INTRODUCTION

The quality of drinking water has been an ever-present concern in the United States and abroad and has sparked a flurry of ongoing research both in water filtration technologies and oxidizing biocides. In August 2002, The World Health Organization (W.H.O.) determined that each year, an estimated 3.4 million people die from disease caused by contaminated water. [1] At least 65% of these deaths could have been avoided with water, hygiene and sanitation interventions.[1] Clearly, there is a need for an economical, easy, non-toxic way to disinfect water sources.

Drinking water quality is a particularly serious problem in India and Bangladesh due to arsenic contamination of the water. The arsenic problem in Bangladesh originated as a result of a microorganism problem. In 1970, sources of surface water were found to be contaminated with microbes, thereby causing outbreaks of cholera and dysentery. To combat the microbe problem, tube-wells were installed. The tubes of the wells were inserted into the ground usually at a depth of less than 200 meters[2] and unknowingly into aquifers rich with naturally occurring sources of arsenic. Arsenic poisoning has now become a disease of epidemic proportions.

Currently, in West Bengal, it is estimated that of the 125 million inhabitants of Bangladesh between 35 million and 77 million are at risk of drinking contaminated water.[2] It has been reported that in some areas in Bangladesh, the arsenic levels are as high as 3500 ppb.[2] This is 350 times the acceptable level of 10 ppb as set forth by the World Health Organization (WHO).[3]

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[1] World Health Organization. Water, Sanitation and Hygiene Links to Health 28 August 2002
[2] Smith, et al. 2000. Bulletin of the World Health Organization. 78(9); 1093.
[3] Apyron Technologies Inc. Website. www.Apyron.com

Initially, arsenic was thought to be introduced into the soil through fertilizers, insecticides, pesticides, herbicides, preservative coatings on wooden electric poles, the tube-well filters, and industrial waste.[4] Further research determined that arsenic had a geological source.[4, 5]

Arsenopyrite (FeAsS), one of three identified sources of arsenic ore, is considered to be the foremost cause of arsenic pollution in Bangladesh.[6] Furthermore, arsenic exists as both organic and inorganic species. Organic species, which may be found in shellfish, are less toxic than inorganic species.[6] Inorganic arsenic occurs in two oxidation states, (As III), and (AsV), in Bangladesh groundwater.[6, 7] Although numerous theories exist as to the causes of arsenic contamination in Bangladesh groundwater, two hypotheses were repeatedly mentioned in the literature: pyrite oxidation and oxyhydroxide reduction.

Both theories involve a redox process where the arsenic is either released or desorbed from pyrites or Fe-Mn oxyhydrides, which causes the arsenic to be released into the groundwater in an anionic form.[4, 8, 9] There appears to be direct correlation between the extent of reduction conditions of the groundwater and the arsenic concentration – "the more reducing, the greater the arsenic concentration."[5]

With an increase in arsenic concentration, the mortality rate is also increased.[10] "The toxic effect of arsenic species depends mainly on their chemical form, route of entry, age, sex, doses and duration of exposure." Most arsenic related ailments involve diseases of the skin, including various carcinomas, but other diseases include liver

[4] Fazal, Abul. 2001. Water International, 26(3); 376
[5] British Geological Survey. 2001 Phase 1 Findings.
[6] Fazal, Abul. 2001. Water International 26(3); 371.
[7] EPA. 2000. EPA 815-R-00-028.
[8] Fazal, Abul. 2001. Water International 26(3); 377.
[9] Smedley, P. J., et al.. Applied Geochemistry. 17; 517-568.
[10] Smith Allen et al. 2000. Applied Geochemistry. 17;517-568.

enlargement, cardiac failure, diabetes, and goiter. The results of these ailments include open ulcers, cancer, limb amputations, and death.[11, 12]

Presently, the Environmental Protection Agency consideres activated alumina as one of the best adsorbents available for the removal of arsenic. Chemical industry now has the technology to develop a selective chemical adsorbent that can be custom designed to remove harmful contaminants from drinking water without eliminating beneficial nutrients. Among the technologies being explored are the specialty type adsorbents; these include metal oxide, iron-based media, and a combination of inorganic, high-porosity metal oxide.[13]

Apyron Technologies Inc. is presently studying a variation of the activated alumina adsorbent media. This technology includes a mixture of colloidal metal or metal oxide, oxide adsorbent and/or catalyst particle, and an acid.[14, 15, 16] The technology founded by Apyron allows the synthesis of known specialty aluminas with oxides of various metals such as copper, silver, manganese, and zinc in combination with various support materials to create an innovative line of chemical media that can be used to purify water.[3]

Independent of the choice of arsenic removal is the need to ensure that the water does not have microbial contamination. If the method of arsenic removal involves stagnant water such as may develop in a filtration system, it is especially important to prevent microbial growth. Chlorine and ozone are two of the more common

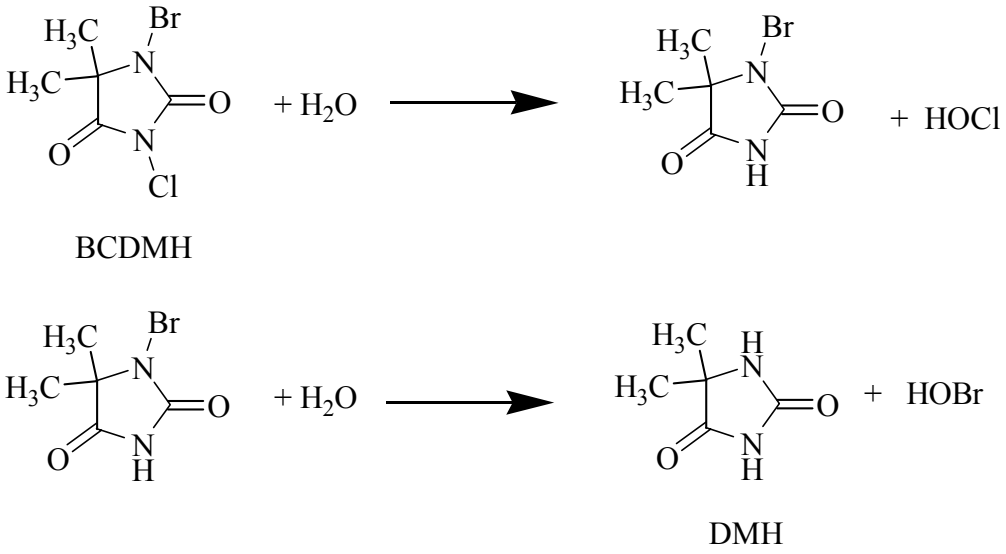
[11] Fazal, Abul. 2001. Water International. 26(3);375.
[12] Dipanker et al. 2002. Talanta. 58;6.
[13] Gilles, Gregory C. 2000. Water Technology. 75-77.
[14] Moskovitz, et al. US Patent Number 5, 948,726. September 7, 1999.
[15] Moskovitz, et al. US Patent Number 5,955,393. September 21, 1999.
[16] Moskovitz, et al. US Patent Number 5,985,790. November 16, 1999.

antimicrobial agents used in water treatment. One other type of antimicrobial agent is the class of compounds known as halamines. These can have some advantages as far as ease of handling (they are typically solids) and their ability to slowly release into the water. Various *N*-halamines and *N,N'*-halamines have been studied and tested for their effectiveness as water disinfectants, and results have shown that many of these compounds exhibit both bactericidal properties and antimicrobial activities.[17, 18]

Of particular interest are the chloramines and bromamines. Under aqueous conditions, these compounds will readily release the halogens thereby producing HOCl and HOBr. These hypohalous acids produce the biocidal effects.[19] In the case of *N*-chloramines, the antibacterial properties are also due to the release of the chlorite ion, which in turn, binds with a cellular receptor directly, interfering with cellular enzyme production.[18]

One of these antimicrobial agents that is used commercially is 1-bromo-3-chloro-5,5-dimethylhydantoin (henceforth referred to as BCDMH). BCDMH has a solubility in water of 0.2% at 77^{o}F, and upon hydrolysis it is thought to immediately release both halogens producing hypochlorous acid (HOCl), hypobromous acid (HOBr), and dimethylhydantoin (DMH) as seen in reaction 1.[19]

[17] Williams, D. E. et al. 1987. Appl. Envirn. Microbio. 53:2082-2089.
[18] Kohl, H. H., et al. 1980. J. Pharm. Sciences. Vol. 69, No. 11, Nov. 1980. 1292-1295
[19] Nalepa, C. J. 1997. Oxidizing Biocides: Properties and Applications. Based on paper presented at the AWT Fall Meeting in Traverse City, Michigan on October 25, 1997. 16-18



(1)

Once hydrated, the BCDMH compound is expected to release the chlorite ion first due to the two electron withdrawing carbonyl groups on both sides of the chloramine. The bromite ion is thought to be released after the chlorite due to the two adjacent methyl groups that are electron donating and act to destabilize an anionic center that would result in an earlier release of the bromite.[20]

BCDMH, is available in briquette form, and is readily added to a water filtration system thereby offering an affordable water filtration technology that can be applied in remote areas, operate with no electricity, and is simple to operate and maintain. Depending on the aqueous conditions, there are qualities of the disinfectant that must be considered, including, solubility, stability and concentration.[20] While the reaction of BCDMH with water is known, the influence of various metals has not been studied.

[20] Worley, S. D., et al. 1983. Water Resources Bulletin. Feb. 97-100.

Because of the importance of the water purification problems, we became interested in the fate of BCDMH under aqueous conditions similar to those of Bangladesh. In order for optimum performance of any adsorbent system, including the specialty adsorbents, the following factors must be considered: arsenic species and concentrations, excess concentrations of iron, cost-effectiveness, and influent water quality.[21] In addition to these factors, the addition of BCDMH into a water filtration system, along with the effects this compound may have on the effluent must also be considered.

As stated previously, arsenite (arsenic III) and arsenate (arsenic V) are the two natural occurring species of arsenic in Bangladesh groundwater. Because of the prevalent reducing conditions, groundwater contains mostly arsenite.[22] Furthermore, an oxidized form of arsenic is more easily removed by adsorbents; therefore, the arsenite may require a preliminary step that includes oxidation.

The pH of the water is a primary concern in adsorbents. This will determine not only the arsenic species, but also influence the efficiency of the adsorbent.[23] While most adsorbent processes will not be affected by pH values within the 6.5-9.0 range, activated alumina has shown optimum pH efficiency for arsenic removal between pH values of 5.5-6.0.[24] The groundwater in Bangladesh has a pH range of 6.5 through 7.6.[5]

Iron concentration is another factor to consider; overwhelming concentrations of iron may foul the media and obstruct arsenic adsorption. In most parts of Bangladesh,

[21] Gilles, G and Odom, S. 2000. Water Conditioning and Purification.
[22] Clifford and Lin "Ion Exchange, Activated Alumina, and Membrane Processes for Arsenic Removal from Groundwater," Proceedings of the 45th Annual University of Kansas Environmental Engineering Conference, February, 1995
[23] Gilles, Gregory C. 2000. Water Technology. 65-66.
[24] EPA 2000. Technologies and costs for Removal of Arsenic from Drinking Water. EPA 815-R-00-028.

groundwater contains dissolved iron concentrations ranging from 2 – 15 ppm.[25] While this may not pose a serious health threat, it may impede arsenic adsorption.[25]

The groundwater in Bangladesh is full of contaminants, ions, and trace metals that could interfere with the effectiveness of the adsorbent and the decomposition of BCDMH. Therefore, simulated Bangladesh groundwater is necessary to mimic the conditions seen in Bangladesh. A formula containing some of the more concentrated contaminants was found in an article by Meng et al.[26] This recipe was based on extensive analysis of Bangladesh groundwater conducted by the British Geological Survey.[5]

Literature searches revealed little information available regarding BCDMH and its decomposition. With the incorporation of the halogenated hydantoin into water filtration systems, there is a need to understand the rate at which the compound decomposes and the effects the ingredients in Bangladesh water may have.

The objective of this work was to evaluate the fate of BCDMH under aqueous conditions similar to those of Bangladesh, specifically, to determine the effects that the various dissolved and particulate constituents in groundwater had on the rate of BCDMH. This required development of a method to quantitatively measure both the decreasing BCDMH concentrations and the increasing DMH concentrations. The variable parameters, specifically, iron concentrations, arsenic (III) and (V) concentrations, reducing versus oxidizing conditions, and a continuous system sample collection versus static sample collection will all be considered while assessing the kinetics of BCDMH to DMH.

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[25] Mamtaz, R. and Bache, D. H., 2001. Journal of Water Supply: Research and Technology-AQUA. 50; 313-24

[26] Meng, Xiaoguang, et al. 2002. Toxicology Letters. 133;103-111.

Although little information was found on BCDMH, an HPLC method for the detection of cyanuric acid, a somewhat similar compound, was used as a foundation for the detection of the dimethylhydantoin.[27] Modifications were made to this method (as described in the Experimental section) and DMH concentrations were quantitatively determined.

Once hydrated, the halogenated hydantoin was thought to rapidly hydrolyze; therefore, another method was needed to follow the disappearance. It was determined the best was to do this was to follow the concentrations of the hypohalous acids. A chemiluminescence method offered sensitivity, speed, and a technique for measuring hypochlorous acid, hypobromous acid and any remaining BCDMH in one measurement.

The chemiluminescence approach was developed based on a method used Rao et al who found that 1,3-dichloro-5,5-dimethylhydantoin reacted with an alkaline luminol solution mixed in equimolar parts with H_2O_2.[28] This technique was applied to BCDMH and the method was optimized.

[27] Cantu, Ricardo, et al. 2001. Analytical Chemistry. 73(14); 3358-64.
[28] Zhiming, Rao, et al. 2002. Talanta. 57(5); 993-8

EXPERIMENTAL

Chemicals and Reagents

Brominating Tablets (96% 1-Bromo-3-chloro-5,5-dimethylhydantoin) produced by Bio-Lab, Inc. (Decatur, GA) were used in the continuous system and in the chamber experiments. 1-Bromo-3-chloro-5,5-dimethylhydantoin, (Fluxa Chemicals, Switzerland) was used in the development phase of the chemiluminescence method. Hydrogen peroxide (30%) and 3-aminophthalhydrazide were purchased from Aldrich Chemicals, (Milwaukee, WI). pH 12 buffer was purchased from Fisher Scientific. Deionized water was used for both the continuous system and in chamber experiments; deionized water (>18MΩ purified by a Milli-Q water system (Millipore, Bedford, MA) was used to prepare the standard solutions.

Synthetic Bangladesh groundwater (SBG) was used in the continuous system and static sample collection. The ingredients are as follows and were all of analytical grade: 0.82 mM $MgCl_2 \cdot 6H_2O$ and 1.1 mM NaCl (Aldrich, Milwaukee, WI); 7.0 mM $NaHCO_3$ and 0.4 mM $Na_2SiO_3 \cdot 5H_2O$ (Fisher Scientific Chemicals, Fair Lawn, NJ); 2.5 mM $CaCl_2 \cdot 2H_2O$ (Sigma, St. Louis, MO); 0.04 mM NaH_2PO_4 (Mallinckrodt, Paris KY); and 0.0062 mM $MnSO_4$ (Acros, NJ).

Method Development: Chemiluminescence

Chromatographic Equipment and Conditions.

All chemiluminescence results were obtained using a Turner Designs TD-20/20 Luminometer (Sunnyvale, CA). A stock solution of H_2O_2 was made by diluting 30%

H_2O_2 with Milli-Q purified water until a concentration of 8.0 x 10^{-2} M was obtained. The luminol stock solution was prepared in a pH 12 buffer to yield a concentration of 2.0 x 10^{-2} M. Both the luminol and H_2O_2 solutions were prepared fresh at the beginning of every experiment.

Equal volumes of the luminol and H_2O_2 solutions were combined and 100 μL of this solution was then placed in a cuvette, which was placed inside the luminometer. The dual automatic injector system in the luminometer delivered 50 μL of sample through each injector. The instrument was set with a delay period of two seconds with an integration period of 4 seconds. Data was collected in a continuous stream using the supplied software.

The CL reaction caused an almost instantaneous flash of blue light that was measured. As seen in Figure 1, the maximum signal is seen at 0.6 seconds. Because the minimal integration setting on the luminometer is four seconds, a continuous data stream collection was used on all samples and the peak maximums were used to generate calibration curves for chemiluminescence. This practice eliminated any erroneous peak area measurements due to the asymptotic section of the graph seen between two and four seconds.

Five chemiluminescence intensities of each sample were measured and the peak maximums were averaged. BCDMH concentration was then derived from a calibration curve, which was constructed based on known BCDMH concentrations and their

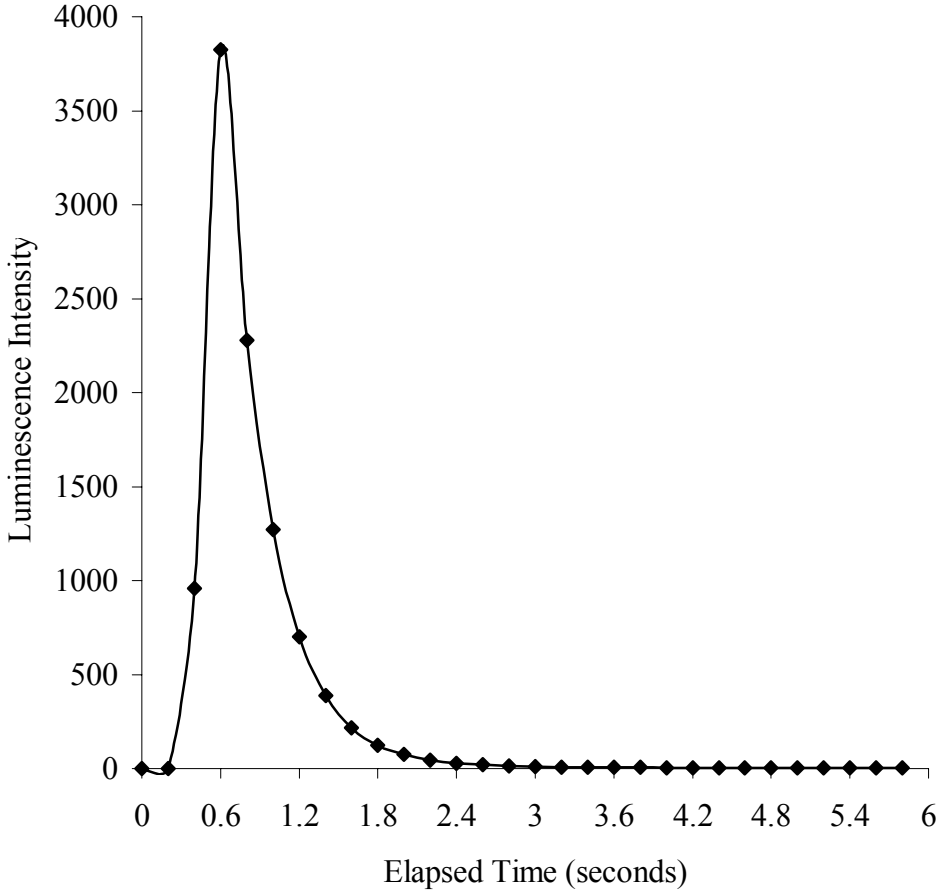

Figure 1: Continuous data stream of luminescence intensity used to determine time interval on chemiluminescence instrument

chemiluminescence intensities; this linear relationship is addressed in Results and Discussion.

Method Development of High-Performance Liquid Chromatography (HPLC)

Chromatographic Apparatus and Conditions.

Data was collected using a Hewlett Packard 1100 HPLC system including a diode array detector, quaternary pump system, equipped with a degasser, auto sampler and ChemStation software. The column used was a Hypersil Hypercarb, 50 x 4.6 mm inner diameter, 5-micron particle size.

The mobile phase consisted of a 0.10 M (aq) KCl solution mixed in ratio (97:3) with methanol. The flow rate was 1.0 mL/ min, the column temperature was 23^{o}C, the sample injection volume was 10 μL, and the UV lamp was set at 210 nm based on the ultraviolet spectroscopy data.

Continuous System Sample Collection

Experimental Apparatus and Sample Preparation

In order to create conditions similar to the tube wells in Bangladesh, a system to mimic the wells was created. As seen in Figure 2, this was done with four 20-liter Nalgene carboys linked with Tygon tubing connected at their spigots. The water flow was regulated by a Cole-Palmer gear pump with a pressure-loaded micropump in conjunction with a variable-flow drive. The water flow was pushed up through the column, which contained the BCDMH briquette, to simulate a well hand-pump and samples were collected periodically from the continuous sample stream.

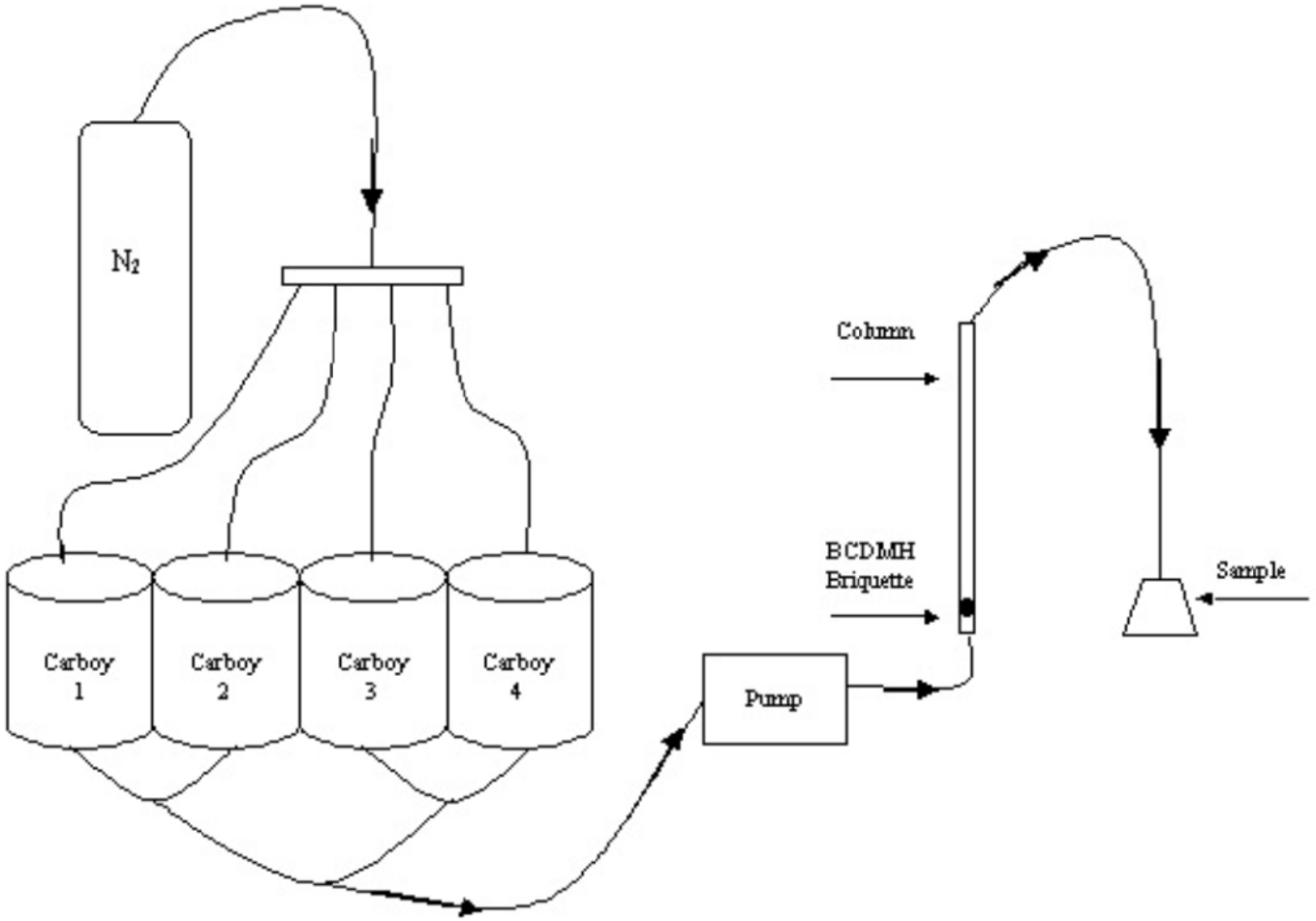

Figure 2: Continuous System Apparatus

Synthetic Bangladesh groundwater (SBG) was used in experiments one through nine. This consisted of $MgCl_2 \cdot 6H_2O$, NaCl, $NaHCO_3$, mM $Na_2SiO_3 \cdot 5H_2O$, $CaCl_2 \cdot 2H_2O$, NaH_2PO_4, and mM $MnSO_4$.[26] Deionized water was used to make these solutions and to bring the carboys to volume. Experiment 9 used only these ingredients. Experiment ten served as a control and used only deionized water with no added metals.

Stock solutions of 6.5×10^{-2} M $MgCl_2$ and 0.20 M $CaCl_2$ were combined while solutions of 3.2×10^{-2} M Na_2SiO_3, 3.2×10^{-3} M NaH_2PO_4, 0.56 M $NaHCO_3$, and 8.8×10^{-2} M NaCl were made in one flask. A stock solution of 2.5×10^{-2} M $MnSO_4$ was also prepared. Stock solutions of 1.8 M As_2O_3, and 2.1×10^{-2} M $FeSO_4$ were made fresh at the onset of any experiment in which they were included (see Table 1). Calculated amounts of these chemicals were added to deionized water purged with nitrogen to maintain the oxidation states of 3 and 2 respectively.

Prior to the addition of these air sensitive solutions to the experiments, the synthetic Bangladesh groundwater in the carboys was purged with nitrogen to minimize air oxidation.

A stock solution of 1.8 M As_2O_5 was prepared using a stirring hotplate. The deionized water was brought to a boil and the calculated amount of the compound was added. A stir bar was added and the solution was mixed until the compound was dissolved.

Table1: The numbered experiments of the continuous system with the correlating contaminant and the respective concentration

Experiment	Addition (Concentration)		
1	Fe (II) (0.27 mM)		
2		As (III) (0.046 mM)	
3			As (V) (0.046 mM)
4	Fe (II) (0.27 mM)	As (III) (0.046 mM)	
5	Fe (II) (0.27 mM)		As (V) (0.046 mM)
6		As (III) (0.024 mM)	As (V) (0.024 mM)
7	Fe (II) (0.27 mM)	As (III) (0.024 mM)	As (V) (0.024 mM)
8	Fe (II) (0.27 mM)	As (III) (0.024 mM)	As (V) (0.024 mM)
9	Synthetic Bangladesh Groundwater		
10	Deionized Water		

Static Sample Collection

Experimental Apparatus and Sample Preparation

Ten 250 mL, wide-mouth amber glass bottles were used in this experiment. Chambers one through nine contained synthetic Bangladesh groundwater in the concentrations given earlier; chamber ten contained deionized water. All chambers contained a BCDMH briquette and chamber eight also included a thin layer of specialty adsorbent.[29] The individual contaminants for each chamber can be seen in Table 2. Volumetric flasks were used in the preparation of the samples and before adding the iron solution to chambers one, four, five, seven and eight, these flasks were sparged with nitrogen. Once the iron solution was added to the flask, the solution was immediately transferred to the chamber whereupon the lid was secured and then covered with Parafilm M®.

Samples were collected every seven to fourteen days. A five mL sample was taken from each chamber and diluted to a volume of 250 mL. Before collecting a sample from chambers one, four, five, seven or eight the approximate volume necessary to bring the dilution to volume was purged with nitrogen. Care was taken not to agitate the chambers while collecting samples. Samples were analyzed as explained in the chemiluminescence and HPLC sections. This experiment was repeated to ensure reproducibility.

[29] Aquabind™ XP, Lot Number F27R2PJ-5. Apyron Technologies, Inc. Atlanta, Georgia.

Table 2: Static sample experimental matrix

Experiment	Contaminant (Concentration)			BCDMH Briquette	BCDMH Briquette
1	Fe (II) (0.27 mM)			21.66 g	19.83 g
2		As(III) (0.046 mM)		16.58 g	19.37 g
3			As(V) (0.046 mM)	15.94 g	19.73 g
4	Fe (II) (0.27 mM)	As(III) (0.046 mM)		18.67 g	18.92 g
5	Fe (II) (0.27 mM)		As(V) (0.046 mM)	20.54 g	20.00 g
6		As(III) (0.024 mM)	As(V) (0.024 mM)	20.30 g	19.72 g
7	Fe (II) (0.27 mM)	As(III) (0.024 mM)	As(V) (0.024 mM)	19.91 g	20.00 g
8	Fe (II) (0.27 mM)	As(III) (0.024 mM)	As(V) (0.024 mM)	20.09 g	19.73 g
9	Synthetic Bangladesh Groundwater			21.71 g	19.78 g
10	Deionized Water			20.76 g	19.68 g

* Jar 8 contained 9.09 g of adsorbent in both set 1 and set 2

RESULTS AND DISCUSSION

Method Development: Initial Approaches

Initially, an HPLC method for the detection of both BCDMH and DMH was attempted. The starting conditions consisted of a YMC C_{18} column (150 x 4.6 mm I.D., 5 μm) with an mobile phase of 78:22 deionized water (purified by a Milli-Q system): acetonitrile. The column temperature was 26^0 C, the flow rate was 1.5 mL, and the wavelength was set at 210 nm. This wavelength was selected based on literature values.[27] These separation parameters were used based on a developed method for a similar compound. Multiple peaks were seen, but peak separation was poor, and both fronting and tailing of peaks was an issue. Several factors were varied to define peak separation and eliminate peak fronting and tailing. However, changes in temperature gradients, mobile phase gradients, and flow-rate changes failed to yield better results.

In an attempt to obtain better peak separation, gas chromatography (GC) was attempted next. A similar method to that reported by Shroff and Huettmann[30] was used, but initial results showed the compound to either be decomposing on the column, or in the water, which was the solvent for the samples. This had not been a problem for Shroff and Huettemann because their samples were dissolved in chloroform and they were analyzing a different parent hydantoin. Both BCDMH and DMH were dissolved in diethyl ether, methanol and acetone and injected on the GC. Acetone proved to be the favored solvent in these experiments because DMH was not soluble in diethyl ether, and there was poor peak separation between the methanol and the sample. The samples dissolved in acetone were injected onto the GC, then spiked with either BCDMH or

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[30] Shroff, A. and Huettemann, R. E. **(1967)** *J. Pharm. Sci.,* 56(11); 1530-31.

DMH and injected again. Based on these results, it was concluded that the BCDMH was decomposing in water rather than on the column.

Liquid-liquid extractions were conducted to determine if the compounds could be removed from the water samples so that GC could be used for analysis. Methylene chloride was used as the organic wash. Known samples were extracted, evaporated to dryness, and weighed. Results were not consistent for BCDMH recovery. Percent recovery ranged among 350% through 12%. Furthermore, DMH did not transfer from the aqueous solution into the organic solution. Because of the inconclusive results with BCDMH and the inability to analyze DMH, no further attempts at extractions or GC were performed.

The next approach involved two different methods for analysis: one for analyzing the starting compound, BCDMH, and a different method for the final product, DMH. A method for quantitative analysis of dichlorodimethylhydantoin by chemiluminescence was found in a literature search.[28] With a modification to this method, as described in experimental, BCDMH was quantitatively measured. An HPLC method for the detection of cyanuric acid served as a starting point for analyzing the dehalogenated hydantoin. Again, modifications were made as described in Experimental, and a quantitative method for the detection of DMH resulted.

Method Development: Chemiluminescence

Selectivity

The hypohalous acids that are produced from the BCDMH briquette initiate the luminescence intensity. Therefore, chemiluminescence is specific for BCDMH and the

presence of DMH will not affect the analysis. Literature searches revealed several proposed mechanisms for the overall reaction between hypochlorite and luminol, as the reaction is not fully understood. The believed path of the reaction is seen in Figure 3.[31]

Linearity

There is a linear relationship between the maximum luminescence intensity and the BCDMH concentration among concentrations. Known concentrations of BCDMH solutions ranging between 1.20×10^{-4} M and 5.0×10^{-7} M were analyzed and a calibration curve was constructed as seen in Figure 4.

Repeatability

Seven samples (n = 7) of 1.00×10^{-4} M BCDMH concentration were used to calculate the relative standard deviation (%RSD). This method showed a 2% RSD for maximum peak height. Data is presented in Table 3. As explained previously, data is collected on a continuous stream with a measurement recorded every 0.2 seconds. Table 3 shows the collected data for seven samples, with the peak maximums, seen at 0.6 seconds, in bold type. The measurements were then averaged; the resulting calculations can be seen at below the continuous stream of data.

Method Development: High-Performance Liquid Chromatography

Selectivity

Before the earlier attempt at HPLC, the absorbance for both BCDMH and DMH were measured by ultraviolet-visible spectroscopy. The BCDMH spectra showed a large,

[31] Rose, A. L. et al. (2001) Analytical Chemistry. 73(24); 5909-20.

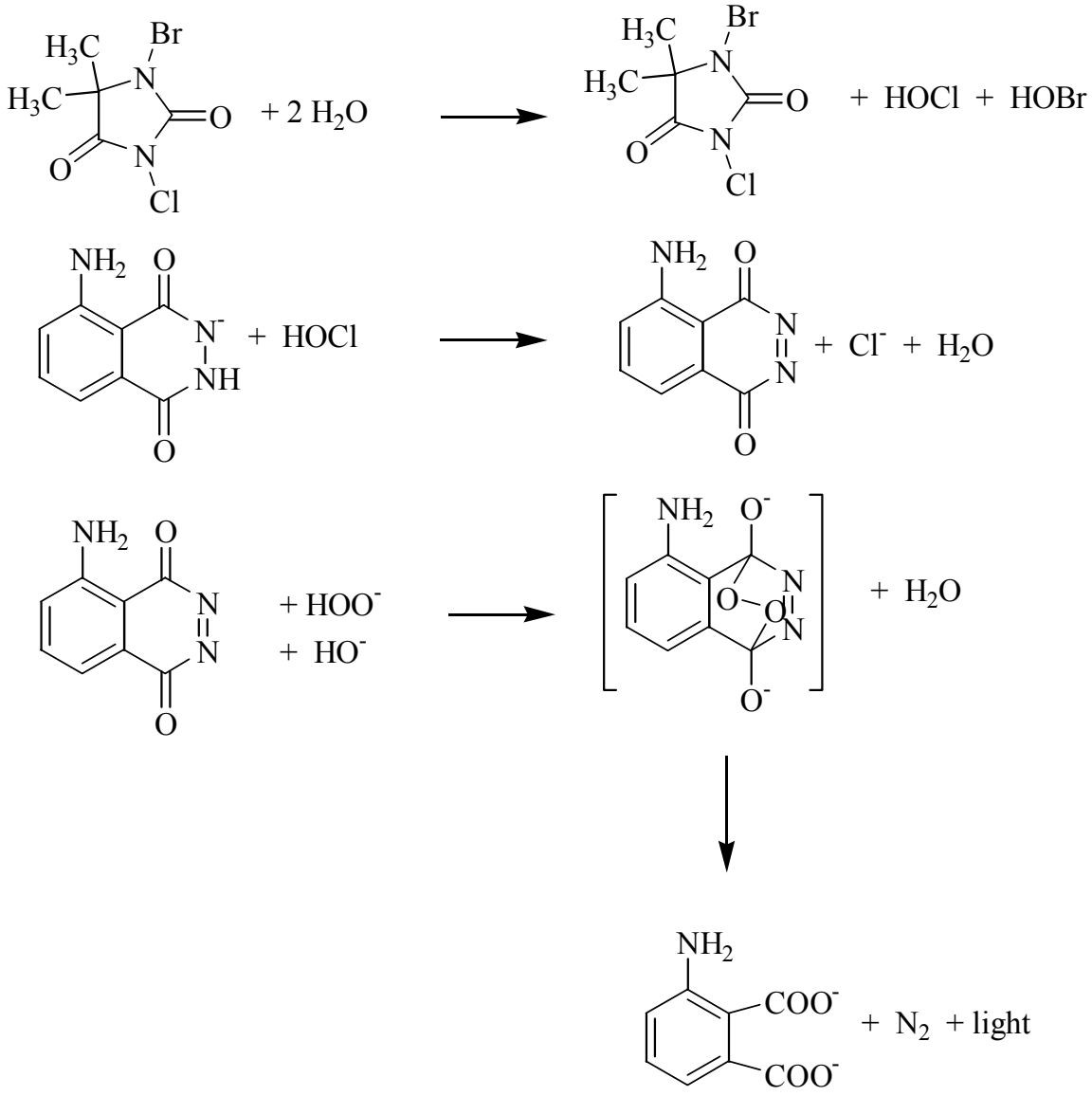

Figure 3: Chemiluminescence reactions involving BCDMH, hypochlorous acid, hydrogen peroxide and luminol in aqueous base. (The bromide ion can react with hypochlorous acid to produce another mole of hypobromous acid.)

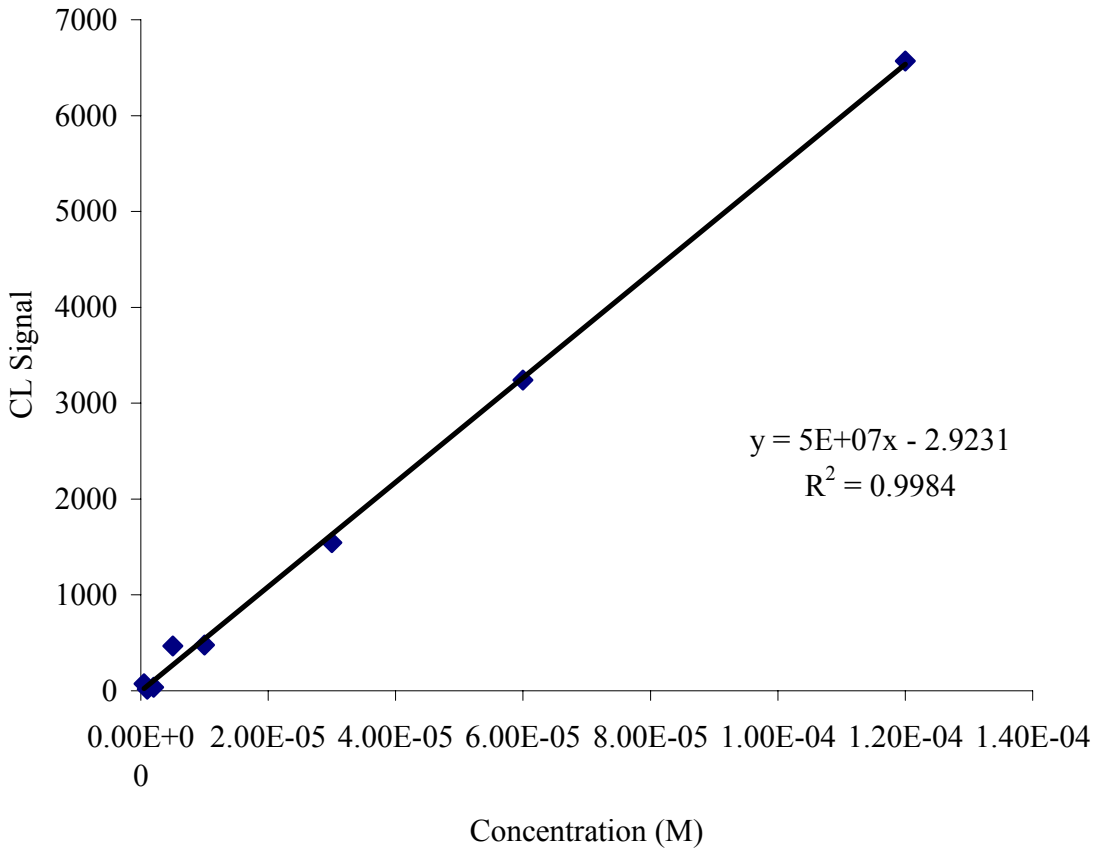

Figure 4. Linear Relationship between Chemiluminescence Intensity and BCDMH Concentrations 1.20 x 10^{-4} M - 5.0 x 10^{-7} M

Table 3: Data supporting the repeatability of the chemlimuminescence method

Time (sec)	Continuous Data Stream						
0	0	0	0	0	0	0	0
0.2	0	0	0	0	0	0	0
0.4	958.1	890.4	1251	1421	851.1	768.7	820
0.6	**3825**	**3716**	**3848**	**3738**	**3778**	**3721**	**3618**
0.8	2278	2266	2324	2284	2315	2277	2218
1	1270	1265	1323	1300	1331	1286	1265
1.2	702.4	700.1	741.8	730.2	756	715.3	709.7
1.4	389.7	387.3	416.6	410.4	429.1	398.8	398
1.6	217.5	215.4	235.7	231.9	244.6	223.2	224.1
1.8	122.5	120.6	134.1	131.7	140.1	125.7	127.1
2	75.88	74.12	83.06	81.54	87.11	77.64	78.64
2.2	45.92	44.3	50.05	49.11	52.8	46.58	47.28
2.4	28.82	27.2	31.02	30.35	32.8	28.76	29.24
2.6	18.98	17.47	19.92	19.43	21.04	18.43	18.75
2.8	13.23	11.83	13.35	13	14.11	12.39	12.58
3	9.865	8.51	9.432	9.189	9.962	8.823	8.919
3.2	7.83	6.543	7.085	6.897	7.426	6.666	6.735
3.4	6.569	5.336	5.648	5.499	5.893	5.377	5.378
3.6	5.796	4.59	4.712	4.591	4.916	4.564	4.524
3.8	5.254	4.115	4.129	4.007	4.292	4.021	3.994
4	4.861	3.749	3.708	3.614	3.872	3.628	3.601
4.2	4.576	3.491	3.397	3.329	3.546	3.356	3.316
4.4	4.345	3.274	3.18	3.112	3.316	3.126	3.072
4.6	4.155	3.112	2.976	2.922	3.126	2.949	2.923
4.8	3.979	2.949	2.827	2.76	2.977	2.827	2.76
5	3.843	2.827	2.705	2.637	2.855	2.678	2.638
5.2	3.721	2.705	2.569	2.515	2.732	2.556	2.529
5.4	3.586	2.623	2.434	2.407	2.624	2.461	2.407
5.6	3.491	2.501	2.352	2.285	2.529	2.353	2.312
5.8	3.382	2.42	2.244	2.217	2.42	2.298	2.231
	Samp44	Samp45	Samp46	Samp47	Samp48	Samp49	Samp50
Average of maximum chemiluminescence intensities: 3749 Standard deviation = 77 Percent relative standard deviation = 2%							

broad peak was seen between 200 nm through 240 nm. Even though the absorbance max for HOCl is 238 nm, the peak was thought to be caused by DMH because no peaks were seen at 270 nm and or 330 nm; the maximum wavelength of OCl^- and OBr^- respectively. This was verified with a spectrum of DMH, which shows a maximum absorbance around 210 nm. This can be seen as Figure 5. A HPLC chromatogram is seen in Figure 6, with a void time around 0.8 minutes and the DMH eluting at 3.465 minutes.

The reaction of BCDMH to DMH has been referred to as instantaneous in the literature.[32] Timed runs were conducted to verify the rate of DMH appearance. The results can be seen in Figure 7. In deionized water, the BCDMH completely decomposed to DMH in approximately 25 minutes.

The effects of pH on the decomposition of BCDMH were also studied and found to have no significant influence on the rate of DMH appearance. As can be seen in Figure 8, in each of the three conditions studied, DMH is rapidly formed. At twenty minutes, more than 50 % of the BCDMH has hydrolyzed and no further changes were observed after 60 minutes.

Linearity

The DMH concentration is linearly related to peak area as seen in Figure 9. Known concentrations of DMH were analyzed between concentrations 1.00×10^{-2} M through 1.00×10^{-5} M. Concentrations outside this range were not analyzed, so the limit of linearity was not determined.

[32] Ware, Elinor. 1950. Chemical Reviews 46(3)

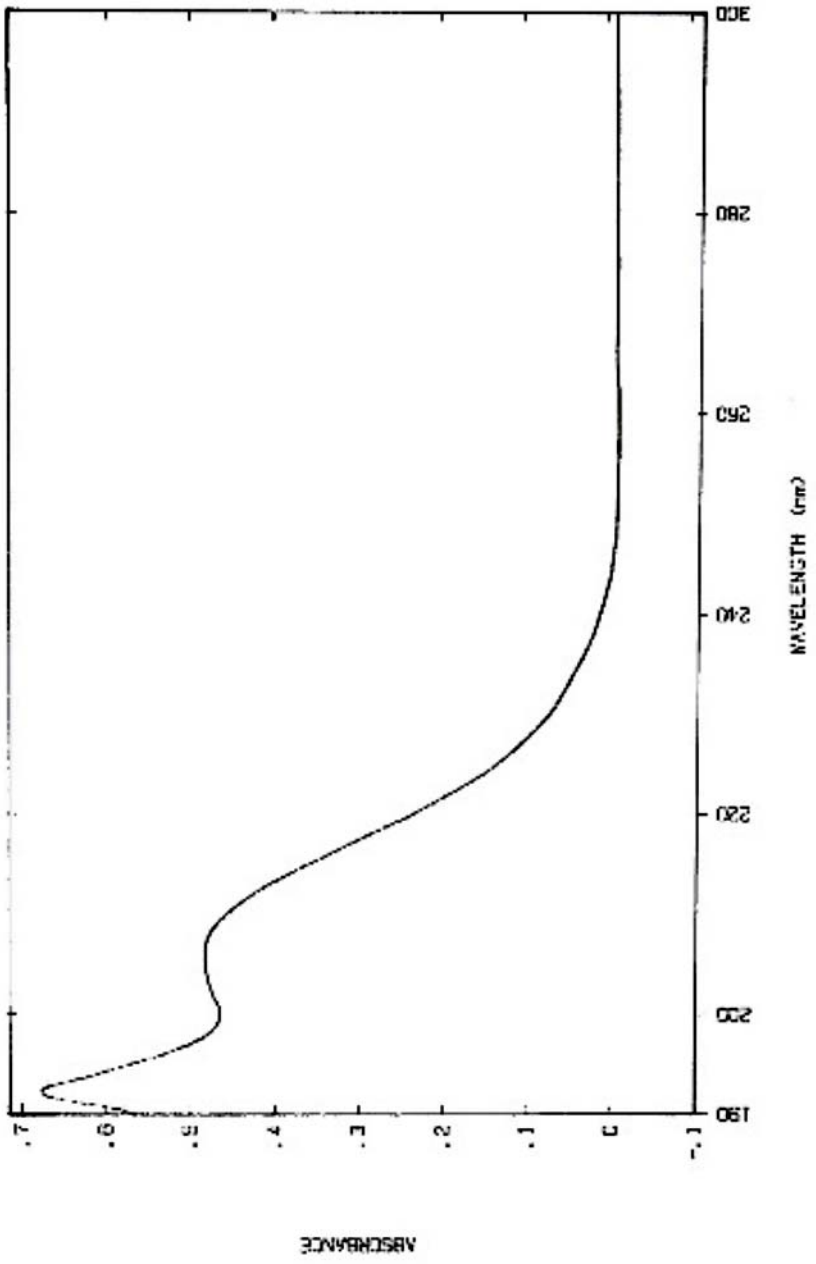

Figure 5: UV-Vis Spectrum of DMH sample. λ_{max} for HPLC method was set at 210 nm.

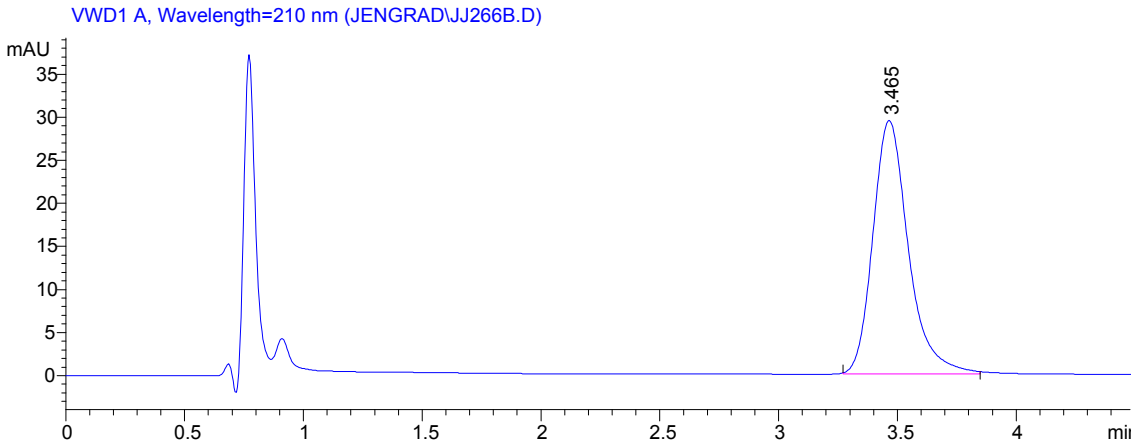

Figure 6: An HPLC chromatogram of DMH peak. The column: Hypersil Hypercarb, 50 x 4.6 mm I.D., 5-micron particle size; mobile phase: 0.10 M KCl solution mixed in ratio (97:3) with methanol; flow rate: 1.0 mL/ min, column temperature at 23^{o}C; sample injection volume: 10 µL, and UV lamp: 210 nm.

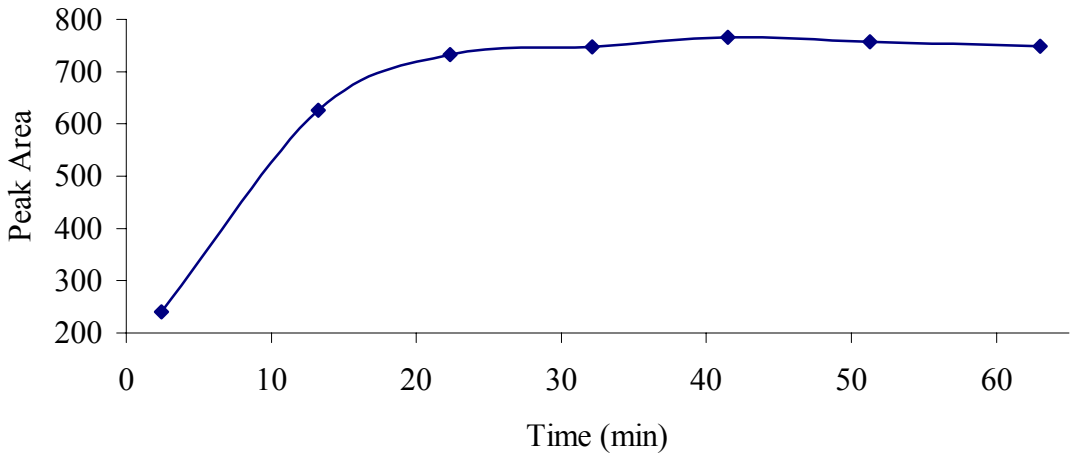

Figure 7: Rate of appearance of DMH when 1.00 x 10^{-4} M equivalent BCDMH dissolved in Deionized water

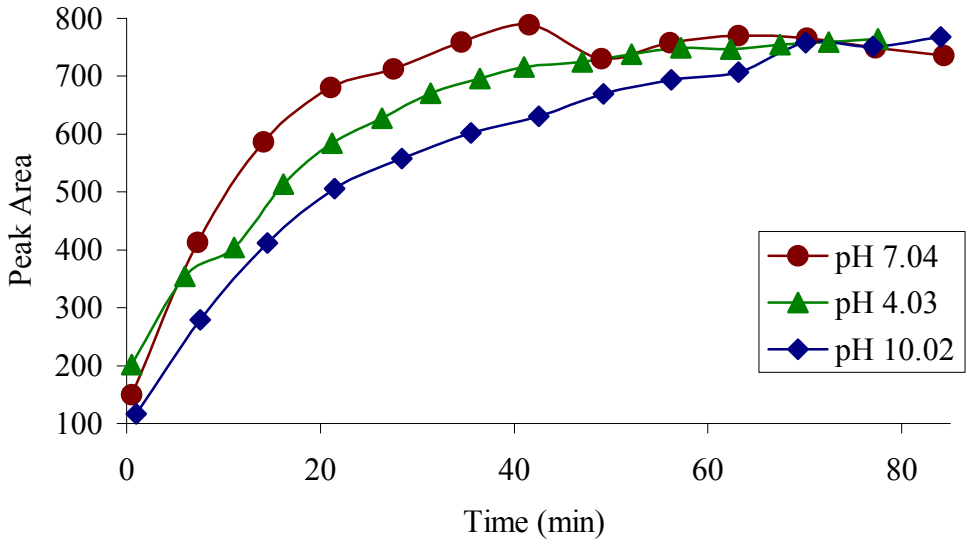

Figure 8: Effects of pH on the appearance of DMH when 1.00 x 10^{-4} M equivalent BCDMH dissolved in respective pH buffer

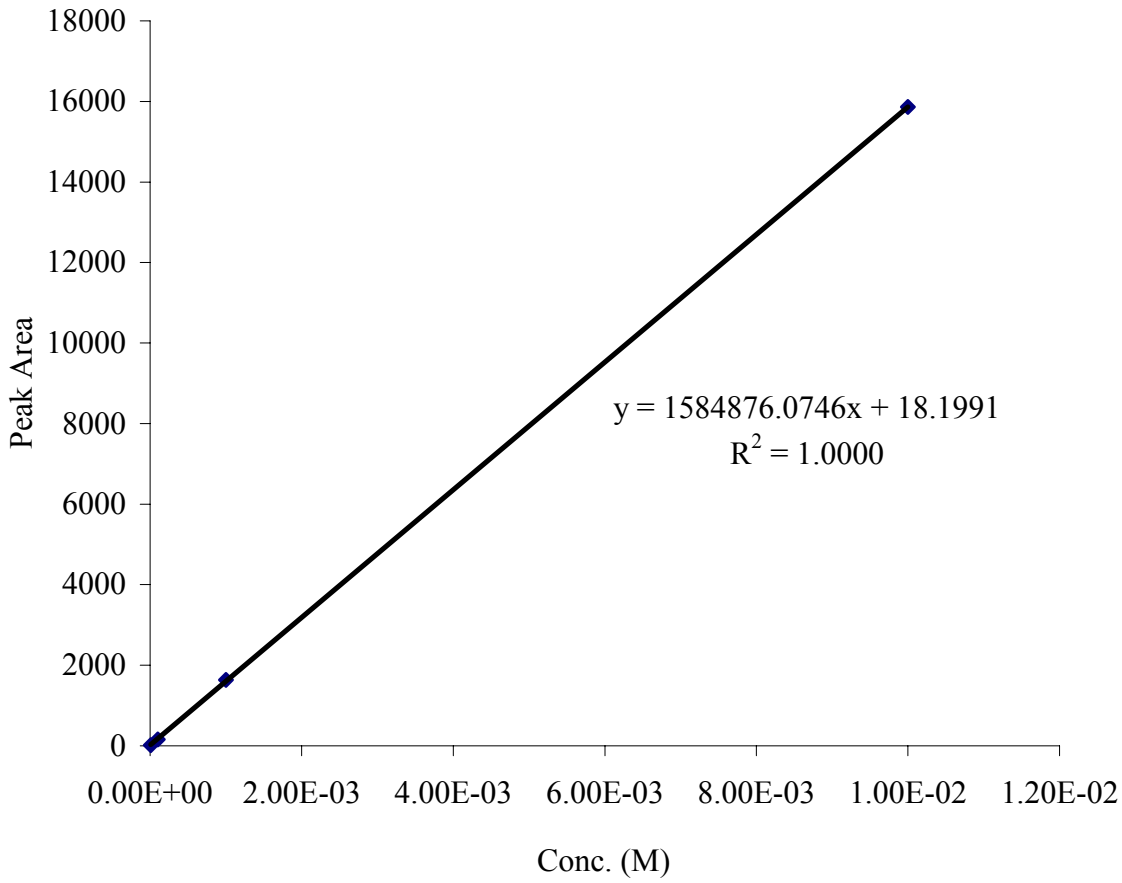

Figure 9: Linear Relationship bewtween HPLC peak area and DMH concentrations 1.00 x 10^{-2} M through 1.00 x 10^{-5} M

Continuous System

Quantitative analysis of DMH by HPLC

The appearance of DMH was monitored by HPLC. Once the concentrations of DMH were calculated based on peak area, they were multiplied by the flow rate and elapsed time for a conversion to grams. The appearance of grams of DMH was then plotted. Figure 10 is a plot of the appearance of DMH during the experiment for continuous system 5, synthetic Bangladesh groundwater spiked with both iron (II) and arsenic (V). Because the initial grams of DMH should be zero, the line of the slope should pass through the origin; Figure 10 shows an intercept of 0.058 grams. Appendices A through J contain graphs for each continuous system plotting the appearance of DMH; all of these graphs show intercepts less than 0.13 grams with an average intercept of 0.06 grams. That the intercepts are all close to the initial 0 grams of DMH is an indication that the HPLC method is accurate. The linear relationship over time proves the dissolution of the BCDMH briquette is uniform over time.

Quantitative analysis of BCDMH by Chemiluminescence

The disappearance of BCDMH was followed by chemiluminescence. Again, once the BCDMH concentration was deducted based on chemiluminescence intensity, the concentration was converted to grams and plotted versus time. Figure 11 is a plot of the disappearance of BCDMH during the continuous system for experiment 9, (synthetic Bangladesh groundwater without additions. Here the intercept is expected to equal the initial mass of the BCDMH briquette. For experiment 9, the starting mass of the briquette was 8.88 grams and the intercept on the graph is 8.86. Appendices A through

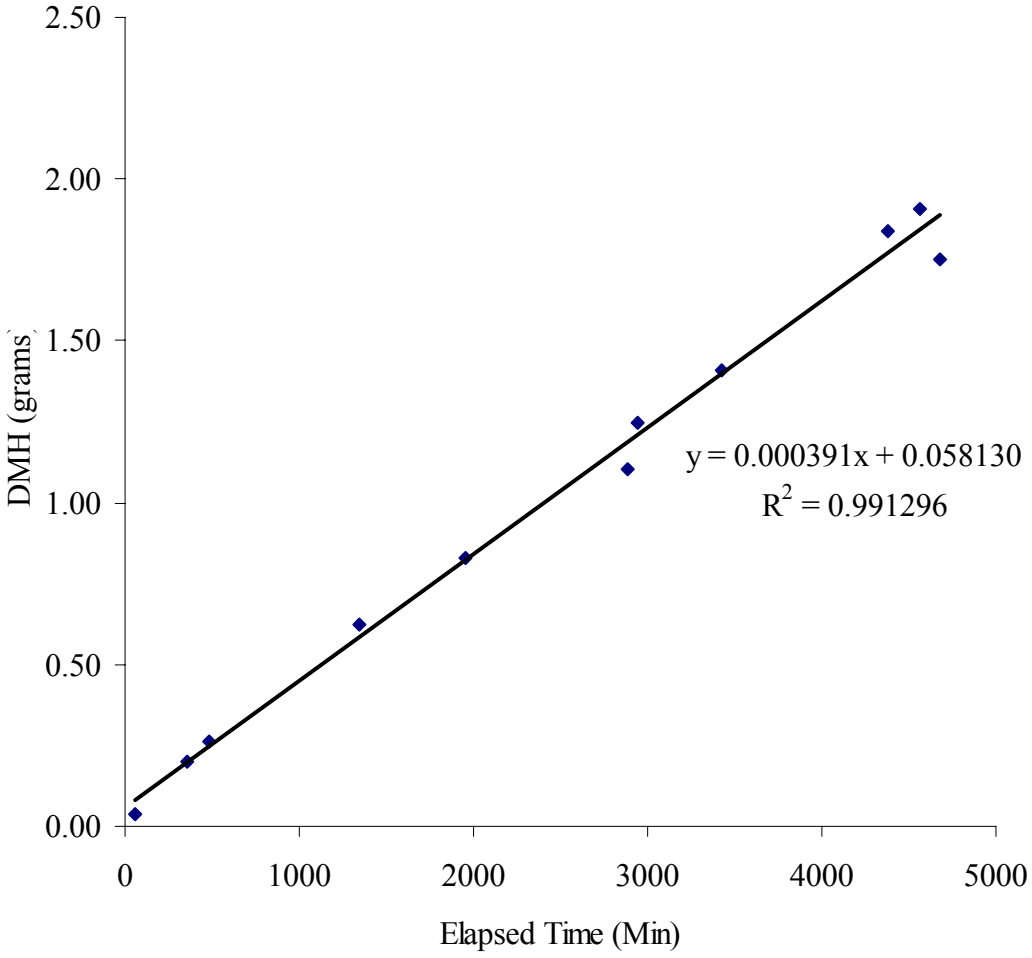

Figure 10: Appearance of DMH in continuous system experiment 5

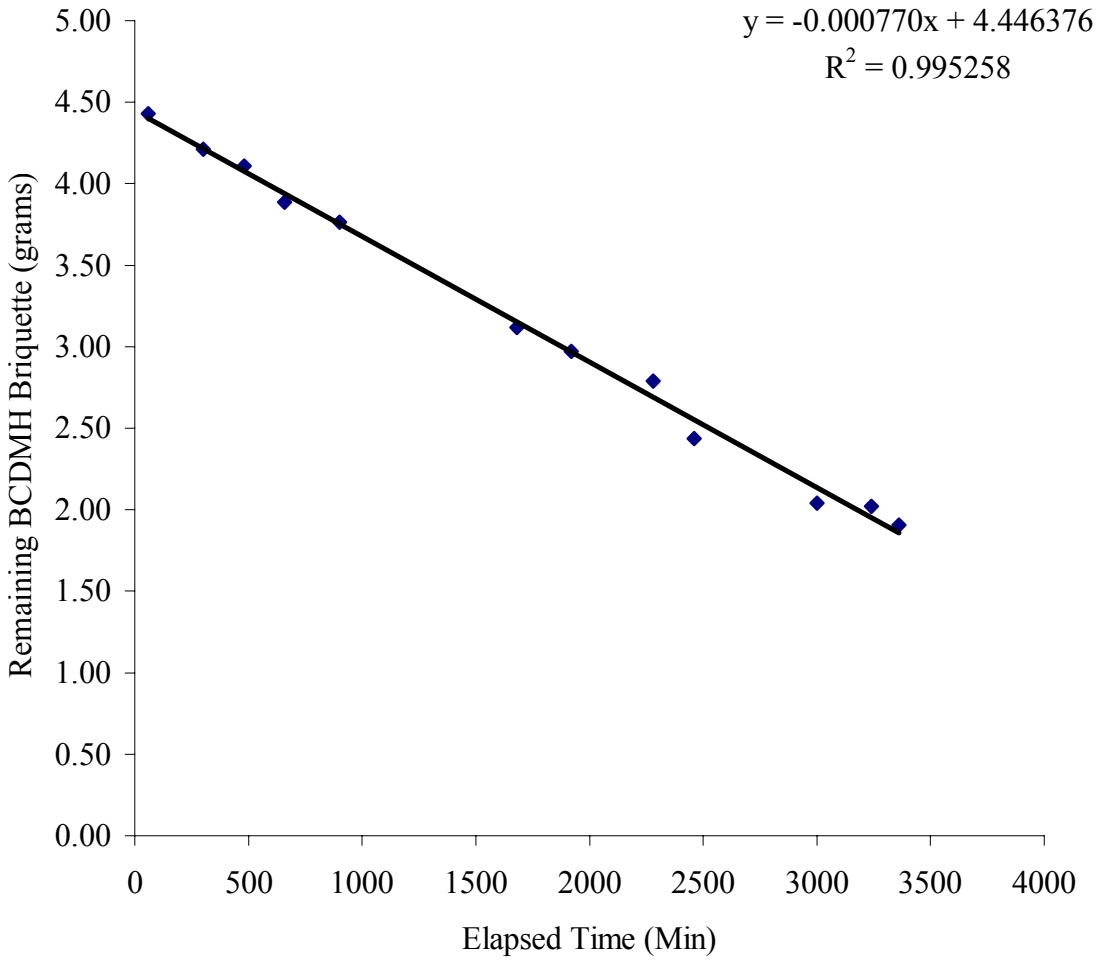

Figure 11: Decomposition of 4.49 gram BCDMH Briquette in continuous system 9

J contain graphs for each continuous system plotting the disappearance of BCDMH, all of these graphs show intercepts within 0.26 grams of their initial mass, with an average deviation from the starting briquette weight of 0.04 grams. Like the HPLC data, the chemiluminescence data indicated a constant dissolution rate.

Comparisons of the two methods

Figure 12 shows a plot of the disappearance of BCDMH based on the measured intensities obtained using the chemiluminescence method along with the loss of BCDMH based on the HPLC method. For the later part of the graph, the derived concentrations of DMH were converted into their corresponding grams; the stoichiometric equivalent of BCDMH grams was then calculated and the difference between the calculated grams of BCDMH and the initial briquette weight were plotted. This graph shows good correlation between the two methods.

Briquette life

Table 4 is a compilation of the data for the ten continuous system experiments. The grams per minute appearance and disappearance of DMH and BCDMH respectively were obtained from the slopes of the kinetic graphs of the individual continuous system experiments, which are included in Appendices A through J. Several factors were found to have an effect on the chemiluminescence results, which yielded inconsistencies in briquette life between the DMH and BCDMH calculations.

In most instances where the metals could be oxidized, systems 1, 2, 4, 5, 7, and 8, the mmol/day of disappearing BCDMH far exceeds the mmol/day of DMH appearing.

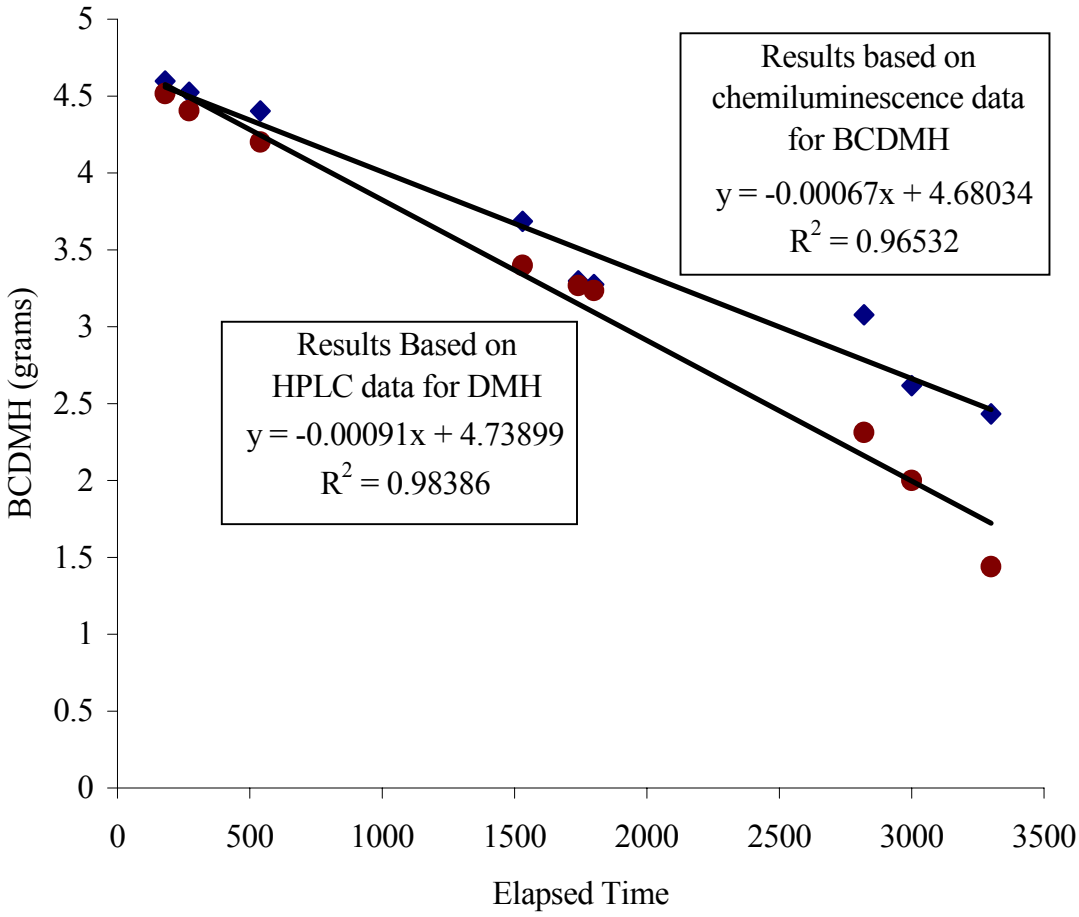

Figure 12: Comparison of chemiluminescence and HPLC Methods for the detection of BCDMH and DMH respectively

Table 4: Data compilation of kinetic results of continuous system experiments

System	Addition	BCDMH Decomposisiton (grams/min)	(grams/ day)	mmol BCDMH/ day	Briquette life (Days)*	DMH Apperarance (grams/min)	(grams/ day)	mmol DMH/ day	Briquette life (Days)
1	Fe (II)	6.80E-04	0.979	4.055	20	5.77E-04	0.831	6.48	12.4
2	As (III)	3.72E-04	0.536	2.218	36	4.33E-04	0.624	4.87	16.5
3	As (V)	1.02E-03	1.47	6.083	13	3.47E-04	0.500	3.90	20.6
4	Fe (II), As (III)	7.21E-05	0.10	0.430	187	3.97E-04	0.572	4.46	18.0
5	Fe (II), As (V)	7.50E-04	1.08	4.473	18	3.91E-04	0.563	4.39	18.3
6	As (III), As (V)	7.24E-04	1.04	4.318	19	4.83E-04	0.696	5.43	14.8
7	Fe (II), As (III) As (V)	1.44E-04	0.207	0.859	94	2.92E-04	0.420	3.28	24.5
8	Fe (II), As (III) As (V)	1.12E-04	0.161	0.668	120	3.94E-04	0.567	4.43	18.1
9	Synthetic Bangladesh Groundwater	1.25E-03	1.80	7.454	11	3.69E-04	0.53	4.15	19.4
10	Deionized Water	2.41E-04	0.347	1.437	56	2.90E-04	0.418	3.26	24.7

*based upon an average briquette weight of 19.40 grams

For example, system 4 shows the chemiluminescence method predicting a BCDMH briquette will last for 187 days while the HPLC method forecasts a briquette will last 18 days. Based on the HPLC results and comparing system 4 results with systems 1 through 8, the briquette lifetime appears credible. Yet, when comparing the briquette lifetimes calculated from the chemiluminescence method, this particular lifetime seems excessive. Something in this experiment must be interfering with the luminescence emission signal as the HPLC method still produces plausible results. This conflict between the two methods is most apparent in experiments 2, 4, 7, and 8. These conflicting results will be addressed individually. In experiment 10, deionized water, the chemiluminescence method also calculates a briquette lifetime twice as long as the HPLC method predicts

.

Effects of As (III)

The effects of As (III) can be seen in continuous system 2 where this was the single contaminant. The synthetic Bangladesh groundwater in the carboys was under nitrogen to minimize the oxidizing conditions to ensure that arsenic (III) was reacting with the BCDMH briquette. The solution in the carboys was colorless, and there did not appear to be any precipitate. The As (III) contaminated solution had decreased chemiluminescence intensities compared to continuous systems 1 and 3, the individual experiments containing Fe (II) and As(V) respectively. This is thought to be caused by the HOCl oxidizing the As (III) rather than oxidizing the luminol. This caused a decreased chemiluminescence emission, thereby, deceptively indicating an increase in the briquette life.

Effects of As (V)

Continuous system 3 was spiked with only As (V). Unlike with arsenic (III), there is no oxidation reaction occurring between the arsenic (V) and the hypochlorous acid. This means there should be no interference with the HOCl oxidizing the luminol as seen in reaction 2 of Figure 3. The chemiluminescence results show a somewhat increased chemiluminescence signal when compared with continuous system experiments 1 and 2, the systems containing Fe (II) and As (III). This increase in signal equates to a seemingly shorter calculated briquette life.

Effects of Fe (II)

The effects of Fe (II) on the decomposition of BCDMH can be seen in experiment 1 in Table 4. Iron (II) quickly oxidizes to iron (III) and precipitates out of solution; therefore, nitrogen gas was used to purge the carboys containing synthetic Bangladesh groundwater. When the reduced iron (II) solution was added to the carboys, the water turned a blue-green color. When this water passed by the BCDMH briquette in the column, a rust-colored precipitate was present both settling on top of the briquette and also floating in the water of the column. Because of the color change when the iron (II) contaminated water passed over the briquette, it was thought the iron (II) was being oxidized, thereby decreasing the chemiluminescence signal and falsely indicating a longer briquette life.

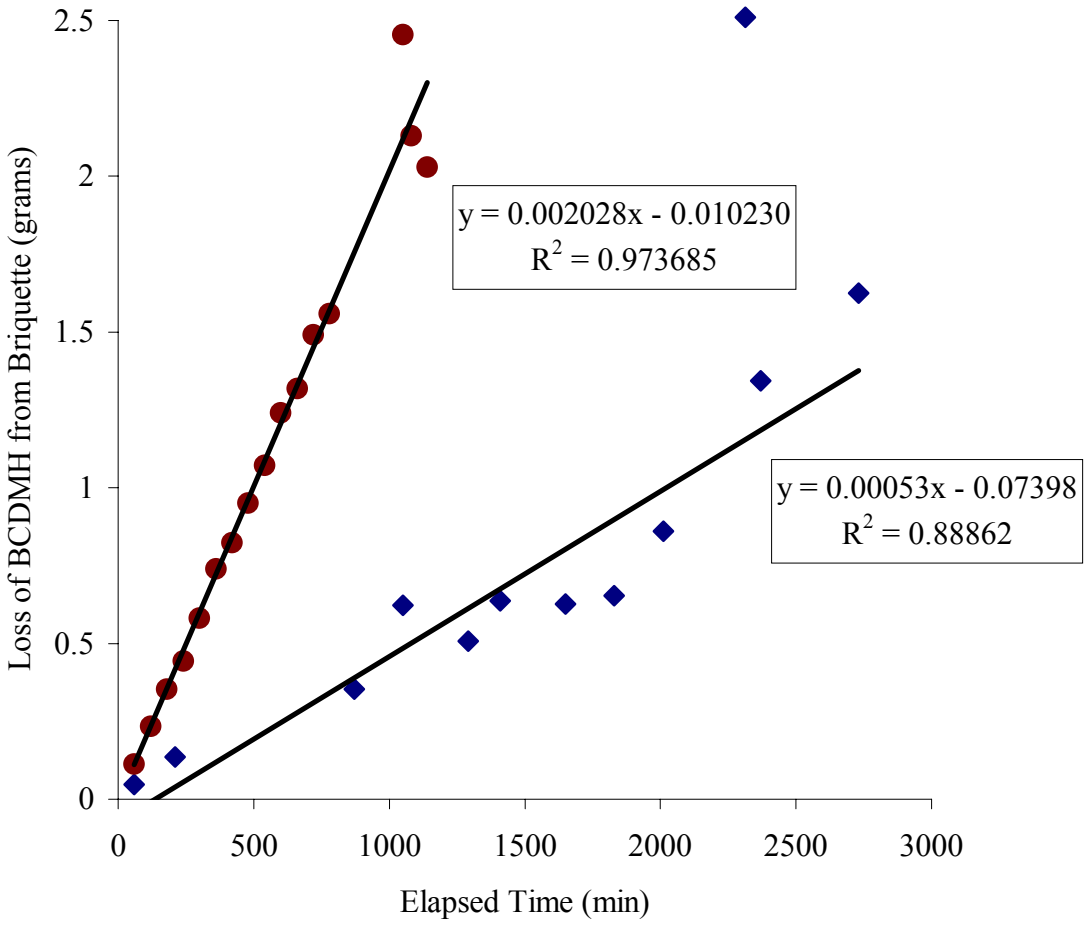

Figure 13: Chemiluminescence Comparison of Continuous System 2; with and without N_2 purging

Effects of Minimized Oxidation Conditions

Figure 13 is a graphic comparison of continuous system 2, synthetic Bangladesh groundwater contaminated with As (III), when the experiment was conducted with and without nitrogen purging to minimize the oxidation conditions. When oxidation was minimized, the apparent rate of BCDMH decomposition is slowed. This is probably caused by the oxidation of arsenic (III) to arsenic (V) rather than the oxidation of the luminol. This would in turn cause a decrease in the chemiluminescence signal and when calculated, indicate longer briquette life. When nitrogen was not used, the effect is not seen. Presumably, this is because the As (III) oxidizes in the solution and then does not consume the hypochlorous acid. This is consistent with the idea that the effect is due to the oxidation of As (III).

Effects of Bicarbonate

Both bicarbonate and manganese were used in continuous systems 1 through 9 because they were included in the synthetic Bangladesh groundwater. Figure 14 shows the effect bicarbonate has on the chemiluminescence intensity of standard BCDMH samples. The bicarbonate causes a noticeable increase in the chemiluminescence measurements. Based on this increase, the calibration curve of BCDMH and bicarbonate, as seen in Figure 14, was applied to the chemiluminescence signals for continuous systems 1 though 9 to calculate the correlating concentration.

Xiao et al explained this increase in chemiluminescence signal due to the carbonate.[33] Xiao et all found that a possible reaction between a superoxide, which

[33] Xiao, C. et al. Analytical Chemistry, Vol. 74, No. 9, May 1, 2002. pp221-2216.

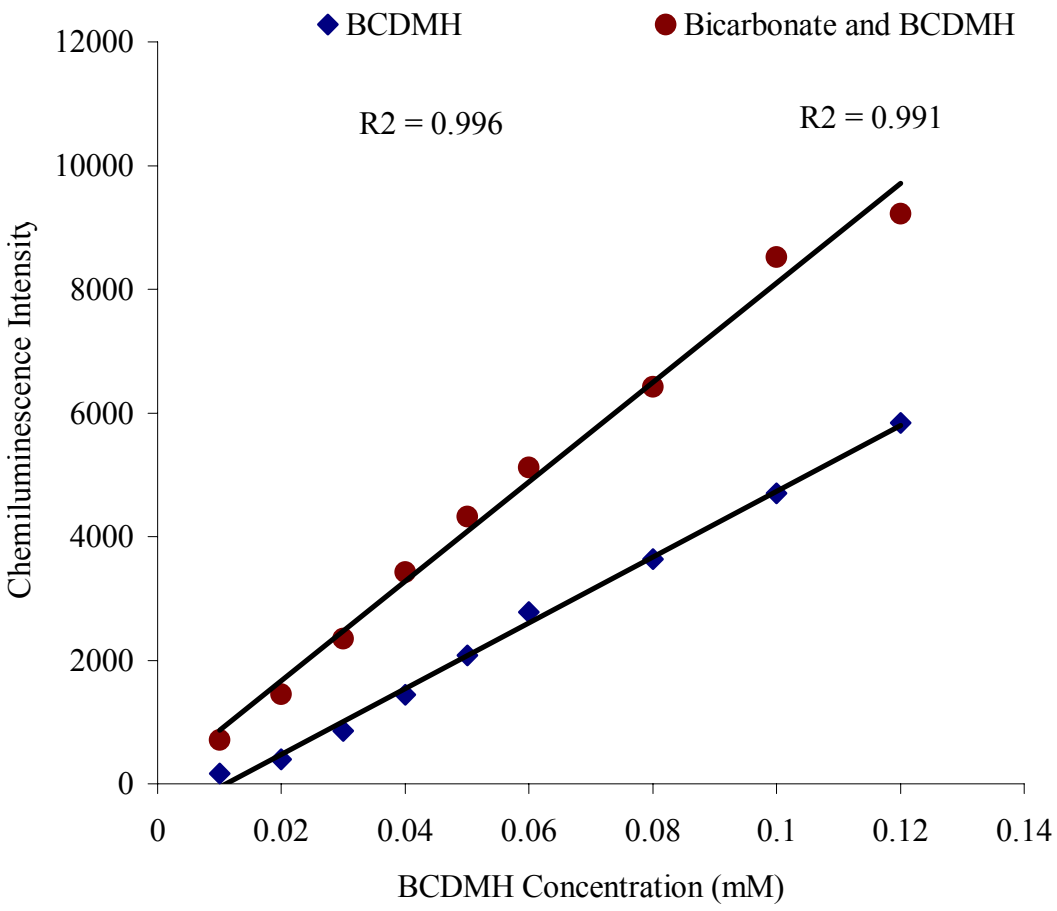

Figure 14: Effects of Bicarbonate on Chemiluminescence/ Bicarbonate Calibration Curve

would be present in the sample, and CO_2 (aq) would form a peroxycarbonate radical, $\cdot CO_4^-$, which would cause an increase in the luminol directed chemiluminescence. Also demonstrated was the oxidation of luminol by a carbonate radical, which can form from reactions 3 and 4.

$$CO_2\,(aq) + HOO^-(aq) \longrightarrow {}^-OOC\text{-}OOH \qquad (3)$$

$$^-OOC\text{-}OOH \longrightarrow {}^-OOC\text{-}OO\text{-}COO^- \longrightarrow 2\cdot CO_3^- \qquad (4)$$

It is speculated that the increased chemiluminescence emissions are due to the carbonate changing the hydroxy radical to the carbonate radical. The carbonate radical reacts with the luminol to form a luminol radical, which in turn produces light emission. Unlike the carbonate radical, the hydroxy radical is not selective towards a particular sight on the luminol compound and will react with any of the carbon atoms in the aromatic ring. This will yield more than one final species, which may not cause the chemiluminescence.[33] While the actual mechanism responsible for the increase in the chemiluminescence signal in this experiment is not known, the effects of bicarbonate are observed and have been considered in this research.

Effects of Manganese

Initially, it was thought that manganese might be affecting the chemiluminescence intensity because it is an easily oxidized metal like iron (II) and arsenic (II). Actually, the

[33] Xiao, C. et al. Analytical Chemistry, Vol. 74, No. 9, May 1, 2002. pp221-2216.

effects of manganese are two-fold. The two competing effects were discovered through a series of experiments. First varying concentrations of BCDMH were mixed with a 6.2×10^{-3} mM solution of manganese solution. The chemiluminescence emission was measured and these results did not show a linear relationship. These results are seen in Figure 15. Next, a range of concentrations of manganese solutions were mixed with a 0.10 mM solution of BCDMH and the chemiluminescence emission of these samples was measured. These results are seen in Figure 16. This test was repeated a few times and the decline in chemiluminescence among the first few samples is always seen.

An explanation for this initial drop in the signal may be due to the low manganese concentration. At low manganese concentrations, the Mn^{2+} will consume the HOCl, similar to the way Fe (II) and As (III) does. With a loss of HOCl, a decrease in chemiluminescence is seen. This effect is seen in reaction 5.

$$Mn^{2+} \longrightarrow Mn^{4+} + 2e^{-} \qquad (5)$$

At increased manganese levels, an increase in chemiluminescence signal is seen because the manganese is catalyzing the decomposition of hydrogen peroxide. The decomposed hydrogen peroxide produces a hydroxyl radical, which immediately oxidizes the luminol, producing the chemiluminescence emission.[34, 35]

[34] Nakayama, E. et al., 1989. Automated Determination of Manganese in Seawater by Electrolytic Concentration and Chemiluminescence Detection. Analytical Chemistry. 61(13); 1392-1396

[35] Okamura, K. et al. 1998. Selective and Sensitive Determination of Trace manganese in Sea Water by Flow through Technique using Luminol-Hydrogen Peroxide Chemiluminescence Detection. Analytica Chimica ACTA. 377: 125-131

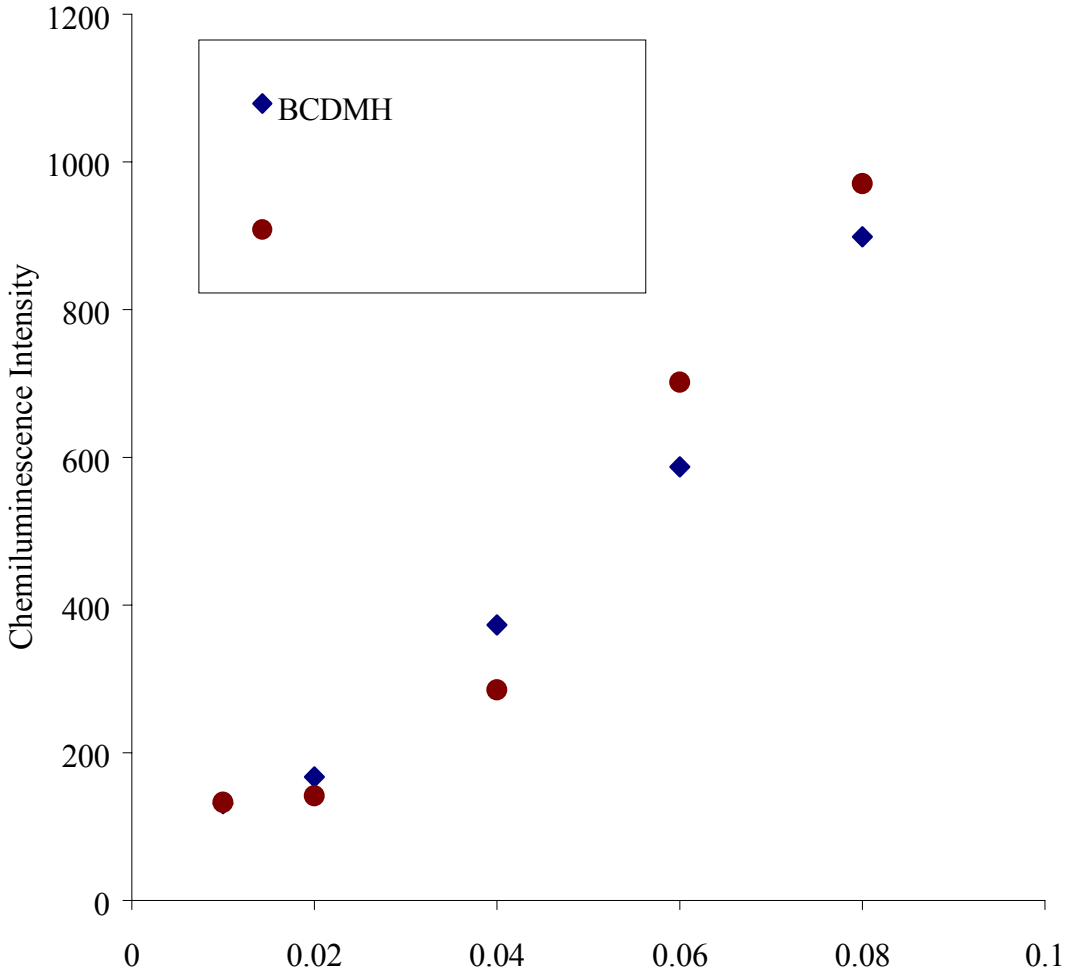

Figure 15: Effects of Manganese (II) on Chemiluminescence Intensity

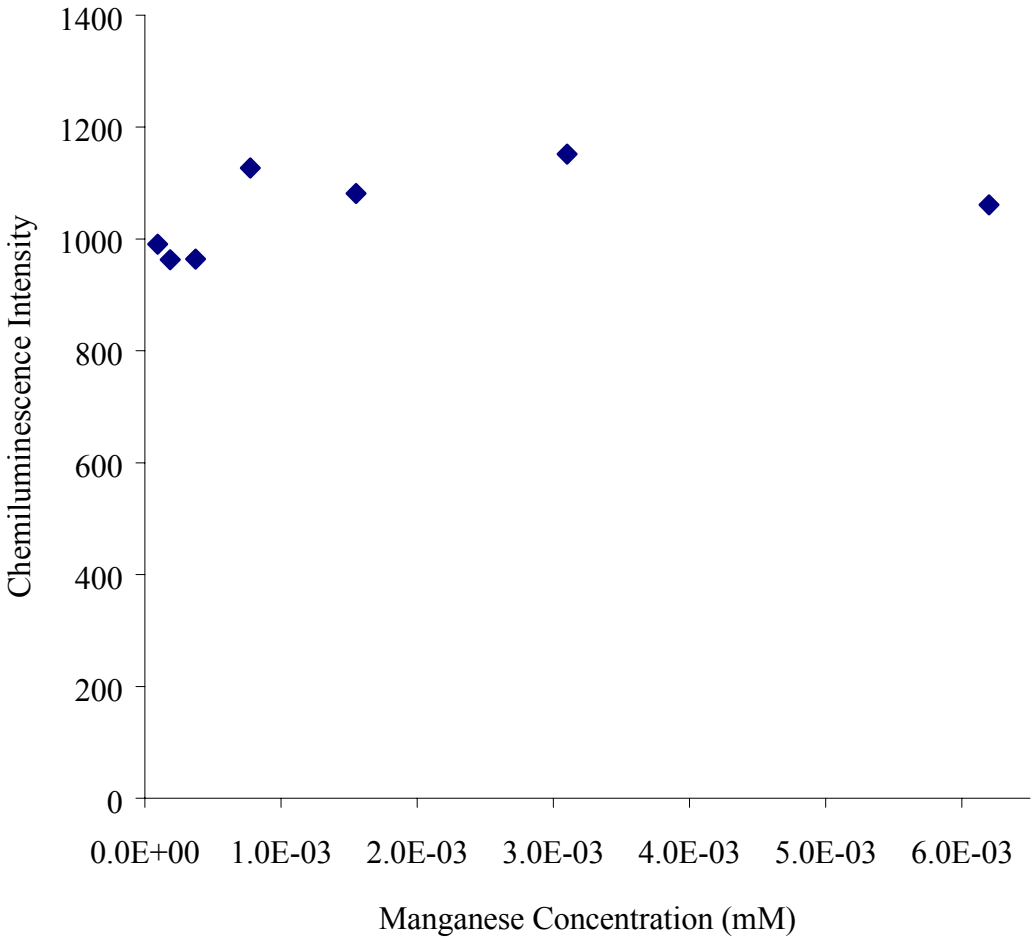

Figure 16: Effects of Various Manganese Concentrations and 0.10 mM BCDMH on Chemiluminescence Intensity

During the continuous runs, a small red precipitate was visible on the briquette and the water in the column was a dark yellow, yet clear. This color change was seen in all the continuous systems except the deionized water experiment, so this occurrence was attributed to a component of the synthetic Bangladesh groundwater, most likely manganese. Because there was no effect on the dissolution rate or interference of the pump flow-rate, this precipitate was not investigated any further.

The effects of the specialty adsorbent

The chemiluminescence intensity is also diminished in this medium. Again, this may be caused by the oxidation of the Fe (II), and As (III). There may also be something in the adsorbent that is contributing to the decreased chemiluminescence signals thereby falsely indicating a prolonged decomposition of the briquette. If the chlorite ions are oxidizing a metal or cation in the absorbent, that would cause a decrease in the available HOCl. Also, because the adsorbent is a ash-gray color that turned reddish-brown as the water passed through the medium and over the briquette, detecting a precipitate would not be easy.

Another approach to explain the continuous system results

Reactions six through ten are the suspected oxidation/reduction reactions occurring at the site of the BCDMH briquette.

$$\mathrm{BCDMH} + 2\mathrm{H_2O} \longrightarrow \mathrm{HOCl} + \mathrm{HOBr} + \mathrm{DMH} \qquad (6)$$

$$HOCl + H^+ + e^- \longrightarrow \frac{1}{2}Cl_{2(g)} + H_2O \quad (7)$$

$$\frac{1}{2}Cl_{2(g)} + e^- \longrightarrow Cl^- \quad (8)$$

$$HOBr + H^+ + e^- \longrightarrow \frac{1}{2}Br_2 + H_2O \quad (9)$$

$$\frac{1}{2}Br_{2(aq)} + e^- \longrightarrow Br^- \quad (10)$$

The reactions show that the decomposition of every 1 mole of BCDMH results in four available electrons. Subsequently, for every 1 mole of BCDMH, four moles of iron (II) can be oxidized to iron (III), or two moles of arsenic (III) will be oxidized to arsenic (V). Therefore, by using the calculated mmol/day of DMH found in Table 5 and converting that value to mmol of BCDMH, then subtracting the BCDMH stoichiometric equivalent of contaminant moles, the difference between the mmol of BCDMH and mmol of contaminant should equal the respective BCDMH concentration calculated using the chemiluminescence method. Figures 17 through 26 are plots of DMH concentrations calculated using the HPLC method along with BCDMH concentrations using the chemiluminescence method versus time, and Table 5 is a compilation of the calculated data.

By considering the effects of the oxidizable metals, the agreement between the HPLC results and the chemiluminescence results is much better. For instance, for continuous run 1 (Figure 17), based upon HPLC, a value of 0.1 mM BCDMH is expected. By taking into account the 0.27 mM Fe (II) in the water, 0.07 mM BCDMH

should be consumed. This gives an unexpected chemiluminescence value of 0.04 mM BCDMH that is in good agreement with the 0.03 mM BCDMH that was experimentally obtained.

Any chlorine gas that is lost would contribute to low chemiluminescence values. That continuous systems 3 and 9 (Figures 19 and 25), both without significant amounts of oxidizable metals, give such good agreement between the HPLC results and the chemiluminescence results, indicates that loss of chlorine does not play a major role.

The agreement is not always perfect. For example, in continuous run 2, the HPLC results indicate 0.08 mM BCDMH. Taking into account that 0.046 mM As (III) should consume 0.023 mM BCDMH, a value of 0.06 mM BCDMH would be expected for the chemiluminescence, whereas 0.03 was obtained. Nevertheless, the agreement is better taking the oxidation of As (III) into consideration. The other continuous run that contains As (III) as the only major oxidizable ion is continuous system 6 (Figure 22), which also gives a somewhat lower chemiluminescence reading than might be expected. Whether this is a real effect due to As (III) or whether it is due to experimental variability is uncertain. Since the chemiluminescence technique is affected by so many factors such as loss of chlorine, oxidizable metals and catalysis by metals, it is to be expected that there would be some variability. Since the HPLC is not affects by so many factors, it is probably the more reliable technique when considering solely the decomposition of BCDMH.

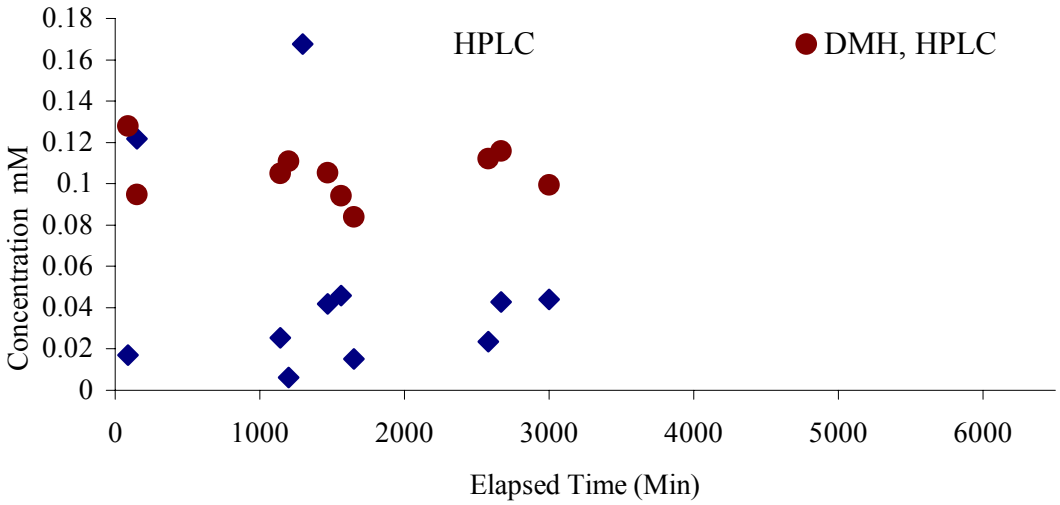

Figure 17: BCDMH and DMH Concentrations
in Continuous System 1, Synthetic Bangladesh Groundwater
Contaminated with Fe (II)

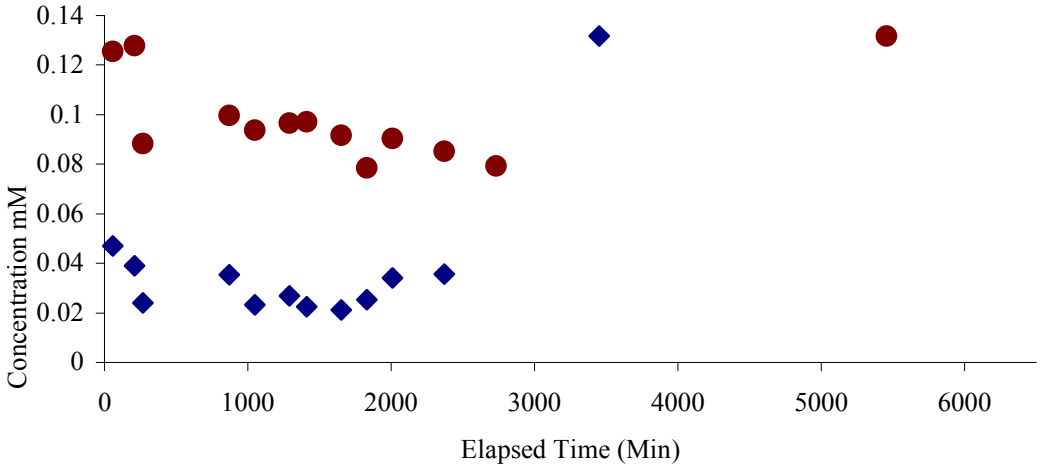

Figure 18: BCDMH and DMH Concentration
in Continuous System 2, Synthetic Bangladesh Groundwater
contaminated with As (III)

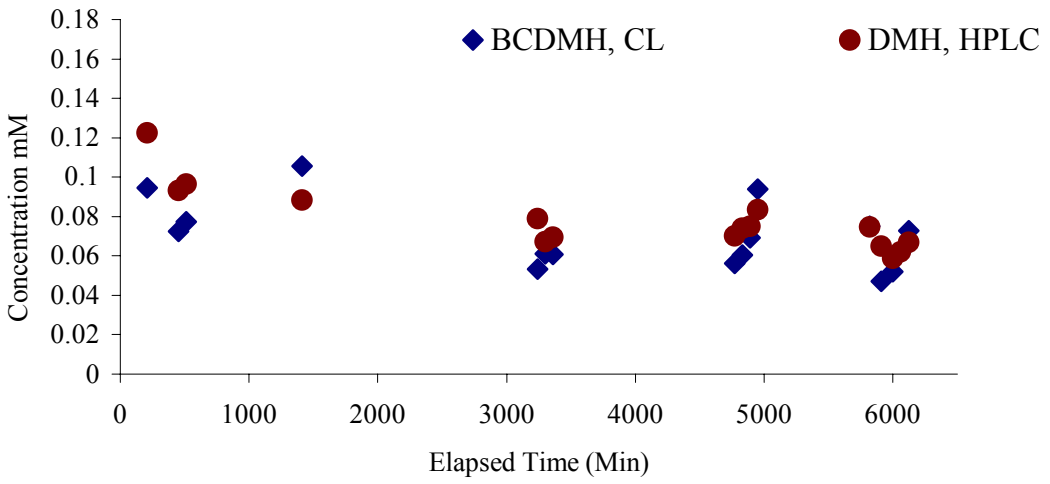

Figure 19: BCDMH and DMH Concentrations
in Continuous System 3, Synthetic Bangladesh Groundwater
Contaminated with As (V)

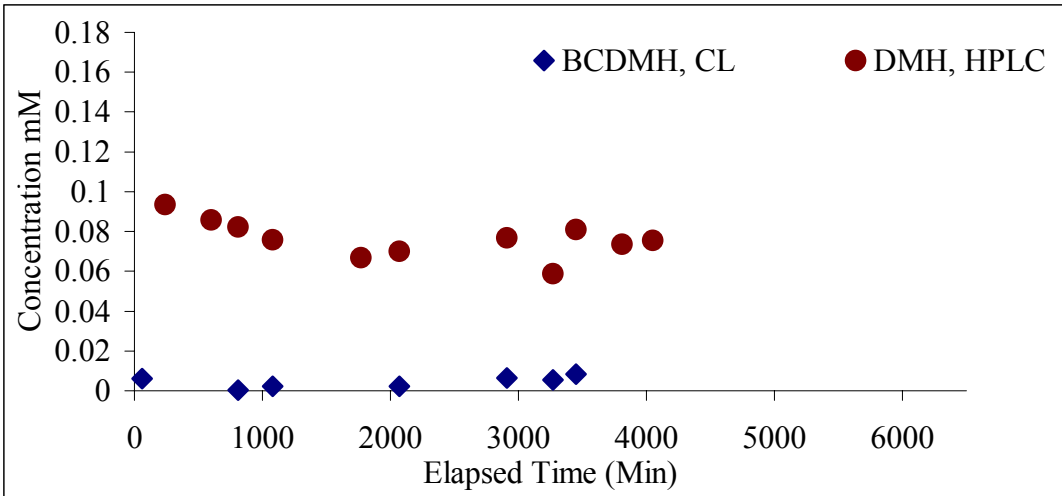

Figure 20: BCDMH and DMH Concentrations
in Continuous System 4, Synthetic Bangladesh Groundwater
Contaminated with Fe (II) and As (III)

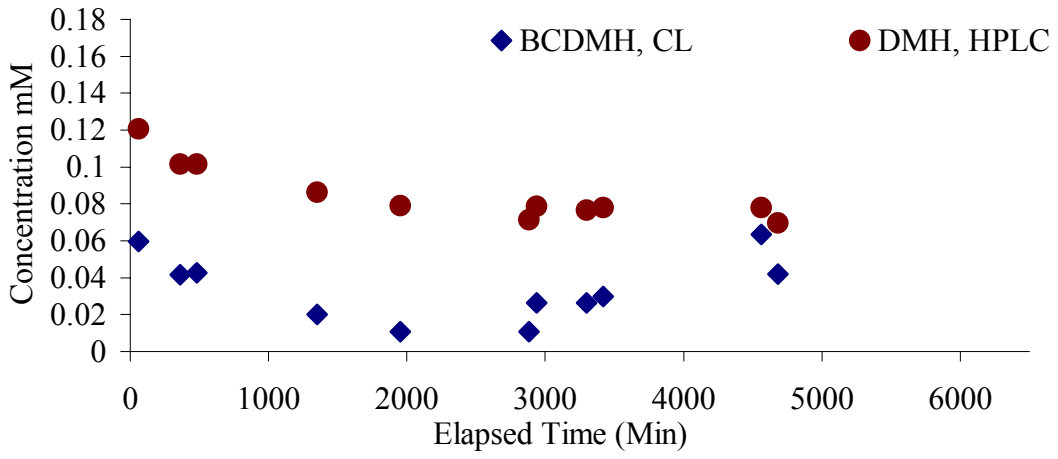

Figure 21: BCDMH and DMH Concentrations
in Continuous System 5, Synthetic Bangladesh Groundwater
contaminated with Fe (II) and As (V)

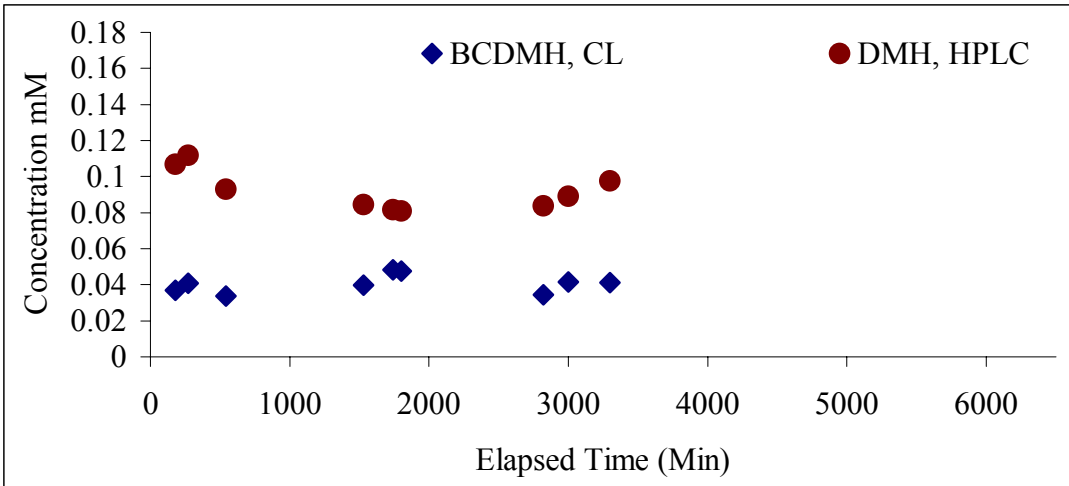

Figure 22: BCDMH and DMH Concentrations
in Continuous System 6, Synthetic Bangladesh Groundwater
contaminated with As (III) and As (V)

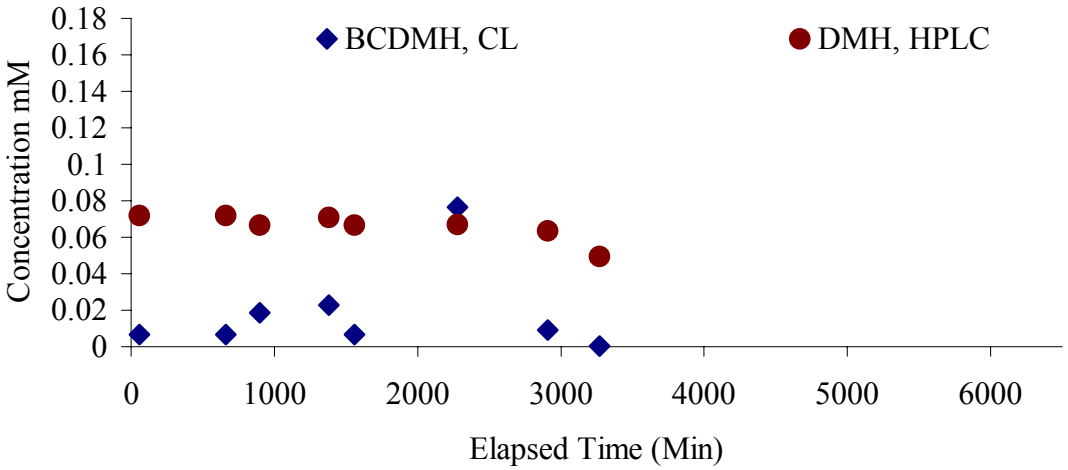

Figure 23: BCDMH and DMH Concentrations
in Continuous System 7, Synthetic Bangladesh Groundwater
contaminated with Fe (II), As (III), and As (V)

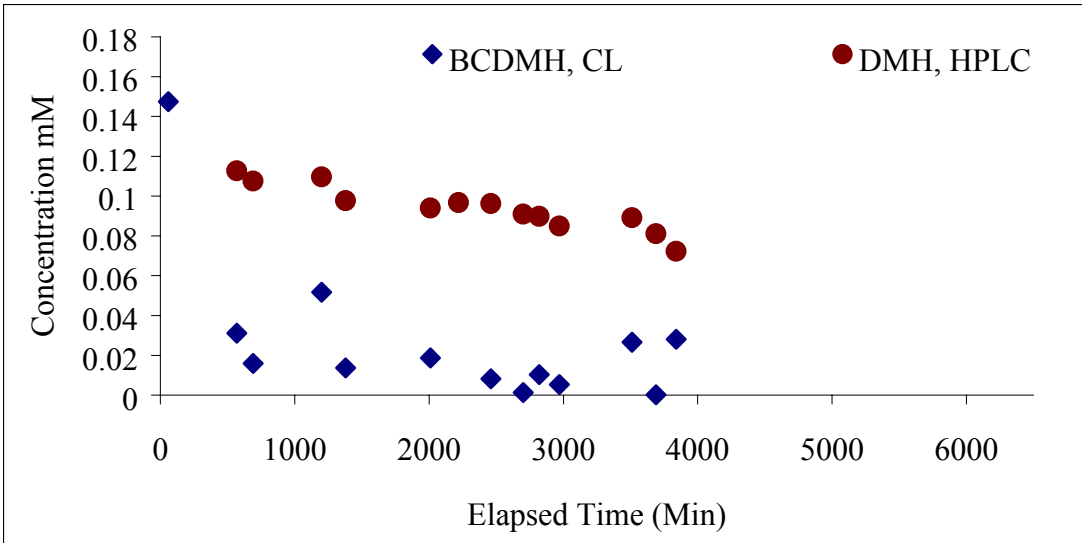

Figure 24: BCDMH and DMH Concentration
in Continuous System 8, synthetic Bangladesh groundwater with
specialty adsorbent, contaminated with Fe (II), As (III), and As (V)

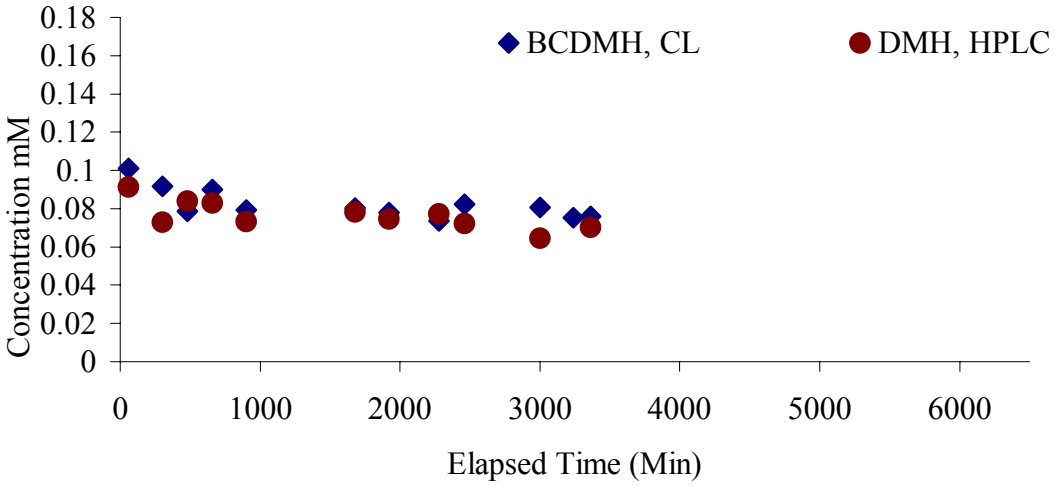

Figure 25: BCDMH and DMH Concentrations in Continuous System 9, Synthetic Bangladesh Groundwater with no additions

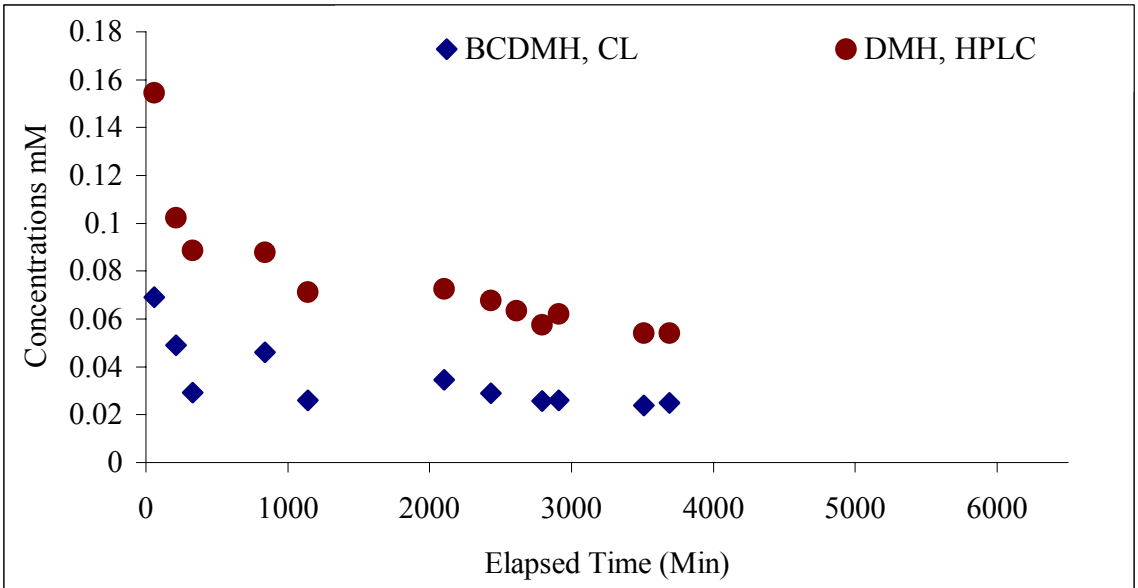

Figure 26: BCDMH and DMH Concentrations in Continuous System 10, Deionized Water

Table 5: Calculated mM of BCDMH from HPLC, mM BCDMH consumed, and expected and experimental chemiluminescence values

Continuous System	Addition	mM BCDMH from HPLC	Calculated mM BCDMH consumed	Expected mM BCDMH CL Value	Experimental mM BCDMH CL Value
1	0.27 mM Fe (II)	0.11	0.07	0.04	0.03
2	0.046 mM As (III)	0.08	0.02	0.06	0.03
3	0.046 mM As (V)	0.07	0	0.07	0.07
4	0.27mM Fe (II), 0.046 mM As (III)	0.07	0.09	0	0.005
5	0.27 mM Fe (II), 0.046 mM As (V)	0.07	0.07	0	0.03
6	0.023 mM As (III), 0.023 mM As (V)	0.09	0.01	0.08	0.04
7	0.27 mM Fe (II), 0.023 mM As(III), 0.023 mM As (V)	0.05	0.08	0	0.01
8	0.27 mM Fe (II), 0.023 mM As(III), 0.023 mM As (V)	0.07	0.08	0	0.01
9	Synthetic Bangladesh Groundwater	0.07	0	0.07	0.08

Static Mode Samples

Because it was not practical to maintain a single continuous system for a month or longer, chambers were used to observe the decomposition of BCDMH for extended periods of time. Figure 27 is a graph showing the concentrations of BCDMH and DMH in the chamber over a 30-day period. Graphs of the 9 other chambers may be found in appendix K. All the chambers show the same trend, which is an increasing gap between the BCDMH and DMH concentrations over time. This is caused by a release of Cl_2 gas each time the chamber is opened as seen in reaction 11.

$$HOCl + HCl \rightleftharpoons H_2O + Cl_2 \qquad (11)$$

Based on reaction 2, there is an equilibrium inside the chambers, but every time the chamber is opened, there is an escape of Cl_2, which causes a decrease in available HOCl, which reacts with the luminol to produce chemiluminescence. With a loss of HOCl, the signal will diminish overtime, which is seen in Figure 27.

Table 6 is a compilation of the data collected from the static mode collection chambers. The number of the chamber correlates to the numbered experiment for the continuous system. The rate of decomposition of the BCDMH briquette is markedly decreased when compared to the rates of the continuous system. This difference may be due to the difference in solution volumes. Based on the daily decomposition and the initial chamber volume of 250 mL of solution, the static samples show a BCDMH release of 4.08×10^{-5} grams per mL whereas the continuous system gives 1.62×10^{-5} grams per mL, based on the flow rate. This shows the continuous system with a two to three times

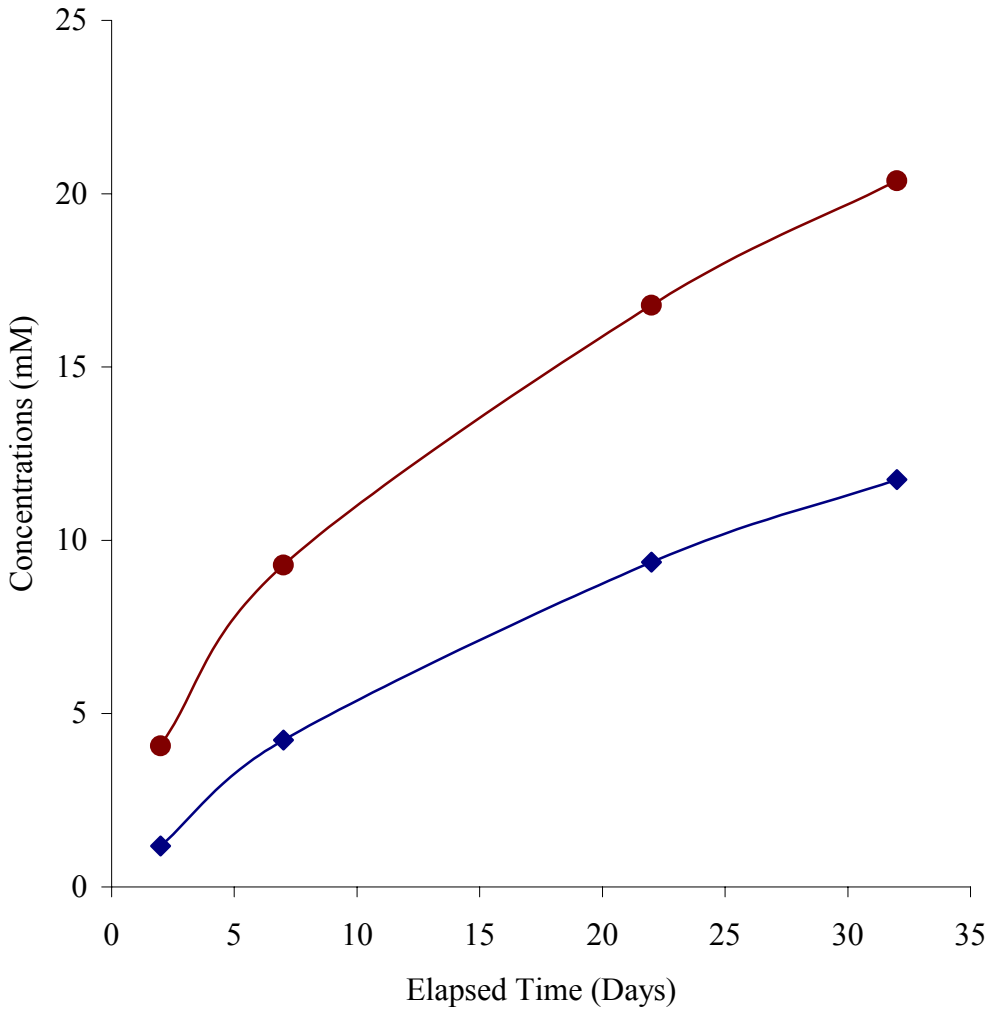

Figure 27: BCDMH and DMH Concentration in Chamber 5

faster decomposition rate than the static samples, probably due to the large difference in water volume of the samples. In the continuous system, a minimum of 160 L of solution is passed over the briquette, whereas the chambers only contain 250 mL of solution.

According to Table 6, based on the chemiluminescence method, the average lifetime of a BCDMH briquette is 5.25 years with a standard deviation of 0.3 years. The small deviation among the 10 sample compositions shows that there appears to be little interference caused by the contaminants. This may be because the moles of contaminant in the chambers are greatly reduced.

Table 7 shows the number of millimoles in a determined volume of solution. The chambers started with a volume of 250 mL that was decreased by 5 mL every time a sample was taken. The continuous system contained four 20 L carboys that were each refilled at least once during the course of a continuous system. The BCDMH briquette along with the effluent in the continuous system had a greater opportunity to be affected by the transition metals.

Because the results for chamber 9, synthetic Bangladesh groundwater, do not differ from the other chambers, it appears as though the contaminants do not have an effect on the rate of decomposition of the BCDMH briquette.

Mass Balance between BCDMH and DMH

Table 8 confirms the theory that a constituent in the synthetic Bangladesh groundwater causes interference with the chemiluminescence signal. In industry, mass balance or material balance is calculated to ensure that one or more degradants are not left on the column, or that the starting material is not degrading into a non-chromophoric

Table 7: The Absolute Mass Balance Deficit (AMBD) and Relative Mass Balance Deficit (RMBD) for the decomposisiton of BCDMH to DMH for the static mode samples.

	Day 2		Day 7		Day 22		Day 32	
Chamber	AMBD	RMBD	AMBD	RMBD	AMBD	RMBD	AMBD	RMBD
1	-14.0%	-885%	-14.3%	-116%	-27.9%	-112%	-23.8%	-69.7%
2	-6.81%	-558%	-15.9%	-163%	-29.2%	-124%	-25.1%	-76.6%
3	-3.61%	-107%	-16.5%	-153%	-16.4%	-63.0%	-20.8%	-70.9%
4	-9.20%	-414%	-15.6%	-144%	-13.9%	-41.0%	-20.0%	-58.7%
5	-8.46%	-237%	-14.7%	-119%	-20.5%	-75.4%	-22.5%	-66.1%
6	-7.60%	-269%	-14.1%	-124%	-21.5%	-83.3%	-26.8%	-78.8%
7	-10.0%	-427%	-17.3%	-115%	-30.2%	-112%	-27.3%	-72.6%
8	-15.3%	-1733%	-17.2%	-218%	-30.2%	-140%	-29.4%	-86.7%
9	-6.93%	-606%	-17.3%	-168%	-16.8%	-54.9%	-25.2%	-79.9%
10	-4.93%	-114%	-17.6%	-163%	-16.1%	-53.1%	-19.8%	-63.8%

Table 7: The millimoles present in corresponding volumes of solution

Contaminant	Millimoles in 0.250 L	Millimoles in 1 L	Millimoles in 20 L	Millimoles in 160 L
Fe (II)	0.0671	0.269	5.37	43.0
As (III)	0.00584	0.0234	0.467	3.74
As (V)	0.00583	0.0233	0.466	3.72

Table 8: The Absolute Mass Balance Deficit (AMBD) and Relative Mass Balance Deficit (RMBD) for the decomposisiton of BCDMH to DMH for the static mode samples.

	Day 2		Day 7		Day 22		Day 32	
Chamber	AMBD	RMBD	AMBD	RMBD	AMBD	RMBD	AMBD	RMBD
1	-14.0%	-885%	-14.3%	-116%	-27.9%	-112%	-23.8%	-69.7%
2	-6.81%	-558%	-15.9%	-163%	-29.2%	-124%	-25.1%	-76.6%
3	-3.61%	-107%	-16.5%	-153%	-16.4%	-63.0%	-20.8%	-70.9%
4	-9.20%	-414%	-15.6%	-144%	-13.9%	-41.0%	-20.0%	-58.7%
5	-8.46%	-237%	-14.7%	-119%	-20.5%	-75.4%	-22.5%	-66.1%
6	-7.60%	-269%	-14.1%	-124%	-21.5%	-83.3%	-26.8%	-78.8%
7	-10.0%	-427%	-17.3%	-115%	-30.2%	-112%	-27.3%	-72.6%
8	-15.3%	-1733%	-17.2%	-218%	-30.2%	-140%	-29.4%	-86.7%
9	-6.93%	-606%	-17.3%	-168%	-16.8%	-54.9%	-25.2%	-79.9%
10	-4.93%	-114%	-17.6%	-163%	-16.1%	-53.1%	-19.8%	-63.8%

moiety. When the measured loss of the initial compound is equivalent to the measured increase in the degradation products, this is considered mass balance.[36] The absolute mass balance deficit (AMBD) is the calculated loss or gain of grams, or more commonly, percent between the degradants and the initial compound. The AMBD for the decomposition of BCDMH to DMH was calculated by first converting the HPLC determined grams of DMH to grams of BCDMH. This product was then subtracted from the difference of the initial weight of the BCDMH briquette that was placed in the chamber and the calculated BCDMH grams from the corresponding chemiluminescence measurement. The AMBD should be near zero, or slightly above if there were other degradants, but Table 8 shows a negative AMBD, verifying an elevated measurement in one of the methods. The relative mass balance deficit (RMBD) is also calculated to express the absolute mass balance deficit as a percentage of the full amount of starting material that has been used consumed. The RMBD was calculated by dividing the AMBD by the grams lost of BCDMH and then multiplying by 100. These results are also found in Table 7. If the BCDMH had been decomposing to another moiety other than DMH, this would have resulted in positive values for the AMBD. Because the values are negative, it is believed that BCDMH is not degrading into any other products besides DMH. Furthermore, an individual DMH sample was tested by HPLC repeatedly over a one-month period and did not show any decrease in peak area. Based on the stability of DMH, this is thought to be the only major degradant.

[36] AAI International Seminar. **2003** Pharmaceutical Stability: Current Regulations and the Analytical Search for Degradants.

Rate Constants

By plotting the natural log of the chemiluminescence intensities versus time, a pseudo-first-order rate constant for the chemiluminescence emission decay could be determined for the 10 different continuous system experiments and the 10 static sample chambers. As seen in Figure 28, x-axis is elapsed time in seconds, the left axis is the chemiluminescence intensity and the right axis is the natural log of the chemiluminescence intensities. Only the decay was plotted in natural log so that a straight line could be obtained. This method was applied to all the different experiments to determine if there was any difference in rate constants or half lives. A compilation of the rate constants and half-lives are seen in Table 9. The remaining graphs for both the continuous system and static samples may be found in Appendices L and M respectively.

Continuous system 5 shows an increased rate constant when compared to the other continuous systems; the reasons for this are not apparent, although it is thought to be caused by experimental error rather than a particular component of the experiment. Aside from continuous system 5, the rate constants for continuous systems 1 though 9 are all similar. This is most likely due to the presence of the carbonate, which has been shown to have a significant influence on the chemiluminescence signal. In the case of the static samples, all 10 continuous systems have similar rate constant. It is thought that there is a loss of CO_2 (g) because a small cloud of smoke escaped when the chamber was opened, and tiny bubbles are seen traveling up the briquette. Therefore, the carbonate does not have the significant effect on the chemiluminescence signal in the static samples as seen in the continuous system samples.

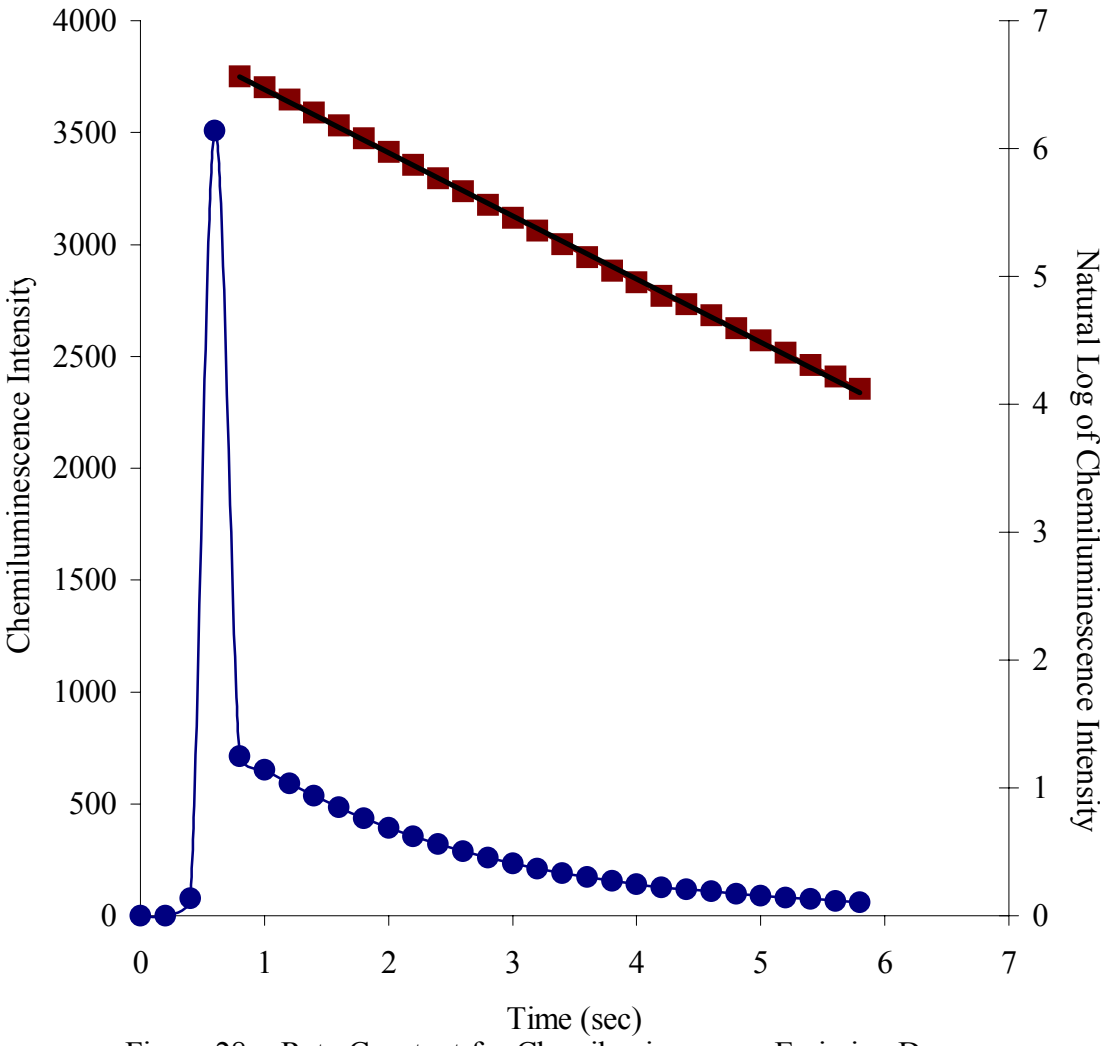

Figure 28: Rate Constant for Chemiluminescence Emission Decay of Continuous System 1

Table 9: Compilation of pseudo-first-order rate constants and half-lives of chemiluminescence intensity decay.

Experiment / Chamber	Continuous System		Static Chambers	
	Rate Constant (s^{-1})	Half-Life	Rate Constant (s^{-1})	Half-Life
1	0.49	1.4	0.58	1.20
2	0.47	1.5	0.58	1.20
3	0.45	1.5	0.63	1.10
4	0.49	1.4	0.59	1.17
5	0.69	1.0	0.61	1.13
6	0.47	1.5	0.58	1.19
7	0.44	1.6	0.60	1.16
8	0.47	1.5	0.58	1.20
9	0.47	1.5	0.62	1.11
10	0.62	1.1	0.59	1.17

CONCLUSIONS

Complementary chemiluminescence and HPLC methods were developed and optimized for the detection of the decomposition of BCDMH into HOCl, HOBr, and DMH. While both methods showed good selectivity, linearity, and reproducibility for standard solutions of the corresponding analyte, the HPLC method produced more reliable results as there were no reducing and oxidizing interferences as seen in the chemiluminescence method.

The complementary methods were useful tools for viewing multiple aspects of the decomposition of BCDMH. If only the HPLC method had been employed, the decrease in the antimicrobial agent would not have been observed. Had chemiluminescence been the only method used, a conclusion may have been that different constituents in the Bangladesh water affect the BCDMH briquettes differently. By using both methods, more complete conclusions can be drawn.

When comparing the static sample results to the continuous system results, aside from the prolonged briquette life, there are no deviations between approaches. This would indicate that the conclusions from the continuous system experiments also apply to longer time periods.

The linearity of the HPLC graphs for the continuing system experiments show the appearance of DMH is uniform. There is a linear relationship between the grams of DMH appearing and elapsed time for the decomposition of BCDMH. Likewise, the correlation coefficients on the chemiluminescence graphs also show a consistent stream of BCDMH being released.

Because the HPLC results did not show any changes with the various contaminants, the contaminants in the water probably did not affect the decomposition of the BCDMH briquette. Also, DMH is apparently stable over an extended period of time. The same DMH sample was injected on the HPLC over a 30-day interval, and only a slight increase in DMH concentration was seen. Therefore, this evidence suggests that DMH is not degrading any further.

Chemiluminescence results showed variations among the water contaminants, but that was due to the different effect the metals had on the hypohalous acid. When these effects were considered, the two methods were in agreement that the composition of the water did not affect the rate of BCDMH briquette decomposition.

Although the chemiluminescence results did show fluctuations in their results, this is not caused by changes in the rate of decomposition of the BCDMH briquette, but rather in the volume of hypohalous acid present in the sample. The contaminants in the sample did affect the presence of the hypohalous acids. In the presence of reduced metals, the acids were consumed before initiating the chemiluminescence reactions. This is what caused the variability in the results. If the HOCl is not available to react with the luminol because the metals are using the HOCl for oxidation, then the actual volume of antimicrobial thought to be present in the water filtration systems will be diminished if not completely consumed. Therefore, to use the BCDMH briquettes as an antimicrobial would not be effective in the presence of large amounts of oxidizable ions such as Fe (II) and As (III).