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# Comparative Analysis of Some Brands of Pesticides Utilized in Eastern Nigerian Environment

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***Abstract:***
*Some pesticide products sold and utilized in eastern Nigeria was investigated for the actual chemical composition aimed at specifying the number of chemical constituents and the actual active ingredient(s) present in the pesticide products. Four pesticide products were bought from Eke Awka Market in Anambra State. Gas Chromatography - Mass Spectrometry (GC-MS) technique was used for the analysis of the products. Results indicates that the sample A contains eight (8) chemical constituents with percentage compositions as follows: Toluene (19.00%), Cumene (6.53%), indane (21.65%), 1-chloro-Indane (8.05%), Endo-8,9-dihydrodicyclopentadiene (16.65%), 9,10-Dimethylene tricycle[4.2.1.1(2,5)]decane (3.41%), 2,3-Anhydro-d-mannosan (3.42%) and 1,14-Tetradecanediol (11.27%) while sample B (100%), C (95.96%) and D (84.90%) contain Dichlorvos as their active ingredient which is in line with the labeled content even though there are other compounds present. Results equally pointed out that none of the identified components in sample A is a pesticide active ingredient. Therefore, it is a matter of public health significance and environmental sustainability to frequently monitor labeled and unlabeled pesticide products sold and utilized in Nigeria in order to ascertain their true chemical composition so as to check the illegal formulation of these pesticides in this region by traders with little knowledge of public health policies.*

***Key words****: pesticide product, chemical composition, pesticide, GC-MS, environmental sustainability*

## 1. Introduction

In nature, there seems to be no pest(s). Humans label as “pests” any plants or animals that endanger food supply, health or comfort. To manage these pests we have “pesticides” (Benbrook, 1991). The biological activity of a pesticide whether chemical or biological in nature, is determined by its active ingredient (AI - also called the *active substance*). Pesticide products very rarely consist of pure technical material. The AI is usually formulated with other materials and this is the product as sold, but it may be further diluted in use. Formulation improves the properties of a chemical for handling, storage, application and may substantially influence the effectiveness and safety (Burges, 1998). Pesticides are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest (US-EPA, 2007). A more elaborate definition of pesticide by Food and Agriculture Organization (FAO) is- “any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit. Also used as substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport (FAO, 2010). They include herbicides, insecticides, rodenticides, fungicides, molluscides, nematicides, avicides, repellants and attractants used in agriculture, public health, horticulture, food storage or a chemical substance used for a similar purpose (NAFDAC, 1996).

Most people eat food grown in a system that uses pesticides and many individuals use pesticides in the house or garden. In places where there are insects whose bites can be a nuisance or a hazard, insecticides are used to make life safer or more comfortable. Yet there has been little acknowledgement of the important beneficial role that pesticides play in world agriculture, or in parts of the world where flies and other arthropod vectors spread dreadful diseases (WHO, 2004).

For all pesticides to be effective against the pests they are intended to control, they must be biologically active, or toxic. Because pesticides are toxic, they are also potentially hazardous to humans, animals, other organisms, and the environment. Pesticides are distributed in the environment by physical processes such as sedimentation, adsorption, and volatilization. They can then be degraded by chemical and/ or biological processes. Chemical processes generally occur in water or the atmosphere and follow one of four reactions: oxidation, reduction, hydrolysis, and photolysis. Biological mechanisms in the soil and living organisms utilize oxidation, reduction, hydrolysis and conjugation to degrade chemicals. The process of degradation will largely be governed by the compartment (water, soil, atmosphere, biota) in which the pesticide is distributed, and this distribution is governed by the physical processes already mentioned (Clark, 1994).

The four main groups of pesticides such as the organochlorine, organophosphate, carbamate, and pyrethroid insecticides (Smith, 2002; Ahmed, *et. al*; 2000) are of particular concern because of their toxicity and persistence in the environment; however several of the banned pesticides are still used on a large scale in developing countries and continue to pose severe health and environmental problems. Farmers in developing regions seem to treat pesticides as substitutes for fertilizers and there is a need to create awareness among the farmers on Integrated Pest Management (Sanzidur, 2003). Pesticide toxicity can result from ingestion, inhalation or dermal absorption. Therefore, people who use pesticides or regularly come in contact with them must understand the relative toxicity, potential health effects, and preventative measures to reduce exposure to the products they use (Eric, 2009).

Some locally made pesticides had caused the death of so many Nigerian families in recent times (Olebunne, 2009) and worldwide (USEPA, 2007), specifically through food contamination (Akunyili, 2007). Children are especially prone to accidental poisoning of this product (Okeniyi, *et. al*; 2007). Also most pesticide preparations include carriers' substances in addition to the active ingredients and also solvents and compounds that improve absorption, etc. These "inert ingredients" are not usually included in any discussion of the effects on health although they frequently comprise a large part of a commercial pesticides product, and their adverse effects may exceed those of the active ingredients without being mentioned on the product label.

Local pesticide makers in Nigeria emphasized the potency of their pesticides by the word "*Ota-piapia*" indicating that such products will completely take care of our little pest problem (Mortui, 2006). Its acceptance and wide spread proliferation in Nigeria have been due solely to its cheap production, efficacy, accessibility and affordability (Essiet, *et. al*; 2009). The product is still not registered with NAFDAC (Akunyili, 2007), but have been commonly used as insecticide, especially for mosquitoes (Foll et al, 1965), food storage, such as grains and preventing insect infestation (FAO, 2001). This is the trend of application in Nigeria. The local formulation of *Ota-piapia* is thought to entails repackaging into a small (about 10 - 15mL) retail bottle of an active ingredient which is unspecified pesticides from those imported, which include cypermethrin, *dichlorvos*, gammalin 20, gammalin super, lindane, capsitox 20 (PAN, 2007). Some may contain homemade cocktail of kerosene, oil, alcohol and any suitable solvent with the pesticide.

Therefore, there is a need to analyze locally formulated pesticide products, both labeled and unlabelled in a Nigeria market to determine their actual chemical constituents.

## 2. Materials and Methods

### *2.1. Study Area*

The entire pesticide products were purchased from Eke-Awka market, Anambra State, Nigeria. The choice of the brand was based on the highest consumption among those available in the market. All reagents, chemicals and solvents such as n-hexane used were purchased from Bridge Head Market Onitsha, Anambra State, Nigeria.

| S/N | TRADE NAME | SAMPLE CODE | STATED ACTIVE CONSTITUENTS |
|---|---|---|---|
| 1 | Kombat | A | Lambda Cyhalothrin |
| 2 | Sniper | B | Dichlorvos |
| 3 | Smash Super | C | Dichlorvos |
| 4 | DD-Force | D | Dichlorvos |

*Table 1: Sampled Products Information*

### *2.2. List of Equipment*

Volumetric flask, measuring cylinder and Gas Chromatography – Mass Spectrometry Machine (GC –MS), model QP2010 PLUS SHIMADZU, made in JAPAN.

### *2.3. Sample Preparation*

Approximately 0.5ml of the product was dissolved in a proper amount of n-hexane which was made up to 100mL in a volumetric flask at room temperature to obtain a clear solution resulting to a stock concentration of 0.5ml/100mL (5mg/L or 0.5% v/v). Pesticide product solution obtained was transferred into 5ml glass vial and was taken to Zaria, Kaduna State, Nigeria for Gas Chromatography – Mass Spectroscopy (GC-MS) analysis.

**3. Result and Discussion**

Figure 1 shows that there are eight (8) peaks which represent eight (8) components present in sample A. Each component has its own mass spectrum and matched spectrum and the respective mass profile of a known compound recommended by Gas Chromatography–Mass Spectrometry (GC – MS) Library for component identification. Table 2 shows the observed retention time and percentage area of each component in the product for determining the amount of each identified component and also it includes molecular formula, compound name and the molecular structure of each component identified from Gas Chromatography – Mass Spectrometry (GC-MS) analysis. The GC-MS analysis of sample A reveals that there are more than one constituent contrary to what the product manufacturer claimed. The specified Lambda Cyhalothrin as the active ingredient in the product was not found.

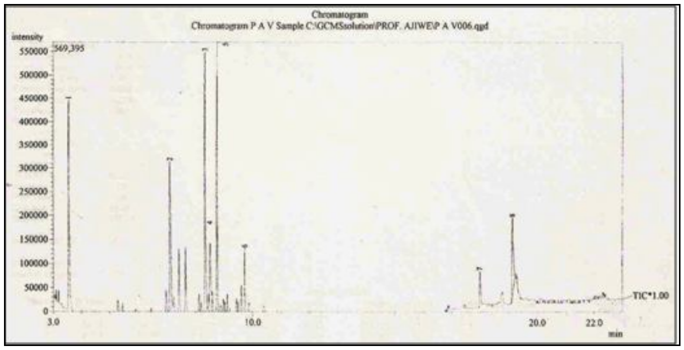



*Figure 1: Gas Chromatograph of the Sample A.*

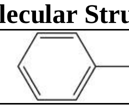
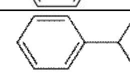
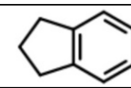
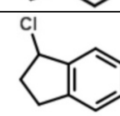
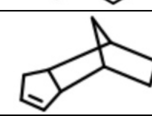
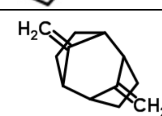
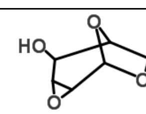
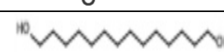
| Peak No | RT Time | Area (%) | Formula | Compound Name | Molecular Structure |
|---|---|---|---|---|---|
| 1 | 3.556 | 19.00 | $C_7H_8$ | Toluene |  |
| 2 | 7.113 | 16.53 | $C_9H_{12}$ | (1-methylethyl)-Benzene(Cumene) |  |
| 3 | 8.338 | 21.65 | $C_9H_{10}$ | Indane |  |
| 4 | 8.511 | 8.07 | $C_9H_9Cl$ | 1-chloro-Indane |  |
| 5 | 8.758 | 16.65 | $C_{10}H_{14}$ | Endo-8,9-dihydro dicyclopentadiene |  |
| 6 | 9.724 | 3.41 | $C_{12}H_{16}$ | 9,10-Dimethylene tricycle[4.2.1.1(2,5)]decane |  |
| 7 | 18.000 | 3.42 | $C_6H_8O_4$ | 2,3-Anhydro-d-mannosan |  |
| 8 | 19.137 | 11.27 | $C_{14}H_{30}O_2$ | 1,14-Tetradecanediol |  |

*Table 2: Identified Compounds in Sample A*

Fifty percent (50%) of the compounds identified in sample A are aromatic hydrocarbons which are the main constituents of Kerosene Oil ($C_{10}H_{22}$-$C_{12}H_{26}$) and when present in the environment at a substantial amount has no or little environmental impact. These chemicals are not likely to persist in the environment, as they will largely partition to the air where they will degrade via photo-oxidation (VCCEP, 2004). According to Material Safety Data Sheet (MSDS) of 1, 14-Tetradecanediol by Sigma-Aldrich Canada, Ltd, 2149 Winston Park Drive Oakville ON L6H 6J8 CA, some of the identified compounds emit toxic fumes under fire conditions with hazardous composition products such as carbon monoxide and carbon dioxide. Also, Indane, Cumen etc are extremely flammable liquid which contains material which may cause damage to the following organs: blood, kidneys, liver, gastrointestinal tract, upper respiratory tract, skin, central nervous system (CNS), eye, lens or cornea, according to their Material Safety Data Sheet (ref: MSDS # 007884 by AIRGAS INC., on behalf of its subsidiaries 259 North Radnor-Chester Road, Suite 100 Radnor, PA 19087-5283, 1-610-687-5253). It has shown that none of the constituents identified is a pesticide active ingredient.

Figure 2 show that there is only one (1) peak which represents one (1) component present in Sample B. The component has a mass spectrum, matched spectrum and the mass profile of a known compound recommended by GC – MS Library for component identification.

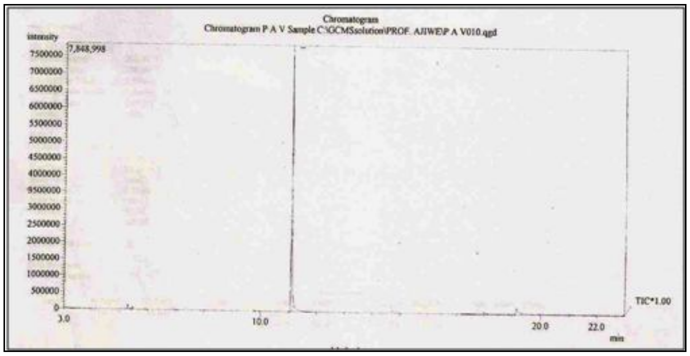



*Figure 2: Gas Chromatograph of Sample B*

Table 3 shows the observed retention time and percentage area of the component in sample B for determining the amount of identified component and also it includes molecular formula, compound name and the molecular structure of the component identified from GC-MS analysis. The GC-MS analysis of this sample of pesticide product reveals that there is only one pesticide active ingredient as stated by the product manufacturer. The Labeled pesticide active ingredient was 99.8%.

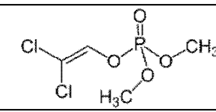
| Peak No | RT Time | Area % | Formula | Compound Name | Molecular Structure |
|---|---|---|---|---|---|
| 1 | 11.092 | 100 | $C_4H_7Cl_2O_4P$ | Dichlorvos |  |

*Table 3: Identified Compound in Sample B*

Figure 3 shows that there are three (3) peaks which represent three (3) components present in sample C. Each component has its own mass spectrum and their respective matched spectrum and mass profile of a known compound recommended by GC – MS Library for component identification.

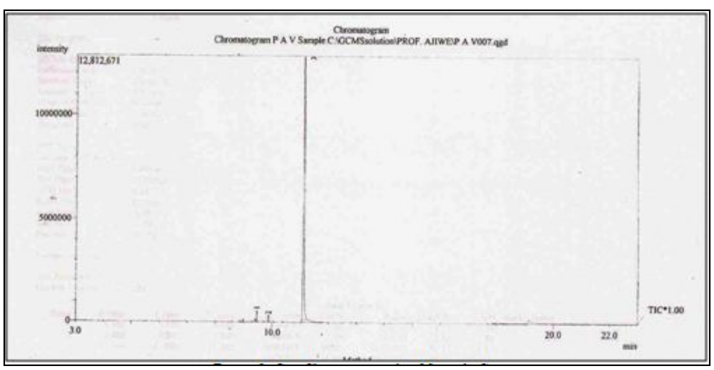



*Figure 3: Gas Chromatograph of Sample C*

Table 4 shows the observed retention time and percentage area of each component in Sample C for determining the amount of each identified component and also it includes molecular formula, compound name and the molecular structure of each component identified from GC-MS analysis. GC-MS analysis of Sample C reveals that there are more than one constituent contrary to what the product manufacturer labeled. Labeled pesticide active ingredient present in the sample was 95.96% Dichlorvos.

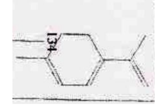
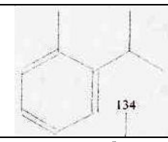
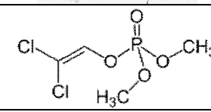
| Peak No | RT Time | Area % | Formula | Compound Name | Molecular Structure |
|---|---|---|---|---|---|
| 1 | 9.456 | 2.56 | $C_{10}H_{14}$ | 1,3,8-p- Menthatriene |  |
| 2 | 9.868 | 1.48 | $C_{10}H_{14}$ | o-cymene |  |
| 3 | 11.104 | 95.96 | $C_4H_7Cl_2O_4P$ | Dichlorvos |  |

*Table 4: Identified Compounds in Sample C*

Figure 4 shows that there are three (3) peaks which represent three (3) components present in Sample D. Each component has its own mass spectrum and their respective matched spectrum and mass profile of a known compound recommended by GC – MS Library for component identification.

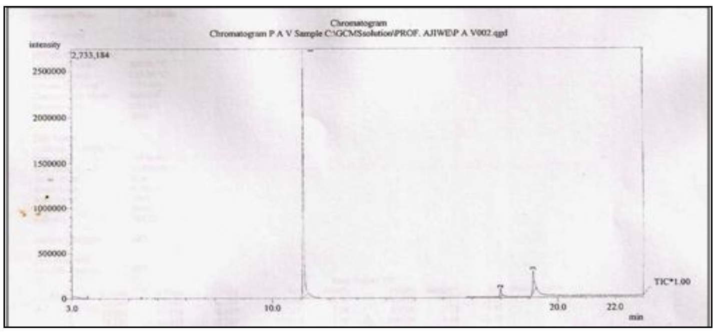



*Figure 4: Gas Chromatograph of Sample D*

Table 5 shows the observed retention time and percentage area of each component in Sample D for determining the amount of each identified component and also it includes molecular formula, compound name and the molecular structure of each component identified from Gas
Chromatography – Mass Spectrometry (GC-MS) analysis. The GC-MS analysis of this Sample D revealed that there are more than one constituent contrary to what the product manufacturer labeled. Labeled pesticide active ingredient present in the sample was 84.90% dichlorvos.

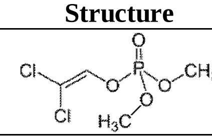
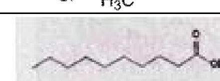
| S | RT Time | Area % | Formula | Compound Name | Molecular Structure |
|---|---|---|---|---|---|
| 1 | 11.084 | 84.90 | $C_4H_7Cl_2O_4P$ | Dichlorvos |  |
| 2 | 17.995 | 3.08 | $C_{10}H_{20}O_2$ | n-Decanoic acid |  |
| 3 | 19.134 | 12.02 | $C_{13}H_{26}O$ | Cyclohexane, [2-(pentyloxy) ethyl] |  |

*Table 5: Identified Compounds in Sample D*

**4. Conclusion**

The analysis indicated the presence of compounds that are not pesticide active ingredients in the analyzed products and the products are registered with the National Agency for Food Drug Administration and Control (NAFDAC) and no pesticide active ingredient was identified in one (sample A) of the product even though the label specified Lambda Cyhalothrin as the active ingredient. None of the compounds identified from the analysis is a banned or restricted pesticide as listed in Nigeria's NESREA regulations of National

Environmental (Sanitation and waste control) regulations of 2009 and such product which does not comply with the claims should not be allowed in our market since its chemical constituents is unknown.

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