

Spectrophotometric Determination of Formaldehyde in Seawater Samples after In-situ Derivatization and Dispersive Liquid-Liquid Microextraction

Nassiri, Mahmoud*⁺

Department of Marine Chemistry, Faculty of Marine Science, Chabahar Maritime University, Chabahar, I.R. IRAN

Kaykhaii, Massoud

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan, I.R. IRAN

Hashemi, Sayyed Hossein*⁺

Department of Marine Chemistry, Faculty of Marine Science, Chabahar Maritime University, P.O. Box 98617-85553 Chabahar, I.R. IRAN

Sepahi, Massoud

Department of Marine Chemistry, Faculty of Marine Science, Chabahar Maritime University, Chabahar, I.R. IRAN

ABSTRACT: In this paper, a simple dispersive liquid-liquid microextraction for the extraction and pre-concentration of formaldehyde in seawater samples followed with spectrophotometric is proposed. Formaldehyde was derivatized in situ with acetyl acetone in the presence of ammonium acetate in a single step. Then it was collected into a mixture of ethanol (disperser solvent) and chloroform (extracting solvent). Experimental parameters which have an influence on the extraction, including type and volume of extracting and disperser solvent, pH of sample solution, the concentration of acetyl acetone and ammonium acetate, reaction time and temperature were evaluated and optimized. Under optimal experimental conditions, good linearity was observed in the range of 1-500 $\mu\text{g/L}$ for the analyte with a limit of detection of 0.29 $\mu\text{g/L}$. The proposed method was applied to the analysis of real seawater samples. For spiked samples, good recoveries in the range of 97.7-101.5% were obtained. The relative standard deviations were below 2.1%. Using this method, formaldehyde content in seawater from several locations in Chabahar Bay (southeast Iran) were determined in the range of 1.4 to 4.8 $\mu\text{g/L}$.

KEYWORDS: Formaldehyde; Seawater; Acetyl acetone; Dispersive liquid-liquid microextraction; Chabahar bay.

* To whom correspondence should be addressed.

+ E-mail: mdnassiri@cmu.ac.ir ; h.hashemi@cmu.ac.ir

1021-9986/2018/1/89-98

10/\$/6.00

DOI:

INTRODUCTION

Formaldehyde (HCHO, FA) is the most widespread carbonyl compound in the atmosphere [1]. It is a common environmental pollutant from natural sources including forest fires and from direct human sources such as industrial activities, fuel combustion, off-gassing from building materials, consumer products, incinerators and car exhaust emission [2,3]. Formaldehyde is usually used as antiseptic in many foods such as beverage, meat, mushroom, bean curd, vermicelli, sea cucumber, fish, tripe, juices and hydrated food to keep them pleasant [4-6]. It is found as a contaminant in foods, i.e. vegetables and fruit (3.3-17.3 mg/L), milk (1.0-3.3 mg/L), cheese (up to 3.3 mg/L), meat (5.7-20.0 mg/L) and fish (1.0-98.0 mg/L) [7]. This compound used illegally in the food industry because the addition of it can increase the storage life for some foodstuffs and give a facelift by changing their color and smell [8]. The World Health Organization has established a maximum daily dose reference of 0.2 mg/kg per day for this compound [9,10]. Formaldehyde is unfavorable for our health because, at low concentrations, it can cause irritation of the eyes, nose, throat, and skin [11]. The mean seawater superficial formaldehyde concentration was reported as 15 $\mu\text{g/L}$ and the concentration along the water column ranges between 4.5-40 $\mu\text{g/L}$ [12]. The presence of this pollutant in Chabahar bay can be due to chemical industries, fuel combustion, and exhaust emission [3]. High-Performance Liquid Chromatography (HPLC) [8], Spectrophotometry (UV-Vis) [13], mass spectrometry [14], and Gas Chromatography-Mass Spectrometry (GC-MS) [15] are common methods used for the measurement of formaldehyde so far. Due to its inexpensive instrumentation, the simplicity of operation and fairly good sensitivity, good precision, the accuracy of analysis and offers the practical, spectrophotometric methods are the most widely used analytical technique [8,16]. However, because of the lack of proper chromophores at the UV-Vis spectra, the complexity of the sample matrix, and the very low concentration of formaldehyde in seawater, the required selectivity and sensitivity it cannot be used directly for the detection of FA. So, a selective separation and pre-concentration step [11, 17] and a preliminary reaction with a highly absorbing derivatizing agent such as 2,4-dinitrophenylhydrazine (DNPH), p-aminoazobenzene, parosaniline, 4-amino-3-pentene-2-one, 4-amino-5-

hydrazine-3-mercapto-1,2,4-triazole (AHMT) and 3-methyl-2-benzothiazolone hydrazine (MBTH) [8,18] prior to the determination of the analyte with the spectrophotometry (UV-Vis) is often required.

A number of modern microextraction techniques were recently employed for HCHO pre-concentration, including Ionic Liquid-Based Dispersive Liquid-Liquid Microextraction (IL- DLLME) [7], Liquid Phase MicroExtraction (LPME) [11], Solid Phase MicroExtraction (SPME) [11] and Cloud Point Extraction (CPE) [19]. Different configurations of LPME have recently emerged, including Single-Drop MicroExtraction (SDME) and Hollow-Fiber-Based Liquid-Phase MicroExtraction (HF-LPME). Various disadvantages, such as the instability of liquid drop in SDME, air bubbles forming in HF-LPME, long analysis time, and relatively low precisions, are often encountered. SPME endures some problems such as sample carryover, relatively high cost, and fiber fragility [7]. The disadvantages of CPE such as time-consuming, unsatisfactory enrichment factors and using large organic solvents, limit their applications [20].

Dispersive Liquid-Liquid Microextraction (DLLME) is an attractive pre-treatment method first reported in 2006 with *Assadi et al.* It has advantages such as short extraction time, ease of operation, low cost, with high enrichment factor and small amounts of solvents used. By means of a 1 mL syringe, a mixture of disperser solvent and extracting solvent which was injected rapidly into the sample solution and shaking the mixture gently for a few seconds. In this technique, extracting solvent is dispersed in a water sample solution with the assistance of a disperser solvent. This solvent could decrease the partition coefficient of the analytes into the extraction solvent. After formation of the cloudy solution, the phase separation was performed by a rapid centrifugation and the extraction solvent containing the target analytes can be easily collected and transferred into the analytical system for analysis [21-25].

In the present paper, a new approach for the detection of formaldehyde is suggested that is based on its derivatization according to Hantzsch reaction, which involves the cyclization between formaldehyde and acetyl acetone in the presence of ammonium acetate. This reaction is very fast and effective which enables derivatization of formaldehyde to be performed in a single step in situ inside the sample before its extraction.

Dispersive liquid-liquid microextraction was employed for the extraction of the derivatized species, before it's a spectrophotometric detection.

EXPERIMENTAL SECTION

Materials

All chemicals in this work were of analytical grade and were used without further purification. Formaldehyde, acetyl acetone, ammonium acetate, acetic acid and sodium hydroxide (NaOH) as reagents, chloroform, dichloromethane, carbon tetrachloride and 1, 1-dichloroethane as extracting solvents, and acetone, acetonitrile, methanol and ethanol, as disperser solvents were purchased from Merck KGaA (Darmstadt, Germany) or Fluka (Buchs, Switzerland). A standard solution of formaldehyde (1000 mg/L) was prepared by dilution of a 37% (v/v) commercial formaldehyde solution in deionized water [26]. The working standard solutions were prepared daily by successive dilution of stock solution with ultrapure water to get required concentrations in the range of 1-500 µg/L. A 0.20 mol/L acetyl acetone and 0.40 mol/L ammonium acetate stock solutions were prepared in purified water. The ammonium acetate buffer was prepared in the range of pH 4-8. All the glassware were previously washed with acetone and water and finally dried in an oven at 250 °C. The required artificial seawater was prepared by dissolving the following salts in 1 L of deionized water: NaF (3 mg), KBr (100 mg), Na₂SiO₃·9H₂O (20 mg), SrCl₂·H₂O (20 mg), KCl (3 mg), MgCl₂·6H₂O (10.780 g), NaHCO₃ (200 mg), H₃BO₃ (30 mg), CaCl₂·2H₂O (1.470 g) and NaCl (23.500 g) [27, 28].

Instrumentals

Spectrophotometry was carried out on a UNICO S2100 UV-Vis spectrophotometer (China) equipped with a 100 µL quartz microcell (model Q-01701, Starna Company, UK). A Centurion Scientific K3 series K241R centrifuge was used to accelerate phase separation. A TPS WP-80 digital pH meter was used for pH adjustments (TPS Pty Ltd, Australia). A 100 µL microsyringe (Hamilton Company, NA, USA) was used for phase separation of collected sediments.

Procedure

First, acetyl acetone and ammonium acetate were added to the sample solution in a way that their

concentration became 0.2 mol/L in artificial seawater. Then the pH was adjusted to 6.0 and the mixture was placed for 12 min in a water bath at 70 °C. The reaction which takes place between formaldehyde and acetyl acetone is presented in Scheme 1 and Fig. 1. After completion of this reaction, it was cooled down in ambient temperature for 15 min. 12 mL of this mixture was transferred into a 15 mL conical bottom glass centrifuge tube. The extraction was performed using a mixture of 500 µL of ethanol as disperser solvent and 200 µL of chloroform as extracting solvent which was injected rapidly into the sample solution and shaking the mixture gently for a few seconds. After formation of the cloudy solution, the phase separation was performed by a rapid centrifugation at 3000 rpm for 5 min. Finally, 100 µL of the organic phase was removed by a microsyringe and transferred to a 100 µL microcell for the measurement of absorbance which was conducted at the wavelength of 412 nm.

RESULTS AND DISCUSSION

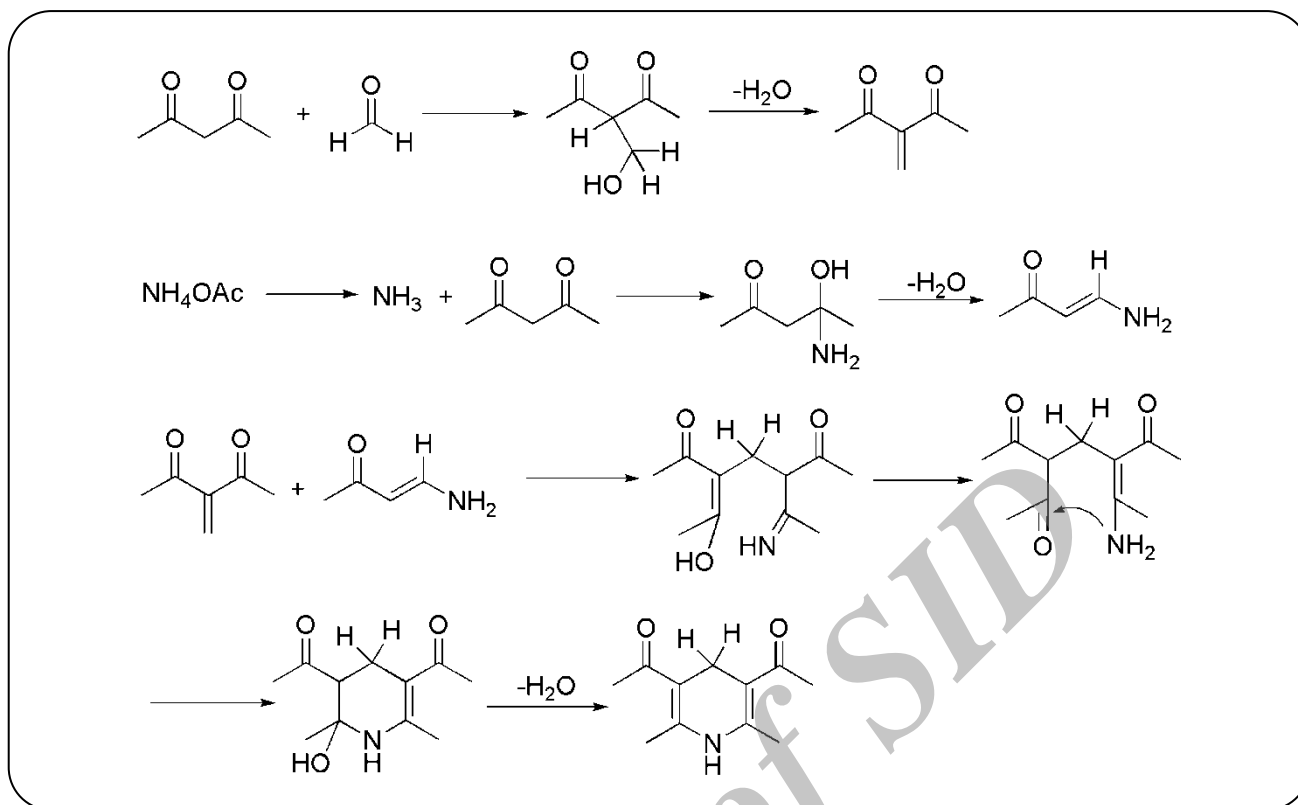
There are various parameters affecting the DLLME performance and efficiency, including the type and the volume of the extracting and disperser solvents, pH of the sample, derivatization condition, and temperature and extraction time. These parameters were investigated carefully, and the optimal amounts were determined as are indicated in the following sections and applied to the extraction of formaldehyde. All optimization were carried out using artificial seawater.

The derivitization reaction is based on the Hantzsch reaction, which was first explained by Nash (1953). The reaction is characterized by a cyclization of acetyl acetone and formaldehyde in the presence of ammonium acetate (Scheme 1 and Fig. 1) [11, 29, 30].

Optimization of the extraction parameters

Selection of extracting solvent

Selection of the extracting solvent is the most important part of all of the microextraction methods. A good extracting solvent should have low solubility in water, extract the target analytes well, and form a cloudy solution in the presence of disperser solvent when injected into the aqueous sample solution. Based on the above requirements four solvents, dichloromethane, chloroform, carbon tetrachloride and 1, 1-dichloroethylene



Scheme 1: Cyclization of acetyl acetone and formaldehyde in the presence of ammonium acetate.

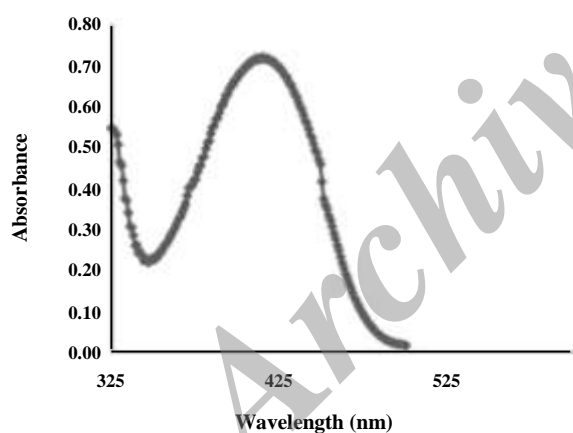


Fig. 1: Absorbance spectra for the product of Hantzsch reaction after extraction. Conditions: sample solution, 12 mL; disperser solvent (ethanol), 500 μL ; extracting solvent (chloroform), 200 μL ; acetyl acetone, 0.2 mol/L, formaldehyde, 200 $\mu\text{g/L}$; pH = 6.

was examined. The results are summarized in Fig. 2 which indicates that chloroform is the best extracting solvent for the extraction of formaldehyde from the seawater.

Selection of disperser solvent

The main point for the selection of a disperser solvent is that it should be miscible in both the organic phase (extracting solvent) and the aqueous sample phase. This decreases the interfacial tension between the two phases and accelerates the formation of the droplets of extracting solvent into the aqueous phase. Thereby, acetone, acetonitrile, methanol, and ethanol were tested as disperser solvents. Fig. 3 shows that the best absorbance was obtained using ethanol. Therefore, ethanol was selected as the disperser solvent for further work.

Effect of extracting solvent volume

In a microextraction procedure, the volume of extracting solvent is crucial by having an important impact on the analytical signals. Commonly, the volume of extracting solvent is selected as low as possible in order to achieve the higher absorbance and the lower toxicity for the environment. On the other hand, it should be moderate to extract as many analytes as possible and to ensure that enough sediment phase volume is being formed for further work. In order to evaluate the effect of

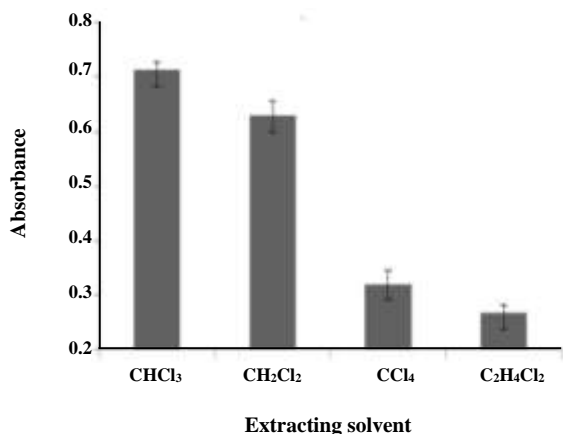


Fig. 2: Effects of extracting solvent on the formaldehyde extraction. Conditions: sample solution, 12 mL; acetyl acetone concentration, 80 mg/L; ammonium acetate, 0.1 mol/L; extracting solvent, 150 μ L; disperser solvent, 500 μ L; formaldehyde, 200 μ g/L; temperature, 70 $^{\circ}$ C and pH = 6.

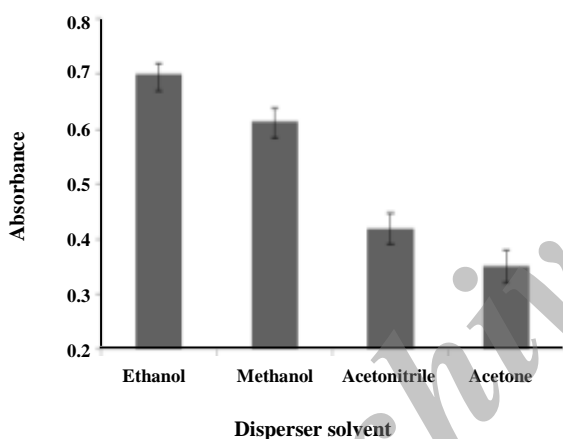


Fig. 3: Effects of disperser solvent on the formaldehyde extraction. Conditions are the same as in Fig. 2.

the extracting solvent volume on the absorbance intensity, additional experiments were performed using 500 μ L ethanol containing different chloroform volumes (100, 120, 140, 160, 180, 200, 220, 240 and 260 μ L). Fig. 4 shows that by increasing the extracting solvent volume from 100 to 200 μ L the absorbance intensity increased, but when the volume of chloroform exceeded from 200 to 260 μ L the absorbance intensity decreased. It was because of that the target compound was diluted by the increase of the resulting upper floating organic solvent volume from the proposed DLLME technique. Thus, 200 μ L of chloroform was selected as the optimum volume of extracting solvent.

Effect of disperser solvent volume

The volume of disperser solvent is also an important parameter that has a significant effect on the extraction efficiency and absorbance intensity. To determine the optimal volume of ethanol, additional experiments were performed using 200 μ L chloroform containing different volumes of ethanol (i.e. 100, 200, 300, 400, 500, 600, 700 and 800 μ L). By increasing the disperser solvent volume from 100 to 500 μ L the absorbance intensity increased, but when the volume of ethanol exceeded from 500 to 800 μ L the absorbance intensity decreased. It was because the target compounds were diluted with the increase in the volume of disperser solvent from the proposed DLLME technique. Therefore, the amount of 500 μ L ethanol was chosen as the optimum volume of disperser solvent for further work (Fig. 5).

Effect of pH

The pH of the sample solution plays an important role in the extraction of organic compounds. In this work, the effect of solution pH on the extraction was investigated in the pH range of 4-8. The results which are presented in Fig. 6 demonstrate that the best pH for extraction of the derivative formaldehyde is 6. The extraction increased by increasing pH, because of the liberation of poron during the condensation is reasonably favorable at higher pH, at pH higher than 5.0 hydrolysis of analytes can be expected. Thereby, pH = 6 was selected for further experiments.

Effect of reaction time

The influence of the reaction time on the absorbance intensity was studied. The results demonstrated in Fig. 7 reveal that the absorbance was constant in the time range of 12-16 min. Accordingly, 12 min was selected for the derivatization of FA.

Effect of temperature

Due to the very low speed of the condensation reaction in room temperature, the effect of temperature was investigated by varying it from 30 to 90 $^{\circ}$ C. The results indicate that the product obtained at 70 $^{\circ}$ C gave the highest intensity and after that, the absorbance was constant. Thus, 70 $^{\circ}$ C was selected as the extraction temperature in the study.

Effect of derivatizing agent concentration

In order to study the effect of the acetyl acetone concentration on the extraction efficiency, different

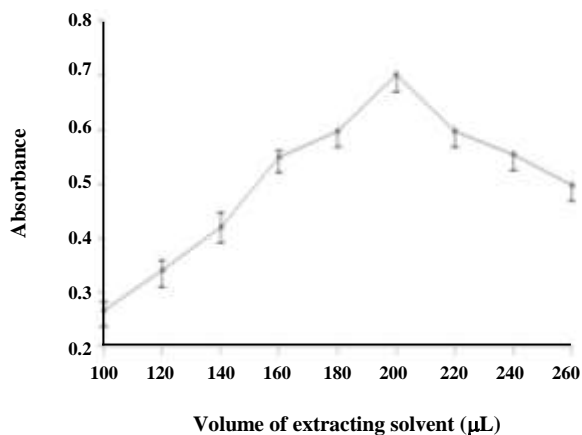


Fig. 4: Effects of extracting solvent volume on the formaldehyde extraction. Conditions: sample solution, 12 mL; acetyl acetone concentration, 80 mg/L; ammonium acetate, 0.1 mol/L; disperser solvent, 500 µL; formaldehyde, 200 µg/L; temperature, 70 °C and pH = 6.

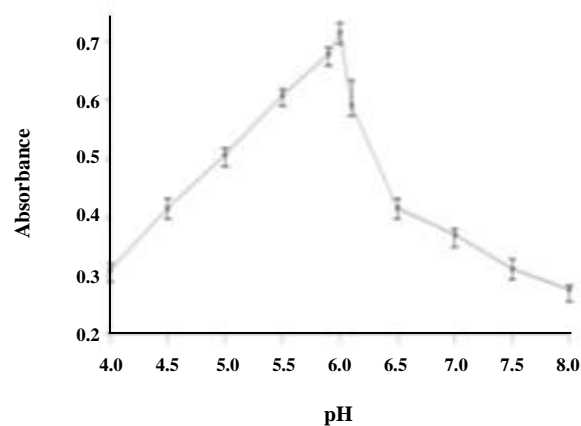


Fig. 6: Effects of pH on the formaldehyde extraction. Condition: 12 mL water sample; Formaldehyde, 200 µg/L; acetyl acetone, 80 mg/L; extracting solvent, 200 µL; disperser solvent, 500 µL; and temperature = 70 °C.

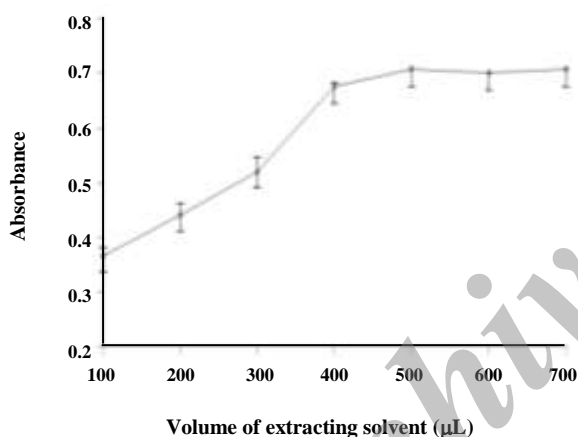


Fig. 5: Effects of disperser solvent volume on the formaldehyde extraction. Conditions: sample solution, 12 mL; acetyl acetone concentration, 80 mg/L; ammonium acetate, 0.1 mol/L; extracting solvent, 200 µL; formaldehyde, 200 µg/L, temperature, 70 °C and pH = 6.

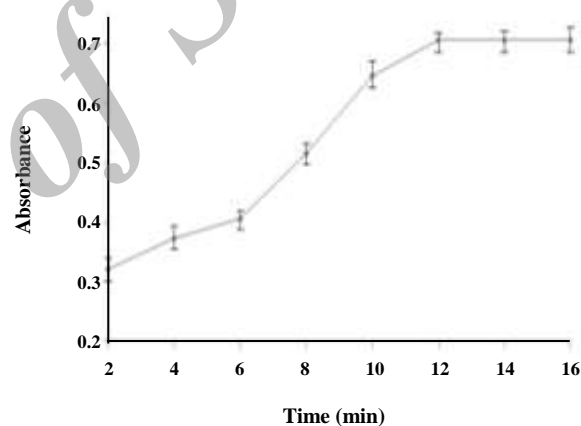


Fig. 7: Effects of reaction time on the formaldehyde extraction. Conditions: 12 mL water sample; Formaldehyde, 200 µg/L; acetyl acetone, 80 mg/L; ammonium acetate, 0.1 mol/L; extracting solvent, 200 µL; disperser solvent, 500 µL; and temperature = 70 °C; pH = 6.

concentrations of acetyl acetone in the range of 20-140 mg/L were examined. The results showed that the best concentration is 80 mg/L.

Effect of ammonium acetate concentration

The effect of ammonium acetate concentration was examined in the ranges of 0.05-0.15 mol/L. By increasing the concentration from 0.05 to 0.10 mol/L the absorbance increased, but when it exceeded from 0.10 to 0.15 mol/L

the absorbance remained constant. Thus 0.10 mol/L was selected for the further experiments.

Analytical performance

Under the selected optimum experimental condition, this method was applied to a series of standard solutions containing various concentrations of analyte, in order to evaluate the efficiency of it. The calibration curve was obtained liner in the concentration range 1-500 µg/L

Table 1: Recovery results for seawater samples obtained from various locations of Chabahar Bay (Iran).

Sampling location	Formaldehyde added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	Recovery (%)
Oman Sea	-	1.8 \pm 0.028	-
	100	101.3 \pm 0.032	99.5
Beheshti	-	4.8 \pm 0.024	-
	100	104.2 \pm 0.026	99.4
Chabahar Maritime University	-	1.4 \pm 0.025	-
	100	100.0 \pm 0.029	98.6
Kalantary	-	4.4 \pm 0.021	-
	100	105.0 \pm 0.022	100.6
Lypar	-	1.5 \pm 0.025	-
	100	100.4 \pm 0.030	98.9
Tis	-	2.5 \pm 0.020	-
	100	104.0 \pm 0.021	101.5
Konarak Desalination	-	1.8 \pm 0.030	-
	100	101.3 \pm 0.033	99.5
Konarak	-	3.6 \pm 0.035	-
	100	101.2 \pm 0.038	97.7

with correlation coefficients (r^2) of 0.998. The least square equation over the dynamic linear range is $Y = 0.003X + 0.037$, which Y and X are absorbance and concentration of formaldehyde in the sample, respectively. The Limit of Detection (LOD) and the Limit of Quantification (LOQ) were 0.29 and 0.98 $\mu\text{g/L}$, respectively; based on the $3S_d/m$ and $10S_d/m$ criteria; in which S_d is the standard deviation of 7 consecutive measurements of the blank and m is the slope of the calibration curve.

Enrichment Factor (EF) and Relative Recovery (RR %) were calculated using the following equations [31]:

$$EF = C_{\text{sed}} / C_0$$

$$RR\% = [(C_{\text{found}} - C_{\text{real}}) / C_{\text{added}}] \times 100$$

Where C_{sed} , C_0 , C_{found} , C_{real} , and C_{added} are the concentration of the analyte in the sedimented phase, initial concentration of the analyte in the aqueous sample, the concentrations of analyte after addition of known amount of standard in the real sample, the concentration of analyte in real sample, and the concentration of known amount of standard which was spiked to the real sample, respectively. The enrichment factor was calculated 149 folds.

Real seawater sample preparation

The applicability of the method was evaluated by extraction and determination of formaldehyde in seawater samples. Seawater samples were taken from the surface layer (25 cm depth) of eight different sites of the Chabahar Bay (southern east of Iran). Sampling stations were 50-100 meters away from the coast. Samples were collected in dark glass bottles and each sample was pretreated by filtering through glass microfibers (GF/C Whatman, UK). All of the samples were stored under dark conditions in a refrigerator at 4 °C before analysis [19]. In order to investigate the effect of sample matrices on extraction efficiency, samples were also spiked at the concentration level of 100 $\mu\text{g/L}$ with formaldehyde. The recoveries for 8 sampling location are also shown in Table 1. The recoveries were obtained from 97.7 to 101.5 with the relative standard deviation of 2.1 % ($n = 7$). These results indicate that the developed method can be successfully applied for the detection of formaldehyde in very complicated matrices such as seawater.

Comparison of this technique with other methods

Some other methods reported in the literature were

Table 2: Comparison of DLLME-UV-Vis with other methods for determination of HCHO.

Method	LOD ($\mu\text{g/L}$)	Linear range ($\mu\text{g/L}$)	Detection method	Ref.
IL-based DLLME	0.12	0.5-50.0	HPLC-UV	7
Condensation of HCHO with hydroxylamine sulfate and subsequent redox reaction with iron (III)-ferrozine complex	1.6	5.3-250.0	UV-Vis	13
Cation-exchange resin	6.0	20.0-5000.0	HPLC-UV	32
DLLME-UV-Vis	0.29	1-500	UV-Vis	This work

compared with the proposed method in Table 2. The results indicated that the proposed method is comparable for determination of formaldehyde in terms of LOD, time of analysis and linear dynamic range.

CONCLUSION

In the present study, a DLLME-UV-Vis method for the determination of formaldehyde in seawater sample has been evaluated. The method is based on the in situ derivatization of formaldehyde which enhances its absorption tremendously at the visible region of spectra. Overall, this method is sensitive, inexpensive, simple and fast and requires only a small volume of organic solvents. This can be used for very complicated matrices as seawater samples.

Acknowledgment

We gratefully acknowledge the financial support received from the Research Council of Chabahar Maritime University.

Received: Aug. 11, 2016; Accepted: Jul. 10, 2017

REFERENCES

- [1] Carlier P., Hannachi H., Mouvier G., *The Chemistry of Carbonylcompounds in the Atmosphere*, *Atmos. Environ.*, **20**: 2079-2099 (1986).
- [2] Agency for Toxic Substances and Disease Registry (ATSDR), "Toxicological Profile for Formaldehyde (Draft), Public Health Service", US Department of Health and Human Services Website (<https://www.atsdr.cdc.gov/toxprofiles/TP.asp?id=220&tid=39>), accessed 21-08-2017.
- [3] "IPCS Formaldehyde", World Health Organization, International Program on Chemical Safety (Concise International Chemical Assessment Document No. 40), Geneva, p. 75. (2002).
- [4] Zhao X.Q., Zhang Z.Q., *Microwave-Assisted On-Line Derivatization for Sensitive Flow Injection Fluorometric Determination of Formaldehyde in Some Foods*, *Talanta*, **80**: 242-245 (2009).
- [5] Li Z.W., Ma H.B., Lu H.H., Tao G.H., *Determination of Formaldehyde in Foodstuffs by Flow Injection Spectrophotometry Using Phloroglucinol as Chromogenic Agent*, *Talanta*, **74**: 788-792 (2008).
- [6] Weng X., Chon C.H., Jiang H., Li D., *Rapid Detection of Formaldehyde Concentration in Food on a Polydimethylsiloxane (PDMS) Microfluidic Chip*, *Food Chem.*, **114**: 1079-1082 (2009).
- [7] Xu X., Su R., Zhao X., Liu Z., Li D., Li X., Zhang H., Wang Z., *Determination of Formaldehyde in Beverages Using Microwave-Assisted Derivatization and Ionic Liquid-Based Dispersive Liquid-Liquid Microextraction Followed by High-Performance Liquid Chromatography*, *Talanta*, **85**: 2632-2638 (2011).
- [8] Li Z., Ma H., Lu H., Tao G., *Determination of Formaldehyde in Foodstuffs by Flow Injection Spectrophotometry Using Phloroglucinol as Chromogenic Agent*, *Talanta*, **74**: 788-792 (2008).
- [9] Afkhami A., Bagheri H., *Preconcentration of Trace Amounts of Formaldehyde from Water, Biological and Food Samples Using an Efficient Nanosized Solid Phase, and Its Determination by a Novel Kinetic Method*, *Microchim. Acta*, **176**: 217-227 (2012).
- [10] Shin H.S., Lim H.H., *Simple Determination of Formaldehyde in Fermented Foods by HS-SPME-GC/MS*, *J. Food. Sci. Tech.*, **47**: 350-356 (2012).
- [11] Arvand M., Bozorgzadeh E., Shariati S., Zanjanchi M.A., *Ionic Liquid-Based Dispersive Liquid-Liquid Microextraction for the Determination of Formaldehyde in Wastewaters and Detergents*, *Environ. Monit. Assess.*, **184**: 7597-7605 (2012).

- [12] Largiuni O., Becagli S., Innocenti M., Stortini A.M., Traversi R., Udisti R., [Formaldehyde Determination in Seawater. Preliminary Application to Coastal Samples at Terra Nova Bay \(Antarctica\)](#), *J. Environ. Monit. Assess.*, **7**: 1299-1304 (2005).
- [13] Teshima N., Fernández S.K.M., Ueda M., Nakai H., Sakai T., [Flow Injection Spectrophotometric Determination of Formaldehyde Based on its Condensation with Hydroxylamine and Subsequent Redox Reaction with Iron \(III\)-Ferrozine Complex](#), *Talanta*, **84**: 1205-1208 (2011).
- [14] Deng B., Liu Y., Yin H., Ning X., Lu H., Ye L., Xu Q., [Determination of Ultra-Trace Formaldehyde in Air Using Ammonium Sulfate as Derivatization Reagent and Capillary Electrophoresis Coupled with On-Line Electrochemiluminescence Detection](#), *Talanta*, **91**: 128-133 (2012).
- [15] Yeh T.S., Lin T.C., Chen C.C., Wen H.M., [Analysis of Free and Bound Formaldehyde in Squid and Squid Products by Gas Chromatography–Mass Spectrometry](#), *J. Food Drug Anal.*, **21**: 190-197 (2013).
- [16] Li Q., Sritharathikhun P., Motomizu S., [Development of Novel Reagent for Hantzsch Reaction for the Determination of Formaldehyde by Spectrophotometry and Fluorometry](#), *Anal. Sci.*, **23**: 413-417 (2007).
- [17] Pebdani A.A., Shabani A.M.H., Dadfarnia S., [Selective Separation and Determination of Diclofenac via Magnetic Molecularly Imprinted Polymer and Spectrophotometry](#), *J. Iran. Chem. Soc.*, **13**: 155-164 (2016).
- [18] Chen L., Jin H., Wang L., Sun L., Xu H., [Dynamic Ultrasound-Assisted Extraction Coupled On-Line with Solid Support Derivatization and High-Performance Liquid Chromatography for the Determination of Formaldehyde in Textiles](#), *J. Chromatogr. A*, **1192**: 89-94 (2008).
- [19] Wang T., Gao X., Tong J., Chen L., [Determination of Formaldehyde in Beer Based on Cloud Point Extraction Using 2,4-Dinitrophenylhydrazine as Derivative Reagent](#), *Food Chem.*, **131**: 1577-1582 (2012).
- [20] Liang P., Zhao E., [Determination of Trace palladium in Complicated Matrices by Displacement Dispersive Liquid-Liquid Microextraction and Graphite Furnace Atomic Absorption Spectrometry](#), *Microchim. Acta*, **174**: 153-158 (2011).
- [21] Berijani S., Ahmadi G., [Ultrasound Assisted Surfactant Enhanced Emulsification Microextraction and Spectrofluorimetry for Determination of Oxadiazon in Agricultural Water Samples](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **33**: 41-49 (2014).
- [22] Chamsaz M., Hossein-Poor-Zaryab M., Arab-Zavar M.H., Darroudi A., [Dispersive Liquid-Liquid Microextraction Based on Solidification of Floating Organic Drop Combined with Flame Atomic Absorption Spectrometry for Preconcentration and Determination of Thallium \(III\) in Water Samples](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **33**: 59-66 (2014).
- [23] Hashemi S.H., Kaykhah M., Dehvari R., [In- Syringe Dispersive Liquid-Liquid Microextraction Coupled with High- Performance Liquid Chromatography for Trace Analysis of Naphthalene Sulfonates in Seawater](#), *Current Chromatogr.*, **4**: 1-8 (2017).
- [24] Soleiman B., Zakerian R., [Ionic Liquid Based Dispersive Liquid Liquid Microextraction and Enhanced Determination of the Palladium in Water, Soil and Vegetable Samples by FAAS](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **33**: 51-58 (2014).
- [25] Hajmohammadi M.R., Hemmati M., [Vortex-Assisted Inverted Dispersive Liquid-Liquid Microextraction of Naproxen from Human Plasma and Its Determination by High Performance Liquid Chromatography](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**: 107-114 (2017).
- [26] Motyka K., Mikuška P., [Continuous Fluorescence Determination of Formaldehyde in Air](#), *Anal. Chim. Acta*, **518**: 51-57 (2004).
- [27] Nassiri M., Zahedi M.M., Pourmortazavi S.M., Yousefzadeh M., [Optimization of Dispersive Liquid-Liquid Microextraction for Preconcentration and Spectrophotometric Determination of Phenols in Chabahar Bay Seawater after Derivatization with 4-Aminoantipyrine](#), *Marine. Pollu. Bull.*, **86**: 512-517 (2014).
- [28] López-Darias J., Germán-Hernández M., Pino V., Afonso A.M., [Dispersive Liquid-Liquid Microextraction Versus Single-Drop Microextraction for the Determination of Several Endocrine-Disrupting Phenols from Seawaters](#), *Talanta*, **80**: 1611-1618 (2010).
- [29] Burini G., Coli R., [Determination of Formaldehyde in Spirits by High-Performance Liquid Chromatography with Diode-Array Detection after Derivatization](#), *Anal. Chim. Acta*, **511**: 155-158 (2004).

- [30] Kidwai M., Chauhan R., Bhatnagar D., Singh A.K., Mishra B., Dey S., [Nafion-Hcatalyzed Synthesis of Polyhydroquinolines Via the Hantzsch Multicomponent Reaction](#), *Monatsh. Chem.*, **143**: 1675-1680 (2012).
- [31] Kaykhahi M., Sargazi M., [Comparison of Two Novel In-Syringe Dispersive Liquid-Liquid Microextraction Techniques for the Determination of Iodide in Water Samples Using Spectrophotometry](#), *Spectrochim. Acta A*, **121**: 173-179 (2014).
- [32] Wang H., Ding J., Du X., Sun X., Chen L., Zeng Q., Xu Y., Zhang X., Zhao Q., Ding L., [Determination of Formaldehyde in Fruit Juice Based on Magnetic Strong Cation-Exchange Resin Modified with 2,4-Dinitrophenylhydrazine](#), *Food. Chem.*, **131**: 380-385 (2012).

Archive of SID