

## Identification of Formaldehyde in Packed Drinking Water

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### ABSTRACT

High performance liquid chromatography (HPLC/UV) and gas chromatography methods to determination of formaldehyde in bottled drinking water were used. Here, GC method was used to determine quantitatively formaldehyde using TCD (thermal conductivity detector) followed by analysis by HPLC / UV, while sensitive UV detection can be non-specific, and is subject to many interferences, and the analysis time can be long, as well as, some laboratories do not have equipments or experts for HPLC analysis. Therefore, gas chromatography method provides an alternative to HPLC, eliminating the need for a solvent mobile phase. Resolution and sensitivity are good for aldehydes evaluated.

Results of this study indicate that the detection for formaldehyde was good even of low concentration in GC. Ten bottled drinking water samples collected from various markets were analyzed. The results were below the guide – line for drinking water quality by WHO (900 ppb).

**Keywords:** packed drinking water, formaldehyde, DNPH derivative, GC, HPLC

### تشخيص الفورمالدهايد في ماء الشرب المعبأة

الخلاصة:

الكروماتوغرافي السائل والغاز يستعملان لتعيين الفورمالدهايد في مياه الشرب المعبأة. عند استعمال HPLC يفحص الفورمالدهايد كمشتق DNPH. وجد ان هناك تداخل وتطابق بين الزمن الاحتجائي للفورمالدهايد واحد مكونات DNPH مما يسبب خطأ في التعيين. ان مقارنة النتائج المستحصلة بطريقة

HPLC مع GC تبيين ان التعين الكمي للالديهيدات بطريقة GC هي المفضلة لكونها لا تحتاج الى تحضير مشتق كما انها اكثر دقة واقل وقت وليس هناك اي تداخل في التحليل. اظهرت النتائج ان النماذج التالبحث عليها قسما منها تحوي على نسبة قليل من الفورمالهايدد أي ضمن الحد المسموح به من قبل منظمة الصحة العالمية(900ppb).

## INTRODUCTION

**B**ottled drinking water has been available in 1981. In recent years, along with prosperous economic development; water pollution is becoming a serious problem. Water quality has public concern about pure and healthy drinking water. Packed water including mineral water, Bottled drinking water, distilled water and reverse osmosis water, with the ready to drink, are there fore full of the market.

The safety of bottled water are public concerns, because of natural biological transformation or photo-thermal chemical reactions as well as artificial industry pollution ozone processing [1]. water could contain low molecular weight aldehyde like formaldehyde [2,3,4]. The high chemical reactivity of this aldehyde has caused serious concern in environmental protection; also, packed water could contain aldehyde due to manufacturing process, unsuitable container, or in complete cleaning of the container [5].

Gas or liquid chromatography is more applicable to detect aldehydes in water with high detection sensitivity. USEPA( environmental protection agency), use HPLC system to detected aldehydes as DNPH derivatives[6]. According to literature[7,8], detection sensitivity can improved by using solvent extraction and solid phase absorption column this way help identify aldehyde by converted to derivative.

The purpose of this research is to establish an analysis method for qualitating and quantization aldehydes by using Gas chromatography to reduce the interference in separation and improved detection sensitivity. This work can be utilized in the investigation of bottled drinking water on market to detect content of formaldehyde can be under stood. Here, GC method was used to determine quantitatively formaldehyde by using TCD (thermal conductivity detector) followed by analysis by HPLC / UV, while sensitive UV detection can be non-specific, and is subject to many interferences, and the analysis time can be long, as well as, some laboratories do not have equipments or experts for HPLC analysis. Therefore, gas chromatography method provides an alternative to HPLC, eliminating the need for a solvent mobile phase. Resolution and sensitivity are good for aldehydes evaluated in this study 10 bottle of bottled drinking water samples collected from markets were analyzed for formaldehyde content. The results were well below the guide line for drinking water quality from various markets quantity were far below the WHO limit (900 ppb).

## Mythology

### Materials and Equipments Reagents

33 % 2,4-dinitro-phenylhydrazine (DNPH), acetonitrile HPLC grade, perchloric acid (analyzer grade), brown wide-mouth reaction bottle 100 ml with screw-capped, formaldehyde (standard fluke), C<sub>18</sub> stainless column (2.46 × 250) mm pre-treated with 25ml of acetonitrile of flow rate 4ml/min and ten bottles of packed drinking water completes were collected from various markets.

Instruments and Measurement condition Technique HPLC / UV detection, column stainless steel, 2.46x250 mm packed with 5µm C<sub>8</sub>, detector UV.360 nm, flow rate 1ml/min, mobile phase acetonitrile /distilled (60/40ml).

GC /TCD, column stainless steel typed with poropack N mesh (80-100), column Temp 80C°, injector temp 150C°, carrier gas H2, current 130 mA, R-column flow 15ml/min, L-column flow 15ml/min. detector temp 150C°.

### Experimental Work

Preparation of reagent

1- Preparation of DNPH reagent: Dissolve 0.645 of 33% DNPH with acetonitrile to make total volume to 100ml.

2-Preparation of 2M per chloride: Dissolve 28 .71 g of 70 % per chloride with Distilled-water to total volume of 100 ml .

3-preparation of sample solution for HPLC analysis packed water sample 50 ml was mixed with 0.5 ml of DNPH reagent and 2 drops of 2M per chloride in a brown wide mouth bottle screw the cap and reacted in 55 C° oven for 1h the reaction solution was passed through a pre-treated column in a flow rate 3ml/min after that the sample solution was eluted by acetonitrile in a flow rate 4ml/min. Adjusted final volume to make 10 ml . 20 µL of sample solution were injected into HPLC and the peak retention time and peak area of sample solution was compared with that of standard sample.

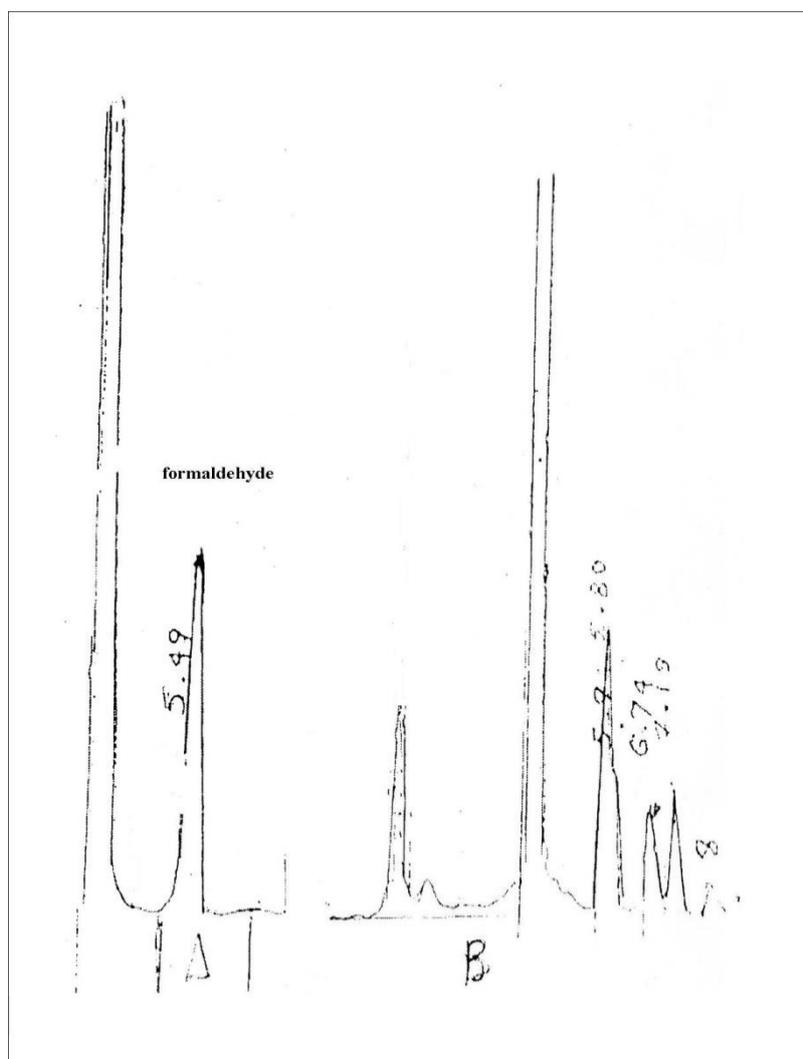
4- Preparation of standard curve (1 – 15) µg /l. was analyzed using GC. , one standard curve was plotted peak area against concentration of free formaldehyde.

5-Identification and quantization test by GC. 20µl of sample solution and formaldehyde standard solution were auto-injected into GC respectively the peak retention time and peak area of sample solution was compared with those of standard solution the conc. Of formaldehyde in sample were calculated according to the equation as shown below:

$$\text{Con. of formaldehyde In ppb} = \frac{\text{Area of Sample}}{\text{Area of standard}} \times \text{Conc. of stand.} \times 1000 \quad (1)$$

### Results and Discussion

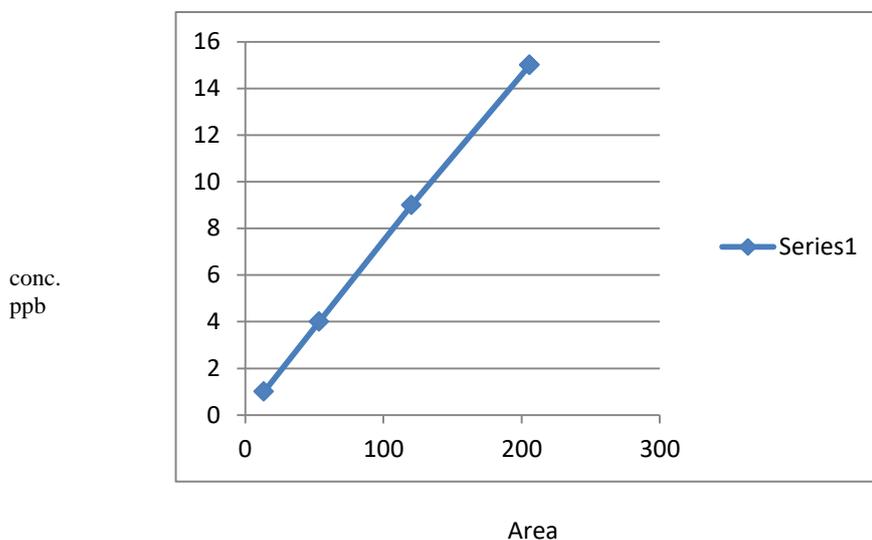
The capability to identify formaldehyde in bottled drinking water by HPLC was investigated. C18 stainless pre-treated purification column was used to improve the qualification of formaldehyde. Figure1. show that DNPH(A) has peak at the relative retention time of formaldehyde DNPH derivative (B) therefore, DNPH needed purification because this is subject to many interference in quantitative measurement , also , the HPLC resolution of the carbonyls can be in consistent and the analysis time is longer than that of the GC analyses , so, the analysis of formaldehyde in bottled drinking water by GC was investigated using standards from (1 – 15)µg/ l. Calibration graph was prepared by peak area vs. µg/l of baldheaded as shown in figure(2). Free aldehyde per sample was calculated according to equation (1). In table (2) the result indicates that the ten samples of bottled drinking water were far below the WHO limit 900µg/l.



Figure(1). HPLC chromatograms of and formaldehyde DNPH derivative (A) and DNPH (B), mobile phase acetonitrile /distilled water (60 /40) ml. With flow rate at 1ml/min and UV detection at 360 nm was used.

Table (1). List the Conc. µg/l and area of standard of formaldehyde by GC.

No. S	Conc. µg/l	Area
1	1.0	13.4
2	4.0	53.466
3	9.0	120.30
4	12.0	160.40
5	15.0	205.8



Figure(1). Show the calibration graph of formaldehyde standard between the peak area Vs conc. In ppb

Table (2) show the conc. of formaldehyde in the samples

No. Sample	Conc. in $\mu\text{g/L}$
1	13.10
2	3.4
3	Nil
4	Nil
5	3.5
6	7.5
7	0.1
8	Nil
9	Nil
10	4.01

**CONCLUSION**

1. GC/TCD can be used to analyze formaldehyde compound in  $0.1\mu\text{g/L}$  or higher
2. Sensitivity of GC/TCD is greater than sensitivity of HPLC.
3. Analysis time is shorter with GC.
4. All detected quantity of formaldehyde in packed drinking water were within WHO limit.

**REFERENCES**

- [1]. Wang, S.M. (Good outlook of packed drinking water market), Food Industries, 29: 70-74, 1997.
- [2]. Ling, Y.C. (Validation of analytical method for organic-aldehydes and glyphosate in water), National-Institute of Environmental Analysis, Environmental Protection Administration, Executive Yuan. Taipei EPA-85-E3S3-09-04, 1997.
- [3]. Velikonja, S., Jarc, I., Kralj, L.Z. and Marsel, J., (Comparison of gas chromatographic and spectrophotometric techniques for the determination of formaldehyde in water), J. Chromatographi. A. 704: 449-454, 1995.
- [4]. Tereshkova, W., (Determination of formaldehyde in foods, biological-media and technological material by headspace gas chromatography), Chromatography 43:625-627, 1966.
- [5]. Keeper, R.J. and Mopper, K. (Determination of Pico molar concentration carbonyl compounds in natural water, including seawater, by liquid
- [6]. U.S. Environmental Protection Agency (EPA), Environmental Monitoring Systems laboratory. (determination of carbonyl compounds in drinking water by DNPH derivation and HPLC, method) 554.Cincinnati, Ohio U.S.A 1992.
- [7]. (NIOSH Manual of Analytical Methods). Environ. Sci. Technol. 24:1477-1481, 1990.. fourth edition, method 2018, issue.1, p (2-10) dated 15 March 2003.
- [8]. Standard Method for the Examination of Water and Wastewater (Liquid-Liquid Extraction Gas Chromatography) American Public Health Association Copyright 1999.
- [9]. World Health Organization Guidelines for Drinking Water Quality. Switzerland 2004.