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Determination of Trihalomethanes in Tap Water by UV-Vis Spectrophotometry

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A simple and sensitive spectrophotometric method based on Fujiwara reaction has been developed for determination of trihalomethanes in water. Determination of trihalomethanes was carried out by adsorption on Amberlite XAD-4 resin, elution with pyridine, addition of KOH to eluate and heating to measure the absorbance at 531 nm. Detection limit and linear range for the proposed method was 187 ng mL^{-1} and 0.2-8 μg mL^{-1}, respectively. This rapid, sensitive, precise and low cost method enables water treatment facilities to respond quickly to investigate water quality.

Key Words: Trihaomethanes, Amberlite XAD-4, Fujiwara reaction, Spectrophotometry.

INTRODUCTION

Most drinking water use chlorine as the primary disinfactant to control waterborne, disease-causing pathogens[1]. Chlorine reacts with naturally occurring matters such as humic substances to from a wide variety of disinfection by-products including trihalomethanes. In addition, bromide in water forms the brominated-trihalomethane *i.e.*, tribromomethane. The most common trihalomethanes are chloroform, bromodichloromethane ($CHBrCl_2$), dibromochloromethanes ($CHBr_2Cl$) and bromoform ($CHBr_3$)[2].

In order to protect public health from possible carcinogen effects[3] of these substances, the USEPA sets the standards at 80 μgL^{-1}, to regulate the concentration of trihalomethanes in drinking water under the Safe Drinking Water Act[2]. Therefore, determination of trihalomethanes in drinking water is of great importance. Recently, researches have been oriented towards the development of inexpensive, simple and efficient sample preparation methods for analysis of trihalomethanes in aqueous samples. The trihalomethanes analytical methods include a variety of different gas chromatography (GC) methods, but the most are not readily adaptable for on line monitoring directly from drinking water distribution system. For example, the most popular USEPA methods used for compliance monitoring includes methods 502.2[4], 524.2[5], 55[6] and 551.1[7] which requires expensive equipment, extensive user training and significant running time (30-45 min). Furthermore, these EPA methods are relatively expensive and may involve laboratory turnaround times (including data

analysis and record keeping) of 2-4 weeks[8]. These methods are based upon clever chemistry and work very well for routine drinking water sampling, where samples are taken on monthly or quarterly schedules. However, when higher sampling rates are needed, perhaps hourly schedules that might be encountered in research or optimization studies, then these methods, especially the two LLE based methods, are not easily and inexpensively automated. None of these provide for sampling directly from water distribution systems and even if these issues were met, they still may not be able to meet the goal of hourly monitoring schedules[9].

Because of these limitations, there is interest in the development of fully automated analyzers and associated analytical methods to monitor trihalomethanes concentrations.

There are a number of analytical methods that have been reported for the analysis of trihalomethanes in water based on Fujiwara reaction[10-14]. Fujiwara reaction and its modifications involve the reaction of pyridine, hydroxide and chlorinated hydrocarbons to give products that absorb strongly in the visible or ultraviolet. The ultimate product in all reactions is (colourless) glutaconaldehyde, obtained by N-alkylation of pyridine followed by complete ring hydrolysis[15]. However, depending on the analyte and on the specific reaction conditions, a number of Schiff base derivatives of glutaconaldehyde may form as reaction intermediates and more than one molecule of glutaconaldehye may be obtained per molecule of analyte.

In the case of trihalomethanes a pink solution may be formed under certain conditions and the structure of the compound responsible for the colour has been determined by Uno *et al.*[16,17]. Although the compound is a reaction intermediate, its stability can be controlled.

This research aimed to utilize the application of the latter method along with solid phase extraction to present a novel method for routine measurement of total trihalomethanes in water plants. The utility of the method as rapid, inexpensive and easy to use method for in-plant total trihalomethanes determination is apparent when the cost and time-to-result is considered. The data presented in this research will demonstrate the sensitivity, precision and performance of the proposed method.

EXPERIMENTAL

All the spectrophotometric measurements were carried out by a DU-6 Beckman spectrophotometer.

Amberlite® XAD-4 (Rohm & Hass company), pyridine, chlororform, potassium hydroxide (Reidel Company) and acetone (BDH company) were used as received.

Polymeric resin clean up procedure: 25 mL of amberlite XAD-4 resin was placed in a flask and 25 mL of acetone was added and shaken vigorously, then the extra solvent was decanted. This procedure is necessary to remove the smallest particle in order to increase bed surface. The remainder of the solvent was removed using vacuum filtering. This procedure was repeated 5 times. Then 2.5 fold bed

volume methanol was added and stirred for 1 h and the resin was filtered by vacuum to remove the methanol and then the resin was rinsed with extra amounts of methanol until the methanol in the output became clear and bright. The resin on the filter was washed with 20 bed volume of deionized water and finally stored under purified water. The purity of the resin was checked by a blank procedure.

Purified water: Deionized water was distilled in glass apparatus. First 10 % of distillate was discarded and the 10-50 % portion was passed through a column containing 10 mL of amberlite XAD-4 at a flow rate of 3 mL min^{-1}. If the resin was taken directly from the methanol extraction, the first 200 mL of the eluate must be discarded.

Preparation of columns: Preconcentration of the samples was carried out using column procedure. 1 mL of the resin was placed in a syringe (8 mm i.d) which its outlet was blocked by crystal wool. The resin was coated with crystal wool.

General procedure: Two procedures are presented here. Procedure A is of general applicability[11], when the chloroform concentration in the water is sufficiently high, whereas procedure B is useful in certain case.

Procedure A: Determination of chloroform present in aqueous solution: To a test tube reagents are added in the following order: 2.0 mL of the test sample, 2.0 mL of pyridine and 4.0 mL of 10 M potassium hydroxide solution, mixing well after each addition, the tube is placed in boiling water for 4 min and then transferred to an ice bath for 2 min. The tube is allowed to remain in the ambient condition for 20 min. The upper phase is then transferred to spectrophotometric cell and its absorbance is measured against a blank prepared by the same procedure.

Procedure B: determination of chloroform extracted in pyridine phase (chloroform present in pyridine): The general procedure involves the addition of potassium hydroxide, heating in boiling water and then kept in ice bath respectively and measuring the absorbance after 20 min. All parameters affecting the signal will be optimized.

RESULTS AND DISCUSSION

The procedure A is only applicable when the concentration of chloroform in water is more than 1 μg mL^{-1}. So, when the concentration is lower than 1 μg mL^{-1}, the chloroform sample should be preconcentrated and extracted into pyridine.

Optimization of Fujiwara reaction's parameters: The parameters to be optimized are: practical wavelength for measurement of absorbances, concentration of potassium hydroxide, volume ratio of potassium hydroxide solution to pyridine and the retention time in boiling water.

Optimum wavelength: The spectrum for the product of Fujiwara reaction is shown in Fig. 1. The optimum wavelength for measurement of absorbance is 531 nm.

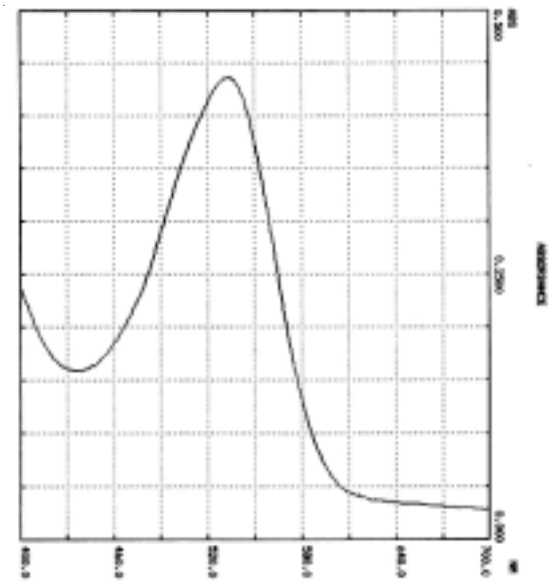

Fig. 1. Absorption spectra of the product intermediate for a solution of 4 ppm chloroform in pyridine which Fujiwara reaction were performed on it

Optimization of potassium hydroxide concentration: Hydroxide ion is involved both in the formation and in the decomposition of the colourful product (intermediate product) as shown in Fig. 2. So, for any given set of reaction conditions, there is a hydroxide concentration that gives a maximum yield of product. As Fig. 3 shows, the sensitivity of the procedure A is increased by increasing the concentrations of alkali to 10 M and diminished at higher concentrations. Therefore, the concentration of 10 M was used as the optimum concentration of potassium hydroxide.

Optimization of the volume ratio of potassium hydroxide to pyridine: The volume ratio of potassium hydroxide solution to pyridine is another important factor that must be optimized. One reason for this is that water content has many effects. At very low concentrations of water, intermediate I is never formed and the reaction rate is fast even at room temperature, chloroform yields a different product than the other trihalomethanes. As the water content is increased, the yield of I increases, but its rate of formation decreases, while it decomposes more readily[8]. As Fig. 4 shows, the 1:1 ratio is obtained to be the optimum volume ratio for the reaction.

Optimization of retention time in boiling water: Heating the sample in alkaline pyridine for 4 min was found to give the highest sensitivity for colour production. On heating the sample with alkali and pyridine for periods of greater than 4 min, however, the sensitivity of the method was dropped sharply (Fig. 5). It is supposed that heating influences both the formation and decomposition of the reaction intermediate (I), so possibly heating more than 4 min will increase the decomposition rate more than the formation rate.

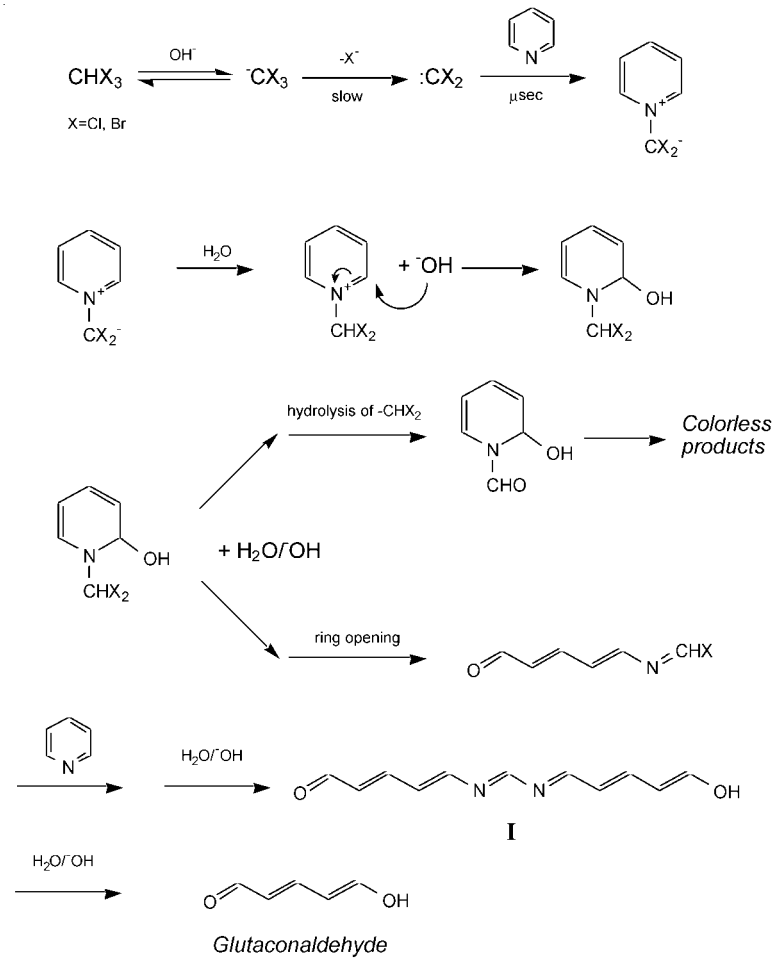

Fig. 2. Reaction pathway that lead to the colourful (pink) product (I)

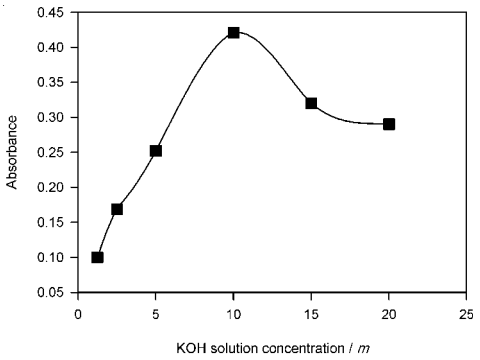

Fig. 3. Optimization of potassium hydroxide concentration

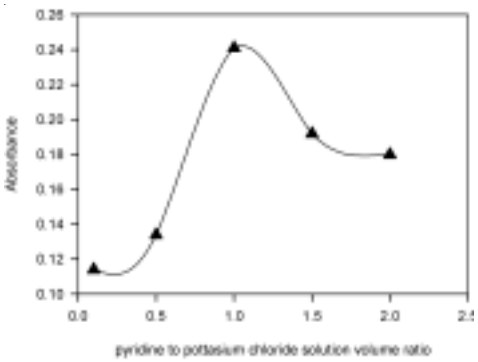

Fig. 4. Optimization of volume ratio of base to pyridine

Calibration curve and figures of merit: Calibration curve was constructed within the range of 0-10 μg mL^{-1}. Regression equation for the plot was:

$$\text{Absorbance} = 0.12\ C\ (\mu g\ mL^{-1}) + 0.0639.$$

Detection limit was obtained to be 187 ng mL^{-1} based on 3 s_b/slope (in which s_b is the standard deviation of the blank) and the linear range for the above method was 0.2-8 μg mL^{-1}.

The important point to be mentioned here is that chloroform was used as calibrator for all trihalomethanes. The reason could be summarized as below: (1) The majority of trihalomethanes formed during disinfection of water consists of chloroform (mainly > % 80). (2) Brominated trihalomethanes are formed only in water with high sources (concentration) of bromine. (3) The sensitivity of the method is maximum for chloroform and bromodichloromethane than chlorodibromomethane and bromoform[8].

Optimization of preconcentration parameters: The reaction is carried out in pyridine, so means must be provided for extracting the trihalomethanes from water into pyridine. The sensitivity of the reaction in pyridine solution reported in the previous section is about 0.2 ppm, whereas seasonal trihalomethane concentrations in drinking water may drop to 20-40 ppb. Therefore a 10 fold preconcentration of trihalomethanes in pyridine was needed in the extraction step. For this purpose amberlite XAD-4 which is a ubiquitous sorbent for the removal of organic contaminants from water[18] was chosen as the solid phase for preconcentration of trihalomethanes. The parameters affecting preconcentration step was optimized as below:

Choosing the eluting solvent: Because the reaction is carried out in pyridine and its capability for dissolving and eluting chloroform from the resin, the natural solvent for eluting chloroform from amberlite XAD-4 is pyridine.

Optimizing the eluting solvent volume: Chloroform in aqueous solution was passed by different flow rates and the column was eluted by pyridine (with 0.1 mL min^{-1} flow rate). Then the eluate was collected in different vials as 1 mL portions. The reagent for production of colour was then added to each portion and analyzed to detect chloroform content. 4 mL pyridine was able to elute the column completely.

Optimizing of sample flow rate: Performance of the column for different sample flow rates was eluted within the range of 0.25-5.00 mL min^{-1} (Fig. 6). Each column was eluted by 4 mL pyridine. After addition of potassium hydroxide to eluate, heating and cooling, the absorbance was measured. The flow rate of 1 mL min^{-1} was chosen as the optimum flow rate.

Optimizing of elution flow rate: Optimizing the elution flow rate (pyridine flow rate) was also carried out using above procedure. Fig. 7 shows, the optimum flow rate is between 0.1-0.2 mL min^{-1}. To obtain higher rates, 0.2 mL min^{-1} flow rate was chosen to minimize the elution time.

Resin capacity and recovery: Fig. 8 shows resin capacity were determined by passing successive 10 mL portion of 1 μg mL^{-1} chloroform solution and collecting

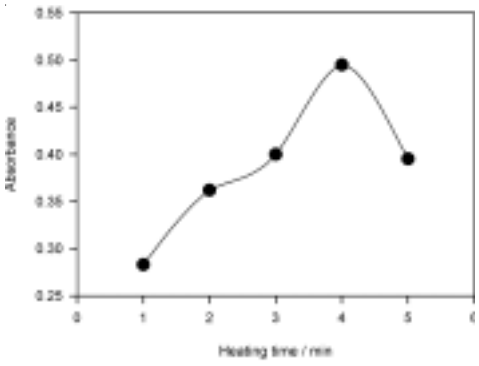

Fig. 5. Optimization of heating time

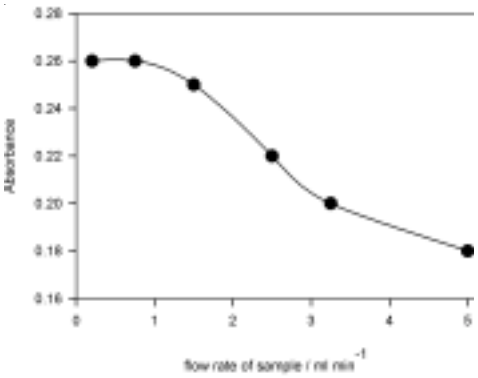

Fig. 6. Optimization of sample flow rate

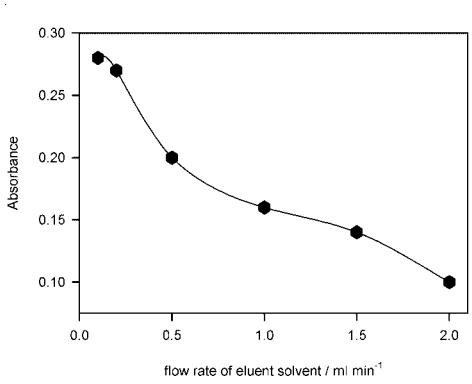

Fig. 7. Optimization of eluent solvent flow rate

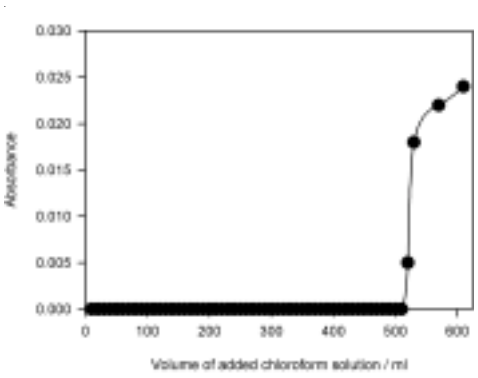

Fig. 8. Resin capacity

collecting the output in separate vial. The procedure A was then used to determine if chloroform is present in water. Resin capacity was 510 µg of chloroform per milliliter of the resin. The recovery of the column was 95 ± 5 % and RSD was 5 %.

Measurement of total trihalomethane in tap water: Sampling procedure was carried out in research analytical laboratory of Ferdowsi University of Mashhad from tap water. A tube connects the cold water tap faucet to the syringe. Before attaching the filter, water was run for several minutes. The out put of syringe was laid in a graduated cylinder, the flow rate of water was adjusted to 1 mL min^{-1} and sampling procedure was continued until the final volume of water collected in graduated cylinder became 1 L. Then the column was disconnected, enclosed in an aluminum foil and stored in a cold place for next steps. In the next step, the column was eluted by 4 mL of pyridine (the enrichment factor was 250), the reagents were added and the absorbance of the product was measured against a blank solution with same procedure. The concentration of trihalomethanes in Mashhad, Iran tap water was determined to be 10.2 ± 0.5 ng mL^{-1}, which was below the critical standards of water.

Conclusion

The proposed method shows an accurate, rapid and low-cost method for measuring the total trihalomethane concentrations in drinking water. The results are comparable to GC methods in regards of sensitivity, precision and accuracy. The main advantages of the method are simplicity, low cost and ability to become easily automated. The data further show that this trihalomethanes Water Test can be used as an in-plant alternative to the conventional laboratory-based methods. The method enables water treatment facilities to respond quickly to changes in water quality and serves as an effective monitoring tool on a routine basis.

REFERENCES

1. M.Y.Z. Aboul Eish and M.J.M. Wells, *J. Chromatogr. A*, **1116**, 272 (2006).
2. US EPA, National Primary Drinking Water Regulations, Stage 2 Disinfectants and Disinfection By-Products Rule: Proposed Rule, Fed. Reg. Nos. 49547-49681, August 18 (2003).
3. H. Norin and L. Renberg, *Water Res.*, **14**, 1397 (1980).
4. USEPA Method 502.2, Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography With Photoionization and Electrolytic Conductivity Detectors in Series, USEPA, Cincinnati, OH.
5. USEPA Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, USEPA, Cincinnati, OH.
6. USEPA Method 551, Determination of Chlorination Disinfection Byproducts and Chlorinated Solvents in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection, USEPA, Cincinnati, OH (1995).
7. USEPA Method 551.1, Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection, USEPA, Office of Water, Technical Support Center, Cincinnati, OH (1998).
8. www.sdi.com
9. M.A. Brown and G.L. Emmert, *Anal. Chim. Acta*, **555**, 75 (2006).
10. K. Fujiwara, *Sitzungsber. Abh. Naturforsch. Ges. Rostock*, **6**, 33 (1916).
11. K.C. Leibman and J.D. Hindman, *Anal. Chem.*, **36**, 348 (1964).
12. J.F. Reith, W.C. van Ditmarsch and T. de Ruiter, *Analyst*, **99**, 652 (1974).
13. K. Okumara, K. Kawada and T. Uno, *Analyst*, **107**, 1498 (1982).
14. D. Reckhow and P. Pierce, A Simple Spectrophotometric Method for the Determination of THMs in Drinking Water, AWWA Research Foundation and American Water Works Association (1992).
14. T. Uno, K. Okumura and Y. Kuroda, *J. Org. Chem.*, **46**, 3175 (1981).
15. H. Miller, F.P. Milanovich, T.B. Hirschfeld and F.S. Miller, Optrode For Sensing Hydrocarbons, U.S. Patent, 4,666,672 (1987).
16. K. Okumura, T. Wada, K. Yamaoka and T. Uno, *Chem. Pharm. Bull. (Tokyo)*, **32**, 174 (1984).
17. T. Uno, K. Okumura and Y. Kuroda, *Chem. Pharm. Bull.*, **30**, 1876 (1982).
18. L. Renberg, *Anal. Chem.*, **50**, 1836 (1978).

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