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Insight of Intrinsic Health Risk from Chemical Profiles in Some Insecticides for Grain Foodstuff Storage in Benue State, Nigeria

E.K.^{1*} Ukpoko, I.S.¹ Eneji, Q. M.² Amua, R.A.³ Wuana

¹Chemistry Department, Faculty of Physical Sciences, Joseph Sarwuan Tarka University Makurdi, Nigeria

²Department of Natural Sciences, British Canadian University Obudu, Cross River State, Nigeria.

³Environmental sustainability Department, Joseph Sarwuan Tarka University Makurdi, Nigeria.

*Correspondence E-mail: ukachiemma@gmail.com

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Abstracts

It is imperative to devise proper control measures for the use of pesticides for good agricultural practices such as appropriate application, detection, and elimination methods for pesticides on foodstuffs. These control measures are required for attainment of food security goals. To attain food security goals, with cautious control measures, the chemical profiles of each particular insecticide commonly use in a particular locality are to be reviewed. This could pave way for precise precautionary measures to eliminate the known toxic substances without missing little in foodstuff before consumption. This research team has reviewed that, three insecticides of Aluminium phosphide, Dichlovos and Permethrin are commonly used insecticides for foodstuff storage in Benue State. Hence the chemical profile of these three insecticides was analysed using Gas-Chromatography couple Mass Spectrophotometer (GC-MS) and X-Ray fluorescence (XRF). The cogent information on the chemical profiles in those insecticide brands used amongst farmers and dealers for storage of foodstuff was revealed. These three brands of insecticides contained different chemicals; Aluminium phosphide 26 minerals and 25 oxides, Dichlovos contains 60 compounds and Permethrin contains 20 compounds. The result was here by presented and discussed, highlighting intrinsic health risk from chemical insecticide application on foodstuffs. When the chemical profiles of the insecticides are known, elimination of the toxic substance from the foodstuff could be an easy task by taking precautionary measures specific for such specific contaminant's removal techniques.

Key Words: Insecticides, Chemicals, Profiles, foodstuff, storage.

Introduction

The increasing awareness of food safety and quality control against residual pesticide concentrations in harvested/stored foodstuff produce is the reason on which this study was under taken. The instrument of Gas – Chromatography couple Mass Spectrophotometer (GC-MS)[1] and X-Ray Fluorescence (XRF)[2] were used to obtain information on the whole chemical profiles of the three common insecticide brands used amongst farmers and dealers for storage of foodstuff in Benue State. The acute health effects of these insecticides include; blisters, blindness, stinging eyes, rashes, nausea, diseases, diarrhea, carcinogens even, death are reported to be caused by residues that remain on agricultural foodstuff commodities and established by the World Health Organization [3]. It is imperative to devise proper control measures for good agricultural practices and appropriate application of pesticide elimination for food security goals [4,5,6]. To attain these goals the chemical profiles of each particular insecticide commonly used in a particular locality must be revealed to pave way for proper precautionary measures of eliminating the toxic substances without missing little in foodstuff before consumption. When the chemical profiles of the insecticides are known, elimination of the toxic substance from the foodstuff could be an easy task. According to

the survey report [7], in a multiple response schedule on commonly used insecticides in Makurdi Benue state, aluminum phosphide tablets ranked 80% as a foodstuff storage pesticide, dichlovos was 60%, DDT 35%. Others such as endosulfan, gamalin, carbofuran, carbendazim, and permethrin were between 5-15%. Also from a yet published surveyed by this team in the 2023, it is shown that three active chemicals of Aluminium phosphide, Dichlovos, Permethrin in different brands names emerged the top patronized insecticides for foodstuff storage aid at 37.50 %, 33.33%, 20.83% respectively, the rests insecticides shared the 8.33% only which is similar to that of survey report [7]. These two recent survey reports are 66.31% similar, about pesticide application in foodstuff storage in Makurdi Town of Benue State. Based on these two reports Aluminium phosphide, Dichlovos and Permethrin are selected as the commonly used insecticide in Benue State for foodstuff storage and hence its chemical profile was investigated. To ascertain and reveal chemical profiles of particular insecticide commonly use in a particular locality to pave ways for proper precautionary measures of eliminating the toxic substances without missing little in foodstuff before consumption.



Materials and Methods

Collection of samples

The documented information from the survey report of [7] and the surveyed by this team was used to sort identified the commonly used pesticide for storage of foodstuff in Makurdi Town as Aluminium phosphide, Dichlovos and Permethrin were selected. These commonly used insecticides were purchased and analysed for chemical composition profiles. This is because domestic and commercial grain foodstuffs are massively shifted into Makurdi Township, the headquarters of Benue State, Nigeria for Storage.

Analysis of chemical profiles in inorganic pesticides complex

A handheld Thermo Scientific NITON XL3t X-Ray Fluorescence (XRF) machine was used to analysed the Chemical profiles of inorganic pesticides. Aluminium phosphide, an inorganic pesticide was purchase and prepared into fine powder. After fixing the battery into the (XRF) machine battery holder, the machine was switched on. The "Mining Cu/Zn" testing mode was selected on the machine menu. The powder sample was measured in the XRF sample cup provided with the machine. The cup was placed on the table to stand then, the machine was placed directly on the sample. It was ensured that the machine's measurement window gauged flushes with the sample and the trigger was held for the testing time of 180seconds which sniff in about 1 gram sample. The XRF machine displayed the reading which was transferred electronically to computer and was printed to a hard copy, while the readings still on the machine's flip-up, touch-screen display.

Analysis of chemical profiles of organic pesticides complex:

The Chemical profile of the homogeneous liquid complex of organic pesticide of Dichlovos and Permethrin was analysed on Agilent 19091S-433UI GC-MS/MS (Triple Quad- S. No. SN: US1447L431) consecutively. The

system, equipped with an HP-5ms Ultra Inert capillary column with a stationary phase (30.0 m × 0.25 mm and a film thickness of 0.25 µm). Different temperatures of the oven were considered to achieve good separation in standard as well as in samples. The instrument was set to an initial temperature of 70 °C and maintained for 3 mins., then in the second stage temperature was allowed to rise by 3 °C/min up to 250 °C, then finally attended 325 °C by expanding the heating rate to 80°C/min. The flow rate of Helium carrier gas was kept at 1.2 mL/min, injection port temperature was kept at 250 °C while the ionization voltage was 70 eV and the linear velocity of the column was 40.37 cm/sec. GC-MS spectra were interpreted by using the NIST 14-MS data-base library stored in Standard Analytical Laboratory (SAL). The Retention Time (RT) and Peak Area where percentage concentrations were ascertained.

Results and Discussion

The results obtained from the activities of this research in the form of images are presented in figures while the numeric data and word remark/ description are presented in tables. Figure 1, is the XRF Chromatograph of Elements and Oxides profile in a branded Aluminum Phosphide insecticide, the chromatograph showed the presence of some excipients and pollutants other than the labeled Aluminum phosphide. Table 1 is the presentation of result from XRF analysis on Elements and Oxides profile in Aluminum phosphide Pesticides. This result clearly presents the high percentage active chemical of Aluminum and phosphide with low percentage of some metals excipients like Chlorine, Iron and Zinc in the profile. Figure 2 present the GC-MS Chromatograph of Qualitative Analysis of Commercial Dichlovos brand in Benue state Markets without the dichlovos as the main branded active chemical though with Chlorpyrifos present with the highest peak. Figure 3 shows the GC-MS Chromatograph of Qualitative analysis of commercial branded Permethrin in Benue Markets. It shows the chromatograph of permethrin at peak fourteen.

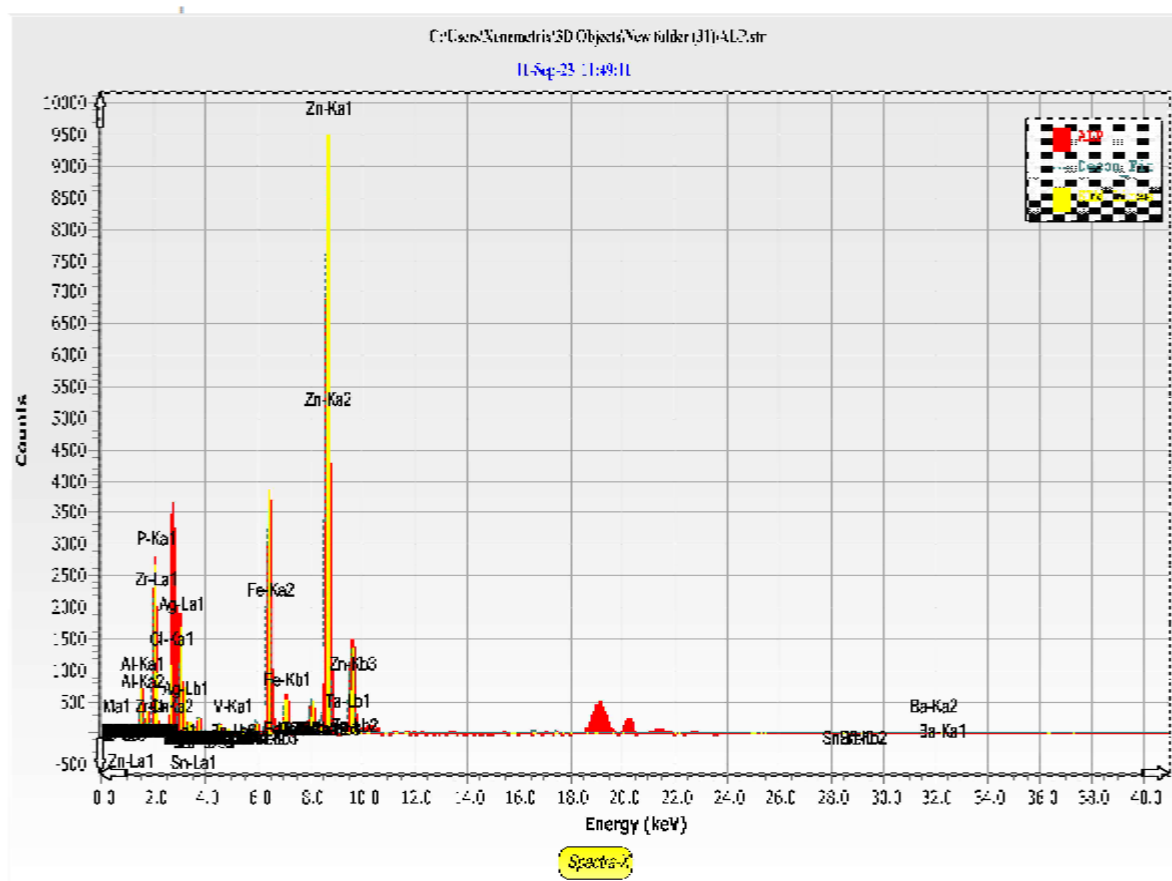


Fig.1: XRF Chromatograph of Elements and Oxides Profile in Aluminum Phosphate Pesticides

Table 1: XRF Elements and Oxides profile in Aluminum Phosphate Pesticides in Benue State Markets

	Elements	Conc.mg/g	Oxides	Conc.mg/g
1	O	48.466	-	-
2	Mg	0.000	MgO	0.000
3	Al	31.573	Al ₂ O ₃	59.655
4	Si	4.202	SiO ₂	8.990
5	P	11.188	P ₂ O ₅	25.636
6	S	0.195	SO ₃	0.487
7	Cl	1.714	Cl	1.714
8	K	0.000	K ₂ O	0.000
9	Ca	0.262	CaO	0.366
10	Ti	0.063	TiO ₂	0.106
11	V	0.001	V ₂ O ₅	0.003
12	Cr	0.029	Cr ₂ O ₃	0.042
13	Mn	0.048	MnO	0.062
14	Fe	0.727	Fe ₂ O ₃	1.040
15	Co	0.021	Co ₃ O ₄	0.029
16	Ni	0.013	NiO	0.017
17	Cu	0.078	CuO	0.098
18	Zn	1.202	ZnO	1.496
19	Zr	0.003	ZrO ₂	0.004
20	Nb	0.010	Nb ₂ O ₃	0.013
21	Mo	0.008	MoO ₃	0.011
22	Ag	0.022	Ag ₂ O	0.024
23	Sn	0.000	SnO ₂	0.000
24	Ba	0.061	BaO	0.068
25	Ta	0.028	Ta ₂ O ₅	0.034
26	W	0.086	WO ₃	0.108
27	Total	100.00	-	100.00



Insecticides chemical profile of aluminum phosphide used in foodstuff; The goals of analyzing the most insecticides used for foodstuff storage in Benue state was successful with the used of XRF for analysis for the inorganic pesticides of aluminum phosphide. The chemical profiles of the aluminum phosphide insecticides were revealed to pave ways for proper understanding of the chemical profiles for specific precautionary measures on eliminating the toxic substances without missing the target by random treatment of foodstuff before

consumption. The insecticide brand of aluminum phosphide analyzed for chemical profile has Twenty-three mineral and oxide which were identified. The six mineral and oxide of most abundance percentages in the profile are, Al: 31.573, Al_2O_3 : 59.655, P: 11.188, P_2O_5 : 25.636, Cl: 1.714, Fe: 1.727, Fe_2O_3 : 1.040, Si: 4.202, SiO_2 : 8.990 and Zn: 1.202, ZnO: 1.496 % respectively. The rest of the minerals and oxide are less than 1% in the brand of aluminum phosphide analyzed and presented in Table 1.

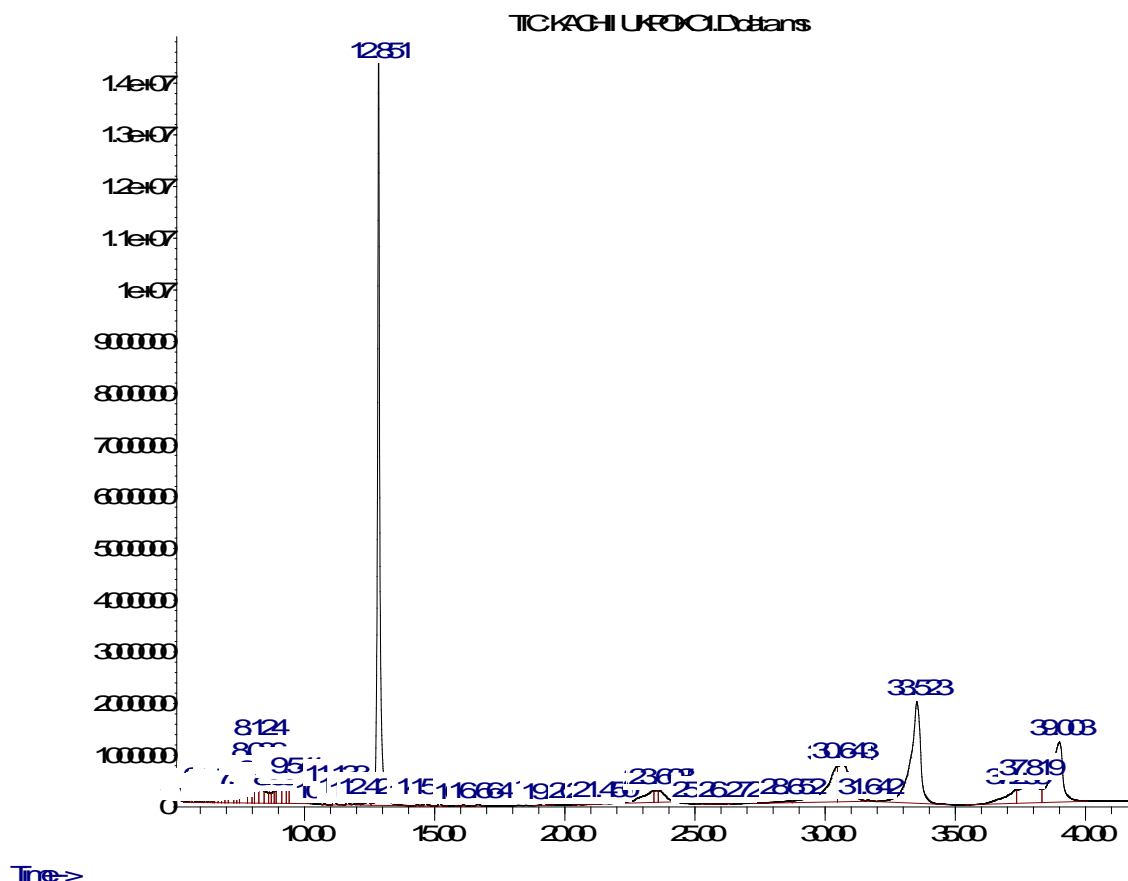


Fig. 2: TIC: KACHII UKPOKOI.D\data.ms is a GC-MS Chromatograph of Qualitative Analysis of Commercial Dichlofos in Benue Markets

**Table 2: GC-MS Analysis of Commercial Dichlovos in Benue State Markets**

Peaks	Compounds Identities	Retention Times	Area Peaks
1	Tetradecane	5.3113	0.0047
2	Metrifonate	5.5374	0.0249
3	Naphthalene, 2,6-dimethyl-	5.6176	0.1269
4	Naphthalene, 1,3-dimethyl-	5.732	0.1461
5	Naphthalene, 1,6-dimethyl-	5.8855	0.0338
6	1H-2-Benzothiopyran, octahydro-, cis-	6.0342	0.0823
7	Dodecanoic acid, methyl ester	6.1831	0.2232
8	17-Pentatriacontene	6.3317	0.0723
9	4(1H)-Oxopyridine-1-carboxylic acid, ethyl ester	6.4501	0.0545
10	2-ethylbutyric Acid, 2,2,2-trifluoroethyl ester	6.5246	0.0607
11	Dodecanoic acid	6.6309	0.1937
12	Dodecane	6.7653	0.3508
13	N-(5-Oxo-tetrahydro-furan-2-ylmethyl)-acetamide	6.8645	0.2345
14	Hexadecenoic acid, Z-11-1H,3H-Pyrano[3,4-c]pyran-5-carboxaldehyde, 4,4a,5,6-tetrahydro-6-methyl-1-oxo-, [4as-(4a.alpha.,5.alpha.,6.beta.)]-	7.0409	0.2033
15	cis-Z-.alpha.-Bisabolene epoxide	7.2288	0.5040
16	Dodecane, 1-chloro-	7.3281	0.4069
17	Dodecane, 1-chloro-	7.4692	0.4172
18	2-Piperidinone, N-[4-bromo-n-butyl]-	7.7809	1.9257
19	1-Nonylcycloheptane	7.9108	1.7698
20	Tridecanoic acid, 12-methyl-, methyl ester	8.0363	1.0596
21	1-Pentadecene	8.1238	1.8802
22	(S)(+)-Z-13-Methyl-11-pentadecen-1-ol acetate	8.2905	1.1686
23	2-Piperidinone, N-[4-bromo-n-butyl]-	8.4735	0.6594
24	Cyclotetradecane	8.6543	0.3770
25	Oleic Acid	8.8103	0.4449
26	Octadecane	8.8826	0.3081
27	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	9.044	1.4314
28	n-Propyl decyl ether	9.1843	1.2461
29	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	9.3364	0.6686
30	Palmitoleic acid	9.5408	2.4141
31	Hexadecanoic acid, methyl ester	10.7535	0.0327
32	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	11.1326	0.4640
33	Benzothiazole, 2-methyl-	11.6413	0.1748
34	1-Octadecanesulphonyl chloride	12.0568	0.0829
35	Chlorpyrifos	12.4211	0.3508
36	Trifluoroacetoxy hexadecane	12.8513	27.1131
37	9,12-Octadecadienoic acid, methylester, (E,E)-	14.3298	0.0624
38	10-Octadecenoic acid, methyl ester	14.5201	0.0405
39	Methyl stearate	14.6384	0.2228
40	9-Octadecenoic acid	15.1819	0.1735
41	9-Methyl-Z,Z-10,12-hexadecadien-1-ol acetate	16.0939	0.0348
42	Methyl 12-hydroxy-9-octadecenoate	16.6637	0.0781
43	Z-8-Methyl-9-tetradecenoic acid	19.1683	0.2736
44	8,8-Dimethyl-7,9-dioxabicyclo[4.3.0]nonane-3-carboxylic acid, methyl ester	19.4454	0.0316
45	2-Trifluoroacetoxytridecane	20.5249	0.0312
46	1-Decanol, 2-hexyl-	21.1888	0.0328
47	n-Propyl Nonyl Ether	21.4496	0.0526
48	Oleic Acid	23.3993	2.1595
49	Oleic Acid	23.5268	0.6636
50	Oleic Acid	23.6031	1.2160
51	Oleic Acid	25.2686	0.0512
52	Lauroyl peroxide	26.2717	0.0175
53	Oleic Acid	28.6522	0.4216
54	Oleic Acid	30.4522	6.2201
55	Hexacosanoic acid	30.6432	6.5788
56	2,6,10-Dodecatrinal, 3,7,11-trimethyl-, (Z,E)-	31.642	0.0583
57	Dodecanoic acid, 1,2,3-propanetriyl ester	33.5229	15.9408
58	Lauric anhydride	37.2948	2.5430
59	Propanamide, N-(3-chlorophenyl)-2,2-dimethyl-	37.8194	5.7320
60	Vinyl lauryl ether	39.003	10.6614
			100.0453



Insecticides chemical profile of dichlovos used in foodstuff

Fig 2: TIC: KACHII UKPOKO1.D/data.ms is a GC-MS Chromatograph of Qualitative Analysis of Commercial Dichlovos in Benue Markets. Table 2 is the GC-MS analysis which has revealed sixty (60) compound and fragment of compounds with different densities of elution time from insecticides of Dichlovos brand. The Nine (9) chemicals compound with the highest percentage amount revealed are Chlorpyrifos with 27.113%, Dodecanoic acid, 1,2,3-propanetriyl ester 15.950%, Vinyl lauryl ester

10.661%, Oleic 6.220%, Hexacosanoic acid 6.578%, Propanamide, N-(3-chlorophenyl)-2,2-dimethyl 5.723%, Benzene 1,1-(3-methyl-1,3-diyl)bis 2.414%, n-Propyl nonyl ester 2.159 and Lauric anhydride 2.543%. The rest of the fifty-one (51) chemicals are below 2 % in the branded Dichlovos analyzed and no specific chemical compound of Dichlovos (DDVP or 2,2-dichlorovinyl dimethyl phosphate) was present as shown in Table 2.

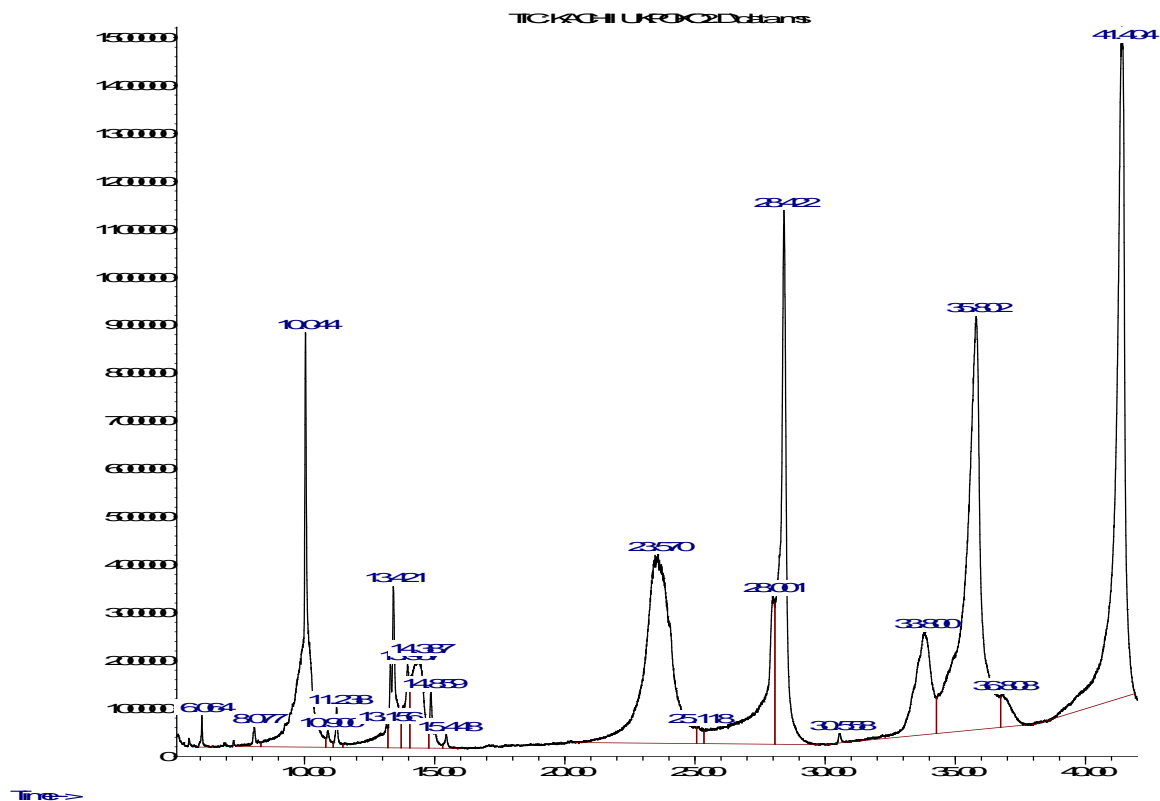


Fig. 3: TIC: KACHII UKPOKO 2 D/data.ms is a GC-MS Chromatograph of Qualitative analysis of commercial Permethrin in Benue Markets

**Table 3: GC-MS analysis of commercial Permethrin in Benue State Markets**

No. Peaks	Compound Identities	Retention Time	Area Peak	% Conc.
1	Nonanoic acid, ethyl ester	6.0637	0.1519	0.1519
2	Docosanoic acid, ethyl ester	8.0772	0.2673	0.2673
3	Hexadecanoic acid, methyl ester	10.0444	8.0767	8.0775
4	1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	10.9004	0.1879	0.1879
5	Hexadecanoic acid, ethyl ester	11.2376	0.3135	0.3135
6	Dodecyl propyl ether	13.1562	0.9950	0.9950
7	10-Octadecenoic acid, methyl ester	13.4213	2.3478	2.3480
8	Methyl stearate	13.9673	1.3265	1.3266
9	6-Octadecenoic acid, (Z)-	14.3874	3.4585	3.4588
10	(Z)-Ethyl heptadec-9-enoate	14.8593	0.6444	0.6444
11	Octadecanoic acid, ethyl ester	15.4479	0.1394	0.1394
12	Oleic Acid	23.5703	16.4220	16.4236
13	Undecylenic acid	25.118	0.3084	0.3084
14	Permethrine	28.0007	6.4172	6.4178
15	Cyclopropanecarboxylic acid, 3-(2,2-dichlorovinyl)-2,2-dimethyl-, (3-phenoxyphenyl) methyl ester, (1R-trans)-	28.422	10.4385	10.4395
16	1,5,9-Undecatriene, 2,6,10-trimethyl-, (Z)-	30.558	0.0785	0.0785
17	Dodecanoic acid, 1,2,3-propanetriyl ester	33.8004	5.5700	5.5705
18	Z-2-Tridecen-1-ol	35.8017	21.1842	21.1863
19	5,5-Dibutylnonane	36.8077	1.0781	1.0782
20	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl Ester	41.4036	20.5941	20.5961
21	Total		99.9999	

Insecticides chemical profile of Permethrin used in foodstuff

Fig. 3: TIC: KACHII UKPOKO 2 D\data.ms is a GC-MS Chromatograph of Qualitative analysis of commercial Permethrin in Benue Markets. Also, Table 3 is the Permethrin brand of insecticide analyzed by GC-MS which revealed twenty compounds, and nine compounds presents ranges from 2- 20.5941 % while permethrin of 6.6172 % amount was present. The rest eleven compounds are below 2% in the brand of permethrin analyzed as shown in Table 3.

Potential health risk implications of chemical in insecticides in foodstuff

Health risk implications; Pesticides have short-term and long-term effects on humans, ranging from simple irritation of the skin and eyes to more severe effects such as affecting the nervous system, hearing, mimicking hormones causing reproductive problems and cancer etc [8,9]. The symptoms of pesticide poisoning depend on the type and amount of pesticide, also the route of contact and intake, there are numerous ways that pesticide poisoning might manifest. Other infections or illnesses brought on by too much heat can mimic the signs of pesticide exposure. If Pesticides poison suspected, do immediately seek for medical help if you experience any of the following symptoms [10,11,12, 13]:

General: extreme weakness and fatigue,

Skin: irritation, burning, excessive sweating or discoloration,

Eyes: itching, burning, watering, difficult or blurred vision, narrowed or widened pupils,

Digestive system: burning in mouth and throat, extreme salivation, nausea, vomiting, abdominal pain, and diarrhea,

Nervous system: reaction such as headaches, dizziness, confusion, restlessness, muscle twitching, staggering gait,

blurred speech, fits and unconsciousness, etc. and sometimes death [11,12,13].

Precautionary measures; Only recommended pesticides should be in circulation for farmers and dealers to purchased, and it should carefully inspect the packages to ensure that the original labels and tamper-evident seals have not been broken or what are on labeled are the actual contents [14]. It is to ensure no purchase or acceptance of any pesticides that have passed their expiration dates, and ask the dealer to show dates of expiration. Avoid purchasing pesticides in unidentifiable repackaging bottles [14]. All these should the challenges to be address under a control agency. The agency should charge to address challenges of pesticides application and precaution awareness such as; before using any pesticide, always read the label and get advice if you are unsure. Verify the pesticide's suitability for the intended purpose, review the safety measures that need to be followed, choose the dosage rate, and take note of the product label's mixing instructions.

Always adhere to the suggested dilutions and dosing rates. Keep in mind that using larger or smaller amounts is a waste of money. Direct application of pesticide on foodstuff in any way or small quantity is not acceptable and etc.

Conclusion

The analyzed chemical profiles of the three insecticides commonly used for foodstuff storage in Benue state have revealed that, one brand of insecticide contains so many chemicals that are harmful to living things; both pests and humans. Such insecticide is branded and package without a clue on the comprehensiveness of other chemical profiles except that of the active chemical ingredient. It is of interest to know that most of the chemicals silently incorporate in an insecticide brand even as excipients are more dangerous to



human health than the main active chemical(s) stipulated on the brand. The worst of these insect packages for retailers do not have written precaution measures for safety handling and application and it is always unreadable even if at all there is such. On some pesticides, the precaution is presented in symbolic signs of toxic, irritants which can be understood by only technocrats, hence naïve foodstuff dealers are using such dangerous chemicals for the storage of foodstuff. The whole of these chemicals in one brand of insecticide are of great potential damages to foodstuff chemical quality apart from preventing pest infestation. The short- and long-term consequences to human health could be disastrous and as such, simple spot tests are needed for identification of pesticides in foodstuffs for precautionary and prevention measures. Now that the chemical profiles of these insecticides are known, elimination of the toxic substance from the foodstuff could be an easy task by taking precautionary measures specifically for such contaminant's base physicochemical properties.

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