Determination of Volatile Organic Compounds in Petroleum Companies using Liquid-Liquid Extraction

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Abstract- The recovery study of volatile organic compounds from effluents of petroleum companies in Ilorin East Local Government Area and its effect on the environmental matrix- surface water, soil, sediment and plant were sampled. The liquid-liquid extraction procedure of two organic solvent (Hexane: Dichloromethane) (50 ml: 50ml) was employed to remove volatile organic compounds from matrix so as to obtain a good recovery and repeatability at 0.01µg/l, 0.02µg/l and 0.05µg/l respectively. Sediment, soil and leaf of plant samples (10 g) were dried and soaked in hexane prior to extraction procedures, after which it was totaled into a 2 ml vial for Gas chromatography analysis. At 0.05µg/l obtained a percentage mean recovery and relative standard deviation for effluent water (82.7±2.5 – 95.0 ±1.0 %), surface water (62.3±2.5 – 97.7±4.2 %), soil (72.7±2.1 – 96.3±3.8 %), sediment (85.7±3.2 – 91.7±2.5 %) and plant (79.3±2.5 – 99.3±2.0 %). Correlation analysis was carried out to establish a relationship between effluent and other matrix, at 0.02 µg/l percentage mean recovery effluent has effect on the sediment at that concentration. The remaining concentration levels did not show any significant relationship with the effluent variables.

Keywords- Recovery studies, Industrial effluent, volatile organic compounds (VOCs)

I. INTRODUCTION

Petroleum is derived from Greek word "petra" (rock) and latin word "oleum" (oil) (Hornby, 2004). Crude oil is a naturally occurring, flammable liquid consisting of a complex mixture of hydrocarbons and other liquid organic compounds that are found in geologic formations beneath the Earth's surface. Petroleum is recovered mostly through oil drilling. This comes after the studies of structural geology - at the reservoir scale, sedimentary basin analysis reservoir characterization - mainly in terms of porosity and permeable structures (Guerriero, 2010). It is refined and separated, most easily by difference in boiling point, into a large number of consumer products like petrol (gasoline), naphta, kerosene, and asphalt (Paul, 2011). Petroleum is used in manufacturing a wide variety of materials, and it is estimated that the world consumes about 88 million barrels each day. Petroleum is called fossil fuel because it was made from plants and animals. The energy in petroleum came from the energy in plants and animals which is from the sun (Speight, 1999). Petroleum keeps us going, but it can damage our environment from organize origin formation exploitation uses of burning oil which can pollute the air. Oil can also pollute the soil and water which injures animals but oil companies work hard to drill and ship oil as safely as possible and try to clean any oil that spills and also making cleaner gasoline and other fuels yearly (Alboudwarej, 2006). Petroleum consists of liquid, gaseous and solid hydrocarbons. Under atmospheric pressure and work - temperature conditions, hydrocarbons such as methane, ethane, propane and butane occur as gases, while pentane and heavier ones are in the form of liquids or solids. However, in an underground oil reservoir the proportions of gas, liquid and solid depend on sub surface conditions and on the phase diagram of the petroleum mixture (Akiner and Aldis, 2004).

An oil well produces predominantly crude oil, with some natural gas dissolved in it. Because the pressure is lower at the surface than underground, some of the gas will come out of solution and be recovered (or burned) as associated or solution gas. A gas well produces natural gas and at surface conditions, these will condense out of the gas to form natural gas condensate. Condensate resembles petrol in appearance and is similar in composition to some volatile light crude oils (Hanson, 1999). Volatile Organic Compounds (VOCs) are class of chemical compounds that share two main properties: they evaporate easily from water into the air and they contain carbon; they are components that have high vapour pressure and low water solubility.

Many volatile organic compounds are human-made chemicals that are used and produced in the manufacture of paints, pharmaceuticals and refrigerants. They are typically industrial solvents such as trichloroethylene; fuel oxygenates such as methyl tetra-butyl ether (MTBE) or by-products produced by chlorination in water treatment, such as chloroform (Craig, 2008). They are often components of petroleum fuels, hydraulic fluids, and paint thinner and dry cleaning agents. They are associated with product such as gasoline, plastics, adhesives, dry-cleaning fluids, biological sources of volatile organic compounds include trees, cows, termite (methanol) and cultivation.

Crude oil tanking can also release volatile organic compounds into the atmosphere. Manufacture of volatile organic compounds has increased dramatically during the past 40-50 years. It is not a surprise that they found their ways into our water supply (Jennings and Sneed, 1996). The United States Environmental Protection Agency (USEPA) estimates

that VOCs are present in one-fifth of the nation's water supplies; more than seven hundred (700) synthetic organic compounds have been identified in various drinking water supply. This contamination originates from a variety of sources, which includes household products and leakage or improper disposal of chemical wastes from commercial and industrial establishments (Rogers and Stalling, 1985).

Liquid-Liquid Extraction is a method used to separate compounds based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid phase into another and a basic technique in chemical laboratories, where it is performed using a separating funnel (Abel et al., 1994). In liquid-liquid extraction there is a feed phase which contains a component to be removed and the addition of a second phase (solvent phase) which is immiscible with feed phase. Some of component (solute) is transferred from the feed phase to the solvent phase. After extraction, the feed and solvent phases are called the raffinate (R) and extract (E) phases respectively. (Ibrahim et al., 1987).

This study was carried out to quantitatively analyze volatile organic compounds using liquid-liquid extraction method of mixed solvent (hexane: dichloromethane) in industrial effluents of two petroleum companies in Ilorin East Local Government Area of Kwara State and other environmental matrix - soil, sediment, plant and surface water close to the companies to generate a good recovery based on various concentration $0.01\mu g/l$, $0.02\mu g/l$, $0.05\mu g/l$ and also to ascertain whether the effluent have influence on the environmental matrix using correlation analysis.

II. MATERIALS AND METHODS

A. Study Area and Sample Collection

Sample from two petroleum companies – Lubcon Company (LC) and Equatorial Coastal Petroleum and Products (EP) along Olorunsogo road, Ilorin Kwara State were assessed in this study. Sampling points were selected based on assumed diversity of input from anthropogenic impacts and pollution level. Triplicate samples were taken from each sampling points at interval of four weeks over a period of three months. Preparation of sample bottles and containers is done prior to sampling based on sample size and type of analysis to be performed. Sample containers were thoroughly washed with metal free detergents and rinsed with tap water. They were then soaked in 1% nitric acid for 24 hours and washed with distilled water and kept intact to prevent contamination. Effluent samples were collected from two different locations and labeled as EW-LC-1 and EW-EP-1 (petroleum companies along Olorunsogo Road), SW-LC-2 AND SW-EP-2 (surface water samples along Olorunsogo road close to the two petroleum companies). Glass bottles were used to sample Volatile Organic Compounds (VOCs). Sediment (SD-LC-3 and SD-EP-3) at those locations was also collected into treated aluminum foil for Volatile Organic Compounds determination using Ekman grab. The same procedure applied to soil (SL-LC-4 and SL-EP-4) but using hand trowel. The collected sediments and soils at each sampling points were kept in an ice-chest before transferring to the laboratory. Plant (PT-LC-5 and PT-EP-5) was collected wet into a transparent nylon and allowed to dry prior to extraction processes.

B. Reagents and solvents

All chemicals used were of analytical grade. Volatile organic compounds mixed standard include propane, hexane, butane, butene, nonene, decene, benzene, ethanoic acid, ethanedioic acid (New Haven, CT, USA).

Solvents of residue grade purity including dichloromethane, chloroform, n-hexane, 1,2-dichlorobenzene, methanol, acetonitrile were obtained from Merck Company. Standard stock solution $0.1\mu g/l$ of mixed volatile organic compounds was prepared in methanol. All solutions were stored in the dark at 4^oC. Working solutions were prepared by dilution of standard stock solution with distilled water.

C. Chromatographic analysis

The determination of the volatile organic compounds was performed by Gas Chromatography/Mass Spectrometry (Agilent Technologies, CA, USA). The features and operating conditions of GC/MS system were as follows: GC Agilent 7890 series installed with HP- 5.5% phenyl methyl siloxane fused silica capillary column (30m length, 0.32mm i.d. and $0.25\mu m$ film thickness). The split/splitness injector was set at 280^oC and operated in the splitness mode (purge delay 1 min, purge flow 30.1 ml/min). Detector temperature was set at 320^oC. The injection was performed by an Agilent 5975C series automatic injector. The oven temperature was 250^oC for 31 mins followed by temperature programmed to 200^oC at $17^oC/min$. Helium was used as carrier gas.

III. LIQUID-LIQUID EXTRACTION PROCEDURE

A. Extraction of VOCs from water samples.

200 ml of sample was placed in a 250 ml capacity of separator funnel. The extraction was carried out three times with 20 ml of dichloromethane. The extracts were combined and dried with anhydrous sodium sulphate. The resulting extract was concentrated to exactly 1 ml using a rotary evaporator and gentle nitrogen stream. Then, GC/MS analysis was performed as described in section 2.3.
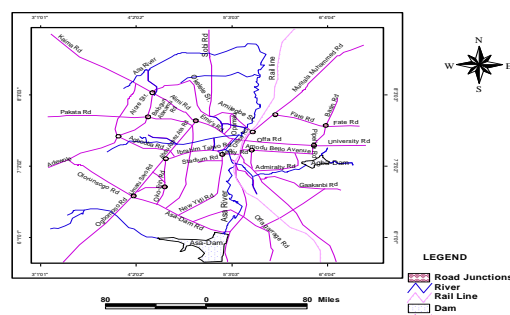

Figure 1. Map showing the study area of Ilorin

B. Extraction and cleanup of VOCs from solid samples

VOCs in sediment, soil and plants were extracted by liquid – liquid extraction. The dry sediments, soil and plant were carefully collected, homogenized and passed through 60 mesh standard sieves. Sample preparation included homogeneous mixing of 10 g of sediment, soil and plant with 0.25 g anhydrous Sodium sulphate to remove moisture and in 10 ml of dichloromethane for 1h followed by centrifugation. Then 3 ml of supernatant was filtered through 2 g of silica gel column with 11 ml 1:1 (v/v) elution of hexane and dichloromethane. The solvent fractions were then evaporated on a rotary evaporator, and exchanged by acetonitrile with a final volume of 2 ml ready for Gas chromatography analysis.

IV. RESULT AND DISCUSSION

A. Quality assurance and quality control

The quality assurance and quality control (QA/QC) requirements included establishing Gas chromatography retention times, method detection limit (MDL) and reproducibility for all compounds analyzed.

In table1, forty volatile organic compounds are listed along with their molecular weight, boiling point, melting point, method detection limit (MDL) and relative standard deviation (RSD) of each volatile organic compound. For volatile organic compounds collected, method detection limits (MDLs) were between 0.2 and 0.7 ppbv. The relative standard deviation was between 1.5% and 4.2% which is well within the limit of ±25%. For quality assurance approximately 25% of the samples were analyzed in triplicate. The reported percentage quality is the amount actually present in the sample.

B. Recovery Studies

Recovery studies with investigated compounds from spiked effluent and surface water, sediment, soil and plant of two petroleum companies were done at three concentration levels. At each concentration level, three determinations were performed. The mean recoveries and relative standard deviations (R.S.D) of alkanes (butane), alkenes (butene), Aromatics (benzene) and carboxylic acids (ethanoic acid) can be seen in table 2 and table 3 respectively.

1) Recovery study on effluent and surface water

Recovery study was done using a known amount of standard volatile organic compounds injected in the sample before extraction to check how much were recovered after completion exercise. The recoveries of volatile organic compounds from spiked effluent and surface water were done at three concentration levels, at each concentration level, three determinations were performed. It was observed at 0.01 µg/l, 0.02 µg/l and 0.05 µg/l respectively, effluent sample recorded a mean recovery range and relative standard deviation (RSD) of [73.7±1.5 - 86.0±4.0, 82.3±2.5 – 93.7±1.5 and 82.7±2.5 – 95.0±1.0] while surface water obtained (65.0±3.0 – 95.3±5.5, 63.3±1.5 – 98.0±4.6 and 62.3±2.5 – 97.7±4.2).

TABLE I. PROPERTIES AND QA/QC FOR TARGETED VOLATILE ORGANIC COMPOUNDS

Groups	VOC specie	MW	BP	MP	MDL	RSD	%Quality
Alkanes	cyclobutane	56	n/a	n/a	0.3	3	97
	1,2-dimethyl-3-pentyl cyclopropane	140	n/a	n/a	0.3	2.5	62
	Methylene cyclobutane	68	42	n/a	0.5	3.8	91
	1,2-dimethyl-cyclopentane(Z)	98	125	-88	0.7	1.5	62
	3-methyl heptane	114	116	-121	0.4	2.5	90
	Cyclohexane	84	81	6.5	0.4	3.5	65
	1,2-diethyl cyclobutane	114	n/a	n/a	0.3	3.2	57
	Pentyl cyclopropane	114	n/a	n/a	0.2	1.5	72
	Butyl cyclopropane	114	n/a	n/a	0.3	4.2	65
	1,5-dimethyl cyclooctane	144	n/a	n/a	0.2	3.5	63
	1-methyl-2-octyl cyclopropane	169	n/a	n/a	0.2	2	87
	1,1,2-trimethyl cyclopentane	114	n/a	n/a	0.2	2.5	53
	4-methylene decane	140	n/a	n/a	0.2	3.2	62
	1-hexyl-2-octylcyclopropane	114	n/a	n/a	0.2	4.2	53
Alkenes	2-butene (Z)	56	3.7	-139	0.4	2.1	91
	2-butene (E)	56	1	-105	0.5	2	91
	1-butene	56	-6.3	-185	0.3	2.1	97
	1-heptene	98	94	-119	0.3	1.5	60
	4-methyl-1-pentene	84	53	n/a	0.2	2.3	93
	2-methyl-1-hexene	98	62	n/a	0.3	2.1	62
	4-methyl-1-hexene	98	n/a	n/a	0.3	1.7	63
	3-methyl-1-pentene	84	54	n/a	0.3	2.1	96
	1-dodecene	169	216	-12	0.4	2.3	65
	1-nonene	126	146	-81	0.5	2.1	50
	1-tridecene	182	232	-23	0.6	2.3	59
	4-ethenyl cyclo hexene	108	126	-101	0.2	1.5	53
	2-cyano-1-hexene	110	n/a	n/a	0.2	3	68
Aromatics	pyridine D5	84	114	-42	0.6	2.5	91
	2,3,4,5-tetrahydropyridine	83	108	-48	0.7	3.2	62
	Perdeuterobenzene	101	n/a	n/a	0.5	2.5	50
	3-phenylpyridine	155	269	69	0.5	2.5	75
	Nitrobenzene-D5	128	88	5	0.2	3.2	73
	2-chlorothiophene	119	127	51	0.7	3.2	83
	3-chlorothiphene	119	137	49	0.7	2.5	91
Carboxylic Acids	dichloroacetic acid	129	194	9	0.3	4	91
	Non-enyl acetic acid	184	234	n/a	0.3	3.2	50
	2,6-diamino-4-hexenoic acid	144	n/a	n/a	0.3	1.5	52
	Undec-10-ynoic acid	184	137	n/a	0.7	3	57

n/a: not available

TABLE II. RECOVERIES FOR EFFLUENT AND SURFACE WATER

VOCs	Conc. (µg/l)	EW-LC-1 MEAN±RSD	EW-EP-1 MEAN±RSD	SW-LC-1 MEAN±RSD	SW-EP-1 MEAN±RSD
Alkanes (butane)	0.01	85.0±3.0	84.7±3.8	72.3±2.5	95.3±5.5
	0.02	82.3±2.5	91.7±1.5	63.3±1.5	95.0±3.0
	0.05	84.3±3.8	95.0±1.0	81.7±3.5	83.0±2.0
Alkenes (butene)	0.01	73.7±1.5	80.0±2.0	82.7±2.5	70.0±2.0
	0.02	90.7±2.1	84.0±1.0	73.0±1.0	74.0±1.7
	0.05	95.3±1.5	88.7±1.5	77.3±2.1	76.7±2.3
Aromatics (benzene)	0.01	ND	82.3±2.5	88.3±2.1	82.7±3.6
	0.02	ND	93.4±3.2	98.0±4.6	65.7±2.1
	0.05	ND	82.7±2.5	97.7±4.2	62.3±2.5
Carboxylic Acids (ethanoic acid)	0.01	86.0±4.0	83.7±3.2	65.0±3.0	71.7±1.5
	0.02	93.7±1.5	88.0±1.0	65.0±1.0	75.7±2.1
	0.05	83.7±3.2	91.7±1.5	69.0±1.0	75.3±3.5

TABLE III.   RECOVERIES FOR SOIL, SEDIMENT AND PLANT SAMPLES

VOCs	Conc.	SL-LC-3 MEAN±RSD	SL-EP-3 MEAN±RSD	SD-LC-4 MEAN±RSD	SD-EP-4 MEAN±RSD	PT-LC-5 MEAN±RSD	PT-EP-5 MEAN±RSD
Alkanes (butane)	0.01	82.0±2.6	78.3±7.6	98.7±1.5	95.0±2.6	67.7±2.5	96.3±1.5
	0.02	89.7±5.5	88.3±7.6	95.7±3.2	72.7±4.2	85.3±4.2	78.0±2.0
	0.05	96.3±3.8	89.3±7.4	86.3±1.5	91.0±3.6	84.0±1.0	93.7±3.5
Alkene (butene)	0.01	ND	ND	97.7±3.2	ND	ND	75.0±3.0
	0.02	ND	ND	77.3±2.5	ND	ND	82.7±2.5
	0.05	ND	ND	90.0±2.0	ND	ND	99.3±2.0
Aromatics (benzene)	0.01	67.7±2.5	72.3±2.5	ND	ND	96.7±2.5	ND
	0.02	74.3±2.1	81.3±3.1	ND	ND	67.0±3.0	ND
	0.05	79.0±1.0	72.7±2.1	ND	ND	79.3±2.5	ND
Carboxylic Acids (ethanoic acid)	0.01	ND	85.0±3.0	70.3±1.5	99.0±2.6	ND	85.0±3.6
	0.02	ND	90.7±2.1	76.7±3.0	74.7±3.5	ND	76.3±1.5
	0.05	ND	83.7±3.2	85.7±3.2	91.7±2.	ND	94.3±2.5

2) Recovery study on soil, sediment and plant samples

The recoveries of volatile organic compounds from spiked soil, sediment and plant were done at three concentration levels, at each concentration level, three determinations were performed. It was observed at 0.01 μg/l, 0.02 μg/l and 0.05 μg/l respectively, soil sample recorded a mean recovery range and relative standard deviation (RSD) of [72.3±2.5 - 85.0±3.0, 74.3±2.1 – 90.7±2.1 and 72.7±2.1 – 96.3±3.8], sediment sample (70.3±1.5 – 99.0±2.6, 72.7±4.2 – 95.7±3.2 and 85.7±3.2 – 91.7±2.5) while plant sample obtained (67.7±2.5 - 96.7±2.5, 67.0±3.0 – 85.3±4.2 and 79.3±2.5 – 99.3± 2.0).
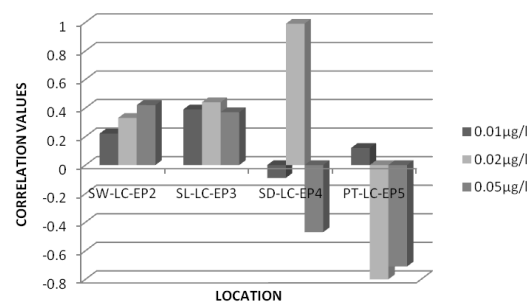
C. Correlation values of volatile organic compounds based on recovery concentration

The table 4 shows the correlation analysis for volatile organic compounds targeted at petroleum companies' effluent with other environmental matrix (surface water, soil, sediment and plant). The degree of freedom is 5, critical table value = 0.754 at 5% significance level.

At 0.01 μg/l for surface water, soil, sediment and plant (-0.1 - 0.4) and 0.05 μg/l (-0.5 – 0.4) rcal < rtable therefore the null hypothesis Ho cannot be rejected and this account show that volatile organic compound from effluent water do not have effect on the environmental matrix at that concentration.

At 0.02μg/l rcal < rtable for surface water, soil and plant (-0.8 – 0.4), while rcal > rtable for sediment (0.99) this implies that the null hypothesis Ho would be rejected and this affirm that volatile organic compound targeted for effluent of petroleum companies at this concentration have little effect on the sediment.

TABLE IV.   CORRELATION VARIABLES OF VOLATILE ORGANIC COMPOUNDS BASED ON RECOVERY CONCENTRATION

EW-LC-EP-1 (μg/l)	SW-LC-EP-2	SL-LC-EP-3	SD-LC-EP-4	PT-LC-EP-5
0.01	0.22	0.39	-0.09	0.12
0.02	0.33	0.44	0.99	-0.8
0.05	0.42	0.37	-0.47	-0.71

Figure 2.   3-D column correlation variables of volatile organic compounds based on recovery concentration

V.   CONCLUSION

The concentration of volatile organic compounds at 0.01 μg/l, 0.02 μg/l and 0.05 μg/l respectively analyzed showed variations for effluent and other environmental matrix.

The volatile organic compounds were determined on effluent sample and other environmental matrix, their percentage quality range are as follows: Alkanes (53-97 %), alkenes (50-97 %), while aromatics and carboxylic acids (50-91%). This reveal the quality of liquid-liquid extraction method used for mixed solvents (Hexane: Dichloromethane) to generate good recovery as aimed. Test significance was carried out using correlation analysis at significance level of 5 % on recovery concentration of volatile organic compounds. Volatile organic compounds of effluent samples were correlated with other environmental matrix and it was discovered that at 0.02 μg/l, the sediment sample was contaminated. It can be seen that volatile organic compounds are characterized by high toxicity, high environmental stability and high hydrophobicity resulting in their accumulation through the tropic chain with final destination in the human body. The distribution of Volatile Organic Compounds in the environment and potential human health risks have become the focus of much attention. Their presence in water bodies combined with other potentially toxic compounds can result in negative effects. In conclusion, though the effluent samples gave a good recovery due to their

concentration being below limit of quantification, it is evident that the study area presents a critical situation, offering risks to environmental compartments and finally to the general populace.

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