

Original Research Article

A Preliminary Study of the Migration of Volatile Components from Crushed Garlic (*Allium sativum*) in to Polyethylene Terephthalates Packaged water

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Abstract: Migration of volatile components from crushed garlic (*allium sativum*) into water packaged in polyethylene terephthalates (sachet water) was studied by extracting the analyte from the water into a liquid solvent phase (liquid-liquid extraction) followed by gas chromatography mass spectroscopic analysis. The bottled and sachet water were stored with the garlic in an air tight container at an average temperature of 30°C. After two days of storage the sample was taken for analysis. The result showed the presence of fifty three (53) different components which includes phthalates, citrate esters, saturated hydrocarbons, siloxanes, amides and other water soluble volatile compounds from garlic. The control result showed only nitrogen. It was concluded that the volatile components of the garlic may have aided the degradation of the polyethylene terephthalate thereby leaching different organic compounds into the water and thus may pose harmful health hazards to consumers of such products.

Keywords: Volatile Compounds, Polyethylene Terephthalates, Garlic, Sachet Water.

INTRODUCTION

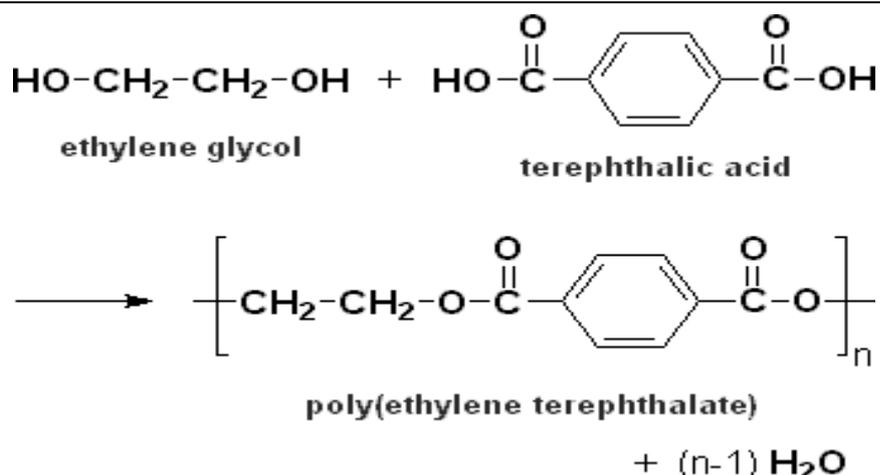
Many years of neglect by government and inadequate investment in public infrastructure has left the public water supply in Nigeria in an unreliable state [1]. One of such local intervention in Nigeria, where portable water supply is unreliable is drinking water sold in polythene sachets [2]. Sachet water is the best drinking water for an average Nigerian considering its availability and cost. About 70 percent of Nigerian adults drink at least a sachet of pure water per day [3]. The polyethylene terephthalate bags used contains 50ml of water and is sold at a very cheap rate. Perusals have been made lately and it is evident that water packaged in polyethylene bags is not safe for drinking when exposed to heat or kept close to volatile materials such as kerosene and benzene [4]. The polyethylene terephthalate sachet used to package water consists of nonpolar, saturated high molecular weight hydrocarbon mainly made from petroleum by-products. Polyethylene (other than cross linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene also when kept to volatiles like kerosene, diesel and so on. Few studies [5-7] have been conducted in recent years on the quality of packaged water in Nigeria.

Vegetables undergo enzymatic reactions, thereby releasing gases or volatiles which are can diffuse with

respect to their concentration. Diffusion in polymers is dependent on the concentration and the solvent power of the penetrating gas [8]. There is every tendency for the volatile components of these materials mentioned to diffuse into the water through the polyethylene terephthalate due to the fact that volatile compounds are of a high vapour pressure at ordinary room temperature resulting from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air [9].

The ability of these volatiles to cause health effects varies from those that are highly toxic, to those with no known health effects. However, it is not advisable to keep water packaged in polyethylene terephthalate with these volatiles as it may be hazardous to human health.

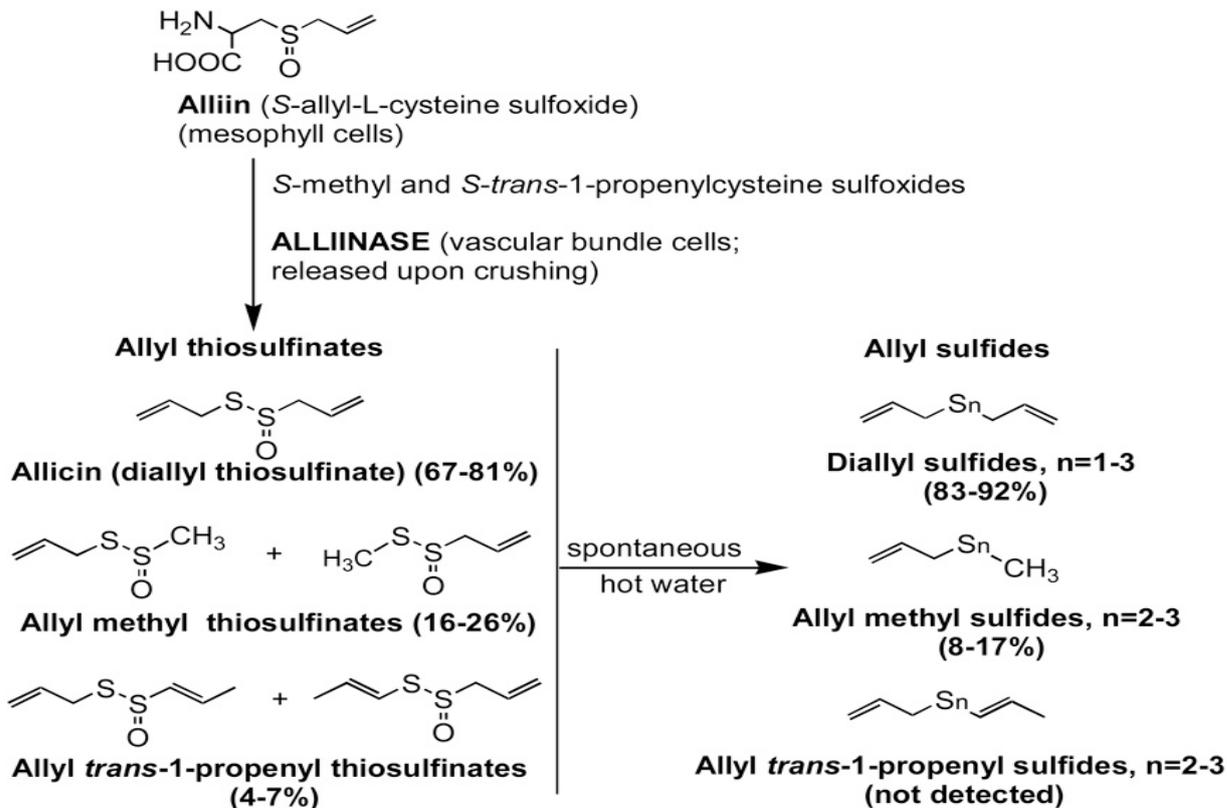
Polyethylene terephthalate is produced from ethylene glycol and dimethyl terephthalate (C₆H₄(CO₂CH₃)₂) or terephthalic acid [10]. The polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/transesterification) with water as the byproduct shown in Scheme 1.



Scheme 1: Polymerization Reaction for the Production of Polyethylene Terephthalate

Garlic (*allium sativum L.*) is a particularly rich source of organosulphur compounds, which are thought to be responsible for its flavor and aroma, as well as its potential health benefits [11]. Aroma development has been reported to be enhanced by tissue disruption and cellular deterioration [12]. Sulphur containing volatiles are formed because of deterioration of the cells in the lipid membranes as well as the loss of intracellular compartmentalization, which allows enzyme-substrate reactions to occur [13].

Typical volatiles of crushed garlic and garlic essential oil includes diallyl sulfide, diallyl disulfide, diallyl trisulfide, methyl allyl disulfide, methyl allyl trisulphide, 2- vinyl-1, 3-dithin,3-vinyl-1, 2-dithin [14] and E, Z-Ajeone [11]. They mostly originate from Allicin (S-allyl-L-Cysteine sulfoxide) as shown in the Scheme 2.



Scheme-2: Pathways of Alliin Breakdown

Alliin is an odorous and extremely unstable compound, specie in the family Alliaceae [11]. It was first isolated and studied in the laboratory by Chester *et al.*, [15]. When fresh garlic is crushed, the enzyme allinase converts alliin to allicin, which is responsible for the aroma of fresh garlic. Allicin is unstable in aqueous solution and rapidly decomposes mainly to diallylsulphide, diallyldisulphide and diallyltrisulphide.

Most times the way bottled and sachet water is stored calls for concern, especially on health issues associated with drinking contaminated sachet water. If volatiles from vegetables and fruits such as garlic, scent leaf, curry leaf, oranges and sometimes banana when stored with bags of sachet water in refrigerators and store rooms can migrate into the water and results to observed change in smell and taste then it is therefore, pertinent to understand whether our storage method affects the quality of water in the polyethylene terephthalate sachet.

Some researchers have studied the migration of volatiles through polyethylene terephthalate containers. Nijssen *et al.* [16] studied the migration of acetaldehyde into mineral water stored in polyethylene terephthalate bottles and concluded that acetaldehyde migrated and resulted in the water contained in the polyethylene terephthalate bottles having sweet and fruity taste. Amiridav and Voutsas [17] also affirm that phthalates are easily released and migrate into food, beverage and water from the packaging materials.

This study aims to investigate the possibility of volatile compounds from garlic migrating into water stored in polyethylene terephthalate sachet.

MATERIALS AND METHOD

The detailed procedures, materials and equipment used in this study are as described in the subsections that follow.

SAMPLE PREPARATION

Garlic bulbs were bought from Amassoma market in Southern Ijaw Local Government Area of Bayelsa State, Nigeria. A bag of sachet water was bought at the shopping complex Niger Delta University, Bayelsa State. The garlic bulbs were weighed, peeled and the cloves were crushed using a china mortar and put in a petri dish. The crushed garlic bulbs alongside with the sachet water were put in a dessicator at an ambient temperature of about 30°C. It was kept for two days (48 hours). A control was set-up in exactly the same way but without garlic.

LIQUID - LIQUID EXTRACTION

The water sample was prepared, by extracting the analyte of interest into a liquid solvent phase (liquid-liquid extraction) using dichloromethane (CH₂Cl₂). The extract concentrated to 1ml and then

analyzed following the procedure described in subsection 2.3.

GAS CHROMATOGRAPHY- MASS SPECTROSCOPIC ANALYSIS

One micro liter (1µl) of the liquid organic sample was injected into a GC-MS GC at an injector temperature of 280°C where it was swept onto a separation column by an inert carrier gas (helium). The analytes in the mixture were carried through the column by the carrier gas where they were separated from one another by the interaction between the coating (stationary phase) on the outside wall of the column and the carrier gas. Each analyte interacted with the stationary phase at different rates. Those that reacted very little moved through the column quickly and exited into the mass spectrometer before those analytes having longer interaction and retention times.

When the individual analytes exited the GC column they entered the ionization area (ion source) of the MS. Here they were bombarded with electrons which formed ionized fragments of the analyte. These ionized fragments were then accelerated into the quadrupole via a series of lenses and separated based on their mass to charge ratio. This separation was accomplished by applying alternating RF frequency and DC voltage to diagonally opposite ends of the quadrupole filter. From here the fragments entered the mass detector (electron multiplier) and were recorded. The MS computer graphed mass spectrum scan showing the abundance of each ionized mass fragment. A combination of mass spectra of all the components of the unknown analyzed sample was then displayed on the computer screen as printable total ion chromatogram. A GC/MS in full scan mode will monitor a range of masses known as mass to charge ratio (abbreviated m/z). A typical mass scan range covers from 35-500 m/z four times per second and will detect compound fragments within that range over a set time period. The unknown analyte spectra were compared to an extensive computer library (NIST library) containing mass-spectra of many different compounds and the components identified.

The condition in which the GC-MS operated are as stated below:

Oven Condition

Initial Temperature: 50°C FOR 5mins
Ramp to 310°C @ 15°C/min for 22mins.

Inlet Temperature:

Heater 280°C
Pressure 40.6psi
Splitless mode
Purge flow 15ml/min at 2min
Septum purge 10.5ml/min

MSD Transfer line Temperature = 300°C

MS Quad Temperature = 180°C

RESULTS AND DISCUSSION

The results obtained from the GM-MS Analysis are as stated in Table 1 below. The result revealed that 53 compounds were identified and quantified using GC/MS including siloxane, alcohols, hydrocarbons, citrate esters, acids, amides, phthalate esters, supraene, pyrene, monosaccharides, diols, azoles, ketones and entrofloxacin as shown in Table 1. According to these results, the components found in greater proportions were 1,2 benzenedicarboxylic acid bis(2-methylpropyl) ester (1.83%), dibutyl phthalate (0.828%) and diisooctyl phthalate (0.188%) which appear to be a component of the polyethylene terephthalate. Amongst the compounds, sulphide compounds from allicin which is the major source of garlic smell/pungent odour were not identified by the GC/MS, however some water soluble compounds from garlic (enrofloxacin and triethyl citrate) were found, according to Artacho *et al.*, [18] who studied the determination of organo-sulphur compounds in of *Allium sativum* (garlic) extracts by gas chromatography and mass spectrometry. In their study, extraction of aqueous solutions with diethyl ether yielded percentage recovery rates ranging from 74.4% (allyl methyl sulphide) to 90.3% (di propyl disulphide).

The phthalates, saturated hydrocarbons, and esters results from the degradation of PET material. Siloxanes were also found showing that the PET was made of silicon polymers. When fresh garlic is crushed, the enzyme allinase converts alliin to allicin, which is responsible for the aroma of fresh garlic. Allicin is unstable in aqueous solution and rapidly decomposes. The extracts from the crushed garlic that were not detected by the mass spectrometer may be due to their volatility and insolubility in water, they may have escaped during the liquid-liquid extraction that was carried out before the GC/MS analysis. Control experiment carried out under the same condition but without garlic. The result shows the presence of only nitrogen. The volatile components from the garlic therefore may have aided the degradation of the polyethylene terephthalates thereby leaching different organic compounds into the water as shown in the result in Table 1.

The importance of storing our water away from volatile materials is now well known as the quantification of the volatile components from the garlic and the degraded product from the polymer can give an idea of what happens when the taste or smell of our sachet water have been altered.

Table 1: GC-MS Quantification of Components in Garlic Contaminated Sachet Water

S/N	COMPOUND	RETENTION TIME (Min)	% COMPOSITION
1	1,2 benzenedicarboxylic acid, bis(2-methylpropyl) ester	14.44	1.83000
2	Dibutyl phthalate	15.15	0.82800
3	Diisooctyl phthalate	18.00	0.18800
4	Oxygen	4.13	0.09720
5	Supraene	18.66	0.07410
6	Silane, diethylheptyloxyoctadecyloxy	21.26	0.03950
7	(1-methoxy-pentyl)-cyclopropane	18.48	0.02940
8	Triethyl citrate	13.14	0.02600
9	Hexanedioic acid, bis(2-ethylhexyl) ester	16.83	0.02340
10	Hexadecane	16.53	0.02220
11	Benzeneamine, 4-(1,1,3,3-tetramethylbutyl)-N-[4-(1,1,3,3-tetramethylbutyl)phenyl]	20.06	0.01930
12	Pyrene	16.74	0.01490
13	Acetic acid, (3,4-dimethoxyphenyl) (trimethylsiloxy)-,methyl ester	17.39	0.01410
14	2-decanol	18.47	0.01320
15	Dodecynediol, tetramethyl, di(2-hydroxyethyl) ether	20.66	0.01220
16	Anthracene, 9-dodecyltetradecahydro	20.66	0.00918
17	Nonane, 1-iodo	13.66	0.00614
18	3-buten-2-one, 4-(2,5,6,6-trimethyl-1-cyclohexen-1-yl)	21.12	0.00604

S/N	COMPOUND	RETENTION TIME (Min)	% COMPOSITION
19	5,5-Dimethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-4,5-dihydrooxazole	20.33	0.00597
20	Octane, 3,4-dioctyl	18.92	0.00575
21	Pentadecane,2,6,10-trimethyl	17.16	0.00544
22	Benzamidine	15.19	0.00537
23	Hexasiloxane, tetradecamethyl	17.19	0.00450
24	Hexane,2,4,4-trimethyl	18.91	0.00386
25	1,1,1,3,5,7,7,7octamethyl-3,5-bis(trimethylsiloxy)tetrasiloxane	15.66	0.00371
26	His-Glu-Arg	16.76	0.00344
27	5,5-Dimethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-4,5-dihydrooxazole	21.06	0.00313
28	Isophthalic acid, oct-3-en-yl propyl ester	20.56	0.00308
29	1,1,1,3,5,7,7,7octamethyl-3,5-(bistrimethylsiloxy)tetrasiloxane	14.84	0.00306
30	1-[t-Butyl(heptafluorobutyryl)amino]-3-(3-methyl-2-nitrophenoxy)-2-propanol	18.56	0.00272
31	Phthalic acid, isobutyl trans-hex-3-enyl ester	14.35	0.00263
32	Levulinic acid	16.29	0.00258
33	Benzeneacetic acid, 2,4,5-tris[(trimethylsilyl)oxy]-trimethylsilyl ester	10.84	0.00249
34	Phenacetin	14.81	0.00237
35	Enrofloxacin	22.18	0.00230
36	Apigenin-8-glucoside, tms	17.90	0.00229
37	2-(2',4'4'6'6'8'8'-Heptamethyltetrasiloxan-2'-yloxy)-2,4,4,6,6,8,8,10,10, nonamethylcyclopentasiloxane	13.01	0.00217
38	3-isopropoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy) tetrasiloxane	12.00	0.00217
39	3-Amino-3-(4-methylphenyl)propionic acid	13.40	0.00206
40	1,1,1,3,5,7,7,7-octamethyl-3,5-bis(trimethylsiloxy)tetrasiloxane	13.96	0.00205
41	2-Methyl-3-hexanol	14.27	0.00165
42	1-Octanol	16.15	0.00150
43	trans-2,3-Dimethoxycinnamic acid	19.91	0.00145
44	Butane, 2,2-dimethyl	12.36	0.00140
45	Ethanone, 1, 3-amino-4-1.1-dimethyl-2,6-dimethyl-5-nitrophenyl	21.11	0.00121
46	N-(2-methyl-2H-tetrazol-5-yl)-acetamide	14.02	0.00112
47	Dodecylamine	18.12	0.00097
48	cis-Aconitic acid	13.16	0.00088
49	D(-)-Lyxose	18.57	0.00077
50	1-Pentene, 4,4-dimethyl-1,3-diphenyl-1-(trimethylsiloxy)	9.52	0.00068
51	D(-)-Lyxose	18.58	0.00058
52	5,5-Dimethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-4,5-dihydrooxazole	21.05	0.00056
53	Phthalic acid, 3,5-dimethyl 4-formPhthalic acid, 3,5-dimethyl 4-formylphenyl ester	19.09	0.00017

CONCLUSION

Fifty three organic compounds were identified and quantified in the PET sachet water stored with the garlic. Three of these compounds with higher proportions in the water were by-products of the degradation of PET which signals danger. Based on the findings, it can be concluded that volatiles from garlic can migrate through and degrade PET and can be potentially harmful storing stuffs that emit organic volatiles with PET packaged foods and drinks. It is therefore important to remain cognizant that our storage methods can also affect the quality of the water and may be hazardous to human health.

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