EFFECTS OF STORAGE MATERIALS ON TRACE METALS CONCENTRATION OF PETROLEUM PRODUCTS

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Abstract

The levels of trace metals (Fe, Cr, Zn, Pb, Cu, Cd and Hg) in petroleum products stored in different materials viz: (polythene containers and brown Winchester bottles) were investigated. Iodine dissolved in MIBK was added to samples prior to aspiration into the premix air-acetylene burner. Results obtained showed that after ten weeks of storage, metals concentration level of products stored in polythene containers increased by three folds; samples stored in brown Winchester bottles showed no significant increase in metals concentration, signifying that inappropriate storage of petroleum products could lead directly to increase in the concentration of metals in the environment above the maximum permissible levels enhancing aerial pollution.

Keywords: Petroleum, trace metals, Winchester bottles, Polythene, pollution.

INTRODUCTION

Heavy metals found in petroleum depend 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 (NNPC/PTI, 2007). 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 (NNPC/PTI, 2007). 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 (Stanisley, 2012). This explains the reason why fuels used by drilling rigs may be the source of heavy metals found in oil producing countries (Holmes and Bames, 2007). The heavy metals in the crude distribute themselves into the petroleum fractions after fractionation and refining, thus accounting for the presence of heavy metals in petroleum products.

Analytical data on the levels of trace metals in petroleum are very useful in deducing the source and the geological origin of crude oils. Such data on petroleum products are useful in assessing the impact of metals such as Ni, Cu, Fe, etc which are deleterious to oils, on the refining or processing of these products (Walker and Wilson, 2016). Often, organometallics such as zinc diethyl dithiophosphate and tetraethyl lead are added to petroleum products such as lubricating oils and gasoline respectively to improve automobile engine performance (Crighton, 2009).

Moreover, there has been a global concern recently about the possible health hazards resulting from the cumulative toxic effects of trace metals such as lead, cadmium and mercury in the environment (Von Lehmden, *et al*, 2000). It was claimed that most of the aerial lead burden is derived from automobile exhaust (Chow, 2003).

In Nigeria, automobile traffic has increased more than ten-fold within the last decade and automobile exhaust would account for about 80% of the air pollution problems in the urban areas (Lahmann *et al*., 2012). The need to know how much impact storage is making on the trace metal composition of these products become very imperative. This will go a long way in providing adequate information and knowledge on how best these products could be stored and handled, so as to minimize the effects and concentrations of these harmful metals in the environment. It is not uncommon to find workers in roadside automobile mechanic workshops and gasoline filling stations washing grease off their hands with gasoline or orally sucking gasoline from containers. There is a dearth of data on the level of toxic metals especially chromium and mercury in petroleum products in the country; and the environmental pollution control laws operating are not being enforced yet. Simple and rapid analytical methods for monitoring toxic metals in petroleum products are therefore desirable.

Nigeria, the sixth oil producing nation in the world is most often threatened by insufficient supply or near non availability of petroleum products in our cities and rural areas as well. Even the oil producing states in the country are not spared of this unfortunate and ugly incidence. As a consequence of this, it is not uncommon to find endless queue of motor vehicles all around the few petrol stations that may be lucky and willing to dispense and sell their products to the numerous buyers. Quite interesting in this regard is the activities of touts storing and selling petroleum products in polythene containers (Jerry cans) so called "black marketers" who freely hawk petroleum products along the major streets. One major concern about these petroleum products hawkers is the environmental hazards this constitute in our society. Apart from the incessant fire outbreak resulting from poor handling of these products, there is the need to critically and analytically assess the methods and manner these products are stored by these hawkers, who know close to nothing about the consequences of storage materials and the methods of storage on the concentration of trace metals in these products. This present study therefore focuses on the effect of storage on the trace metal composition of petroleum products.

MATERIALS AND METHODS

Samples Collection

All the samples were collected directly from the metering pumps in filling stations into already cleaned containers according to the methods developed by ASTM (2011). All the samples were stored at room temperature.

Chemicals/Solvents

All chemicals and reagents used were of analar grade. Standard stock solution which contain 1000mg metal per litre were prepared by dissolving the appropriate amount of dried analar grade metal nitrate or sulphate in distilled water, sometimes with concentrated analar grade nitric acid to aid dissolution. Working standards were prepared by diluting the stock solutions with methylisobutylketone (MIBK)

Sample Preparation

Each sample was thoroughly shaken before pipetting $1cm^3$ into a $50cm^3$ standard flask. Iodine dissolved in MIBK was added to make the solution to the mark. The solution was thoroughly mixed and aspirated into the premix air-acetylene burner. Calibration graphs were made for the standard solutions by diluting stock solutions with the iodine/MIBK solvent. 50cm3 of MIBK solvent into which 3mg of iodine was added served as the blank.

Sample Analysis

The samples were analyzed using Varian spectra AA10 Atomic Absorption, Spectrophotometer with an air/acetylene flame. With the exception of Hg, which was determined by a modification of the AAS, total mercury was determined by a cold-vapour technique after wet washing. The total mercury was reduced to metallic form when it could be volatilized by aeration and measured by flameless AAS.

RESULT:

Table 1: Effect of Sample loss by Vaporization on the Level of Metals in Petroleum products (Concentrations in ppm)

	Fe			Cr			Zn			Pb			Cu			Cd			Hg		
Samples	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
Total Super	0.6±0.1	0.7±0.1	0.6±0.2	0.3±0.1	0.9±0.1	0.2±0.1	0.4±0.2	0.5±0.2	0.4±0.1	0.9±0.2	1.9±0.3	0.8±0.3	0.3±0.1	0.5±0.1	0.4±0.1	ND	ND	ND	0.4±0.1	0.6±0.1	0.3±0.1
Mobil Super	0.7±0.2	0.9±0.3	0.7±0.1	0.4±0.2	0.9±0.1	0.5±0.2	0.3±0.1	0.5±0.1	0.3±0.1	0.9±0.3	1.9±0.2	0.9±0.1	0.2±0.1	0.5±0.2	0.3±0.1	ND	ND	ND	ND	ND	ND
Total Diesel	0.9±0.3	1.4±0.2	0.9±0.4	0.5±0.2	0.8±0.2	0.6±0.2	0.9±0.3	1.0±0.4	0.8±0.2	0.8±0.1	1.0±0.2	0.9±0.3	0.4±0.2	0.7±0.2	0.6±0.1	0.3±0.1	0.5±0.1	0.4±0.1	0.1±0.0	0.1±0.0	0.1±0.0
Mobil Diesel	0.8±0.1	1.2±0.4	0.7±0.2	0.6±0.1	1.2±0.4	0.7±0.1	0.5±0.1	1.0±0.3	0.7±0.1	0.9±0.2	1.5±0.6	0.9±0.1	0.7±0.1	1.3±0.2	0.9±0.2	ND	ND	ND	ND	0.2±0.0	0.1±0.0
Kerosine	0.9±0.2	1.5±0.3	1.0±0.3	0.7±0.1	1.3±0.5	0.9±0.1	0.8±0.1	1.3±0.4	0.9±0.3	0.8±0.1	1.4±0.3	0.9±0.2	0.6±0.1	1.1±0.5	0.8±0.3	ND	ND	ND	ND	ND	ND
LPFO	0.3±0.1	0.9±0.2	0.4±0.1	0.9±0.2	1.1±0.3	0.9±0.2	0.3±0.0	0.9±0.1	0.3±0.1	0.8±0.1	1.5±0.2	0.9±0.4	0.3±0.1	0.9±0.3	0.4±0.2	ND	ND	ND	ND	ND	ND

NOTE: ND = Not Detected. Results of Triplicate

KEY

X = Initial Metals Concentration

Y = Concentration of Metals after Ten (10) Weeks of Storage in Polythene Bottles

Z = Concentration of Metals after Ten (10) Weeks of Storage in Winchester Glass Bottles

DISCUSSION

The concentration levels of Fe, Cr, Zn, Pb, Cu, Cd and Hg in various petroleum products are shown in Table 1.

The data showed that the metal contents increase on proceeding from light to heavy petroleum distillates (Gasoline > Kerosene > Diesel > LPFO). This is in agreement with the results reported by France (2014), in his study of trace metals in petroleum products. The results obtained showed that pretreatment of sample with iodine and dilution with MIBK gave better and reliable results for most metals especially, Cr, and Fe. The addition of iodine probably increased metal response by converting organometals into inorganic halide with subsequent improvement in instrument response (Trent, 2013; Lukasiewicz *et al.*, 2015).

Comparing the results obtained showed that samples loss by vapourization occurred enhancing metal concentration levels to about three fold, when samples are stored in polythene bottles. Good sample preservations was obtained when brown Winchester glass bottles were used as there seem to be no significant difference between the initial metal concentrations and results obtained after ten weeks of storage.

Most publications on trace metals determination do not contain information on sample storage problems. The result obtained in this study has however shown that metals such as lead and chromium have the greatest significant increase in concentrations resulting from poor storage.

Cadmium was not detectable in most of the samples analysed, in accordance with the reports of Robin and Waker, (2011) that this metal occurs at ppb level in Nigeria petroleum products, which is below the detection limit of conventional AAS for this element.

Analysis of variance showed that there is a significant difference in the individual metal concentrations in various products. Also, there is a significant difference in the heavy metals content of the products under the different storage methods.

High concentration of metals in petroleum products could directly lead to environmental pollution problems as they are released into the environment during combustion (Winster and Harry, 2015: Henry and George, 2015). According to the W.H.O, chromium concentration in the air above 2.0ppm could be harmful to humans and animal health, also lead atmospheric concentration greater than 1.0ppm can lead to toxicity (Nriagu, 2017).

The soil and water are usually the sink for most heavy metals when they are released in the environment. Concentration of metals in petroleum products due to poor and inappropriate storage could therefore lead to pollution of these environmental compartments as they are deposited in water (MacGrath, 2014), and soils (Idodo-Umeh and Ogbeibu, 2010).

CONCLUSION

A comparison of the two storage materials studied indicated that petroleum products could better be stored in brown Winchester bottles than the current polythene containers being used. It is therefore recommended that appropriate storage materials should be used in order to protect the environment from the impact of pollution resulting from petroleum products combustion.

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