Asian Journal of Chemistry Vol. 20, No. 2 (2008), 849-852

Determination of Formaldehyde in Environmental and Other Aqueous Samples

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The present method described an analytical procedure for determination of formaldehyde in environmental aqueous samples. The water samples are first derivitaized with 2,4-dinitrophenylhydrazine then extracted with dichloromethane. The extract is concentrated and analyzed with HPLC using ODS zorbax column and UV detector.

Key Words: Formaldehyde, Derivatization, Environmental pollutant, HPLC.

INTRODUCTION

Formaldehyde is classified as a human carcinogen and has been linked to nasal and lung cancer and possible link to brain cancer and leukemia. Short-term exposure to low levels of formaldehyde may cause respiratory difficulty, eczema and sensitization. The common method for measuring formaldehyde is to use 2,4-dinitrophenylhydrazine to convert formaldehyde into 2,4-dinitrophenylhydrazone derivative which is detectable using UV detector[1].

The derivative is extracted using dichloromethane and then analyzed by high- performance liquid chromatography (HPLC) equiped with UV-Vis detector (360-380 nm). 2,4-Dinitrophenylhydrazine derivatization with HPLC analysis have been applied in a laboratory course experiment to quantify formaldehyde in aqueous samples.

In the aqueous matrix, 2,4-dinitrophenylhydrazine traps formaldehyde and selectively derivatize it to 2,4-dinitrophenylhydrazone which is then extracted with dichloromethane using liquid-liquid extraction method. The final extract is analyzed by HPLC.

EXPERIMENTAL

Hydrazone derivative is measured with an Agilent 1100 series HPLC. Solvents used for HPLC analysis were acetonitrile (HPLC grade, Merck, Germany), water (HPLC grade, Germany). Acetic acid, formaldehyde (37 %) and 2,4-dinitrophenylhydrazine were purchased from Merck, Germany.

Condensation reaction with 2,4-dinitrophenylhydrazine: 2,4-dinitrophenylhydrazine (DNPH) is insoluble in water. A little conc. H_2SO_4 is used to dissolve the orange DNPH solid[2].

A common analytical procedure employed in the speciation and quantification of carbonyl compounds involves their reaction with an acidic solution of 2,4-dinitrophenylhydrazine to form the corresponding 2,4-dinitrophenylhydrazone precipitate. In the solution of DNPH add the target analyt (formaldehyde) in molar excess of the DNPH. Filter the 2,4-dinitrophenylhydrazone derivative and wash the percipitate with 2 N HCl then wash with water and finally allow to dry in air[3].

Check the purity of the 2,4-dinitrophenylhydrazone derivative by its melting point (164-165 ºC) or HPLC analysis. If impurity level is not acceptable, recrystallize the derivative in acetonitrile. Repeat the purity check and recrystallization as needed until 99 % purity is achieved[3].

Standard preparation: Stock standard solution-prepared by dissolving 0.010 g of the solid hydrazine derivative in 100 mL of acetonitrile. Secondary dilution standard was prepared in acetonitrile using the individual stock standard solution. Calibration standards prepared from the secondary dilution standard at 0.5-2.0 µg/L.

Sample preparation: To 100 mL water sample add 4 mL acetate buffer and adjust the pH to 5.0 ± 0.1 with 6 M HCl or 6 M NaOH. Add 6mL of DNPH reagent, seal the container and place in a heated (40 ºC), orbital shaker for 1 h. Adjust the agitation to produce a gentle swirling of the reaction solution. [The 2,4-dinitrophenylhydrazone retention time is around 2.1 min the 2,4-dinitrophenylhydrazine elutes just before it. If the concentration of unreacted 2,4-dinitrophenylhydrazine is too high, the corresponding peak will mask or cover the 2,4-dinitrophenylhydrazone peak. Therefore, it is recommended for samples with low concentration of formaldehyde less 2,4-dinitrophenylhydrazine solution be used (*e.g.*, 0.5 mL DNPH solution instead of 6 mL)].

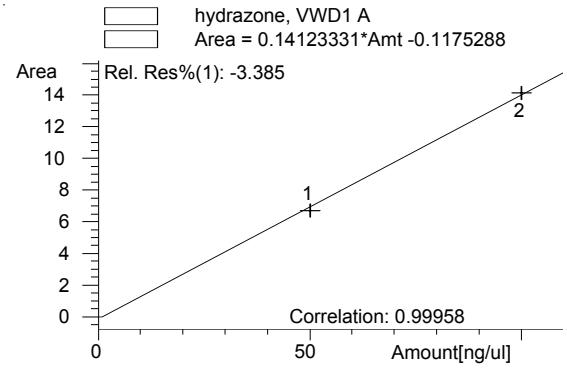

Fig. 1. Calibration curve

Extract the solution serially with three 20 mL portion of methylene chloride using a 250 mL separator funnel. If an emulsion forms upon extraction, remove the emulsion by centrifuging the sample at 2000 rpm for 10 min. Combine the methylene chloride layers in a 125 mL Erlenmeyer flask containing 5 g of anhydrous sodium sulfate. Shake the contents to complete the extract drying process. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporator flask. Pour the extract into the evaporator flask being careful to minimize transfer of sodium sulfate granules. Wash the Erlenmeyer flask with 30 mL of methylene chloride and wash to the evaporator flask to complete quantitative transfer.

Add one to two clean boiling chip to the evaporative flask and attach a three ball Snyder column. Prewet the snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90 °C)and wait to complete the concentration process in 10-15 min. When the apparent volume of liquid reaches less than 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Quantitatively transfer the sample to a 5 mLvolumetric flask using a 5 mL syringe with an attached acrodisk 0.45 μm filter.

HPLC analysis: Inject 20 μL of prepared sample into an HPLC system using the following conditions:
(i) HPLC column-reversed phase ODS zorbax (ii) mobile phase - 70 % acetonitrile/30 % water (iii) flow rate - 0.5 mL/min (iv) injection volume - 20 μL of sample (v) detector UV-wavelength - 360nm (vi) column temperature - room temp (25 ºC).

The formaldehyde concentration in unknown samples can be determined by using the following procedure:

$$\text{Formaldehyde concentration} = \frac{\text{Area sample} \times R_f \times \text{g mol}^{-1} \text{ formaldehyde}/\text{g mol}^{-1} \text{ DNPH volume (5 mL)/sample volume (100 mL)}}{}$$

RESULTS AND DISCUSSION

Formaldehyde concentration = $14.048 \times R_f \times 30$ g mol^{-1}/209 g mol^{-1} × 5 mL/100 mL = 0.71 ppb. Since the true concentration value of the unknown sample is 0.8 ppb therefore the per cent recovery is as follow:

% Recovery = calculated conc./true conc. × 100
= 0.71/0.8 × 100 = 88.75

% Recovery is in the acceptance limit for formaldehyde.
Retention time for the derivative was 2.096 min.

The analysis was repeated and the standard deviation for the derivative at room temperature was: $sd_{rt} = 0.0558$.

Standard deviation of sample area was found to be (sd_{Area}) 0.11.

The per cent recovery in the analysis, respectively was 88.75, 83.13 and 84.44. Retention time for the derivative was 2.096 min.

Conclusion

This method is appropriate for measuring formaldehyde in aqueous samples. The per cent recovery of spiked samples show over 83 % recovery of formaldehyde. It can easily be analyzed in any laboratory equipped with HPLC to measure formaldehyde which is a known environmental pollutant.

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(*Received*: 19 September 2006; *Accepted*: 26 September 2007) AJC-5906