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**BIOMARKER FINGERPRINTING
ANALYSIS:**
AN ANTIDOTE TO POLLUTANTS GENERATED
FROM INDUSTRIAL ACTIVITY

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ANALYSIS:**

*An Antidote to Pollutants Generated from
Industrial Activity*

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BY

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BIOMARKER FINGERPRINTING ANALYSIS: AN ANTIDOTE TO POLLUTANTS GENERATED FROM INDUSTRIAL ACTIVITY

The Vice-Chancellor, Deputy Vice-Chancellor, Registrar and other Principal Officers, Dean of Faculty of Pure and Applied Sciences and other Deans present, Learned Colleagues, Beloved Students, Gentlemen of the Press, Distinguished Ladies and Gentlemen.

Introduction

I feel strongly delighted and privileged to stand before this distinguished audience to deliver the 5th Inaugural lecture of our great university. I quite appreciate the willingness of the Vice-Chancellor to grant my request to present today's lecture, which indeed is the first from the Department of Pure and Applied Chemistry and the second from the Faculty of Pure and Applied Sciences. In the course of this lecture, I will be sharing with you some of the significant breakthroughs and challenges faced in my research goals to date. My focus however shall primarily be on my research orientation and findings in my chosen profession, which is in the field of industrial and environmental chemistry.

My topic is: **Biomarker-Fingerprinting Analysis: An Antidote to Pollutants Generated from Industrial Activity.** Pollutants are no less than the "inevitable disease" of any industrial sector worldwide and as such demand urgent attention to secure their cure. As with most dreadful human diseases like HIV/AIDS, which claims millions of human lives, no effective antidote has been proffered to eradicate them. This lecture identifies and recommends biomarker-fingerprinting analysis as an antidote to pollutants generated from industrial sectors. The oil spill fingerprinting and environmental monitoring of polluting substances can be subdivided into two major categories: first, chemical/analytical methods, which entail quantitative statements for chemical compounds concentrations and characterisation; secondly, ecotoxicological methods (biotests, markers, sensus), which involve integrated statements about the concentration and effects of the polluting substances. Therefore, biomarker-fingerprinting analysis (BFA) is an interactive process, which combines both methods. The methods involved have been widely used to identify toxicologically relevant organic and inorganic pollutants in environmental samples. BFA also helps to gain an insight into the chemical nature of petroleum and coals for more efficient processing of these minerals for industrial development.

There are numerous oil fields in the Niger Delta (Ughelli, Kokori and Otorugo), which make a significant contribution to

Nigeria's crude oil output. Also, there are various coalmines in places like Enugu and Plateau states as well as bitumen deposit in Agbabu area of Ondo State, which also contribute to Nigerian economy. Exploration and processing of these minerals have impacted negatively on the people and economy of these areas. Periodical spills have resulted in destruction of farmlands, rubber plantations and aquatic biota, thereby undermining the rural economy and leaving the people of these areas unemployed. Also, as a result of pollution of streams and rivers by crude oil and petroleum-like materials, mainly resulting from lapses of oil producing companies, the fishery resources of many rivers have been decimated. This has rendered fishermen jobless and they have had to migrate to cities in search of jobs, thereby worsening social problems in these towns.

Source Identification of Pollutants using Biomarker Fingerprinting Technique

Crude oil contains primarily carbon and hydrogen, but also contains smaller amount of nitrogen, sulphur and oxygen as well as metals such as nickel, vanadium and iron. The infinitely variable nature of these factors results in distinct chemical differences between oils. Because of dissimilarities in the characteristics of crude oil feed stocks and variation in refinery processes, petroleum and refined oils and petroleum products, to some extent,

have chemical compositions that differ from each other. This variability in chemical compositions results in unique chemical "fingerprint" for each oil and provides a basis for identifying the source(s) of spilled oil.

Biomarker fingerprinting has historically been used by petroleum geochemists in the characterisation of marine oils in terms of source rock, genetic family, migration and maturation properties and in identification of petroleum deposits. Chemical analysis of source-characteristic and environmentally persistent biomarkers generates information of great importance in determining the source of spilled oil, differentiating oils, monitoring the degradation process and weathering state of oils under a wide variety of conditions. In the past decade, use of biomarker fingerprinting techniques to study spilled oils has greatly increased, and biomarker parameters have been playing a prominent role in almost all oil spill work.

A wide variety of instrumental and non-instrumental techniques are currently used in the analysis of oil hydrocarbons, which include gas chromatography (GC), gas chromatography-mass spectrometry (GC/MS), high performance liquid chromatography (HPLC), size exclusion HPLC, infrared spectroscopy (IR), thin layer chromatography (TLC), ultraviolet (UV) and fluorescence spectroscopy, isotope ratio mass spectrometry, nuclear magnetic resonance spectroscopy (Wang *et al.*, 1999a). Of all these, GC techniques are the most widely

used and have been enhanced by more sophisticated analytical techniques, such as GC/MS, which is capable of analysing the oil-specific biomarker compounds and polycyclic aromatic hydrocarbons. Several reviews (Sauer and Boehm, 1995; Krahn, *et al.*, 1993; Whittaker *et al.*, 1995; Kaplan *et al.*, 1997; Wang *et al.* 1999a; Stout *et al.*, 2002) have been published on the analytical methodologies for characterisation and identification of oil hydrocarbons using various analytical techniques.

Depending on chemical/physical information needed, the point of application and the level of analytical detail, the methods used for oil spill study can be, in general, divided into two categories; non-specific methods and specific methods for detailed component analysis. In the non-specific methods such as the US EPA methods 1614 and 418.1, only groups or fractions of chemical hydrocarbons such as measurement of total petroleum hydrocarbons (TPH) and EPA priority PAHs -are determined.

In response to the oil spill identification need and specific site investigation needs, attention has been focused on the development of flexible, tiered analytical approaches which facilitate the detailed compositional analysis by GC/MS, GC-FID and other analytical techniques that determine a broad range of individual petroleum hydrocarbons. A variety of diagnostic ratios, especially ratios of PAH and biomarker compounds, for interpreting chemical data from oil spills have been proposed for

oil source identification and monitoring of weathering and biological degradation processes in some of my research activities as shall be seen in the latter part of this presentation.

Effects of Weathering on Oil Hydrocarbon Fingerprinting

When crude oil or petroleum products are accidentally released to the environment, they are immediately subject to a wide variety of weathering process (Jordan and Payne, 1980). These weathering processes can include evaporation, dissolution, microbial degradation and other processes such as dispersion and water-oil emulsification, photooxidation, adsorption onto suspended particulate materials and oil-mineral aggregation. Weathering causes considerable changes in the chemical and physical properties of spilled oils. The degree (lightly, moderately, or highly weathered) and rate of weathering is different for each spill and is controlled by a number of spill conditions and natural processes such as type of the spilled oil, spill site and environmental condition as well as microbiological activities. Major chemical compositional changes due to weathering can be measured with IR, GC, ED-XRF (for multielemental analysis) as demonstrated in the course of my research activities, which shall be treated at the latter part of this presentation.

Heavy Metals and Persistent Organic Compounds

Contamination of heavy metals in the environment is of major concern because of their toxicity and threat to human life and the environment (Purves, 1985). Anthropogenic and natural sources led to an increasing input of heavy metals into the biosphere. Anthropogenic sources of heavy metals include industrial wastes (Gibson and Farmer, 1983); automobile emissions (Fergusson *et al*, 1980); mining activity (Culbard and Johnson, 1984) and agricultural practice (Colbourn and Thornton, 1978); while geochemical sources are the main natural source of heavy metals in the environment.

The insidious accumulation of heavy metals over large areas and long periods, resulting in slow damage to living organisms, necessitates careful monitoring of the input, movements and effects of such pollutants in the environment. Atmospheric heavy metal pollution has been monitored with the method of bioindication, using plants as biomonitors. Plants are sensitive to environmental conditions and their element compositions actively respond to changes in the state of the environment (Vtorova, 1991; Kabata-Pendias and Pendias, 1989). Bioindicators offer the possibility to trace the emission and deposition of individual heavy metals, even for large-scale areas (Moriarty, 1988). They also allow the tracing of point source emitter as well

as following long-distance transport of individual metals (Steinness, 1993). Plant organisms like mosses have been used regularly and successfully as bioindicators for monitoring the emission, atmospheric transportation and deposition of heavy metals over wide areas because of their morphological and physiological properties (Frost, 1990).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent organic pollutants, and have been identified as important pollutants in the environment and could cause significant environmental risk (Menzie, 1992). Polycyclic aromatic hydrocarbons released into the environment arise mainly from anthropogenic sources. They are mainly formed as bi-products of incomplete combustion of organic materials. PAHs have been identified in many emission sources, such as vehicle exhausts, power plants, chemical-, coke-, oil shale industries and urban sewage. Primary natural sources of PAHs are forest fires and volcanic activity (Shabad and Ilitskii, 1979). PAHs are important environmentally because many individual PAHs are genotoxic (White *et al*, 1998) and many cause mutations and certain types of cancer. PAHs are quite resistant to degradation and when the release of PAH into the environment exceeds their degradation capacity, a significant accumulation of PAH is observed in the environment. The existence of permanent pollution sources results in the accumulation of PAH in the soil, sediments, plants and water bodies.

Porphyryns and metalloporphyryns are another class of compounds that are persistent in geological samples, such as coal, petroleum and bitumen. Owing to the development of geoporphyry separation and characterisation techniques and to the progress of the knowledge on their origins, these biomarkers are increasingly used by geochemists as indicators of sediment maturity, in the determination of the deposition conditions and in oil-oil and oil-source rock correlations (Barwise and Park, 1983). Furthermore, the presence of these porphyry complexes, mainly vanadyl and nickel derivatives, in the crude oils and other geological samples, is of importance in the further processing of oils or their derivatives. Indeed, vanadium traces can damage the catalysts used during the hydrotreatment operation of heavy oil fractions (Baker, 1969; Filby, 1975 and 1982).

My Research Interests and Findings

Oil, refined products and pyrogenic hydrocarbons are the most frequently discovered contaminants in the environment. To effectively determine the fate of spilled oil in the environment and to successfully identify source(s) of spilled oil and petroleum products, development of oil hydrocarbon fingerprinting and identification techniques is extremely important in many oil related environmental studies and liability cases. Crude oil and petroleum products possess high social and economic significance. The characterisation and determination of the

chemical composition and physicochemical properties of these products are major analytical challenges. The extremely high complexity of these products calls for the use of various analytical techniques, including chromatographies (GC, HPLC), spectroscopies (IR, UV, NMR, MS), specific tests and empirical measurements of physical and chemical properties of interest.

Mr. Vice-Chancellor, sir, my research focus in the past 16 years has been geared towards detailed characterisation and compositional analysis of Nigerian crude oils and their products using various spectroscopic analytical techniques, for planning the most effective utilisation of these fractions as feedstock in petrochemical industry. Impact assessment of organic and inorganic polluting substances in environmental samples (soil, water, sediments etc) was also investigated. Accordingly, my research activities and programmes are organised around two interrelated topics, with the following specific areas:

1. Structural Characterisation of Nigerian crude oils and their products together with coal-porphyrins, using a combination of spectroscopic analytical techniques.
2. Analysis of organic and inorganic pollutants in environmental samples.

At this juncture, I wish to humbly present a synopsis of my noteworthy contributions to knowledge in my chosen field of research.

Petroleum and Coal

Both petroleum and coal originate predominantly from organisms of the plant kingdom and both are subject to the same geological processes of bacteria action, burial, compaction and geothermal heating that constitute diagenesis and catagenesis (Tissot and Welte, 1978). There are however, some essential differences between the mode of coal and petroleum formation. Basically, coal is found at its site of deposition as solid and relatively pure massive organic substances whereas petroleum is liquid and migrates readily from its place of origin into porous reservoir rocks. Both minerals contain, in varying proportions, carbon and hydrogen as major elements, with small percentages of nitrogen, sulfur and oxygen and trace elements.

As part of a policy of controlling discharges of oil at sea, it is necessary to be able to prove that a particular oil slick or deposit was caused by one of several possible tankers, cargo ships, offshore oil wells, natural seeps or other potential sources. Nowadays, as most environmental protection agencies are adopting the policy of "polluter pay principle", polluters may want to ascertain their responsibility. This requires accurate identification of spilled oils.

Infrared spectroscopy appears to be the most simple, rapid, reliable and inexpensive of the instrumental techniques employing for fingerprinting oil types. Some workers (Simkhaev *et al.*, 1988; Drobot and Glushkova, 1988; Said *et al.*, 1988) have explored the

use of infrared spectrometry to characterise crude oils, whilst others (Brown *et al.*, 1975; Lynch *et al.*, 1975) have used this approach to identify the source of petroleum. **Olajire** and Oderinde (1992) described the applicability of infrared spectrophotometric technique to characterisation of crude petroleum, middle distillate and heavy residual (> 387°C) oils from various locations in Nigeria. Their results showed that infrared absorbance ratio serves as a good criterion for distinguishing crude petroleum and their products from different locations. Davis and Gibbs (1975) also described the effects of weathering on Kuwait crude oil, but only with respect to changes in chemical composition and physical properties such as specific gravity and viscosity. The study carried out by **Olajire** and Oderinde (1993) was the first to investigate the effects of weathering on the infrared characteristics of Nigerian crude petroleum. In their study, the infrared spectra of samples of fresh and weathered crude petroleum were interpreted. According to them, the large difference in the spectral of naturally weathered oil and the fresh crude petroleum shows that infrared analysis of the whole crude cannot give enough information necessary for fingerprinting the source of oil spill. A correct matching between weathered (two- day weathered oil) and fresh sample can be accomplished with infrared spectrophotometry by submitting the fresh and weathered oil to be compared to distillation or to some other vapourisation procedure, which induces comparable volatility

losses in the oils, and the spectral fingerprint of the nonvolatile components can then be compared.

The present trend in the catalytic cracking is in the direction of utilising heavier oil as feedstock; hence the concentrations of metal contaminants in the heavy residual oil call for great attention. Energy dispersive X-ray fluorescence spectroscopy was used by **Olajire** and Oderinde (1993) for multielemental analysis of crude petroleum and their heavy residual oil boiling above 387°C (729°F) from different oil producing companies in Nigeria. The distribution pattern of the two major contaminants, i.e. vanadium and nickel in the crude petroleum and heavy residual oils was established by making a plot of the V/Ni ratio of the crude petroleum against that of the residual oils. The equation generated around the common line predicts that the V/Ni ratio of the residue to be three-quarters of that of the crude petroleum. The results show unequivocally that vanadium and nickel present in the crude petroleum are concentrated in the residue. The utilisation of such residue as feedstock will therefore possess a lot of industrial problems, as these elements including sulfur poison the catalyst used in the refinery, resulting in poor product yield and cause corrosion of processing units. The refiners are therefore advised by the authors to find a means of keeping such contaminants under control. In a follow-up study, a simple and rapid spectrophotometric method for the determination of vanadium (V) concentration in heavy crude oils was described by **Olajire**

(2000). The method is useful for analysing a large number of similar heavy crude oil samples. **Olajire** and **Oderinde** (1994) further investigated the effects of weathering on the trace metal contents of Nigerian crude oils, with a view to assessing the applicability of some elemental ratios for fingerprinting the source of oil spill. The main conclusion of the work was that the ratios of concentrations of vanadium to nickel, iron, cadmium and manganese respectively in an oil sample were unaffected by weathering to any significant extent and thus allowing their use in fingerprinting the source of an oil spill (**Olajire**, 1997).

Detailed compositional characterisation of petroleum aliphatic and aromatic fractions is of fundamental interest and instrumental in the development of widely used techniques in analytical chemistry. **Sazonova et al** (1986) used multidimensional gas chromatography for determining the fractional composition of crude oils and natural gas condensates and for defining the detailed light hydrocarbon ($C_1 - C_9$) content. In a related study, **Olajire** and **Oderinde** (1996) measured fingerprints of the major oil components such as individual resolved n-alkanes and major isoprenoids. In this study, detailed analysis was carried out on the Nigerian crude oil saturated hydrocarbon biomarkers using $SiO_2 : Al_2O_3$ (2 : 1) liquid chromatographic technique followed by computerised gas chromatographic analysis of the n-hexane soluble fractions. The authors found that the ratios Pr/Ph , C_{17}/Pr , C_{17}/C_{18} and CPI are

greater than unity, evidence in support of strong predominance of odd-numbered carbon atoms over the even-numbered carbon atoms, which is indicative of petroleum-free plants. The method used in this study is particularly suited to the identification and differentiation of crude oils, distillate fuel oils and other petroleum fractions, which contain significant concentration of n-alkanes fraction of moderately low boiling point (**Olajire**, 1996). It is much less suitable for the identification and differentiation of heavy residual oils because they contain mainly the high boiling constituents. **Olajire** (1994) also investigated the composition of aromatic fraction of Nigerian middle distillate oils using adsorption column chromatography followed by mass spectrometric analysis. The study showed that the aromatic fraction of Nigerian middle distillates are not only the aromatic hydrocarbons, but are extremely complex mixtures of aromatic compounds containing nitrogen, oxygen and sulphur atoms. In a related study, **Jewell et al** (1972) reported a separation scheme that separates heavy-end petroleum distillates into acid, base, neutral nitrogen, and saturate and aromatic fractions. The analytical techniques used include anion and cation exchange chromatography, coordination chromatography and adsorption chromatography. The separation scheme was adopted by **Olajire** and **Oderinde** (1998) to provide a detailed analysis on the chemical composition of Nigerian heavy residual oils. In their study, a combination of analytical techniques were carried out on

heavy residual oil boiling above 387°C using coordination chromatography, ion-exchange chromatography and a single dual-packed adsorption column chromatography containing silica gel and alumina, followed by infrared and ultraviolet studies of the neutral aromatic fractions of the oil. The ultraviolet portion of the analysis was used to analyse the polynuclear aromatic types and to determine their specific absorptivities at each matrix wavelength, while the infrared analysis was used to characterise the aromatic compounds. The UV-IR technique used in this study enabled the determination of the high boiling aromatic hydrocarbons present in heavy fractions for oil pollution awareness. In contrast with gas chromatographic technique, the approach described in this study is only applicable to oils that contain significant concentration of aromatic hydrocarbon compounds that are highly absorbing. There is, however, an abundance of such structures in the heavier oils and particularly in the residual oil. A further advantage of the UV-IR technique used in this study is that it helps in the determination of the degree of separation achieved and the validity of the four compound type concentrates obtained in the silica-alumina adsorption procedure. According to the authors, the variations in the values of the specific absorptivity ratios of the aromatic fractions of the heavy oil also serve as a basis for the applicability of the ultraviolet technique for fingerprinting of heavy oil types.

In view of reports of major ecological disruptions caused by oil pollution and as a follow-up of my study, **Olajire** (1995) isolated and quantitatively determined the major soluble aromatic hydrocarbons in Nigerian heavy oils using ultraviolet spectrophotometric technique. In this study, seawater was mixed with heavy residual oil with slow stirring for 12 hours; the aqueous phase was extracted with methylene chloride to remove all the dissolved hydrocarbons, which were then fractionated by SiO_2 liquid chromatography. Some of the soluble aromatic hydrocarbon types detected includes naphthalene, phenanthrene, triphenylene, 3,4-benzofluorene and 1,2-benzanthracene.

The use of NMR spectroscopy for the determination of a series of parameters describing the average molecular structure of the aromatic fraction in Nigerian middle distillates (250 – 337°C) was also reported (**Olajire**, 1998). The method used were adaptation of the techniques developed for the characterisation of aromatic fractions in petroleum. Calculations of structural parameters indicate an average molecular model of two and three fused aromatic rings for all the distillates. The aromatic fraction of Forcados distillate oil, with the highest average molecular weight ($MW = 229$) has the highest average number of aromatic ring carbon atoms per molecule ($\#C_a = 3.16$) and per cent substitution of alkyl groups on non-bridge aromatic carbon ($\%AS = 84.36$). The aromaticity values (f_a) of all the fractions are the same. A review article by **Olajire** and Oderinde

(1996) with 25 references covers studies on the applicability of some analytical techniques for fingerprinting oil types. On the basis of the criteria used in this review for judging the appropriateness of an analytical technique for fingerprinting oils, a rating scheme was proposed which enabled an objective critical comparison of the analytical techniques.

The porphyrins as well as metalloporphyrins are of varied importance. They serve as biological markers to geological samples (coal, oil, bitumen and shales), and also provide information on geochemical transformation or degradation products of chlorophyll and hemin (Manskaya and Dryozdova, 1968). Porphyrins and metalloporphyrins have been found in coals in relatively low abundance. The low abundance of these compounds in coals compared with that in many crude oil deposits has been suggested to be consistent with more drastic thermal conditions believed to be necessary for coal formation (Didyk *et al.*, 1975). **Olajire** and Adabanija (2000) carried out a preliminary characterisation of metalloporphyrins in Nigerian coals. In their study, metalloporphyrins were isolated from Nigerian coal minerals by solvent extraction followed by SiO_2 liquid chromatography. Electronic absorption spectrophotometry was used in the determination of the nature of the isolated complexes. The major elements as determined by atomic absorption spectroscopy were manganese, iron and gallium. Rhodotype visible spectra were obtained for some of the fractions, and the

presence of rhodofying groups were confirmed by the carbonyl absorption band at 1715 cm^{-1} ($5.8 \mu\text{m}$) in their infrared spectra. Levels of inorganic elements in coal is important in view of the impacts of these elements on coal combustion systems in their operational (corrosion, slagging, fouling) and environmental (emission of toxic metals) performance. In a similar study, **Olajire et al.** (2006) carried out geochemical studies of metals and porphyrins in some Nigerian coal minerals. In their study, the metal contents of Nigerian coal minerals were analysed with atomic absorption spectrophotometer, while the porphyrins were qualitatively characterised by a combination of thin layer chromatography (TLC), infrared and ultraviolet-visible spectrophotometers. Okaba coal, with the highest degree of mineralisation and toxic metals, is not environmentally friendly especially for use in coal processing industry, when compared with other coals studied. Comparatively at international level, Nigerian coal minerals are more environmentally friendly than foreign coals on the basis of toxic metals analysed in this study. Porphyrins isolated from Nigerian coal minerals were characterised by means of infrared and UV-visible spectrophotometric techniques. In this work, we demonstrated the utilisation of infrared spectroscopy as a useful analytical technique for structural characterisation of porphyrins. The differences observed in the spectra demonstrate the value of this approach in the identification of geologically significant

etioporphyrins. The UV-visible spectra of these coal porphyrins are in accordance with a metal-free porphyrin structure.

Environmental Impacts of Inorganic Elements

The increasing input of heavy metals into the biosphere from anthropogenic and natural sources requires constant global monitoring of these pollutants. In the last few decades, due to rapid industrial and technological growth, the emissions of these metals from various human activities have increased. Consequently, the translocation of these toxic metals from the environment to living systems, and their accumulation are the concern of most environmental protection agencies. **Olajire** and **Ayodele** (1997) investigated the level of heavy metals contamination of roadside soil and grass of Ibadan metropolis, the largest city in Africa, and two highways linking Ibadan. In their study, the concentrations of Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb in roadside soil and grass were determined. In order to deduce the possible sources of the metal contaminants, the authors determined correlation coefficients between elements in the sample taken from high traffic density and low traffic density areas. The low correlation coefficient found between metal pairs considered in both groups suggests that sources other than the motorcar also influence the levels of these metals in the roadside soil. According to the authors, in addition to motor traffic, other probable sources of these metals in soil and grass samples are

admissible concentration. The high Cr content can be due to leaching of wastes from metal plating industry located in the study area into the rivers. Also, a non-common source of the metals was suggested by the authors from the low correlation that existed between some of the metals. The probable sources of the metals in the river water and groundwater samples, according to the authors, varied widely and may include leachates from wastewater generated domestically, industrially or municipally, and intentional dumping of agricultural waste or waste materials from industrial metal scraps, furniture, automobiles into the river water and from the natural weathering of rocks on land and volcanic activity, which eventually get eroded as run-off into the river. The water quality of Osun River in terms of inorganic nutrients was also assessed (**Olajire** and **Imeokparia**, 2001). Their investigation provides data of some ions, namely Na^+ , Ca^{2+} , NH_4^+ , Cl^- , NO_3^- , CN^- and PO_4^{3-} on water samples of River Osun, selected rivers in the region and ground waters. The pH, temperature, electrical conductivity, total dissolved solids, total hardness and total carbon (IV) oxide have also been determined to assess the chemical status and pollution levels of these water sources. The higher values of certain parameters with respect to the acceptable standard limits for drinking water indicate the pollution in both groundwater and river water samples of the study area, and make the waters unsuitable for various applications. The correlation coefficients between the quality parameter pairs of both the river water and groundwater

samples were calculated in order to indicate the sources of polluting substances. It is evident from our findings that the causes and sources of water pollution in the study area are due to agricultural land use, anthropogenic activities and industrialisation. The major occupation in the study area is farming. This is seen as the main source of the high ammonium (measured as NH_4^+) and phosphate ion concentrations. Domestic and industrial discharges into the river are probably responsible for the observed high concentration values of electrical conductivity, total hardness, total dissolved solids and chloride ion.

The transport of nutrients and chemical elements from soils to leaves occurs mainly via trees, where they are prone to leaching, and eventually transferred to urban surfaces. Urban land run-off has been known to be a major source of lake phosphorus. In a study reported by Olajire and Olanipekun (2000), leaves of different tree species, collected at Ogbomoso (Nigeria) were leached with distilled and rain waters in order to simulate the release of phosphorus. The results showed that the amounts of leachable and total leaf phosphorus varied significantly among the tree species but were not significantly affected by the tree diameters. It was also observed that rainwater caused better leaching of phosphorus than distilled water, while fragmented leaves released more than twice as much phosphorus as intact leaves. From all available evidence at our disposal, it was

concluded that tree leaves are indeed a major source of urban run-off phosphorus. In a related study, Olajire *et al* (2004) characterised trace metal leachability from highway construction solid waste using the toxicity characteristic leaching procedure. In this work, the authors addressed the potential risk of soil surface and groundwater contamination by trace metals leached from highway construction solid wastes by evaluating trace metal leachability, toxicity of the leachates to aquatic organism and environmental impacts of highway construction solid waste (HCSW). The kinetics of metal release was determined using the cascade-leaching test (CLT) with water at pH 4. According to the authors, with the exception of zinc in the first fraction, metal concentrations in all consecutive leaching fractions remained below the maximum permissible level in water for human consumption. The result of the toxicity test also showed that the leachates were in concentrations that did not exceed the toxic concentration level for aquatic toxicity tests. Our findings indicate low risk of surface and groundwater contamination resulting from highway construction solid wastes. Comparative evaluation of EDTA, pyridine and acetic acid for the assessment of available heavy metals from domestic and industrial sludges was also carried out by Olajire *et al* (2006). In their study, various sludge samples from different domestic and industrial wastewater treatment plants were analysed by Flame Atomic Absorption Spectrometry to evaluate their total and available contents of heavy

metals (Pb, Hg, Cd and Zn). From our findings, a more extraction efficiency was obtained using EDTA in domestic and industrial sludges, however acetic acid and pyridine gave a better extraction efficiency for Zn in industrial sludge than EDTA. Similarly, pyridine and EDTA gave a better extraction for Hg in industrial sludge than acetic acid. The variation in extraction efficiency of the EDTA, acetic acid and pyridine, essentially reflected the differences between sludges in their contents of the four heavy metals. According to the results of this work, the application of EDTA, acetic acid and pyridine single extraction provide valuable information about the mobility, lability and availability of the four heavy metals from domestic and industrial sludges under different environmental conditions. The interest of this application is useful in the determination of leaching behavior of pollutants from different types of sludges, in order to assess their environmental impact and consequently select the best methods of disposal and possible re-use of such sludge for agricultural purposes without severe impact on plants.

Analysis of Organic Compounds in Environmental Samples

Environmental samples such as soils, sediments and water in industrialised cities have been reported to have a greater tendency to be polluted with traces of many substances including Cd, Pb, Sb, polycyclic aromatic hydrocarbons, polychlorinated

roadside deposition of the residues of motor oil, battery wastes and car tires, a common practice of our roadside mechanics, battery smelters and tire vulcanisers.

The usefulness of tree bark and leaves in detecting atmospheric metals was reported by various investigators for various species of trees. Fatoki and Ayodele, 1991 used zinc and copper levels in Nigerian tree barks as indicators of environmental pollution. The pollution was reportedly due to vehicle exhaust. The atmospheric pollution levels of heavy metals in Ogbomosho, the second largest city in Nigeria and a tourist centre, were investigated (Olajire and Ayodele, 2003) by analysis of tree bark and leaves in automobile parking lots where vehicular emissions are frequent and pollution levels important. In their study, the concentrations of Pb, Cu, Zn, Ni, Fe and Mn in leaf and bark samples of seven tree species at 22 sampling locations with different pollution levels were investigated. According to the authors, the high-pollution automobile parking lots showed higher levels of these elements. This study provides greater awareness to the people of Ogbomosho and its environs about the atmospheric pollution levels in most automobile parking lots.

The great majority of moss species were found to have the special advantage that they take the nutrients they require almost exclusively from the atmosphere, as they have not developed a real root system or water conductive tissue. A comparison of heavy metal deposition in selected Eastern Europe countries using moss-

monitoring method was first reported by Markert *et al* (1996). In a similar study, Olajire (1998) used the elemental analyses in moss samples to predict the atmospheric deposition of heavy metals. In this study, the bioaccumulation of Sb, Sn, As, Fe, Ni, Mn, Pb, Cu and Zn in mosses from polluted and unpolluted areas of the southern part of Nigeria was reported. Results of the moss samples show strong variations in the concentration of metal ions with type of sampling sites. The highest levels of heavy metals were found in Lagos (both industrial- and residential type areas), where there is a high level of industrialisation. The low level of heavy metals in the samples collected from rural-type environment could be understood from the low level of industrialisation in these areas. The author also noted that the concentration of accumulated heavy metals differs in various moss species from the same biotope. *Bryidae mnum* was found to be a better accumulator of heavy metals than *Tetraphidae tetraphis*, as evidenced from the interspecies calibration between the two moss samples.

Waste generation is one of the consequences of advancement in technology. Wastes and their disposal are the cause of a great deal of environmental pollution (Alloway and Ayres, 1994). Of special concern is the concentration of heavy metals in solid municipal wastes, their transformations during disposal practices and their accumulation in food chain (Keefer *et al*, 1979; Rhode, 1974). In Nigeria, Sridhar and Bammeke

(1986) measured the heavy metal contents of some solid wastes produced in residential areas, a market, a cafeteria and the compost in Ibadan. In a similar study, the concentrations of heavy metals present in the municipal refuse collected from major cities and suburban areas in the western part of Nigeria were determined (Olajire and Ayodele, 1998). In this study, the heavy metal contents of solid municipal wastes produced at various sites in Lagos, Ibadan, Ogbomoso, Ilorin, Osogbo, Ile-Ife, Ejigbo, Iwo and Oyo were measured. According to the authors, the Cd levels of waste samples from Lagos and Osogbo and Hg level of waste from Lagos, Ibadan, Osogbo and Iwo exceed the European community maximum permissible concentration of Cd (3 ig/g) and Hg (1 ig/g) (EC, 1986; MAFF, 1992). These sites could constitute great health hazards in the event of leak into surface water or the soil and groundwater. The significance difference between the two means of the elements analyzed was demonstrated by means of student t-test. The values for the student "t" calculated from these data ($p < 0.05$) showed the difference between the waste samples produced in the high and low density towns for iron, zinc and cadmium. The high concentration levels of iron, zinc and cadmium could be attributed to socio-economic life styles coupled with commercial and industrial activities in these towns. In a follow-up study, Olajire *et al* (2003) investigated the distribution and chemical fractions of cadmium, lead, copper, nickel and zinc in four contaminated soils, differing

in soil properties using sequential extraction scheme developed by Tessier *et al* (1979). Their results showed that lead (Pb) was significantly associated with non-residual fractions in soils studied, indicating that this metal was potentially more bioavailable than other metals analysed. Cadmium and nickel were found mainly in the residual or the exchangeable fractions in most of the soils, while Cu and Zn were mainly associated with the organic fractions. The distribution of the five studied metals in the various fractions confirms their difference in mobility and bioavailability. The mobility index of copper and nickel correlated strongly and positively with their total metal content, indicating that the anthropogenically added metals remained in relatively weakly-bound forms.

In view of the important role water plays in most ecosystems, its inorganic chemical characterisation is of great interest. A study of the water quality of the Osun River was carried out by Olajire and Imeokparia (2000). In the study, the concentrations and distributions of Cd, Cu, Ni, Pb, Cr and Zn in Osun River, selected rivers in the region and groundwater were studied, in order to establish the current levels of pollution. The concentrations of Cd, Cr, Cu, Pb and Zn are compared with maximum admissible concentrations recommended for drinking water quality. The results showed that Cd, Cu, Pb and Zn contents in all water samples were below the maximum admissible concentrations except Cr, which exceeded the maximum

and anthropogenic (e.g. bitumen and synthetics) sources to the aliphatic hydrocarbon load in soil and water samples from Agbabu bitumen field.

Recommendations

It is customary on an occasion of this nature, to make some recommendations based on my experience and findings. Such recommendations, which have been incorporated in the appropriate sections of this lecture, will be useful for geochemist and environmental chemists working in petroleum companies and allied chemical Industries. The recommendations are itemised below for the ease of reference.

1. Studies on characterisation of Nigerian crude petroleum and their products were performed to evaluate the applicability of various analytical techniques for fingerprinting the oil types. The evaluated analytical techniques include infrared spectroscopy, gas chromatography, energy dispersive X-ray fluorescence spectroscopy, proton nuclear magnetic resonance spectroscopy and ultraviolet absorption spectroscopy
 - a. The aromatic/aliphatic infrared absorbance ratios calculable from the infrared spectra of the oil samples serve as good fingerprint indices for distinguishing oils from different locations and between crude oils and their products. This method is suited for the identification and differentiation of crude oils, distillate fuel oils and other petroleum fractions

b. The gas chromatographic technique was employed to analyse the alkane fraction in Nigerian crude oils. The variations in the determined values of oil compositional parameters make the technique suitable for fingerprinting the oil types. This method is particularly suited for fingerprinting of crude oils, distillate fuel oils and other petroleum fractions, which contain significant concentrations of saturated hydrocarbon fraction of moderately low boiling point. It is much less suitable for fingerprinting of heavy residual oil types because they contain mainly high boiling constituents.

c. Energy dispersive X-ray fluorescence spectroscopy was used for multi-elemental determination of trace-metals in the oil. The trace-metal indices have proven to be a good parameter for differentiating oils from various locations. The fingerprinting of oil types by means of trace-metal indices is, however, subject to serious ambiguities because these metals are commonly present in petroleum in forms that may be volatile.

d. Proton nuclear magnetic resonance spectroscopy was employed to determine a series of average molecular structure parameters of aromatic fractions in Nigerian middle distillate oils. The parameters provide a meaningful description of the aromatic fraction in the distillates in terms of the "average molecule". The variations in the values of the determined parameters then suggest the proton nuclear magnetic resonance technique as an additional means of fingerprinting distillate oils.

e. The ultraviolet absorption technique was used to determine the specific absorptivities of the high boiling aromatic hydrocarbons present in the heavy fraction. In contrast with gas chromatographic technique, the ultraviolet absorption technique described in these studies does not provide any information concerning the saturated hydrocarbons or other compounds that do not absorb light, and is, therefore only applicable to oils that contain significant concentrations of aromatic hydrocarbon compounds, that are highly absorbing. There is, however, an abundance of such structures in the heavier oils and particularly in the residual oil. The variations in the values of the specific absorptivity ratios of the aromatic fractions in the heavy oil thus suggest a basis for recommending the applicability of the ultraviolet absorption technique for fingerprinting of oil.

f. On the basis of the scoring technique used in these studies, infrared spectroscopic technique was recommended to be the best for fingerprinting of oil, followed by the gas chromatographic technique, ultraviolet absorption spectroscopy, energy dispersive X-ray fluorescence spectroscopy and proton nuclear magnetic resonance spectroscopy. It should be noted, however, that a single analytical technique would not suffice for proving the identity of oil; hence a technique should be further confirmed with one or two other techniques for generating authentic data that would confirm the identity of oil.

2. The results of trace metal analysis in Nigerian crude petroleum

and heavy oils show that vanadium and nickel present in crude petroleum are concentrated in the residue. The utilisation of this residue as feedstock will therefore possess a lot of industrial problems, as these elements, including sulfur poison the catalyst used in the refinery, resulting in poor product yield and cause corrosion of processing units. The refiners should therefore find a means of keeping such contaminants under control.

3. It has been evident from our findings that causes and sources of water pollution in the study area are due to agricultural land use, anthropogenic activities and industrialisation. Domestic and industrial discharges into the river are probably responsible for the observed high concentration values of electrical conductivity, total hardness, total dissolved solids and chloride ions. Proper treatment of effluent from industrial processes to the acceptable levels, discouraging stagnation of domestic sewage on the ground surface, availability of sewage treatment plant along with proper sewerage system as well as thorough analysis and study of any water sources before being used for domestic applications are recommended to minimise health risk.

4. As evidenced from our study, the leachable P levels were higher with rainwater than distilled water and this was attributed to the presence of dissolved ions and gases in rainwater. Burning and storing of leaves in the street gutter or roadside prior to pick up should be discouraged as they evolve gases that lead to acid formation and may facilitate nutrients including P transport to

biphenyls, polychlorinated dibenzo-*p*-dioxans and furan by aerial and other inputs (Jones, 1991; Olajire and Ayodele, 1997), but polychlorinated benzenes and polycyclic aromatic hydrocarbons are considered to constitute the greatest health hazard of organic compounds normally encountered in environmental samples (Alloways and Ayres, 1994). Olajire *et al* (1999) reported a preliminary evaluation of the presence, composition and characterisation of organic compounds in compost-amended soil from waste dumping sites in Lagos metropolis, a highly industrialised city in Nigeria using a combination of spectroscopic analytical techniques. From their study, analysis of the *n*-hexane fraction using gas chromatography showed the presence of a mixture of aliphatic hydrocarbons, ranging from C_9 – C_{25} , while ultraviolet analysis of the toluene fraction suggested

1,2-benzanthracene, 2,3-benzphenanthrene, chrysene and pyrene as polycyclic aromatic compounds present in samples analysed. The results of this work indicated the occurrence of large hydrocarbons in appreciable concentrations in the samples analysed despite the losses from atmospheric weathering, and we concluded that continued accumulation of these hydrocarbons in these sites can lead to deterioration of the ecosystem if leaching occurs. Olajire *et al* (2005) assessed the extent of environmental contamination and sources of polycyclic aromatic hydrocarbons (PAHs) compounds to sediments of the Niger Delta (Nigeria) using combined chemical analysis and toxicity bioassay

techniques. Concentrations of two- to six-ring PAHs of molecular mass 128-278 and toxicity to *Vibrio fischeri*, and *Lemna minor* are considered in this investigation. From this study, the authors concluded that the measured PAHs content of the Niger Delta sediments is well below values found in grossly polluted areas around the world. The PAH group profile showed the predominance of 2-3 ring PAHs in almost all the samples. Moreso, the PAHs in the sediments of the Niger Delta were characterised mainly by petrogenic source but contributions of pyrolytic sources cannot be excluded. Fractionation and subsequent biotesting with *V. fischeri* indicated non-polar aliphatic rather than aromatic compounds as a major cause of toxicity in the sediments. This, according to the authors, may be due to alkanes and alkenes; a contribution of elemental sulfur cannot be excluded. The concentrations of PAHs in sediments are not a measure of sediment toxicity because of the poor correlation that existed between the TPAHs concentrations and toxicity bioassays of the sediments. In a related study, ecotoxicological assessment of Niger Delta sediments using Duckweed (*Lemna minor*) growth inhibition test was reported (Olajire et al, 2003). In their study, the toxicity of sediments of the Niger Delta to *Lemna minor*, a sensitive aquatic weed regularly used for ecotoxicological studies was evaluated. This study wanted to determine if *Lemna minor* can be used as an effective bioassay

organism by oil companies and chemical industries in Nigeria. Essentially, the experimental approach involved exposure of *Lemna minor* under standard laboratory conditions to sediments, and toxicity is presented as per cent inhibition of growth of *Lemna minor* cultures after 7 days. The results of this study showed that there is differential toxicity among the sediments tested in a modified Steinberg-medium. The plants exposed to two of the sediments (SDWRR and SDOGN) were chlorotic and lost their roots, indicating the very high toxicity of the soluble contaminants in these sediments. The authors concluded that *Lemna minor* has proven to be a good practical bioassay organism because the toxicity test is simple, sensitive and cost effective. The distribution and sources of PAHs in soils as well as PAHs profile in areas with anthropogenic pollution in the Niger Delta such as Warri and Ugehelli were investigated (Olajire and Brack, 2006). The authors concluded that typical Niger Delta soils were contaminated with PAH above the natural level and this was attributed to long-range atmospheric transport of PAH from the hotspot to these sites. Also, the PAHs in soils of the Niger Delta were characterised by both petrogenic and pyrolytic sources. The PAH group profile showed the predominance of 2-3 ring and 4-6 ring PAHs in soil samples analysed. In a follow-up study, Olajire et al (2006) analysed qualitatively and quantitatively water and soil samples from the vicinity of Agbabu Bitumen field of Southwestern Nigeria for 10 parent polycyclic aromatic

hydrocarbons (PAHs) using gas chromatography coupled by flame ionisation detector (GC-FID), in order to gather information on the degree of contamination by bitumen exploration and processing in this area. According to the authors, the total PAH levels in water samples from all the sampling stations were sufficiently high ($> 10 \mu\text{g/l}$) to cause acute toxicity to the exposed organisms. The authors also concluded that water samples from these areas were more grossly polluted than soil samples. This, according to the authors, was due to the fact that water column receives direct PAH inputs from various sources, including both petrogenic and pyrolytic. Discharges of industrial and domestic wastes into the water body are other local sources of PAHs in water. The PAHs in soils and water samples were mostly dominated by 3-ring PAHs. In a similar study, *Olajire et al* (2006) investigated anthropogenic and natural organic inputs in soil and water samples from Agbabu bitumen field using aliphatic hydrocarbon markers. Soil and water samples from Agbabu bitumen field of Southwestern Nigeria were analysed by GC-FID for aliphatic hydrocarbons, in order to gather information on the degree of contamination by bitumen exploration and processing and other biogenic contributions. Unresolved complex mixture (UCM) and anthropogenic aliphatic hydrocarbons, like hopanes and stearanes, were not detected in any of the samples. The results of their study show contributions of both natural (e.g aquatic input)

lakes and streams from urban runoff.

5. Relative to those observed in the urbanised and industrialised locations around the world, the measured PAHs content of the Niger Delta sediments is well below values found in grossly polluted areas. Information from this study revealed that the remediation strategies embarked upon by the community of the Niger Delta and Shell Petroleum Development Company of Nigeria might be effective, to some extent but more efforts are needed in this direction for environmental protection and management of oil spills in the Niger Delta to better the living conditions and economy of the study area.

6. The concentrations of individual and total PAH in water samples of Agbabu bitumen were sufficiently high to cause acute toxicity to certain exposed organisms. There are implications on the quality of seafoods from many aquaculture locations meant for human consumption. Our findings point to the need to establish a monitoring programme for persistent organic pollutants, such as PAHs, not only in water but also in organisms themselves, to ensure that any exceedence in concentration levels over environmental quality standards is quickly and adequately addressed.

Concluding Remarks

Mr. Vice Chancellor sir, the three major functions of an academic in the University system are teaching, research and

service to the Community.

In the area of teaching, I have taught many generations of students in diverse areas of chemistry, some of whom are in various specialised fields of agriculture, pharmacy, engineering, medicine and allied disciplines. I quite appreciate the sound training received from my teachers at various levels of my tutelage, and permit me to single out Prof. R.A Oderinde who supervised my Master's project and Doctorate thesis. I have published two standard textbooks currently in use as teaching materials nationwide and abroad for students of higher institutions of learning; they are *Introductory Physical Chemistry* (University Series A) [Olajire and Ayodele, 1999] and *Introductory Organic and Inorganic Chemistry* (University Series B) [Olajire *et al*, 2000], popularly known as "Small and Big Abass" by LAUTECH Students. I also have a text in press, entitled "Principles and Applications of Spectroscopic Techniques". The book covers aspects of qualitative and quantitative spectroscopic analysis.

My research activities in industrial/environmental chemistry have constituted the main subject of this lecture. The five-tiered levels of analysis and data treatment used in my research studies are as follows:

- Tier 1:** Determination of total petroleum hydrocarbons (TPH) and heavy metal contents.
- Tier 2:** Separation of four compound types concentrates

in the silica alumina procedure.

Tier 3: Distribution pattern recognition of target PAHs and biomarker components.

Tier 4: Determination and evaluation of diagnostic ratio for fingerprinting source of oil Spill.

Tier 5: Ecotoxicological studies of sediments and wastes using *Lemma minor* and *Vibro. fischeri* and toxicity characteristic leaching procedure (TCLP).

This tiered approach helps in gathering information necessary to address site- or incident-specific questions about the nature and extent, and ultimately source(s), of hydrocarbon and heavy metal contaminations

It is significant to mention, however, that I co-authored some articles with colleagues in other fields within and outside the department on the synthesis of some organosulphur compounds that have industrial applications as agrochemical (Ayodele and Olajire, 1999; Ayodele *et al*, 1999, 2001, and 2003); kinetics of periodate oxidation of tris-(4,4'-dimethyl-2,2'-bipyridine) iron (II) in acid medium (Ayodele *et al*, 2000); potency of paracetamol tablets after the expiry dates using spectrometric technique (Ajanaku *et al*, 2000); application of first law of thermodynamics in the re-heating furnace of Osogbo Steel Rolling Company (Nigeria) [Olajire *et al*, 2005] and on the studies of lycopene in Tomato fruits and their products (Olajire *et al*, 200, 2006; 2006). I have supervised three

master's candidates and four postgraduate diploma students, specializing in Environmental Chemistry. I am currently supervising two doctoral and three Master's students.

In the area of administration and service to the community, I have served a three-year – term in acting capacity as the head of department of Pure and Applied Chemistry in addition to serving in various committees at the departmental, faculty and university levels. I am also serving as a consultant to the International Community on the Management of Waste Dumping sites in Cotonou, the Republic of Benin. I am currently serving on the highest decision-making body of the university- the university Governing Council.

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thank you very much.

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What would have been my gain if on my return, my home is in ruin? My children are too young to understand my sojourn in academic life, yet I do see sparks of joy in their small eyes whenever I return home with success. I thank you, also my children, for being happy to welcome me back home on my arrival. May you all grow to be greater "Professor Olajires".

I also wish to appreciate the contributions of my parents, teachers and lecturers, especially at the undergraduate level, for all I have achieved academically. Special thanks to my Ph.D supervisor, in person of Prof. Rotimi A.Oderinde. To all my friends and well wishers, let me say, you are all extremely wonderful.

Mr. Vice-Chancellor, Sir, eminent academic and administrators from LAUTECH, and others from far and near Universities, Polytechnics and Colleges of Education, students,

ladies and gentlemen, here present, I humbly and sincerely thank you all for your love for me and my achievements in life.

I thank you all for your rapt attention and may God bless you all. AMEN.

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