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STUDY OF THE MIGRATION OF ACETALDEHYDE FROM PET BOTTLES CONTAINING NANO SILVER PARTICLES USED IN THE PACKAGING OF DRINKING WATER

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ABSTRACT

Polyethylene Terephthalate (PET) is a polymeric material with broad applications in food packaging. PET, due to chemical neutral nature and physical properties is suitable in a wide range of food products packaging, especially drinking water. However, the migration of acetaldehyde from PET bottles into drinking water is a risk factor for the health of the consumer, so a suitable method for the quantitative detection of acetaldehyde in drinking water is essential. The nano technology is now offering high potential for food packaging and materials at the nano scale aid to increase the shelf life of food. The purpose of this study was to evaluate the migration of acetaldehyde from PET bottles containing nano silver into the drinking water. Headspace chromatography was used to identify acetaldehyde. The method was validated for the limit of detection, the limit of quantification and the accuracy. Calibration curve showed good linear relationship (r^2 = 0.999). The detection limit and the value limit are 3.62 and 12.08 micrograms per liter, respectively. The accuracy of the method was evaluated by testing the repeatability and showed relative standard deviation of 4.54. To validate accuracy, the recovery of 95.12% was obtained. Migration of acetaldehyde in PET bottles containing nano silver showed a significant difference compared to PET bottles free of nano silver (control). The results demonstrated that in the presence of nano silver particles, migration of acetaldehyde in PET bottles increases.

Keywords: Polyethylene Terephthalate – Nano silver - Acetaldehyde - Headspace gas chromatography

INTRODUCTION

Food contact material, especially items used in packaging are among materials with important effect on the safety of the food chain. According to Europe Commission definition food contact materials are those that are intended to contact with food including packing material, tableware, processing machinery and materials as well as containers for contact with potable water. Polyethylene Terephthalate (PET) is a polymeric food contact material. It is a large polymer chain belonging to the family of polyesters [1] that constitutes the terephthalic acid intermediate compounds, (TPA) and ethylene glycol (EG), both derivatives of petroleum with a wide application in packaging various types of non- alcoholic beverages in the world [2]. Its strength and impermeability are excellent properties for packaging beverages, and its resistance to chemicals is high with a high degree of transparency, as well [3]. In Europe, sale of water packaged in PET allocated 44% of soft drinks market volume, with an average consumption of 105 liters per year per person in 2009 [1]The first choice for packaging of mineral water and drinking water in the world is not far from the addition of nano-materials. Social change, globalization and the need for strict safety measures have increased pressure to produce a new packaging system able to transport food with traceability in the food distribution chain, therefore nano structure materials are included to enhance mechanical properties, inhibitory properties and prevent damage caused by light in food contact polymers [4]. It is necessary to ensure minimum migration of substances such as acetaldehyde since the transmission of harmful material to health between packaging materials and food, or vice versa is on the values that addition of nano-particles in polymers can rise large changes in the material properties with impact on harmful emigrants because of physicochemical and biological behavior changes emerge by material size reduction. Acetaldehyde is a chemical compound with the CH_3CHO formula and the most volatile product that is produced during thermal decomposition of PET. Acetaldehyde is obtained when polymer melts (from heat chemical reactions). Cases such as polyethylene terephthalate occurred during thermal decomposition of various reasons including lack of temperature control during the production process (more 300 ° C) or insufficient pressure in the bottle blowing and the lack of satisfactory raw materials purity; consequently, the amount of acetaldehyde in the final product increases. It is very important to control the level of acetaldehyde because they will be able to be added to food or alter the food taste packed in PET. This substance has considerable risks to consumer health, so that in the twelfth edition of the carcinogenicity report in 2011 acetaldehyde was mentioned. It is necessary to achieve the safety and quality of food to monitor and supervise it in order to achieve new technologies for producing food packaging in response to customer needs as the driving force for the development of new concepts and improved packaging that increases the storage time [5]. As a result, food security regulatory is being changed and modified. In fact, in order to achieve these laws there has always been new methods parallel to the developments, the methods to identify and determine the limits of even small amounts of excipients transferred to the food. Accordingly, the objective of the current study is to use headspace gas chromatography and validation of methods to ensure the safety of PET with the addition of nano silver - particles in the polymer, as a suitable method for measuring pollutants such as acetaldehyde and determine their migration of PET bottles containing nano silver particles used in packaged drinking water.

MATERIALS AND METHODS

Nano silver -particles were provided from American manufacturer, American Elements, Chromatography Vials were made of Millipore, a US company, acetonitrile and acetaldehyde were made of Merck, Germany, and chromatographic gas column was provided from Roshk, a German manufacturer.

Preparing the bottle

Samples were prepared in the packaging factory using polymeric materials packaging automated systems. 10% of the total weight of PET chips was mixed by nano silver particles in the mixer manufactured by IKA German model 3 / 654779Z and then added to the mixture of PET to gain a homogeneous mixture of PET and nano silver particles. Next, PET bottles were produced using injection blow with the wind injection and perform Ararat 2135RS model manufactured by an Iranian company in 2 stages of perform production and shaping.

Nano particles were used at 5 different concentrations in packaging as the treated samples. Sample free of nano silver particles (control); numbered 1:treated with

0.050 nano silver, numbered 2: treated with 0.075, numbered 3: treated with 0.100 nano silver, numbered 4: treated with 0.125 nano silver, numbered 5: treated with 0.150 nano silver, respectively.

Sample preparation for chromatographic analysis:

10 mL of deionized water was added to clean Headspace Vials chromatography gas at the volume of 25 mL [6] and then a piece at the size of a square centimeter in one square centimeter of samples packaging container and nano silver treatments were precisely cut by a cutter so that entere in the vials separately. The Vial cap with a septum was pressed so that the gas cap vials were fully sealed [7]. Samples were held for 6 months [8] at room temperature away from sunlight [8],[1] and the experiment was repeated three times.

Before chromatography experiments, the analysis of various studies were collected and evaluated and optimized using Design Expert 7 Software using Plackett- Burman method.

Conditions of chromatography, detector and headspace settings:

Chromatography device made of the American manufacturer, Varian; model 3800 CP with flame ionization detector was used for measuring acetaldehyde by headspace gas chromatography method.

Chromatographic device and detector conditions:

Internal temperature: 45° C, shelf life 1 (Holding 1): 1.3 min, increasing temperature rate: 45° C / min, final temperature: 150° C, shelf life 2 (Holding 2): 0.6 min, injection temperature: 100° C, Liner: Zero dilution, split: 25mL / Min, flame ionization detector temperature: 150 ° C

Headspace conditions and setting:

Samples temperature incubator: 60° C, needles temperature: 80° C, canal temperature: 100 ° C, equilibrium time: 15 minutes, pressure time: 1 minute, infusion time: 0.1 min, departure time: 0.0 min

Statistical analysis:

Mean and standard deviation were used in the descriptive analysis of survey data. For statistical analysis, after data normality approval by the Levene test and Kolmogorov- Smirnov, One-way analysis of variance was used to identify significant differences between the means. Duncan's test was used to compare treatment significant means in the case of significant differences between treatments. Pearson correlation was used to determine the linear relationship and the amount of relationship between quantitative variables. Moreover, t tests were used to detect significant correlation coefficients and regression. In all tests, the significance level of (p value <0.05) was considered.

RESULTS AND DISCUSSION

Linearity of test method:

Linearity was assessed by linear regression analysis. The enriched samples at 20, 40, 60, 80, and 100 mg/lit concentration levels and the control were injected 3 times under the same conditions. The calibration curve equation was obtained by y= 0.049 x+0.109 and correlation coefficients of $R^2 = 0.999$ (Figure 1).

LOD limit of detection and limit of quantification LOQ:

To calculate and display the sensitivity of the method two limit of detection (LOD) and limit of quantification (LOQ) values were used that have been calculated by $LOD = \frac{3\times s}{b}$ and $LOQ = \frac{10\times s}{b}$ equations, respectively. (Table 1)

b: the slope of the regression line and s: SD intercept of regression line

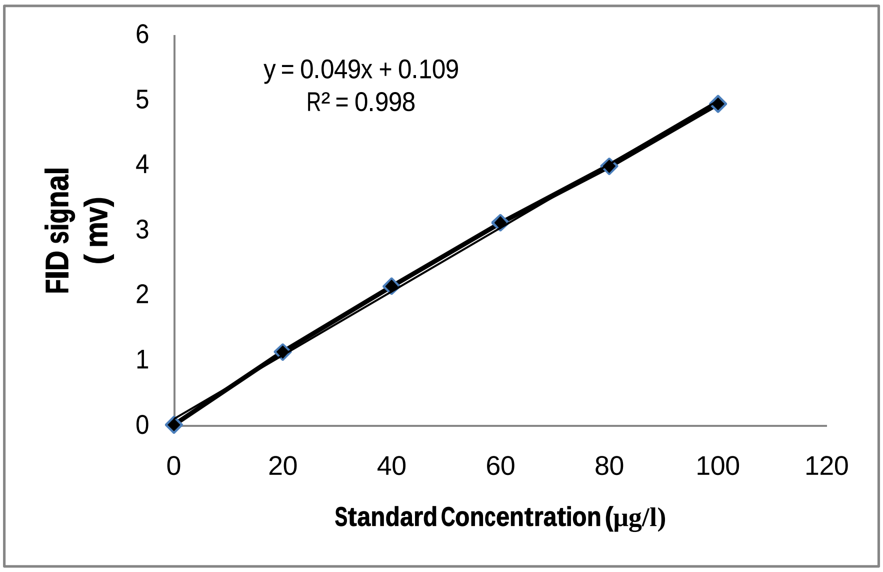

Figure 1: Calibration curve at 5 concentrations of 20.40, 60, 80 and 100 micrograms per liter

Table 1: Results of validating analytical methods

Parameter	Value
LOD	**3.62 (micrograms per liter)**
LOQ	**12.08 (micrograms per liter)**
Repeatability (RSD)1	**4.54%**

[1]-Relative Standard Deviation

Linearity Range:

Since the least amount of determination is 12.08 ppb, so the range of linearity to the concentration is limited to 12.08 to 100 ppb.

Accuracy of the method:

To prove the validity of the test, a square centimeter of a nano containing container number 4 (containing 0.0100 nano silver) with (6, 12 and 18 micrograms per liter) concentrations of acetaldehyde in 3 replications was used in the same vial. Average percent of recovery, which is the proof of method, is 95.12 ± 3.08 that was in the acceptable recovery range of 95.12 ± 3.08.

The results of manually and stepwise acetaldehyde addition

Instead of distilled water used in vial 1, 10 ml of standard solution of acetaldehyde in the 2, 4, 6, 8 and 10 mg per liter acetaldehyde concentrations was used, respectively. 1 sq cm of vial number 4 (0.100 treated with nano silver) was added to all the vial groups, and the FID signals were measured.

With stepwise increase of acetaldehyde, the FID signal was increased and there was a significant positive correlation (0.999) between the amount of used acetaldehyde and the FID signal (Figure 2).

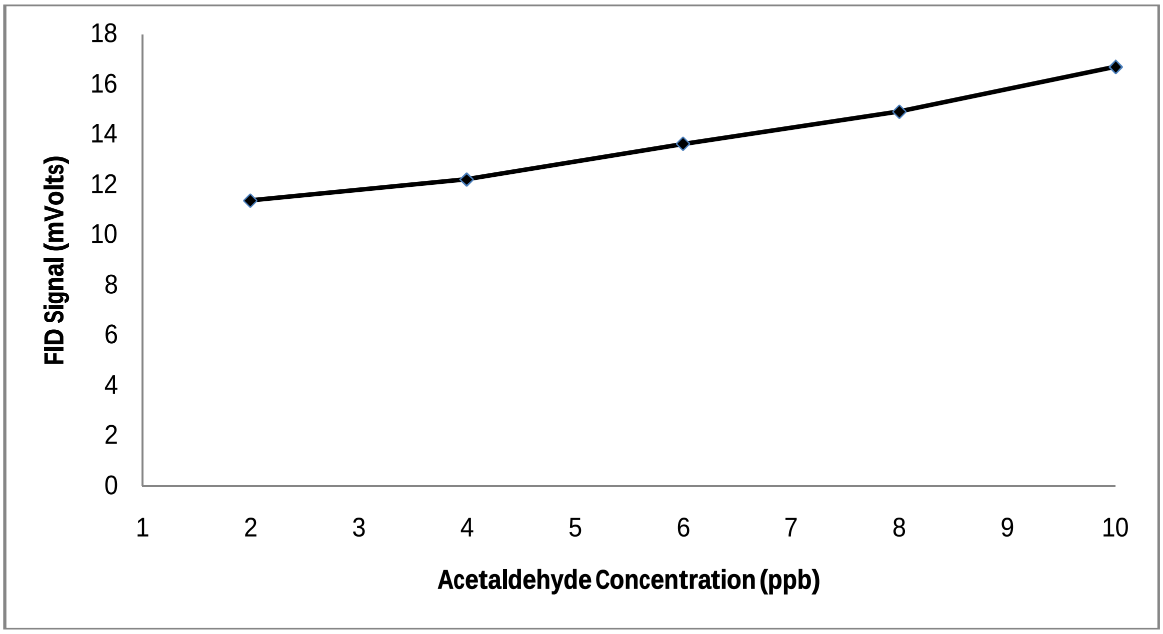

Figure 2: The FID signal with various amounts of acetaldehyde

Results of acetaldehyde changes in PET containing various amounts of nano silver:

Different treatment of PET with 5 levels of nano silver (0, 0.05, 0.075, 0. 100, 0.125 and 0.150 percent) was constructed and entered the test to determine the amount of acetaldehyde. The experiment was performed with 3 replications.

Increase in the percentage of nano silver in PET showed a significant increase in signal level and actually acetaldehyde at every level (Table 2).

Results of acetaldehyde changes in PET containing the same amounts of nano silver particles:

Different levels of PET (1, 2, 3, 4 and 5 sqm) containing 100% nano silver (treatments most commonly used in packaging) were tested with the same condition. The results showed that with the increase of PET, the FID signal increases with a correlation coefficient 0.998 (Figure 4)

Table 2: Results of Duncan test at 5% level for acetaldehyde mean comparison at treatments

Treatment (% of nano silver in PET)	**0 (control)**	**0.05**	**0.075**	**0.1**	**0.125**	**0.150**
Acetaldehyde level (micrograms per gram)	**0.01± 0.28^{f}**	**0.26±2.32^{e}**	**0.05± 5.52^{d}**	**0.12±12.32^{c}**	**0.08±18.43^{b}**	**0.11 ±27.55^{a}**

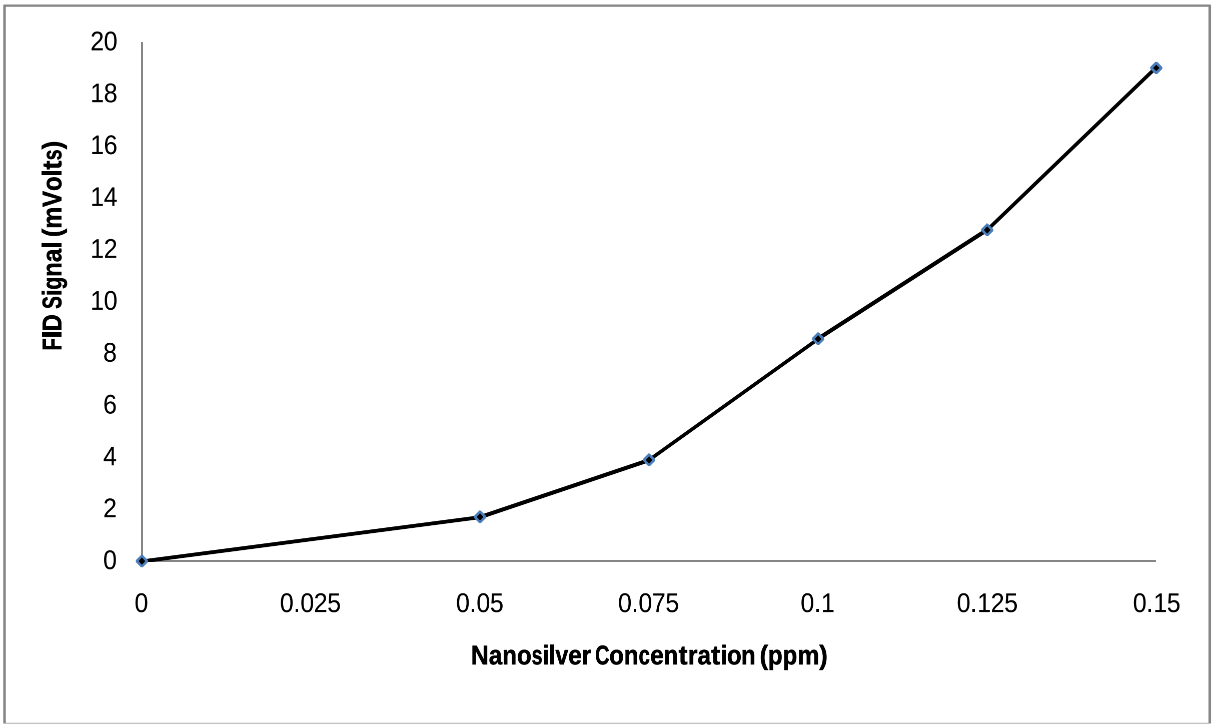

Figure 3: Changes in signal level by increasing the percentage of nano-silver in PET

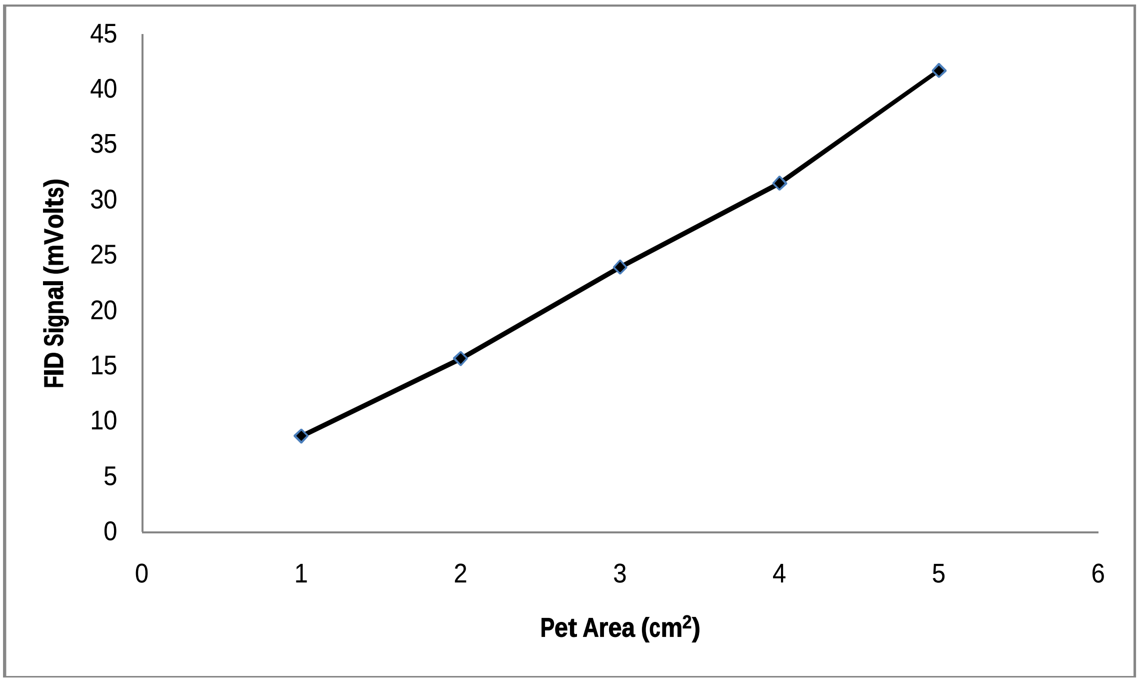

Figure 4: FID signal intensity changes with different levels of PET containing equal treatment

To know the linearity of the relationship, PET levels were considered as the independent variable and the signal intensity was the dependent variable. Linear regression analysis was performed. According to the coefficient of determination in Table 4 (0.996), the independent variable of PET level explained 99.6 % of signal intensity changes in the dependent variable. Linear regression analysis was a suitable model for variables in our study, given the significant level of analysis of variance (0.000) and the relationship between these two linear variables and regression equation was obtained as:

Signal intensity = 8.186* Pet Area-0.222

Table 3: Regression coefficient of the independent variable, PET, on the dependent variable of FID signal intensity

Statistics	The multiple correlation coefficient	The coefficient of determination	Modified coefficient of determination	Standard error estimates
Value	0.998	0.996	0.994	0.9812

Table 4: Results of independent variable linear regression analysis of PET levels verses dependent variable of FID signal intensity

Model	Non-standardized coefficients		Standardized coefficients	t	Significance level
	B	Standard error	Beta		
(constant)	-0.222	1.029		-0.216	0.843
PET Level	8.186	0.310	0.998	26.382	0.000

In this study, the calibration curve indicated good linear relationship with (correlation coefficient = 0.999). In a study of carbonated water by static HS-GC method, a correlation coefficient of 0.99 and linear equation equal to $y=0.97 \times 10^3 x+5.6\times 10^3$ were obtained, respectively [9]. [8]studied carbonated non-alcoholic beverages + N +

2 g of sodium chloride by HS-GC method obtained linear calibration curves of 0.969 correlation coefficient. [3] studied derivation of acetaldehyde in non-carbonate mineral water by HS-GC + and obtained a linear calibration curve of 0.999 correlation coefficient.

The limit of detection and the limit of quantification were obtained 3.62 and 12.08 micrograms per liter, respectively. In a study by (O ¨ zlem, 2008) [8] LOD = 10ppb, LOQ =3.33 ppb and in a study by Redžepović [3] LOD = 0.3 ppb and LOQ = 1ppb were obtained, respectively.

The accuracy of the method was evaluated by repeatability test and showed relative standard deviation of 4.54. To validate accuracy, the recovery of 95.12% was obtained. [8] reported repeatability of 11.7% and recovery percentage of 93.94. [3] reported repeatability of 2.604% and recovery percentage of 92.99.

The research findings suggest headspace gas chromatography as a rapid, automated, sensitive method without derivatisation for the quantitative detection of acetaldehyde in mineral water and the method was validated [2]. As in most studies, the concentration of acetaldehyde in conventional PET bottles (no nano) was considerably lower than the permissible level of immigration according to the guidelines 72/2002 / EEC (less than 6 ppm), (Dong et al., 1980) [10] =0.5-6 ppm, [11]=2.6-3.12 ppm, [12]= 1.3-5.65 ppm, [2]=0.2 ppm; in this study, the amount of acetaldehyde in the control sample (no nano-silver) was 0.28 micrograms per gram (ppm)

The minimum level of acetaldehyde in bottles containing nano silver was 2.32 micrograms per gram that was of the PET samples containing 0.05 nano silver and maximum amount of acetaldehyde (27.55 micrograms per gram) was of the PET samples containing 0.15 nano silver. There are significant differences in the amount of acetaldehyde in PET bottles free of nano silver and those containing nano silver. Acetaldehyde levels in samples containing nano silver shows a significant difference with control samples and nano silver particles percentage increase significantly increases acetaldehyde.

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