Determination of Heavy Metal Contents in Refined Petroleum Products

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Abstract: Heavy metals were determined in petroleum products sold in Agbor, Delta State. Metals analysed for include Cd, Cr, Cu, Pb and Zn. Petroleum products sampled were kerosene, diesel and gasoline respectively. Samples were digested with a mixture of nitric, sulphuric and hydrochloric acid to make the metals available for determination and the concentration levels of the metals analysed using Atomic Absorption spectrophotometer(A.A.S, Buck Scientific Model VGP-210). Anomalous values were found for Cu and Pb except for Cd, Cr and Zn which fell within permissible levels. Petroleum products analysed were perceived to be highly polluted in Cu and Pb from the results obtained. Kerosene showed a higher degree of pollution in Pb than the others. High levels of Pb and Cu could be attributed to anthropogenic sources such as additives applied during refining process, absorption of the metals from storage tanks and supply vessels as well as natural presence of the metals in the source rock from which the crude was obtained. This high level could pose serious ecological and environmental threat within the vicinities where these products are utilized.

Keywords: Petroleum Products, Heavy Metals, Kerosine, Diesel, Gasoline, Pollution.

I. Introduction

Petroleum hydrocarbons are important environmental pollutants. Pollution from these sources emanates from two major routes, releases of the hydrocarbons into the atmosphere from combustion processes and direct spill of the hydrocarbons into the environment. Various potentially toxic elements such as heavy metals are present in crude oil and elevated concentrations of these compounds are known to affect soil, its toxicity and associated components(1, 2).

One of the major anthropogenic sources of heavy metal enrichment in terrestrial habitats of oil producing areas of Niger Delta Nigeria is the frequent spills of crude oil on land and gas flaring(7). Major crude oil spillage has adversely affected inorganic levels of soils. Heavy metals found in petroleum depends on the geological location in which the crude is being formed. Some metals present in crude oil are as a result of the type of metals present in the source rock. These metals dissociates in the pore water of these rocks, which in turn is absorbed into the crude oil. These heavy metals may possibly play an important role as catalyst in conversion of organic matter to petroleum(3). Therefore many trace metals found in crude oil are simply a reflection of those picked up during migration of the source rock to the reservoir rock(3). Another possible source of heavy metals in crude oil is the introduction of drilling mud fluids into the oil well during crude oil extraction. These chemicals are added directly to the crude oil and invariably act as contaminants in the soil(4). This explains the reason why fuels used by drilling rigs may be the source of heavy metals found in oil producing countries(5). The heavy metals in the crude distributes themselves into the petroleum fractions after fractionation and refining thus accounting for the presence of heavy metals in petroleum products.

This study therefore tends to examine the presence and distribution of heavy metals in diesel, kerosene and gasoline with a view to comparatively evaluate the concentration levels of these metals so as to see if they meet desirable standards or otherwise.

II. Materials And Methods

SAMPLING:- Petroleum products (diesel, kerosene and gasoline) were randomly and systematically obtained from three different service stations (Total, Conoil and Oando) in Agbor. True representative samples (composite samples) of each were obtained by mixing each product to homogenise after which one litre was measured out into small plastic jericans and corked properly.

SAMPLE PRESERVATION:- The samples were preserved in a refrigerator to avoid volatilization until they were taken for analysis

III. Sample Preparation And Analyysis

10 ml of each product was digested with a mixture of 20ml HNO₃ and H_2SO_4 (ratio 4:1) and heated 4 hours daily slightly in a water bath at a temperature of $80^{\circ}c$ for 9 days to ensure complete digestion. The digestion method was adopted to avoid inflammation due to the volatility of the samples. The digested samples

were then taking for A.A.S analysis. Samples were analysed at an environmental laboratory(Edo Environmental Consult and Laboratory, Benin- City) and the metal content of each digested samples determined by aspiration(air/acetylene flame) using an Atomic Absorption Spectrophotometer(Buck Scientific Model VGP-210) at appropriate wavelengths of 324.8nm, 283.3nm, 357.9nm, 213.9nm and228.8nm for Cu, Pb, Cr, Zn and Cd respectively. Their concentrations were obtained from the absorbances read.

Quality Control and Assurance- Replicate analyses were performed on samples to yield a mean which was used to determine trueness and also standard deviation of the mean to measure precision(9, 10). Procedural blanks and standard solutions were also included for analytical quality control to assure the accuracy and reproducibility of the results.

	IV.	Results	And	Discussion
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Mean concentration levels of heavy metals in the petroleum products are given below.

Sample	Zn	Cu	Cr	Pb	Cd
Gasoline(ppm)	1.43	1.74	0.54	0.24	1.68
Kerosene(ppm)	2.63	1.98	0.33	0.41	1.33
Diesel(ppm)	2.87	1.77	0.86	1.01	1.50
standard limits	5.00	0.10	1.00	0.075	5.00

The standard deviations were calculated to be approximately ± 0.014 for all the metals determined. The relative percent differences (RPD) for duplicate analyses were less than 20% which is the control limit between duplicate as set by United States Environmental protection Agency (10) indicating high precision. The results obtained for Cu and Pb in the three samples exceeded the permissible standard limits as recommended by <u>www.Detoxmychild.org/heavymetal(6)</u> for petroleum products except for Cr, Cd and Zn. Various reasons could be adduced for this. Anomalous levels of Pb and Cu could be attributed to anthropogenic sources such as; additives applied during refining process, absorption of the metals from storage tanks and supply vessels as well as natural presence of these metals in the source rock from which the crude was extracted.

Sources of these metals in the petroleum products could also account for the presence of the other metals which fell within permissible levels even though they pose no pollution risk.

This disturbing levels of Pb and Cu found in the petroleum products possess problem of pollution and significant health risk to the local population and environment where these petroleum products are utilized.

The released of these metals into the environment and atmosphere as oxides during its combustion could threaten the existence of the local population. Also, spillage of these products releasing the metals into the environment and water body could be deleterious to the ecosystem and aquatic life.

A survey of the three products shows that kerosene sample had a higher concentration of Copper thus indicating higher degree of pollution in copper than the others while diesel had a higher concentration of lead thus suggesting more level of lead pollution.

V. Conclusion

The findings of this study shows that petroleum products analysed for heavy metal concentration indicated high and disturbing levels of lead and copper in them since they exceeded the standard limits. It is therefore suggested and recommended that since the nation rely more on imported petroleum products, the appropriate agencies and regulatory bodies should ensure that both imported and internally refined petroleum products meets the regulatory and permissible standards of these heavy metals to avoid further pollution of the environment with these metals.

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