

Gas chromatography elemental analysis of some corrosion-coat-protective bitumen from Nigerian resources

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Abstract-The chemical composition of a coating material greatly determines its corrosion-protection level and other desirable service attributes. Previous studies have shown that Nigeria is blessed with large deposits of natural bitumen and potentials for sustained production of bitumen in large quantity with crudes which can be coat-utilized to economically reduce corrosion in her petroleum-dependent economy that is subjected to costly corrosion ravages. Reliability, handling, and modifications in technological usage of bitumen harvested from different sources demands that proper information on physicochemical properties of each per se should be consulted and applied instead of general information on bitumen. This paper supplements previously determined quantitative elemental compositions of three bitumen samples - Ondo S.A, Ondo S.B, and KPB harvested from critical resource sites in the country by neutron activation analysis as part of their physicochemical characterization. This

I INTRODUCTION

Corrosion of carbon steel as a prime structural material is the most important corrosion problem to contend with in all quarters worldwide, and the most important method to counteract it is by paint or organic coatings. Coatings of grease, plasticizer, bitumen, resins, polymers, rubber latex, corrosion-resistant paints or metals, etc provide protection by acting essentially as impervious barriers to water, oxygen and

was achieved by oxidatively degrading each prepared sample at about 1002°C with oxygen to produce carbon dioxide, sulphur dioxide, water, nitrogen gas and oxides of nitrogen which contained the desired elements to be assayed amidst other products. Helium was used to carry the products, as they were processed along an arranged path to remove unwanted products. This was followed by column separation and detection by thermal conductivity detectors and elemental quantification of the volatile products using the 540 PerkinElmer gas chromatograph interfaced with ancillaries that included an IBM-PC with analysis software. The result showed that the carbon, hydrogen, nitrogen, oxygen and sulphur contents of the bitumen samples ranged from; 83.49 to 87.7, 9.35 to 10.51, 0.13 to 0.72, 1.25 to 1.72, and 1.14 to 1.32% by weight respectively.

Keywords: Corrosion of carbon steel, coat-protection with Nigerian bitumen, elemental analysis, gas chromatography method, benefits.

other agents of corrosion of the substrate. It is estimated that about 90% of all steel are corrosion-protected by paints or organic coatings based essentially on their comparative advantages in cost, versatility and availability. The chemical compositions of coating materials however determine several desirable properties such as adhesion to the substrate, wear and abrasion resistance, corrosion-protectiveness, thermal

behaviour, weather resistance, handling and processing properties, etc; of coatings produced from them. It is therefore important to provide information on distinct chemical composition of every coating material for better understanding and possible modifications to improve its service performance and usage [1]. Bitumen is a cheap, common, and important material in today's technological world. It was also used in ancient times as far back as over 3,500 BC for many purposes including corpse preservations such as the Egyptian mummifications of the Pharaohs and water proofing of baskets. It is primarily used today for paving roads and parking lots, roofing, corrosion protection, general industrial and special purposes. Oxidized bitumen is used in pipe coating, manufacture of paints, hydraulic applications, under sealing for concrete pavement, etc. A majority of pipelines today are coated with hot-applied plasticized coal tar or petroleum bitumen and coatings based on proper bitumen show excellent resistance to industrial pollutions. The current world use of bitumen is put at over 220 million tonnes per annum [2, 3, 4, 5 and 6]. The chemical composition of bitumen is a great determinant of its grade or quality. Bitumen gotten from different sources, or produced with different manufacturing processes and/or crudes can have wide variations in chemical compositions and other physicochemical properties with different levels of service benefits. Any bitumen whose chemical composition and other physicochemical properties deviates significantly from compositions of bitumens of standard grades or known acceptable qualities can be unreliable in service for most engineering applications or cause unpredictable problems in its service usage [6, 7, 8 and 9]. Bitumen is a highly viscous, black, sticky and chemically complex material whose detailed chemical

composition is still not possible despite many recent advances in analytical chemistry. ^{13}C nuclear magnetic resonance spectroscopy (C-NMR), proton nuclear magnetic resonance spectroscopy (H-NMR), gas chromatography, X-ray diffraction, infrared adsorption spectroscopy, and distillation are the techniques that have the most significant impact on determining the chemical composition of bitumen. More complex advanced chemical methods such as ruthenium ion-catalyzed oxidation and pyrolysis analytical techniques have also been used to elucidate the complex structure of bitumen [9, 10 and 11].

Corrosion is preponderant in the oil and gas industries. Nigeria's economy is about 85% dependent on petroleum and a lot of wastages occur in the economy through corrosion processes. A previous study has however shown that the country is blessed with large deposits of natural bitumen in her Ondo, Lagos, Ogun, Edo, and Enugu States with a combined proven reserve of over 14.86 billion barrels and capability of synthesizing large quantities of bitumen from crudes which can be used to economically reduce corrosion in her economy. The characteristics and suitability of her bitumen resources need to be studied, understood, and documented for better technological applications including corrosion protection. Geologically, the country's main bitumen belt occurs on the eastern margin of a coastal sedimentary basin known as the Benin basin, which extends through Togo and Benin Republic to western Nigeria. The crystalline basement rocks form the foundation of the whole area [12, 13 14 15 and 16]. Ondo State is the most noted area of bitumen activities in the belt and has offices of Nigerian Bitumen Development Project located at Akure and Ore. The bitumen content of Nigerian soil is not the same but varies from location to location. Generally some distinct bitumen-

impregnated hydrocarbon types of occurrence have been identified within the bitumen belt from topsoil downwards and location to location as outcrop, sands, lean sands, shales and heavy crudes [17].

Tarsands with 5 to 10% by weight bitumen content are designated as good or medium grade. The average bitumen content of Nigerian tarsand is about 20% by weight. Very rich natural bitumen deposits are found in Ondo State around the region of Idiobilayo, Foriku, Agbabu, Okitipupa, and Aiyibi. Generally, the country's tarsand is composed of bitumen, water and some mineral accessories [17 and 18]. Kaduna Refining and Petro-Chemical Company (KRPC) is the most important synthetic bitumen outfit in the country. It has installed capacity for synthesizing large quantity of bitumen with blends of Nigerian crude which per se is not suitable for bitumen production and imported suitable crudes such as; Lagomar from Venezuela, light Arabian from Saudi Arabia, Basara from Iran, and the Kuwaiti ones [19]. The social, economic and technological benefits of exploiting all these bitumen resources to the country are enormous [20]. Instrumental neutron activation analysis (NAA) of elemental weight compositions and X-ray diffraction (XRD) analysis of two clear

natural bitumen samples named Ondo S.A and Ondo S.B harvested in a waterlogged area and underground through an extraction hole respectively within the region of Agbabu village; and a KRPC-synthesized sample, named KPB, with the blend of Nigerian and Iran's Basara crudes have previously been undertaken by [6 and 21]. The NAA of the samples was part assessment of their physicochemical properties and the XRD analysis was meant to understand the microcopies of the structures of their coating treatments on low carbon steel. The NAA indicated that the bitumen contained different quantities of trace elements of aluminum, titanium, manganese, and vanadium. Although NAA is a high-efficiency method for precise quantitative and qualitative analysis of main-component and trace elements in different samples compared to most methods of analysis, only up to about 40 elements essentially metals can be analyzed by it [23, 24 and 25]. The objective in this paper is to supplement the NAA results reported by [6] with results for carbon, hydrogen, sulphur, oxygen and nitrogen which do form the main elemental weight compositions of good-grade bitumen through gas chromatography analysis

II. METHODOLOGY

A Elemental analysis, position and principle of gas chromatography method

Elemental composition is an important chemical characteristic and its determination is the first essential step in investigating the structures of chemical compounds. Elemental analysis is used extensively across a wide range of applications including pharmaceuticals, oil related products, catalysts and foods. Its main purpose is for quality control or assuring standards. For example, some fine chemical and food industries will not tolerate even very minute traces of some elements in their

products. Generally, the elements typically of interest are carbon, hydrogen, sulphur, nitrogen, chlorine, bromine, iodine and oxygen. In some instances, phosphorus may also be of interest. The standard micro-methods of elemental analyses not involving gas chromatography are available for use and have reached a high degree of perfection and give high accuracy. Such methods are however complicated, time and labour consuming, require special laboratory environments and highly skilled personnel. Typically, they require sample weight of at least 3mg and time of 1.5 to 3hrs to analyze a single organic sample [25].

Over the past decades, researchers have been largely concerned with the development of micro-scale methods. However, the gravimetric determination is bound to thwart all attempts to reduce the weight of samples further. The development of reliable automatic instruments based on classical gravimetric methods appears to be a formidable task, and therefore efforts have been concentrated on new rapid physicochemical methods of elemental micro-analysis. Chemical micro-analysis is normally carried out in two stages: first, the quantitative chemical conversion of the sample into sample products, and second, the quantitative determination of these products with the use of an appropriate technique. Elemental analysis involves production of a simple mixture of gaseous and volatile products, which can be quickly and effectively broken down into individual components to which a highly accurate and sensitive gas chromatographic detector can be applied [25 and 26].

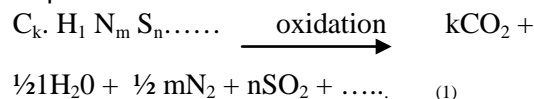
At one time, gas chromatographic analysis was less accurate than classical elemental analysis, but the development of simple reliable and sensitive thermal conductivity detectors (TCDs), flame ionization detectors (FIDs), photo-ionization detectors (PIDs), special electronic integrators and small computers has now brought the reproducibility of chromatographic peak-area measurements to at least $\pm 0.2\%$ and the accuracy of chromatographic elemental analysis close to that of standard gravimetric methods, which is normally $\pm 0.3\%$ [25, 27 and 28].

The use of gas chromatography in elemental analysis provides a sharp increase in the rate of analysis and makes it possible to produce relatively simple automatic and semi-automatic instrumentation. Today, many manufacturers of chromatographic equipment offer instruments for elemental analysis featuring gas chromatography determination of the products of chemical degradation. At present there is a variety of gas chromatography methods that can be used for the determination of a number of elements in organic compounds including, carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine, bromine, phosphorous and arsenic [25

and 29]. When based on gas chromatography, the elemental analysis of organic compounds normally consists of the following, steps;

- i. The preparation and introduction of a sample into vent.
- ii. Chemical conversion of the sample into volatile products.
- iii. Chromatographic separation of these products.
- iv. Detection of the separated products and quantitative processing of result.

The sample is normally weighed in a trough of aluminum, platinum or tin foil, and then a small amount of a catalyst is added. Today many instruments are equipped with automatic sample introduction devices. The purpose of chemical degradation is to obtain sample products, each containing one or more of the elements to be determined present in the products. For example oxidation of a compound containing carbon, hydrogen, nitrogen and sulphur can be calculated as follows:



The commonest chemical degradation reactions are oxidation and reduction. Usually oxidation takes place in an atmosphere of inert gas. Table 1 below shows characteristic of some reactions used in gas chromatographic elemental analysis.

Table 1: Characteristic of some Reactions used in Gas chromatographic Elemental Analysis [25 and 29]

Element to be determined	Reaction	Volatile Reaction products	Carrier gas
C, H	Oxidation	CO ₂ , H ₂ O, CH ₂ , C ₂ H ₂	O ₂ , He
C, H, N	Oxidation	N ₂ , CO ₂ , H ₂ O	He, Ar
O	Reduction (carbon Contact)	H ₂ O, CH ₄ , NH ₃	He, Ar, N ₂ , H ₂
O	Reduction And Oxidation	SO ₂ , CO ₂ , H ₂ O, H ₂	He
O	Reduction	H ₂ O, CH ₄ , NH ₃	H ₂
S	Oxidation	SO ₂ , CO ₂ , H ₂ O, H ₂	He
S	Reduction	H ₂ S, CH ₄ , H ₂ O, H ₂	H ₂
H (halogen)	Oxidation	Cl ₂ , Br ₂ , I ₂ , CO ₂ , SO ₂	He
H (halogen)	Reduction	HCl, HBr, HI, H ₂ S	H ₂
As	Reduction	ASH ₃	H ₂
P	Reduction	PH ₃	H ₂

B. Test procedure

The two natural bitumen samples- OndoS.A, OndoS.B and the synthetic sample-KPB collected and used by [6, 12, 13, 14, 15 and 21] which remained were used for the analyses. Figure 1 shows the block diagram of the set up.

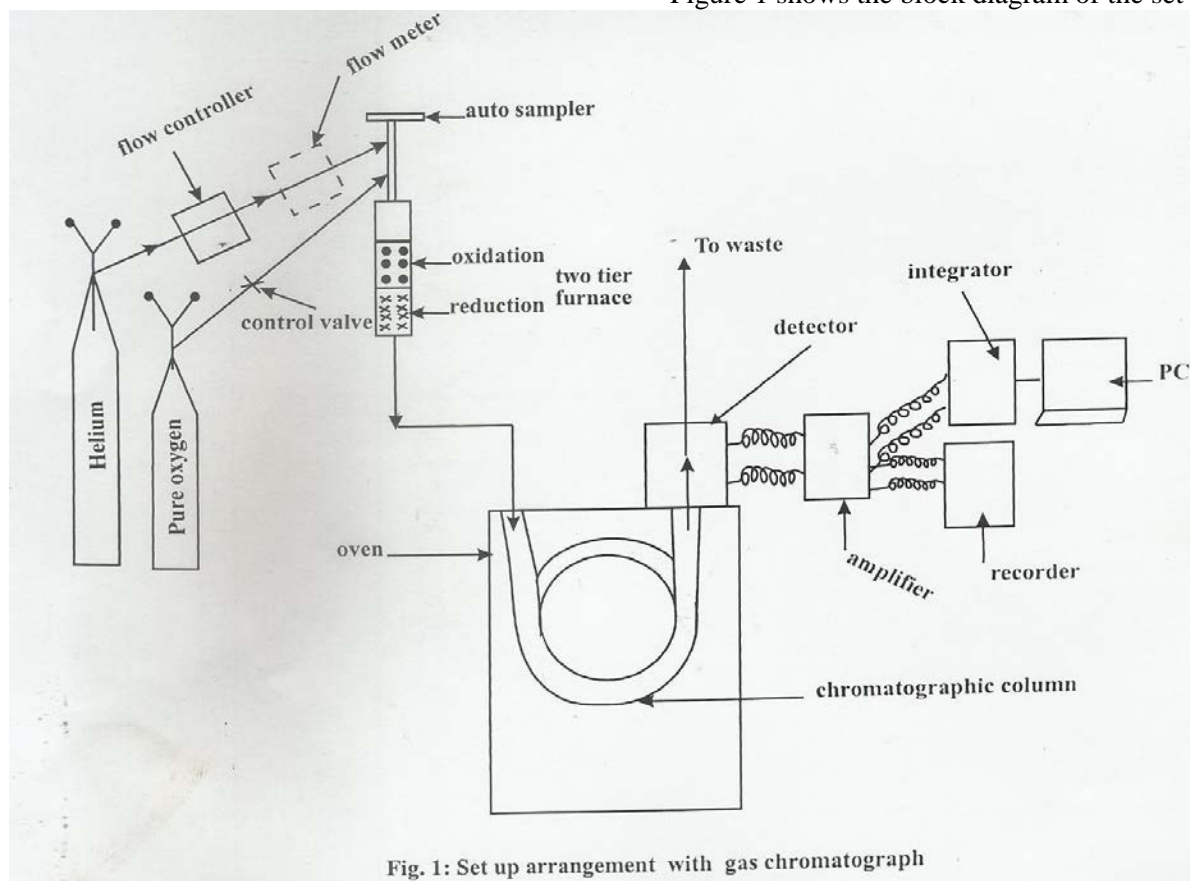


Fig. 1: Set up arrangement with gas chromatograph

Samples were analyzed in principle with the methods used by [30, 31, 32 and 33]. The set up

consisted of pure pressurized oxygen supply from a tank for sample combustion and another

pure pressurized helium gas from a separate tank to act as the mobile phase and some means of controlling and measuring the gas's flow rate, a mean of introducing the sample into the combustion tube where chemical degradation occurred, a single two-tier combustion furnace tube in which each tier was heated electrically and maintained at desired temperatures, a gas chromatography column contained within a thermostated oven where separation of a mixture into distinct chemical compounds occurred, and thermal conductivity detector to register the presence of the separated chemicals as they emerge from the column. The detector also had ancillary equipment interfaced with it to provide a permanent record of the analysis and to manipulate the data. Detected reaction products and their chromatograms were manipulated by a transducer that served to change them into proportional electrical signals. The amplifier served to increase low-level signals from the transducer to levels sufficient for recording with a voltage measuring instrument. The integrator was to calculate the area under each chromatogram as a determinant of mass of each chemical product and use the results to determine the relevant elemental contents.

Since bitumen is viscous and sticky and not suitable for direct introduction for processing, about 20-microgram sample of Ondo S.A was weighed out in thin properly pre-cleaned 5 x 9 tin capsules using an automated and computer controlled microbalance and sealed. A rotating auto-sampler delivered the tin encapsulated sample into the top of a quartz combustion tube into a pure oxygen environment in the tube in which the oxygen had been introduced under static condition at 1002°C. The thermal energy from the combustion of the tin and sample material generated a temperature of 1780°C at the moment of flash combustion as indicated by equipped pyrometers. All combustible materials in the sample were burned and the flash oxidize-converted the carbon in the sample to carbon dioxide, hydrogen to water, sulphur to sulphur dioxide, nitrogen to nitrogen gas/oxides of nitrogen and other present elements to other combustion products. A variety of absorbents were used to remove undesirable products that were not required or relevant. The remaining combustion products were swept out at the

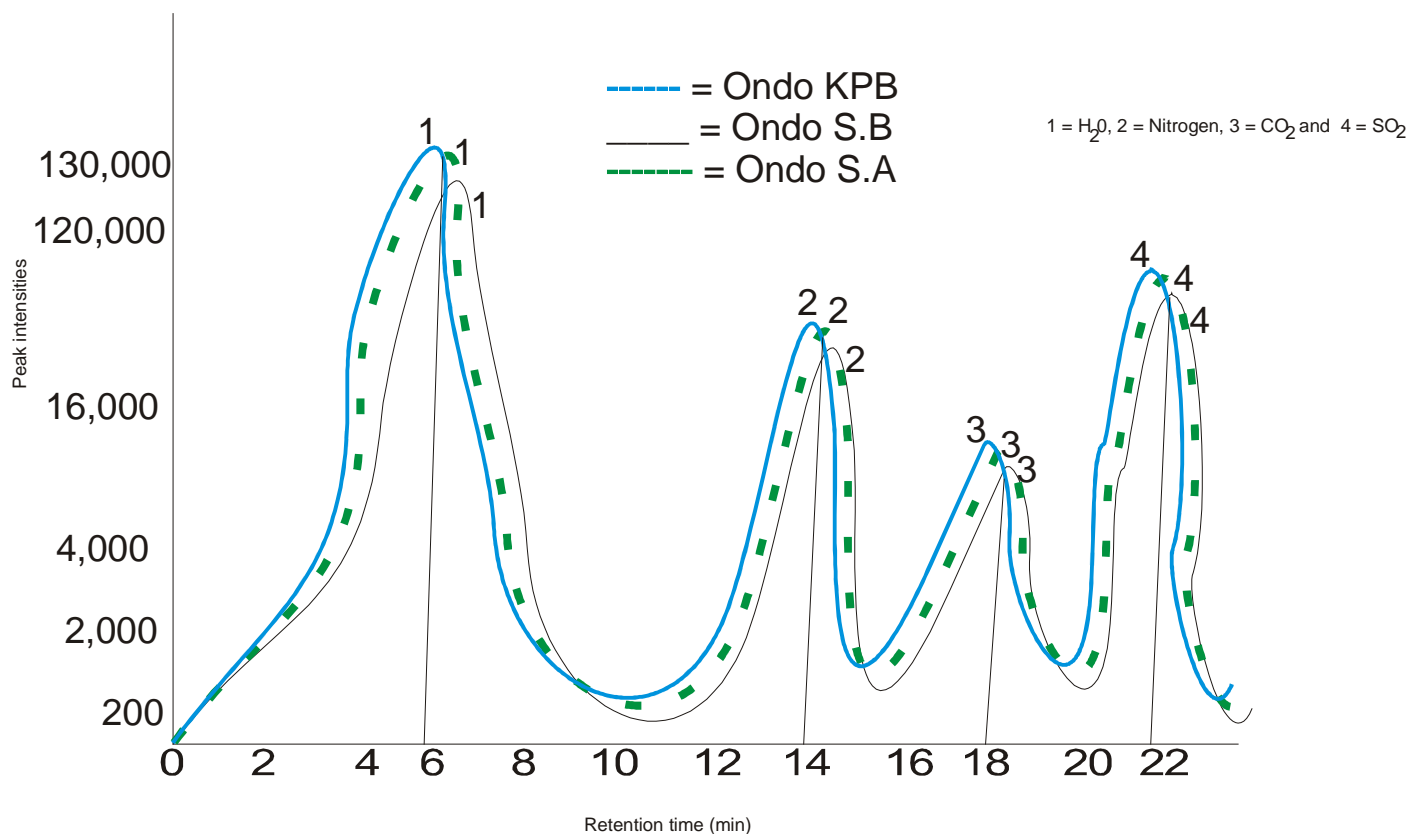
bottom of the upper combustion tube by a constant stream of non-reactive helium carrier gas and passed to the lower two-tier tube furnace filled with high purity chopped copper wire that was heat-maintained at 640°C. Both the catalysts/absorbents used and copper metal were packed into readily exchangeable tubes made of ceramic material. The copper removed any oxygen that was not consumed in the initial combustion and converted any oxides of nitrogen to nitrogen gas. The gases were then passed through absorbent traps that left only carbon dioxide, water, nitrogen and sulphur dioxide. Separation and detection of the gases were thence carried out using the Perkin Elmer gas chromatograph model 540. Separation was effected in a chromatographic column maintained and encased in a well thermostated oven. The initial oven temperature was maintained at 40°C for 5.2 min, increased at a constant rate of 14°C/min to a final oven temperature of 358°C and held there for 7.6 min. The detector was maintained at 500°C throughout the analysis. The choice of helium as the carrier gas was because of its high thermal conductivity which differs considerably from that of compounds that usually result from chemical separations so as to preclude it from detection among the analyte gases by the thermal conductivity detector accordance to [6 and 30] and shown in Table 1. The helium carrier gas flow rate was adjusted to 55cm/s at a pressure of about three bars throughout the test and discharged to waste after column separation. A 0 to 200mV instrumentation amplifier with logger Pro 3 data collection software was used to amplify signals from the detector such as peak retention times, peak areas, etc. The amplified signals were then sent to an IBM-PC through a Hewlett-Packard 3396 Series II integrator using a Hewlett-Packard file server programme, where they were digitized and stored to disk. In addition software allowed the results to be displayed in an automated manner. By this the C, H, N, O, S contents of Ondo S.A were automatically quantitatively analyzed in about 29 minutes in a single run. This was repeated with Ondo S.B and then KPB

III. RESULTS AND DISCUSSIONS

The pattern of the chromatograms with Ondo S.A, Ondo S.B and KPB are shown in figure 2 while the computer printout of results of the elemental analyses are presented in Table 2.

Table 2: Elemental composition by weight of Ondo S.A, Ondo S.B and KPB as obtained by gas chromatography method of analysis

Element	Bitumen Sample used		
	Ondo S-A	Ondo S-B	KPB
C [%]	87.78	86.91	83.49
H [%]	9.35	9.37	10.51
N [%]	0.13	0.66	0.72
O [%]	1.25	1.74	1.62
S [%]	1.32	1.23	1.14



Fig'2: Pattern of the chromatograms obtained with the bitumen samples

Results in Table 2 show that, generally, the carbon contents of the bitumen samples is highest, followed in order to the least content by hydrogen, sulphur, oxygen and nitrogen as can be observed from the table. The chemical compositions of five other different and clear natural bitumen samples from other locations in the Nigerian bitumen belt have been reported in the paper by [20]. The chemical elements and percentage ranges of their contents by weight were; carbon (82.96 to 86.02%), hydrogen (10.26 to 10.61%), nitrogen (0.47 to 0.67%) oxygen (1.21 to 1.98%), and sulphur (1.11 to

1.2%). It can therefore be appreciated that the percentage of these elements as obtained for Ondo S.A, Ondo S.B and even KPB fall in these respective ranges. Typical elemental analysis of petroleum shows 83 to 87% carbon, 10 to 11% hydrogen, 1 to 5% sulphur, 0.3 to 1.1% nitrogen, 0.2 to 0.8% oxygen, 4 to 1400 parts per million (ppm) vanadium, and 0.4 to 11ppm nickel [34]. Compositions of bitumen produced with the Mexican blend, Arkansas Rousiana, Boscan, and California crude sources has been reported by [9] to quantitatively contain 83.77 to 86.77% carbon, 9.91 to 10.94% hydrogen, 0.28 to 1.10

nitrogen, 0.99 to 5.25% sulphur, 0.2 to 0.77% oxygen and minute traces of vanadium and nickel. Analysis of Whiterocks, Asphalt Ridge, PR Spring and Sunnyside bitumens by [34] showed that they contained within 86.8 to 87% carbon, 10.8 to 11.6% hydrogen, 1.1 to 1.7% nitrogen and 0.4 to 0.7% sulphur by weight. It can therefore be observed from Table 2 that the compositions of all the test bitumen samples are comparable to these bitumens. Furthermore, the average compositions of most bitumen as given by [9] lie in the range of 79 to 88% carbon, 7 to 13% hydrogen, traces to 3% nitrogen; 8% sulphur; 8% oxygen by weight. From this it can also be seen that the compositions of the bitumen samples are comparable with the average composition. Finally the elemental weight composition of 83.49 to 87.78% carbon, 9.35 to 10.51% hydrogen, 0.13 to 0.72% nitrogen, 1.25 to 1.74% oxygen, and 1.14 to 1.32% sulphur of the bitumen samples are comparable 83% carbon, 8% hydrogen and 6% sulphur respectively as per IS-73: 2006 for 80/100 penetration grade bitumen [35]

IV. CONCLUSION

The use of gas chromatography in elemental analysis is beneficial in using smaller sample mass, increasing the rate of analysis with relatively simple automatic and semi-automatic instrumentation with equally high accuracy compared to standard gravimetric methods of analysis. Quantitative elemental assay of carbon, hydrogen, sulphur, oxygen and nitrogen contents of two clear natural bitumen samples harvested from underground and on the ground surface in a waterlogged area around Agbabu village in Ondo State and synthetic bitumen from KRPC in Nigeria has been conducted through the gas chromatography method. The result showed that the contents of the bitumen samples varied in proportions from; 83.49 to 87.7 carbon, 9.35 to 10.51 hydrogen, 0.13 to 0.72 nitrogen, 1.25 to 1.72 oxygen, and 1.14 to 1.32% sulphur respectively. The results also show that, by the elemental weight composition; bitumens from which the samples were obtained are all comparable with one another, reputable bitumens from other locations in the world and the 80-100 penetration grade bitumen.

V. RECOMMENDATIONS

The following recommendations are made from the paper:

- i. The presented results in this paper in conjunction with previously reported ones with the test bitumen by [6, 13, 14, 15 and 21] show that clear natural bitumen deposits within the region of Agbabu village and the KRPC-manufactured bitumen with the country's crude blended with Basara crude as feedstock in Nigeria are of very high quality for corrosion protection of steelworks and are recommended as the basis for assessing the quality of bitumen from other locations.
- ii. The overall series of information is basic and posited for consideration towards properly coat-utilizing Nigeria's abundant bitumen as dependable resources for economical reduction of steelwork corrosion in her economy, and by extension for other technological applications.

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