap and groundwater samples from southern Nigeria satisfied the WHO standards. However there were individual violations of Cadmium, Chromium, Mercury and Selenium in some of the tap water

samples, and Selenium, Barium, Aluminium and Manganese in some of the borehole waters.

The higher than – normal levels of Cadmium in some of the tap water samples are due to corrosion of galvanized Iron storage tanks, those of Barium, Manganese and Aluminium are due to weathering of bedrock and soil into the groundwater, and high levels of Selenium and Mercury in some of the tap waters are due to contamination of the source water from agricultural wastes.

Even though the incidences of these violations are very few (e.g only 7% for Selenium, 1.2% for Cadmium, 2% for Manganese , 2% for Barium etc) they are still cause for concern because of their health implications. For example, high levels of Aluminium in drinking waters have been linked to Alzheimers disease (Craum 1990; Epstein 1990; Flaten 1990), Cadmium to Osteomalacia (Piotrowski and Coleman, 1980), Barium to cardiovascular problems (Kojola *et al*, 1978) and Mercury to central nervous system disorder (Tsuboki and Irukayama, 1972).

For further insight into the sources of trace elements in the drinking waters, our data were subjected to Principal Component Analysis (PCA). The result shows that 6 factors account for 70% of the total variance. Factor 1 contains As, Cd, Cr, Hg and Ni. This factor is due to anthropogenic sources from industrial effluents dumped into surface waters which are the sources of water for a lot of State Water Corporations (e.g Abesan, Iju in Lagos). Some of the Cr and Cd might also be from corrosion of pipes and plumbings. The dominant elements in factor 2 are Cu and Zn whose major source is galvanized Iron from storage tanks. The third factor is made up principally of Pb and Mn whose major source is not very clear but might be due to corrosion products from steel pipes used for external piping and solders used to join the pipes. The last 3 factors are apparently due to background sources of the elements in the source water.

The trace element data of the drinking waters were analyzed for seasonal variations. Ordinarily, metal concentrations in the public taps were expected to be higher during the wet season than the dry season due to increased runoff into the source waters. However, the reverse was the case. Most of the variations were small but marked differences (> 50%) were found for Cd, As, Ni, Cr and Zn which were all higher in the dry season. A possible explanation for this finding is that increased inflow of rainwater far outweighs the effects of wash – in of trace metal contaminations into the surface waters from runoff.

Seasonal variations in the groundwater (borehole) samples were opposite to those of the public tap waters which are sourced from surface waters. Most of the elements had relatively higher mean concentrations in the wet season than the dry season samples. This is most likely due to leaching from already weathered materials which is enhanced during the wet season.

It is usually not the total concentration of an element that is crucial from the toxicological point of view. Rather, what is most crucial is its speciation or actual chemical form. Thus we carried out a speciation study of some of the tap water samples.

The speciation analysis shows that 90% of the Zn in these samples exist in the chelex - labile form while Cu is evenly distributed between the chelex – labile and inert forms, in agreement with other studies which show that divalent Cu ions associate strongly and Zn ions relatively weakly with both organic matter and

colloidal Iron oxide (Sholkovitz, 1978). Most of the Cd (57.2% – 60%) and Pb (0.55% - 0.61%) exist in the chelex- labile fraction possibly as simple inorganic ions or simple complexes.

The health implications of these results are very clear. In general, the concentrations of Zn and Cu in these waters are relatively low hence they are not of toxicological interest. However for the toxic trace elements like Cd and Pb which are found predominantly in the chelex – labile fraction, even though their total concentrations too are quite low in these waters, they could still be toxic. At the pH of the stomach, Cd and Pb could exist as free metal ions and more available for absorption than the Cd and Pb in foodstuffs. The only remedy for this is replacing the existing galvanized tanks with other materials such as fibre – glass or high – density propylene containers.

2.2.3.2 Surface Waters

Surface waters (in form of lagoons, canals and regular rivers) are the most widely utilized of all water systems. They serve as a means of transportation in some areas, recipients of industrial sewage discharge, washing/ laundry, marine food source, and primary sources of drinking water in other areas.

There is growing evidence of trace element pollution of these waters worldwide as a result of increasing anthropogenic activities in and around these water systems (Kobayashi 1971; Salmons & Forstner, 1984; Murozumi *et al*, 1969; Ndiokwere & Guinn, 1983; Nriagu 1986; Nriagu, 1999).

Because of the importance of the Lagos lagoon to the residents of Lagos, Nigeria's commercial capital, we decided to study it in detail from trace element/chemical speciation perspective.(Nkono *et al*, 1999).

The Lagos lagoon waters were sampled at 15 different stations during the dry seasons of 1991/1992. The mean concentrations of most of the trace elements were more than 10 times (> 100 times in some cases) higher in the Lagos lagoon than world average values for unpolluted rivers. This is obviously due to anthropogenic activities in and around the lagoon from various sources. Average levels of Cd, Cr, Co, Mn, Pb, and Zn were significantly higher in the dry season than the wet season. This is attributed to high dilution of the water from an increase in runoff from roadside and adjoining rivers as a result of increase in influx of rainwater during the rainy season. The same increase in runoff into the lagoon during the rainy season is responsible for the higher Fe concentration in the rainy season, the runoffs being rich in suspended particulate load which is highly enriched with Iron oxides.

Multivariate statistical analysis (factor analysis) of the data identified 3 factors as being responsible for the sources of the trace elements in the lagoon . Factor 1 includes, among others, elements like Cr, Cu, Fe, Mn and Ni which most likely originate from metal processing industries in Lagos discharging their wastes (treated and untreated) through various canals and drains into the lagoon. This factor was then attributed to industrial/ domestic wastewaters. Factor 2 has high loadings in (among others) Ca, K, Li, Mg and Na (mostly major and minor elements) whose concentrations are normally much higher in seawater than continental water. This factor was thus attributed to seawater intrusion into the lagoon from the Atlantic Ocean. Factor 3 which

has loadings in Zn only, is attributed to surface runoff from tyre wear and galvanized roofing sheets being discharged directly into the lagoon from roadsides and canals, particularly during the rainy season. Over 90% of houses in Nigeria have galvanized iron sheets as roofing materials which corrode rapidly in the tropical weather particularly during the rainy season.

Most of the Fe, Mn, and Pb were found in the particulate fraction which is generally not available to marine organisms. On the other hand, Cu, Cd, and Zn were mainly in the soluble (chelex – labile) fraction which is generally bioavailable. This has significant health implications for consumers of fish from the lagoon waters. Cd is usually considered as one of the three (along with Hg and Pb) most dangerous trace elements in water. It is biopersistent, and once absorbed by an organism, remains resident in it for many years. Long – term exposure to it may lead to renal dysfunction, obstructive lung disease and even bone defects. Even though Cu is an essential element, it can cause anaemia, liver and kidney damage at high concentrations. Zinc too is also an essential element but its toxicity arises from its synergistic properties with very toxic elements like Hg and Cd. Studies have shown that presence of Zn in some aquatic organisms leads to greater accumulation of these highly toxic metals, with their attendant health complications.

2.2.3. Wastewaters

The input of trace metals from wastewaters, particularly from industrial processes, has been of much concern to regulatory agencies because of the possible ecological consequences around the discharge points as well as on the receiving waters. The first known case of metal poisoning from this type of source occurred in Minimata bay in Japan in 1953 when a factory using mercury compounds discharged its effluents into the surrounding river. This led to the death of many people who ate fish from the river (Inskip & Piotrówski, 1985). Since then, a lot of efforts have gone into enforcement of limits/ guidelines for toxic trace elements in wastewaters by regulatory agencies such as the United States Environmental Protection Agency (USEPA).

With the issuance of guidelines/ limits on trace elements discharge from industrial wastewaters in Nigeria by the Federal Environmental Protection Agency (FEPA, 1991) it became important to identify major point sources and determine the levels of trace metals in them.

In Lagos, the industrial capital of Nigeria, raw or partially treated effluents from industries and wastewater treatment facilities containing some of these metals are discharged into surface waters either directly or indirectly through canals. The city thus became the logical choice of our study of trace elements in wastewaters (Nkono & Asubiojo, 1999). Wastewater effluents from auto – battery, metal works, paints and textile factories were studied. In addition, samples were collected from a central industrial wastewater treatment plant and some small domestic sewage treatment plants.

As expected, the trend of mean trace element concentrations followed the order: Metal works > Auto Battery > Paints > Textile > Ikeja Central Treatment Works H" Domestic Sewage Treatment Works.

Iron and Mn were particularly high in the metal works plants. The mean concentrations of these metals were 101,400mg/l and 5,740mg/l respectively, compared to the FMEnV effluent limits

of 20mg/l and 5mg/l respectively. This is because the raw materials in these industries are composed mainly of Fe and its alloys, and apparently very little treatment of the effluents is carried out before discharge. Although Fe is not classified as a toxic metal, its concentration and chemical form can influence the speciation of Pb (a very toxic metal) and hence its toxicity. Fe and Mn normally act as scavengers, due to their tendency to form colloidal particulate hydrous oxides (Stumm & Morgan, 1970; Mill, 1980) which have strong adsorption affinities for certain metals like Pb and Cd (Gadde & Laitinen, 1974). In this way dissolved Pb can be transferred onto the particulate phase, hence becoming less bioavailable and mobile.

The mean value of Pb in the battery effluent was 3770ug/l which exceeded the FMEnV specific metal limit for auto battery effluents by over 400-fold. The high Pb level at this plant is because the main operations are secondary smelting of Lead and the fabrication of Lead batteries. Other elements with higher – than normal values in this effluent are Fe, Ni, As, and Cd. Ni and Cd are minor components of Lead alloys.

Effluents from the Paints and Textiles industries were relatively low in trace metal concentrations. In the Paints industries, the production process involves mainly organic reagents with very little additions of inorganic pigments like lithophone (a mixture of ZnS and $BaSO_4$) which is responsible for the fairly high levels of Ba (270mg/l) and Zn (127mg/l) in the effluents.

Similarly, in the Textile industries, the only processes involving substantial trace element involvement are the dyeing and printing processes which discharge much less wastewater than the main processes of desizing, scouring, mercerizing, bleaching and finishing which utilize mainly organic compounds with minimal trace element contents. Pollutants of major concern in the Paints and Textiles industries are organic in nature and generally biodegradable and hence less toxic.

Trace element concentrations of the Domestic Sewage Treatment wastewaters were very low. This is due to a combination of factors, viz normally low trace element concentrations of domestic wastewaters, dilution of the domestic wastes with storm water runoffs, and sedimentation of the particulate fraction of the wastewaters prior to reaching the treatment plants, and effectiveness of the sewage treatment plants themselves.

Similarly, effluents from the Central Industrial Treatment plant of Ikeja Industrial estate are also very low in trace element concentrations. This facility collects mainly industrial effluents from sewers in the Ikeja Industrial estate. The volume ratio of effluents from the metal processing industries compared to other industries (breweries, food processing, textiles, etc) is usually very low, hence there is a dilution of effluents with high metal concentrations as they move towards the wastewater treatment facility. This factor coupled with flocculation treatment at the plant, leads to much reduced heavy metal concentration of the final effluents. The government of the old Western region of Nigeria deserves commendation for its foresight in putting in place this central wastewater treatment plant which reduces considerably the environmental burden due to the many industries in the area.

Industrial wastewater treatment

Having determined the types and concentrations of trace elements in Nigerian Industrial wastewaters, we felt it was not enough to just identify the problem without looking for solutions. Thus studies were carried out at proffering solutions to the problem.

There is a lot of existing data in the literature on methods of heavy metal removal from industrial wastewaters. Among these are Chemical precipitation (Anderson *et al* 1973; Ajayi 1978), Electrodeposition (Peter *et al*, 1976), Cementation (Gould *et al*, 1986), Ultrafiltration or reverse Osmosis (Winfield, 1979), Ion exchange (Vogel, 1962), Activated Carbon Adsorption (Patterson, 1975), e.t.c. However, these methods are all expensive and may not be affordable for many Nigerian industrial concerns, especially with the large volumes of wastewaters they generate. There was thus the need to devise equally or almost equally efficient but cheap methods of industrial wastewater treatment.

Some workers had reported on the use of natural adsorbents for removal of heavy metals from laboratory – made solutions of heavy metals (Okiemen *et al*, 1986; Krishnan *et al*, 1987; Al – Hashimi *et al* 1992). We explored the efficacy of this relatively cheap technique for removing heavy metals from the large volumes of industrial wastewaters. The use of locally available plant material such as paddy husk, corn cob, wheat bran, peanut skin as well as human hair as scavengers of heavy metals from real – life industrial wastewaters from some industries in Lagos was investigated. All the plant materials and human hair investigated are good scavengers of heavy metals from industrial wastewaters, with overall mean percentage removal of 87.6% - 92.2%

(Asubiojo & Ajelabi; 2001). They are as good, if not better than some of the conventional expensive commercial materials currently used for industrial wastewater treatment. Their mechanism of action was proposed to be similar to the top – of – the –line commercial Ion Exchange Resins and they can thus be used as cost-effective scavengers of heavy metals from industrial wastewaters.

2.3 Trace Elements in Biology and Medicine

Mr. Vice Chancellor Sir, I have reported on some of my trace element studies in rocks, crude oils, soils, plants, air and water – essentially covering all parts of the Nigerian ecosystem. This audience might be wondering; how about Trace Elements in Biology and Medicine? I hasten to report Sir, that these too were not left out in my studies.

The importance of trace elements in human and animal nutrition has been widely documented in the literature (Underwood 1971; WHO 1973, Bowen 1979). As reported earlier in this lecture, while some elements such as Cobalt, Chromium , Iron, Manganese, Molybdenum, Nickel, Selenium, Tin, Vanadium and Zinc in moderate concentrations are essential for growth, elevated levels of most elements, including these essential ones, can cause morphological abnormalities, stunted growth, increased mortality and mutagenic effects in humans (Pier & Bang, 1980). In view of these, biological and medical applications were not left out in my "Adventures in the world of trace elements".

Nature provides the required amounts of trace elements needed by infants through breast milk. However, it has become a status symbol in Nigeria and some other developing countries to subject

infants to commercial milk and cereal formulas in place of mother's milk. It thus became necessary at some point to investigate the adequacy (or lack of it) from trace element considerations. of the commercial milk and cereal formulas as well as a locally grown cereal(Guinea Corn) which is also widely in use for infant feeding in Nigeria.

A total of 17 trace elements were determined in the infant milk and cereal formulas and the locally grown cereal (Asubiojo and Iskander. 1988). The commercial milk formulas were found to contain adequate amounts (from WHO standards) of most of the essential trace elements but the cereal formula is deficient in Iron. The locally grown cereal (Guinea corn) is adequate in some but deficient in other essential elements such as Calcium and Iron. The Iron deficiency is worthy of note because of its important role for oxygen transportation in blood. However, the adequacy of Guinea Corn for supply of some essential elements is also noteworthy as it is used only as a supplement to regular breast feeding among the low income group. Among this group, breast milk would take care of those essential trace elements in which the local cereal is deficient.

In the area of human health, Sickle Cell Anaemia (SCA) is the commonest inherited hemoglobinopathy of clinical importance among the black race. It is particularly common in Nigeria, where it affects about 2% of the population. With the well established role of trace elements in health and disease (Prasad, 1976) and some inconclusive reports on the role of some trace elements in North America and West African SCA patients (Brewer *et al*, 1974; Prasad *et al* 1975; Olatunbosun *et al* 1977), we felt that detailed trace element study on Nigerian SCA patients and control subjects could provide some useful information in efforts to combat the disease.

Besides human blood which sampling has some socio-cultural constraints, hair and nail have been found to be very useful in the study of trace element accumulation in the body because both are keratinized tissues with low metabolic turnover. Hair in particular has been shown to be a reliable and atraumatic method of assessing trace element stores (Strain *et al,* 1966; Othman and Spyrou, 1979). Hence hair and fingernails of some Nigerian SCA patients and control subjects were analyzed for trace elements (Oluwole, Asubiojo, Adekile, 1990; Ojo, Oluwole, Asubiojo & Adekile, 1992). The results were subjected to rigorous statistical treatment for possible correlation between specific or a group of elements and the genotypes as well as between different tissues. Among the results obtained was that, while many elements (Na, Co, Cu, Br, and Cr) were positively correlated across both hair and nails for control groups, they were essentially negatively correlated for the sickle cell group. This indicates some disorder in trace element metabolism in the sickle cell group resulting in some elements trying to replace others that are probably deficient or somehow unavailable. This work has since been continued by analyzing whole blood, plasma and erythrocytes of blood of SCA patients compared with regular patients and controls (Ojo, Oluwole, Durosinmi & Asubiojo, 1996). It was found that there were much closer regulations of elemental ratios in the SCA patients compared to the control subjects. While the implications of these findings are not very clear at the present time, they nevertheless provide useful background knowledge on this subject, and further work along this line could be useful in efforts on the management of affective disorders.

3.0 Recommendations

It is customary on an occasion of this nature, to make some recommendations based on one's experience and findings. Such recommendations have indeed been incorporated in the appropriate sections of this lecture, hence they will only be itemized here for ease of reference.

1. Our analyses of Nigerian air particulates, roadside dust and vegetation revealed anomalously high levels of Lead in some parts of the Nigerian atmospheric environment, which is attributed to the wide use of leaded gasoline in the country. In order to prevent or at least reduce the adverse health effects of Lead inhalation, particularly on roadside workers, the Federal government is being urged to phase out the use of leaded gasoline in the country. Also, the various Lead smelting and battery manufacturing factories should be made to install better air pollution control devices to reduce the level of Lead exposure of their workers, as well as the level of Lead emissions into the surrounding environment.

2. In view of the fact that some of the violations of heavy metal concentrations in Nigerian drinking waters arise from corrosion of galvanized iron storage tanks, it is recommended that, where these are still being used, they should be replaced with fibre – glass or high – density polypropylene containers which are more heavy metal friendly.

3. Indiscriminate discharge of industrial and domestic wastes into the Lagos lagoon has been implicated as the major

source of the anomalously high concentrations of some heavy metals in the lagoon waters. Some of these toxic heavy metals are in bioavailable forms to aquatic organisms, some of which are consumed by the local populace. The Lagos state government is thus being advised to devise some means of controlling the indiscriminate discharge of untreated industrial and domestic waste into the lagoon via the adjoining canals and streams.

4. The central industrial wastewater treatment plant at Ikeja Industrial Estate was found to be doing a good job of considerably reducing the levels of heavy metals being discharged from the various industries in this estate into the neighbouring aquatic environment. While the old Western region government of Nigeria is being commended for its foresight in putting this treatment plant in place, such treatment plants are being recommended for all other major estates in existence or being proposed anywhere in the country.

5. As a result of the proven effectiveness of some locally available plant materials and even human hair for heavy metals removal from industrial wastewaters, these materials are being recommended to small and medium – scale industrial establishments as a cost – effective method of heavy metals removal from their wastewaters prior to discharge into the environment.

6. Exploitation of the large deposits of Nigerian bituminous sands is bound to commence in the near future. However, in view of the high concentration of some toxic trace

elements in these deposits, they would have to be closely monitored during exploitation of the bituminous sands.

4.0 Concluding Remarks

Mr. Vice Chancellor Sir, the 3 main functions of an academic are Teaching , Research, and Service to the community.

In the first area, I have taught many generations of students, some of whom, in addition to the Chemistry graduates, have gone on to specialize in fields as diverse as Agriculture, Education, Engineering, Pharmacy, Medicine and allied disciplines. Quite a few of such former students are even in this audience today as Professors and lecturers in their different disciplines. I am proud to say that I teach in virtually all branches of Chemistry, be it Physical, Inorganic, Organic, Analytical, and even Nuclear – thanks to the broad and sound training that I received as an undergraduate here at O.A.U and at that world - renowned University, Stanford University, as a graduate student. I have a basic Organic Chemistry text in press, and I am currently co-authoring another for use at Secondary school level.

My research exploits have constituted the main subject of this lecture. It is significant to note however, that my research career did not actually start in the area of Applied Analytical Chemistry of which Trace element research is a part. My doctorate research was in the field of "Organic Reaction Mechanisms in the Gas Phase" where I co- authored 4 top –of-the-line papers with my supervisor (Asubiojo, Blair & Brauman, 1975; Asubiojo *et al*, 1977; Asubiojo, Brauman &Levin 1977; Asubiojo & Brauman, 1979). With the advent of the Nigerian nuclear programme in the late 1970's of which O.A.U was declared a Centre of excellence, the University authorities, through Prof. Oluwole, who was then the Director of the Nuclear Technology programme, asked me to undergo postdoctoral training in the field of Nuclear & Radiochemistry and applications. This launched me into the area of Applied Analytical Chemistry with the use of nuclear- and atomic- based techniques for most of my work, in collaboration with Prof. Oluwole. In the course of my research activities, I have co-authored a monograph in addition to several journal articles and refereed Conference proceedings. I have supervised 4 doctoral and 4 masters graduates and I am currently supervising another 4 doctoral and 2 masters students.

In the area of administration and service, I have served a 3 year - term as Head of Department in addition to serving in various committees at Departmental, Faculty and University – wide levels. Indeed, I have served on the highest decision-making body of the University – the University Governing Council. Outside of the University, I have contributed my own quota in various forms at local, state and national levels, serving as a resource person, as well as providing environmental consultancy services to various industries and government agencies.

Mr. Vice Chancellor Sir, from the totality of my contributions in these designated functions of an academic, I am satisfied that even if I quit the stage today —— I have paid my dues.

Mr. Vice Chancellor Sir, distinguished ladies and gentlemen, I thank you all for listening to my various 'Adventures in the World of Trace Elements'.

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