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Bromination of aromatic compounds by residual bromide in sodium chloride matrix modifier salt during heated headspace GC/MS analysis

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ABSTRACT

Analytical artifacts attributed to the bromination of toluene, xylenes, and trimethylbenzenes were found during the heated headspace gas chromatography/mass spectrometry (GC/MS) analysis of aqueous samples. The aqueous samples were produced from Fenton-like chemical oxidation reactions and contained aromatic compounds, hydrogen peroxide (H_2O_2), and ferric sulfate. Prior to GC/MS headspace analysis, the samples were acidified ($pH < 2$), and sodium chloride was amended to the headspace vial as a matrix modifier. The brominated artifacts were generated during heated headspace analysis. Further, when samples were spiked with a mixture of volatile chlorinated and aromatic compounds (50 μg/L), poor spike recoveries of toluene and xylenes occurred, and in some cases complete loss of trimethylbenzenes and naphthalene resulted. Where poor recovery of aromatic spike compounds occurred, brominated aromatic compounds were found. The only significant source of bromine in the reaction scheme is the bromide typically present ($< 0.01\%$ w/w) in the sodium chloride amended to the samples. Conversely, brominated artifacts were absent when a buffered salt mixture composed of sodium chloride and potassium phosphate dibasic/monobasic was used as a matrix modifier and raised the sample pH ($pH \sim 6$). This indicated that the brominated artifacts resulted from the reaction of the aromatic compounds with BrCl, which was formed by the reaction of H_2O_2, chloride, and bromide under acidic conditions. An alternative matrix modifier salt is recommended that prevents the bromination reaction and avoids these deleterious effects on sample integrity during headspace analysis.

1. Introduction

Over the last two decades, thousands of oxidant-related, environmental laboratory- and field-scale studies have been conducted where oxidants are amended to aqueous solutions (i.e., surface water, ground water, and soil slurry) for the purpose of transforming organic contaminants into less harmful chemical by-products. The objectives of these studies range from the investigation of fundamental oxidative mechanisms to chemical oxidation optimization and feasibility assessment in the purification of water, wastewater, ground water, soil and other contaminated matrices[1,2]. The oxidants predominantly include permanganate (MnO_4^-), hydrogen peroxide (H_2O_2), persulfate ($S_2O_8^{2-}$) and ozone (O_3) [1]. Results from these studies have been published in >600 journal articles, theses, and reports [3]. An integral component in such studies is the collection and analysis of aqueous samples to assess oxidative treatment performance. In many cases, aqueous samples contain the oxidant and the organic contaminants in a "binary mixture." The commingling of organic contaminants and oxidants in binary mixture aqueous samples represents a condition in which there is significant potential for oxidative transformation of the contaminants after sample collection, and/or during analysis. The presence of residual oxidant in aqueous samples introduces a wider range of potential interfering reactions. For example, binary mixtures of residual oxidants including permanganate and persulfate have been shown to negatively impact the quality of aqueous samples causing "false negative" analytical results using headspace and purge and trap gas chromatography mass spectrometry (GC/MS) [4–6]. In these cases, transformation of volatile organic compounds (VOCs) occurred in the sample (1) during the time frame between when the samples were collected (i.e., in either the field or lab) and analyzed, or (2) during analysis when the oxidant was thermally activated. False negative results describes the condition where contaminants were originally present in the sample matrix, but

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was transformed as described above and consequently, not detected by the analytical instrument. Sample preservation guidelines and methods have been developed for these two oxidants to eliminate the impact of the binary mixtures on the quality of these samples [4–6].

The role of binary mixtures involving H_2O_2 and VOCs and their impact on headspace GC/MS analytical results has not been investigated in detail. Fenton-like reactions are initiated by the reaction between ferric iron (Fe^{+3}) and H_2O_2. The classic Fenton reaction involves the reaction between ferrous iron (Fe^{+2}) and H_2O_2 to generate hydroxyl radicals ($\cdot OH$) which oxidize a wide range of organic contaminants (Table 1; R1–R4) [2]. The progress of VOC transformation during Fenton and Fenton-like oxidation reactions can be monitored by heated headspace gas GC/MS analysis. In heated headspace analysis, aqueous samples in sealed vials are heated at elevated temperatures so that the VOCs equilibrate between the aqueous and vapor phase. An aliquot of the headspace is transferred to the injection port of a GC and the concentrations of organic compounds are determined from calibration curves of authentic standards. Enrichment of the VOCs in the headspace and method sensitivity can be increased by heating the sample and adding matrix modifiers that "salt-out" the organics and enhance mass transfer from the aqueous phase to the headspace. Matrix modifiers can be common salts such as sodium chloride, sodium sulfate, and calcium chloride. The matrix modifier can also include a salt such as trisodium phosphate (TSP) or a phosphate buffer that neutralizes the sample pH when acid or base is added for preservation. Care must be taken to ensure that the preservation does not cause hydrolysis of compounds during storage or during heated headspace analysis. Hydrolysis of ether oxygenates including methyl *tert*-butyl ether, *tert*-amyl methyl ether, and ethyl *tert*-butyl ether can occur when heated headspace analysis is done on samples whose pH is adjusted to less than 2 with hydrochloric acid [7–10]. When ether oxygenates are preserved with trisodium phosphate [7–10] hydrolysis does not occur during heated headspace analysis. However, the use of TSP cannot be considered a universal preservative as catalyzed base hydrolysis of halogenated compounds such as bromomethane, 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane can occur during sample storage.

In preliminary studies involving the chemical oxidation of aromatic compounds under Fenton-like conditions, the unexpected detection of brominated compounds was observed using GC/MS heated headspace analysis methods. The objectives of this study were (1) to investigate the source and mechanism of brominated aromatics formation and appearance in mass chromatograms resulting from GC/MS analysis of aqueous samples containing aromatic compounds, H_2O_2, and matrix modifier salts under acidic conditions, and (2) to develop an alternative method of analysis that eliminates the mechanism that causes the bromination step and to ensure the integrity of aqueous samples.

Table 1
Fenton-like/Fenton and related reactions, and proposed bromination mechanism.

Fenton-like/Fenton related reactions		
R1	$H_2O_2+Fe^{+2}\rightarrow Fe^{+3}+OH^-+OH$	$k_1=76\ M^{-1}\ s^{-1}$
R2	$H_2O_2+Fe^{+3}\rightarrow Fe^{+2}+O_2^-+2H^+$	
R3	$O_2^-+Fe^{+3}\rightarrow Fe^{+2}+O_2$	$k_3=3.1\times 10^5\ M^{-1}\ s^{-1}$
R4	toluene+OH→toluene'	$k_4=3.0\times 10^9\ M^{-1}\ s^{-1}$
Proposed aromatic bromination mechanism in Fenton-like test reactors		
R5	$H_2SO_4+2NaCl\rightarrow 2HCl+Na_2SO_4$	
R6	$HCl+H_2O_2\rightarrow H_2O+HOCl$	[13]
R7	$HOCl+Br^-\rightarrow HOBr+Cl^-$	[14–15]
R8	$HOBr+HCl\rightarrow BrCl+H_2O$	
R9	Toluene+BrCl→Br-toluene+HCl	

2. Methods and materials

For Fenton-like reactions [11–12], batch reactors were prepared using borosilicate glass vials (20 mL) with Teflon-lined septa. The samples typically contained solutions of ferric sulfate (5 or 30 mM as Fe^{+3}), NaOH (to raise the pH to pH=3), toluene or individual xylene isomers (0.08–0.88 mM) and H_2O_2 (0.6–60 mM). After adding the reagents in the order listed, the sample vials were immediately capped to prevent volatilization of the aromatic compound. The reactors were sacrificed at various times during the reaction. The Fenton-like reaction was quenched at the time of sampling by adding concentrated sulfuric acid at ~1% v/v.

2.1. *Analytical*

Two methods of headspace analysis were used to determine the concentration of toluene and xylenes remaining after the Fenton-like oxidation reactions. Both methods follow the general procedures outlined in EPA Method 5310a/8260c [7]. In one method, a CombiPal headspace autosampler and an Agilent 6890 gas chromatograph/5973 quadrupole mass spectrometer were used. Here, the aqueous sample (10 mL) was added to headspace autosampler vial (20 mL) containing the NaCl matrix modifier salt (2 g) (USP grade). Before the sample vial was sealed, an internal standard/surrogate mixture containing fluorobenzene, p-bromofluorobenzene, and 1,4-dichlorobenzene-d_4 was added. The headspace vial was heated in an agitator/incubator module (80 °C for 30 min). A syringe (2.5 mL) was used to transfer 1.0 mL of headspace to the injection port of the gas chromatograph. The syringe was enclosed in a heated syringe module and was heated at 85 °C. The capillary column used for target compound separation was an Agilent DB624 column (length 30 m; 0.25 mm inner diameter; and 1.5 μm film thickness). Typically all the samples in the analysis queue were prepared at the same time and placed in the autosampler tray.

In the second headspace method, a Tekmar 7000 static headspace autosampler and Varian Saturn 2100T gas chromatograph/ion trap mass spectrometer were used. Here, the sample (10 mL) in the headspace autosampler vial (20 mL) was heated in the platen (80 °C for 30 min). The septum of the headspace vial was pierced with the autosampler needle and the headspace was pressurized with helium. After equilibration, the sampling valve was rotated and the pressurized headspace was directed to a 1.0 mL sample loop. A back pressure regulator connected to the vent of the sampling valve allowed the headspace to flow through the sample loop until the vial pressure dropped to a set point pressure controlled by the regulator. The valve was actuated again and the headspace vapor in the sample loop was directed to the injection port of the gas chromatograph. As in the first headspace method, an identical Agilent DB624 capillary column was used for gas chromatography. In this method, the matrix modifier was a buffer salt mixture composed of NaCl (50 wt%) (ACS), K_2HPO_4 (42 wt%), and KH_2PO_4 (8 wt%). The buffer salt neutralized the pH of samples prior to analysis. All salts were purchased from Aldrich Chemical. When the salt buffer (2 g) was added to the acidified sample (10 mL), the pH was ~6.

In the mechanistic investigation, each of the samples was analyzed using the Varian Saturn 2100T. The samples were prepared and immediately analyzed, unless otherwise noted. The reaction occurred for exactly 30 min, the time that the sample was heated in the headspace autosampler. Samples analyzed using the Agilent 6890 GC/MS rested in the autosampler tray for varying amounts of time depending on how many sample were in the sample queue. The spike recovery samples were usually placed at the end of the sample queue. The reaction times were the sum of the time that the samples rested in the autosampler tray at room temperature and the time that they were heated (30 min at 80 °C).

3. Results

The mass chromatograms of samples from the Fenton-like reactions of *m*-xylene, *p*-xylene and *o*-xylene, and toluene are

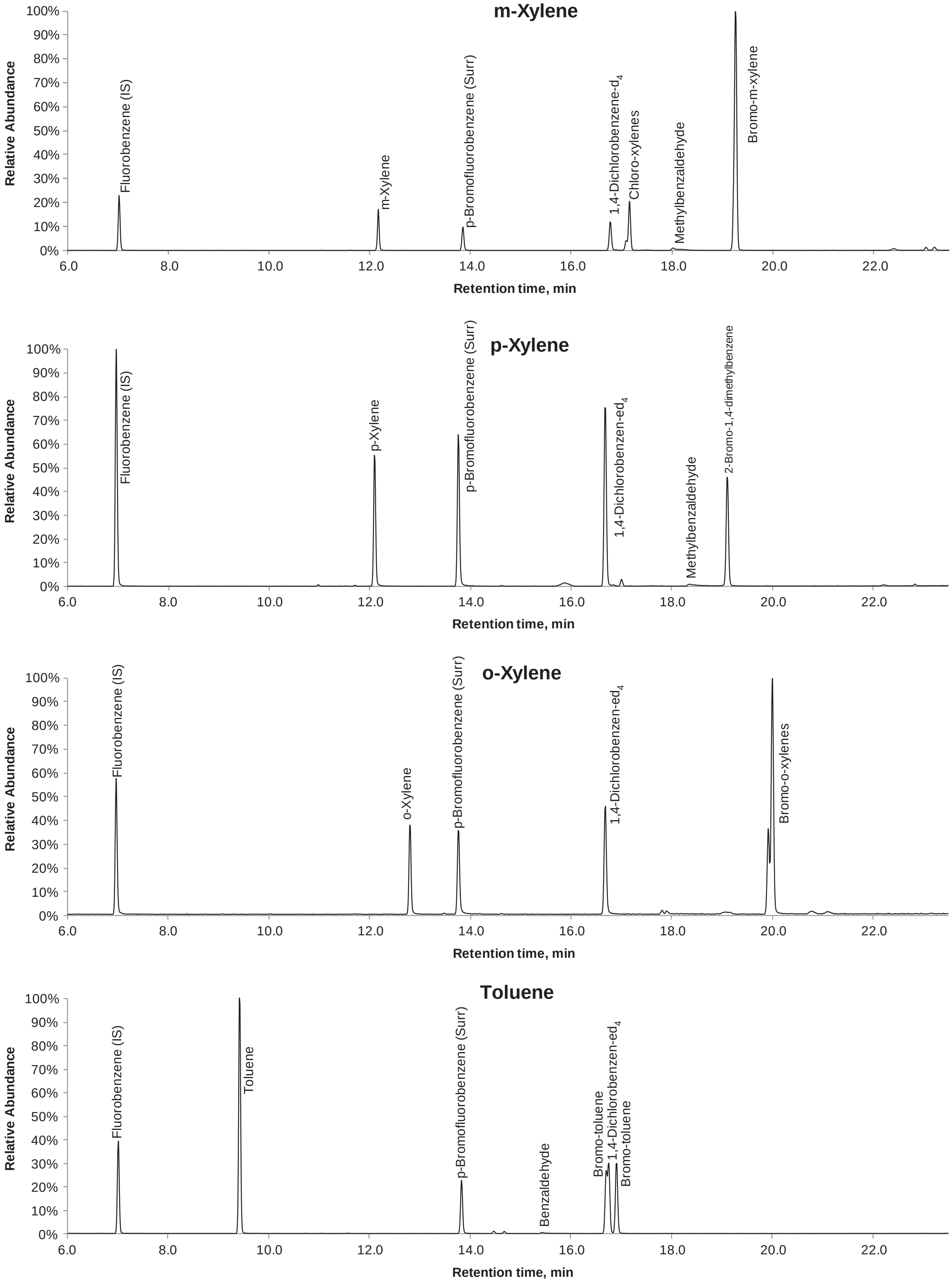

Fig. 1. Heated headspace mass chromatograms (Agilent GC/MS) illustrating the brominated reaction byproducts resulting from aqueous samples containing VOCs (m-xylene, p-xylene, o-xylene and toluene). Aqueous samples were from test reactors containing VOCs, H_2O_2, pH < 2 (resulting from quenching using H_2SO_4 (conc.)). Prior to analysis, samples were amended with sodium chloride (matrix modifier) containing bromide impurities.

total ion chromatograms (TIC) (Fig. 1). These samples were analyzed using the Agilent headspace GC/MS system. The plots reveal the presence of intense chromatographic peaks whose mass spectra correspond to brominated toluene or brominated xylenes. The identity of each brominated compound was confirmed by comparing the retention times and mass spectra of the compounds found in the samples with the authentic reference standards of the mono-brominated isomers of toluene and each of the xylenes. Some di-brominated xylenes and chloro substituted aromatics were also found in the chromatograms but at significantly lower levels.

Matrix spike samples were included within each analysis queue. These were prepared from split samples of the Fenton-like reactions which were spiked with the same VOC standard mixture that was used to prepare the calibration curves. This spike mixture contained 29 VOCs including the aromatic compounds: benzene, toluene, ethylbenzene, *m*-,*p*-,*o*-xylene, 1,2,3-,1,2,4- and 1,3,5-trimethylbenzenes (TMBs), and naphthalene. Mass chromatograms of the VOC standard mix (50 μg/L), a sample from the Fenton-like reaction of *o*-xylene, and the same *o*-xylene sample spiked at 50 μg/L with VOC compounds are provided (Fig. 2). In the chromatogram of the Fenton reaction of *o*-xylene, two brominated compounds were found: 1-bromo-2,3-dimethylbenzene and 4-bromo-1,2-dimethylbenzene. When this sample was spiked with the VOC standard mixture, peaks corresponding to trimethylbenzenes and naphthalene disappeared from the mass chromatogram and brominated aromatic compounds appeared. The spike recoveries of these aromatic compounds were determined in numerous Fenton-like reaction samples under different conditions where toluene or one of the

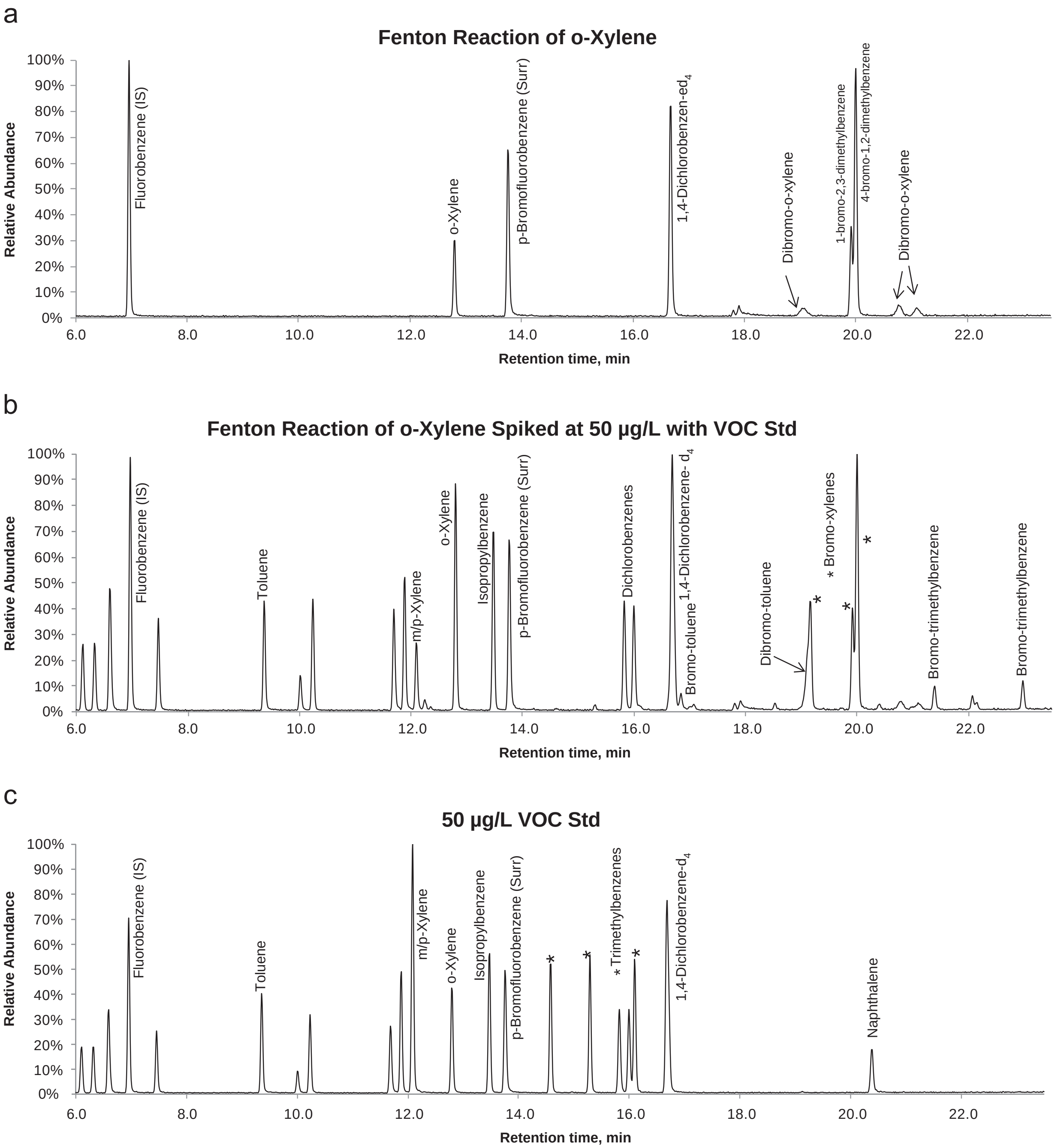

Fig. 2. Heated headspace mass chromatograms (Agilent GC/MS) of Fenton-like reaction mixtures containing H_2O_2, pH < 2 (Conc. H_2SO_4), ferric sulfate, sodium chloride used as matrix modifier, and (a) o-Xylene, (b) o-Xylene spiked with a VOC standard (50 μg/L), and (c) a VOC standard (50 μg/L).

Table 2
Percent (%) recovery of aromatic compounds spiked into Fenton-like mixture using the Agilent Headspace GC/MS system. Prior to analysis, the pH was adjusted (pH 2) with H_2SO_4 and the sample (10 mL) was added to headspace vials (20 mL) containing a sodium chloride (USP) matrix modifier. The determination of the matrix spike recovery was based on a Fenton-like reaction sample (10 mL) that was spiked (50 μg/L) with a chlorinated and aromatic VOC mixture.[a]

Reactant	Sample	Benzene	Toluene	m+p-Xylene	o-Xylene	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	Naphthalene	Brominated peaks
m-Xylene	50 μg/L spike	85	90	8.5	73	11	0.0	17	30	yes
	50 μg/L spike	87	88	57	57	6.3	0.0	6.8	8.5	yes
	50 μg/L spike	85	65	11	4.5	0.0	0.0	0.0	0.0	yes
p-Xylene	50 μg/L spike	100	59	37	25	0.7	7.1	5.0	0.0	yes
	50 μg/L spike	101	82	29	35	4.3	3.5	5.0	0.0	yes
	50 μg/L spike	100	85	35	46	6.5	3.6	6.0	0.0	yes
o-Xylene	50 μg/L spike	105	76	25	75	0.0	4.3	0.0	14	yes
	50 μg/L spike	110	61	27	41	0.0	6.2	0.0	22	yes
	50 μg/L spike	105	70	20	25	0.0	0.0	0.0	12	yes
Toluene	50 μg/L spike	100	160	13	1	0.0	0.0	0.0	0.0	yes
	50 μg/L spike	98	112	19	1.6	0.0	0.0	0.0	0.0	yes
Toluene	50 μg/L spike; no H_2O_2	106	116	105	103	100	102	104	128	no
	50 μg/L spike; no H_2O_2	101	108	104	101	101	104	98	118	no
	50 μg/L spike; no H_2O_2	101	102	97	102	92	91	95	92	no
	50 μg/L spike; no H_2O_2	95	97	95	96	81	81	85	82	no

Spike recoveries which are greater than the acceptable limit of ± 30% of the spiked concentration.

[a] Each sample contained sodium chloride salt (USP) containing bromide impurities as the matrix modifier; TMB = Trimethylbenzene.

Table 3
Percent recovery (%) of aromatic compounds spiked into Fenton-like reaction samples with different matrix modifiers, reaction times and reagents. These analyses were performed using the Varian Saturn Headspace GC/MS system. Prior to analysis, the pH was adjusted (pH 2) and the sample (10 mL) was added to headspace vials (20 mL) containing salts (2 g) (either NaCl (USP) (Fisher Scientific), NaCl (ACS) (Aldrich), or NaCl/phosphate mixture (50% w/w NaCl (ACS); 42% w/w potassium phosphate dibasic; 8% w/w potassium phosphate monobasic) (Aldrich)).[a]

Sample	Benzene	Toluene	m+p-Xylene	o-Xylene	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	Naphthalene	Brominated peaks
NaCl(USP)	96	97	100	93	51	71	70	28	yes
NaCl(USP)	95	99	104	99	78	75	81	49	yes
NaCl(ACS)	96	100	110	106	82	84	94	84	yes
NaCl(ACS)	95	97	108	105	85	84	92	84	yes
NaCl/PO_4 mix	95	97	108	99	94	93	95	76	no
NaCl/PO_4 mix	96	100	113	104	96	94	96	79	no
NaCl(USP); 8 h storage[b]	98	54	37	36	0	7.9	3.7	0	yes
NaCl(USP); no Fe^{+++}	94	97	103	102	78	81	81	55	yes
NaCl(USP); no Fe^{+++}	96	100	103	102	80	83	85	57	yes
NaCl(USP); no H_2O_2	94	100	109	108	96	95	105	90	no
NaCl(USP); no H_2O_2	93	99	109	107	95	90	101	90	no

Spike recoveries which are greater than the acceptable limit of ± 30% of the spiked concentration.

[a] TMB = Trimethylbenzene.

[b] The 8 h storage sample was prepared at the beginning of the sample queue but not analyzed until 8 h later; sample rested at room temperature until analyzed; all other samples were prepared and immediately analyzed.

xylene isomers was the starting aromatic reactant (Table 2). A correlation was established between the decrease in recovery of spiked aromatic compounds and the presence of brominated aromatic compounds (last column). The matrix spiked samples were usually analyzed at the end of the analysis queue. Poorer spike recoveries were found for aromatic compounds having increased number of methyl substitution (i.e. TMB's) and for naphthalene. The spike recovery of benzene was always within the desired quality assurance, quality control (QA/QC) acceptance criteria. In several examples, the matrix spike was done on samples that did not contain H_2O_2. The spike recoveries of aromatic compounds in these samples ranged from 81% to 128% (avg: 99%, std. dev: 10%.) All of the spike recoveries in these samples were within the QA/QC criteria of ± 30% of the expected spike concentration.

When the analysis of the Fenton-like samples was done using the Varian Saturn headspace GC/MS system, brominated compounds were not found in any of chromatograms of samples or matrix spiked samples. The one significant difference between the two headspace methods was the matrix modifier. In the Tekmar/Saturn system, the matrix modifier was the buffer salt mixture consisting of NaCl, K_2HPO_4, and KH_2PO_4. In the CombiPal/Agilent method, the matrix modifier was sodium chloride. When the buffer salt was used, the pH of the sample increased to ~6. The acidic nature of samples ($pH < 2$) containing un-buffered sodium chloride (i.e., NaCl only) was attributed to the small quantity of H_2SO_4 (conc.) used to quench the Fenton/Fenton-like reactions. No brominated toluene or xylene compounds were found in samples where the matrix was modified with the buffer salt.

Given the reagents used in the Fenton-like reaction experiments and in the headspace analysis, the only source of bromide (Br^-) was the trace amount present in the sodium chloride salt added as a matrix modifier. In USP and ACS grades of sodium chloride, the manufacturer's specifications indicate that Br^- is present at < 0.01% w/w. Since 2 g of sodium chloride is added to the 10 mL of sample, Br^- at levels less than 0.2 mg could be present in the sample. Relative to the amount of aromatic compounds spiked into the sample, the concentration of Br^- would likely be in significant excess of the aromatic compounds. Assuming a concentration of 0.01% w/w of Br^- in the NaCl salt, the bromide would be present at 250 μmol/L compared to 45 μmole/L of aromatic compounds.

3.1. Mechanistic Investigation

Several experiments were done to determine the critical reagents in the bromination reactions. The basic Fenton-like reagent mixture was prepared using ferric sulfate (5 mM), H_2O_2 (6 mM), and pH 3 using NaOH (to raise the pH to pH=3), and subsequently acidified (pH <2; H_2SO_4 (conc.)) prior to analysis to simulate actual reaction and preservation conditions. Aliquots (10 mL) of the acidified Fenton-like reagent mixture were added to separate headspace vials that contained different matrix modifiers (2 g): sodium chloride (ACS grade), sodium chloride (USP grade), and sodium chloride with a phosphate buffer (pH ≈ 6) (i.e., 50% w/w sodium chloride (ACS), 42% w/w potassium phosphate dibasic and 8% w/w potassium phosphate monobasic) (Aldrich). Each sample was spiked with the VOC mixture (50 μg/L) and internal standard/surrogates were added (100 μg/L). In one experiment, the spiked sample containing acidified Fenton-like mix and the USP sodium chloride was allowed to sit at room temperature for 8 h before the headspace analysis was started. In two other experiments, ferric sulfate or H_2O_2 were omitted. The Tekmar/Saturn headspace GC/MS system was used to analyze these samples. The sample that was allowed to react for 8 h (i.e., allowed to sit on the autosampler tray for 8 h at room temperature followed by headspace heating at 80 °C for 30 min) had complete loss of 1,3,5-trimethylbenzene and naphthalene and significant losses of toluene, *m*-,*p*-,*o*-xylenes, and 1,2,4- and 1,2,3-trimethylbenzenes (Table 3). Comparison of the samples that were heated at 80 °C for 30 min and contained USP sodium chloride or ACS sodium chloride revealed more loss of 1,3,5-trimethylbenzene and naphthalene in the USP sodium chloride sample. This may be due to a greater concentration of bromide in the USP sodium chloride. When ferric sulfate is absent, the loss of aromatic compounds still occurs to approximately the same extent as when it was present. When ferric sulfate was present but H_2O_2 was absent, no loss of aromatic compounds occurred during the heated headspace analysis indicating that ferric sulfate is not needed for the bromination to occur. Finally, the bromination effect documented in the Agilent GC/MS system using NaCl as the matrix modifier was duplicated in the Saturn GC/MS system. These results indicate that when NaCl is used for the matrix modifier, bromination of the aromatic compounds occurs at room temperature and during the time that the sample is heated in the headspace analyzer. This result indicates that the extent of aromatic compound loss depends on the amount of time that the sample rested on the autosampler tray before analysis and explains the differences between spike recoveries for aromatic compounds found in Table 2. Specifically, samples analyzed using the Varian Saturn 2100T were prepared and immediately analyzed, unless otherwise noted (i.e., 8 h storage sample set, Table 3), and samples analyzed using the Agilent 6890 GC/MS rested in the autosampler tray for varying amounts of time depending on how many sample were in the sample queue. Therefore, greater reaction time occurred in samples analyzed using the Agilent system and resulted in greater bromination and less recovery of the aromatic compounds.

4. Discussion

4.1. Bromination reaction mechanism

A mechanism for the bromination of aromatic compounds under the conditions reported here is supported by previous research involving treatment of aqueous systems containing Cl^-, Br^-, and H_2O_2, under acidic conditions [13–15] (Table 1; R5–R9). When acid is present, Cl^- from sodium chloride is protonated to form hydrochloric acid. In the presence of H_2O_2, hydrochloric acid reacts to form hypochlorous acid (HOCl) [13]. Hypobromous acid (HOBr) is then produced by the very fast and irreversible oxidation of Br^- by hypochlorous acid. When excess Cl^- is present in water containing HOBr, BrCl is formed. BrCl is a strong brominating reagent that is more reactive than HOCl, Cl_2, HOBr or Br_2. Voudrias and Reinhard [15] have reported that in the presence of HOCl (5×10^{-5} M) (pH 3; 3 h reaction), Cl^- (5×10^{-4} M), Br^- (2.5×10^{-5} M), and *p*-xylene (10^{-6} M), approximately 93% of the original *p*-xylene is converted to halogenated products with 92% of them being bromo-*p*-xylene and 1% being chloro-*p*-xylene. When the same reaction was done at pH 5.0, less than 5% bromination of *p*-xylene occurred. They further reported that in HOCl solutions containing Br^- and Cl^-, acidic protons and both Br^- and Cl^- ions catalyze the bromination of *p*-xylene. Even at relatively small Br^- concentrations as is found in NaCl salt, the initial bromination rate is higher than the initial chlorination rate. This is due to the superior electrophilic power of BrCl and H_2OBr^+.

4.2. Functionality dependency

The extent of bromination of the aromatic compounds increases as the number of methyl groups increases on the molecule. Methyl groups in aromatic compounds direct electrophilic aromatic substitution to the 2,4-positions relative to the methyl group. In toluene, the expected bromated compounds are 2-bromotoluene and 4-bromotoluene. The isomeric distribution in the bromination of toluene was reported as 33% 2-bromotoluene, 0.3% 3-bromotoluene and 67% 4-bromotoluene [16]. In 1,3,5-trimethylbenzene each of the methyl groups directs bromination equally toward each of the three open positions (2,4,6) for electrophilic substitution of bromine. This is evident when the relative reactivities of methyl substituted benzenes are compared. The relative reactivity toward bromination for benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene and 1,3,5-trimethylbenzene are reported as 1: 605: 2520: 5320: 5×10^5: 2×10^8 [16]. The spike recovery data (Table 2) for the aromatic compounds show the same trend with no bromination of benzene and complete or nearly complete loss of 1,3,5-trimethylbenzene occurred in all eleven spike recovery determinations. Similar trends are seen with 1,2,4-TMB and 1,2,3-TMB. It is suggested that the high reactivity of 1,3,5-trimethylbenzene toward BrCl could be used as a means to determine low concentrations of bromide ($<0.01\%$) in sodium chloride salt. Specifically, this would require that acidic conditions (pH <2), the presence of H_2O_2, and 1,3,5-trimethylbenzene would need to be present in excess of the bromide. The Br^- concentration could be determined by heated headspace GC/MS by reaction of an excess concentration of 1,3,5-trimethylbenzene with the Br^- impurity in sodium chloride. A standard curve could be prepared to determine the bromide in the USP and ACS sodium chloride involving the addition of incremental concentrations of sodium bromide with plots of the peak area of 2-bromo-1,3,5-trimethylbenzene. Similarly, pentamethylbenzene could be used as the bromination reagent since the bromination reaction of this compound is four times greater 1,3,5-trimethylbenzene [16].

4.3. Problem resolution

The use of a sodium chloride/phosphate buffer salt as a matrix modifier and neutralization reagent of acid/base preserved samples is a better option than using sodium chloride. Specifically, two cases are now known where neutralization of the acidified samples before heated headspace analysis prevents reactions that cause target compound loss. The first case involved the acid hydrolysis of fuel ether oxygenates: MTBE, TAME and ETBE, to form the corresponding *tert*-butyl alcohol, *tert*-amyl alcohol, ethanol and methanol [7–10]. The second case of compound loss due to a heated headspace reaction under acidic conditions is reported here and involves the reaction of aromatic compounds with BrCl formed by the reaction of H_2O_2, Cl^-, and Br^-.

Notice

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