Fluorimetric determination of bromoform via its photochemical reaction with diphenylamine in aqueous Triton X-100 medium

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A new fluorimetric method based on the photochemical reaction of CHBr₃ with diphenylamine (DPA) in aqueous Triton X-100 (TX-100) medium is described for the determination of bromoform (CHBr₃). The fluorescence intensity of the product at 480 nm (λexc: 400 nm) is a direct measure of CHBr₃ concentration. The calibration graph is linear in the range of 0-21.8 ppm of CHBr₃. The limit of detection (LOD) is 0.1 ppm of CHBr₃. The effect of reagent concentration, TX-100 concentration, time of irradiation, interfering substances, and statistical parameters are discussed.

Chlorination is the most widely used technique for disinfection of drinking water, which leads to the formation of trihalomethanes (THMs). The THMs include chloroform (CHCl₃), dichlorobromomethane (CHBrCl₂), chlorodibromomethane (CHBr₂Cl) and bromoform (CHBr₃) all of which have been enlisted as priority pollutants due to their carcinogenic behaviour, by the US Environmental Protection Agency. The formation of THMs takes place due to the reactions of chlorine with naturally occurring organic materials such as humic and fulvic acids. Several studies have shown that the formation of THMs and their ratio depends on a number of parameters such as the concentration of precursor materials, bromide ions, water, temperature, pH and chlorine dose. It has been observed that due to the presence of bromide, the yield of THMs is increased for a particular chlorine dose and also it influences the composition of by-product mixture. Bromoform, thus, among all THMs could be dominant (even to 71% of total THMs) species formed during chlorination in the case of high bromide contained water; the remaining THMs formed being CHBrCl₂ and very little CHBrCl₃ and CHCl₃.

The occurrence of bromide in natural water is not abnormal. It can enter source water either through natural process or due to human activities. Methyl bromide is widely used in agriculture to fumigate crops and soil. Ethylene dibromide is used as an additive in common gasoline. A degradation product of ethylene dibromide is methyl bromide, which is converted to inorganic forms before transport to natural waters. Bromide may also appear as a trace impurity in chloride used for water disinfection. Also, bromide-based disinfectants, such as HOBr are sometimes used. All these lead to occurrence of CHBr₃ in higher concentrations and thus it is always useful to develop a simple and reliable technique for its quantification.

The four main techniques involved in the analysis of THMs are head-space, liquid-liquid extraction, adsorption-elution (purge-trap) and direct aqueous injection. The final step in each case involves separation by gas-liquid chromatography with detection generally by electron capture and sometimes with mass analysis. Most of these methods, although very sensitive, require specialized personnel with sophisticated instrumentation and are relatively time-consuming. During the last few decades, the photochemical reactions between aromatic amines (such as, diphenylamine (DPA)) and various chlorinated compounds such as carbon tetrachloride (CCl₄) , polychlorinated biphenyls (PCBs) , chlorinated pesticides , trichloroacetic acid (TCA) , etc. have received considerable attention due to their simplicity and efficiency. But the reaction of bromine containing THMs has remained totally unexplored for analytical purposes.

Here is reported, for the first time, a new fluorimetric method for bromoform quantification based on its photochemical reaction with DPA in aqueous poly(oxyethylene) iso-octylphenyl ether (known as Triton X-100 or TX-100) medium. The reaction leads to a fluorescent product having...
fluorescence emission at 480 nm (λ<sub>ex</sub>: 400nm) and the fluorescence intensity of the product is a measure of bromoform concentration. The method described is quick, reliable, and simple and does not need an extraction step.

Other chloroorganic compounds such as CHCl<sub>3</sub>, CCl<sub>4</sub>, TCA, dichloroacetic acid (DCA), monochloroacetic acid (MCA) which commonly occur in drinking water systems do not respond to the reaction under the proposed reaction condition. However, CHBr<sub>2</sub>Cl and CHBrCl<sub>3</sub> did produce similar but weak fluorescence. The determination could tolerate the presence of the above said bromine containing THMs in 2-fold excess.

**Experimental Procedure**

All fluorimetric measurements were performed on a Perkin-Elmer LS-50B Spectrofluorimeter equipped with a 9.9 W Xenon flash lamp and a photomultiplier tube with S-20 spectral response. The spectrofluorimeter was linked to a personal computer and utilized the Perkin-Elmer FLDM software package for data collection and processing. Photochemical reactions were carried out in well-stoppered quartz cuvettes. Cuvettes filled with samples were placed horizontally for UV irradiation under a portable germicidal lamp (15-W; Sankyo Denki, Japan) at a distance of 3 cm.

Analytical Reagent grade CHBr<sub>3</sub>, CHBrCl<sub>3</sub>, CHBr<sub>2</sub>Cl, DPA and TX-100 are purchased from Aldrich Chemicals. A stock solution of CHBr<sub>3</sub> (786.5 ppm) was prepared in a 1:1 (v/v) methanol: water mixture. TX-100 solutions were prepared by dissolving its appropriate volumes in known volumes of double distilled water. TX-100 (10<sup>-2</sup> M) solution saturated in DPA was used as the reagent.

Aliquots of stock CHBr<sub>3</sub> solutions were placed in quartz cuvettes and each was mixed with 0.2 mL of the reagent solution and 1.9 mL of distilled water so that final CHBr<sub>3</sub> concentration varied from 0.7 to 21.8 ppm. A blank containing no CHBr<sub>3</sub> was also prepared. Each was then irradiated for 1 min. After the irradiation, the fluorescence intensities were measured at 480nm using λ<sub>ex</sub>: 400nm after a 30-min wait. The excitation and emission slits used were 5 and 5 nm.

**Results and Discussion**

In the presence of a suitable sensitizer, such as DPA, illumination of halogenated organic compounds with UV or visible light causes photochemical reactions leading to either coloured<sup>13,14,18,19</sup> or luminescent complex<sup>13,14,18,19</sup>. Such types of reactions might have enormous use in photography<sup>20,21</sup>. The reactions largely depend on the sensitizer, the light and the conditions used for the reaction. All the reactions reported above are carried out either in purely organic phase or on solid support. The organic solvents used are acetone, alcohol, cyclohexane, acetonitrile etc. For solution phase reactions, careful choice of the solvent is necessary so that the reagent, analyte and the product remain in homogeneous phase and also to attain selectivity and sensitivity. Because solvent plays an important role in photoreaction, choice of solvent is a critical step to make such reactions feasible. Another important aspect is that since most of these substances usually occur in water systems, an added step of extraction is necessary using a suitable organic solvent, and this makes the process more time consuming and tedious.

Micelles, being well-known membrane mimetic agents<sup>22</sup> can function in many ways. As a consequence micelles have tremendous application in chemistry. This is either to enhance the solubility of organic compounds in water owing to their incorporation in the hydrophobic core of the micelle<sup>23</sup> or to catalyze reactions due to "concentration effect" in the micellar pseudo-phase<sup>24</sup>. Micellar environments can also alter reaction pathway<sup>25</sup>. These micellar
effects have tremendous application in analytical chemistry. Another advantage for using a micellar medium is that the emission intensity of analyte in this media is usually many times greater than the corresponding aqueous phase. Lower detection limits and longer range of linearity is also obtained in the cases where micelles are used. All these facts have prompted us to undertake the present study.

Photoreaction of CHBr₃ in presence of DPA either in purely organic or aqueous media is hitherto unknown, although reaction of carbon tetrabromide with DPA has long been used in photography. CHBr₃ and DPA on 1-min irradiation with UV light in aqueous TX-100 medium produced a yellow-green fluorescent compound (λₑₓ: 480nm, λₑₘ: 400nm) of which the excitation and emission spectra (curve A and curve B respectively) have been shown in Fig.1. The fluorescence intensity is proportional to CHBr₃ concentration. Under similar conditions DPA alone (curve C), or CHBr₃ in the absence of DPA did not show any fluorescence. The reaction could tolerate up to 2.5% of MeOH without affecting the fluorescence intensity of the product. UV light of shorter wavelength (≤ 254nm) or visible light did not produce the complex. Cells made of glass were found unsuitable for the purpose. The reaction could be done at lower pH ≥ 2 but not at higher pH ≥ 8. When the reaction was carried out at lower temperature (−5 °C) the fluorescence intensity did not change much. The reaction did not occur in the absence of O₂. The fluorescence compound was stable for > 24 h.

The reaction may involve either radical or radical cation like those involving CCl₄ or CHCl₃ with DPA under photo-irradiation. It is expected that, because both CHBr₃ and DPA are hydrophobic in nature, they remain in the hydrophobic core of the micelle and come in close contact. This facilitates the photochemical reaction to take place in a much more efficient way. This has been corroborated by the fact that when the reaction is carried out in a pure methanol medium, the photoreaction occurred but not so efficiently. Thus it can be assumed that the "concentration effect" in the micellar pseudo-phase might be operating in this case. To have a clearer insight into the mechanism, however, further studies are needed.

The use of surfactant is vital, as without this, DPA is not soluble in aqueous phase. If the reaction is
carried out in aqueous phase without surfactant, and containing slight MeOH and DPA the reaction does not occur. The reaction also did not occur in presence of other surfactants such as sodium dodecyl sulphate (SDS, a well-known anionic surfactant) and cetyltrimethylammonium bromide (CTAB, a well-known cationic surfactant) above their critical micellar concentration. The DPA-CHBr_3 photoreaction, however, proceeds very well in aqueous TX-100 in the concentration range of 10^{-4}-10^{-1} M and it was found that 1 \times 10^{-3} - 5 \times 10^{-3} M TX-100 is optimum.

The relative concentration of the reagent with respect to CHBr_3 is important for the reaction. For the concentration range of 0.7-21.8 ppm of CHBr_3 the reaction was studied where volume of TX-100 (10^{-2} M) saturated in DPA was varied. TX-100 concentration (final) in each case was kept fixed at 2.5 \times 10^{-3} M. It has been observed that 0.2-0.5 mL reagent was optimum for the working range of CHBr_3. In the higher range of DPA concentration the solution turned hazy. And in the lower range much decreased fluorescence is noticed, which might be due to the presence of insufficient DPA.

A linear calibration graph is obtained in the range of 0-21.8 ppm of CHBr_3 concentration (final). The fluorescence intensities are obtained after subtracting the blank. The equation for the straight line is \( I_f = 11.5 \times C \) ppm \(-1.78\). The correlation coefficient found was 0.994. The limit of detection (LOD) is 0.1 ppm. For CHBrCl and CHBrCl also the calibration curves were generated in the same way. They were linear in the range of 0-192.0 and 0-97.6 ppm, respectively. The corresponding equations were \( I_f = 1.16 \times C \) ppm \(+ 9.88\) and \( I_f = 2.35 \times C \) ppm \(+ 12.71\) respectively. The LODs for CHBrCl and CHBrCl2 were 0.8 and 0.4 ppm, respectively. All LODs were calculated as LOD = 3 \( \sigma_b \)/m (\( \sigma_b \) = standard deviation of the blank, \( m \) = slope of the calibration graph). The precision of the method (RSD, 5 determinations) is found to be \( \pm 5.4\% \) for 3.7 ppm of CHBr_3.

To examine the selectivity of the method, a brief investigation was made with possible interfering substances like TCA, DCA, MCA, CCl_2, and CHCl_3. None of them gave, under the stated reaction conditions the fluorescent photo product as given by CHBr_3. Under the proposed condition, the determination of CHBr_3 was possible in presence of 5-fold excess of TCA and MCA, and 3-fold excess of DCA, CCl_2 and CHCl_3. CHBr_2Cl and CHBrCl_2, as stated earlier, gave similar product but could be tolerated up to 2-fold excess concentration. The other substances tolerated up to 3-fold excess were Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} ions, and 1-fold excess of Fe^{3+} Cl ions and 6-fold excess of urea.

### Conclusion

A new fluorimetric method is developed for CHBr_3 quantification. It is based on the photochemical reaction of CHBr_3 with DPA in aqueous TX-100 medium. The reaction leads to a fluorescent product. The method is simple and quick, and it utilizes environmentally benign chemicals and does not need an extraction step.

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### References