Electronic Supplementary Information

Applications of 1,3,5-trimethoxybenzene as a derivatizing agent for quantifying free chlorine, free bromine, bromamines, and bromide in aqueous systems

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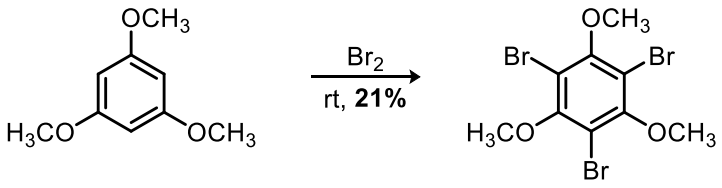
Reagent information

Table S1. List of reagents by purity and source.

Chemical	Purity/Grade	Source
1,3,5-trimethoxybenzene (TMB)	≥ 99.0 %	Sigma-Aldrich
1-bromo-2,4,6-trimethoxybenzene (Br-TMB)	98%	Oakwood Chemical
1-chloro-2,4,6-trimethoxybenzene (Cl-TMB)	98%	Sigma-Aldrich
1,3-dibromo-2,4,6-trimethoxybenzene (diBr-TMB)	> 98%	synthesized previously[1]
1,3-dichloro-2,4,6-trimethoxybenzene (diCl-TMB)	> 98%	synthesized previously[1]
1-bromo-3-chloro-2,4,6-trimethoxybenzene (BrCl-TMB)	> 99%	synthesized previously[1]
1,3,5-tribromo-2,4,6-trimethoxybenzene (triBr-TMB)	> 98%	synthesized (this work)[a]
1,3,5-trichloro-2,4,6-trimethoxybenzene (triCl-TMB)	> 98%	synthesized (this work)[a]
2-bromoanisole	97%	Sigma-Aldrich
2-chlorobenzonitrile	≥ 98%	Sigma-Aldrich
2,4,6-trichlorophenol	98%	Fisher Scientific
2,6-dichlorophenol	99%	Oakwood Chemical
4-bromoanisole	99%	Sigma-Aldrich
4-bromo-2,6-dichlorophenol	98%	Oakwood Chemical
acetonitrile	HPLC grade	Fisher Scientific
aluminum chloride anhydrous	98.5%	Acros Organics
ammonium chloride	99.5%	Fisher Scientific
anisole	99.7%	Sigma-Aldrich
bromide certified standard solution[b]	1003 mg L^{-1}	Sigma-Aldrich
dimethenamid-P	95.4%	ChemService Inc.
bromo-dimethenamid-P	> 98%	synthesized[1]
chloro-dimethenamid-P	> 98%	synthesized[1]
formic acid	HPLC grade	Fisher Scientific
hydrochloric acid	Certified ACS plus	Fisher Scientific
hydrochloric acid	Certified ACS Plus	Fisher Chemical
hydrochloric acid	ultrapure	J.T. Baker
iron (III) chloride anhydrous	98%	Acros Organics
iron (III) chloride hexahydrate	≥ 99%	Acros Organics
iron (III) chloride hexahydrate, lump	≥ 98%	Fisher Scientific
methanol	99.9%	Fisher Scientific
nitric acid	ACS grade	Fisher Scientific
N,N-diethyl-1,4-phenylenediamine sulfate (DPD) solution	99%	Ricco Chemicals
potassium iodide	99%	J. T. Baker
potassium iodate	99%	J. T. Baker
sodium bicarbonate (ACS reagent)	≥ 99.7%	Acros Organics
sodium bicarbonate (extra pure)	≥ 99%	Acros Organics
sodium bromide	99.5%	Sigma-Aldrich
sodium chloride (higher purity)	99.999%	Sigma-Aldrich
sodium chloride (lower purity)	≥ 99.0%	Fisher Scientific
sodium chloride (pool salt)	not reported	Clorox
sodium chloride (table salt), no added iodide[c]	not reported	Morton Salt
sodium hydroxide	50%	Fisher Scientific
sodium hypochlorite solution	5.65-6%	Fisher Scientific
sodium iodide dihydrate	99+%	Acros
sodium nitrate	≥ 99.0 %	Sigma-Aldrich
sodium phosphate dibasic	ACS reagent	Acros
sodium sulfate anhydrous	99.9%	Fisher Scientific
sodium tetraborate decahydrate	99.5%	Acros
sodium thiosulfate pentahydrate	99.5–101.0%	Alfa Aesar
starch	ACS reagent	Fisher Scientific
toluene	99.9%	Fisher Scientific

[a] Synthetic method and characterization details provided below.
[b] Aqueous solution with a certified concentration of bromide traceable to National Institute of Standards and Technology (NIST, USA) primary standard NIST SRM 999b.
[c] Contains calcium silicate as an anticaking agent; amount not specified by manufacturer

Synthesis of 1,3,5-tribromo-2,4,6-trimethoxybenzene



To a 20 mL vial was added neat bromine (1.07 mL, 20.8 mmol, 7.00 eq.). Solid 1,3,5-trimethoxybenzene (500 mg, 2.97 mmol, 1.00 eq.) was added cautiously in a single portion behind a blast shield, the vial was tightly capped, and a vigorous reaction ensued. Initially, some black solid remained on the sides of the vial, but this was gradually rinsed down by carefully rotating the vial. After two hours, a homogeneous dark red solution was obtained. The uncapped vial was then left in the back of a fume hood overnight so that the excess bromine could evaporate. The resulting orange solid was partitioned between diethyl ether and 10% aqueous sodium sulfite solution. The layers were thoroughly mixed and separated, and the aqueous phase was extracted with one additional portion of diethyl ether. The combined organic phases were then dried over anhydrous magnesium sulfate. TLC (3:1 hexanes / ethyl acetate, UV / anisaldehyde stain) showed complete consumption of the 1,3,5-trimethoxybenzene (R_f =0.50, stains red) and formation of several products, including the desired tribromide of R_f = 0.25 (does not stain). The solvent was removed under reduced pressure to give 1.17 g (97%) of the crude product as an off-white solid. This material was recrystallized once from 95% ethanol and dried under high vacuum to afford the pure product as fluffy white needles (258 mg, 21%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 60.9, 110.3, 155.1.

This synthesis was based on a procedure reported by Kiehlmann and Lauener.[2]

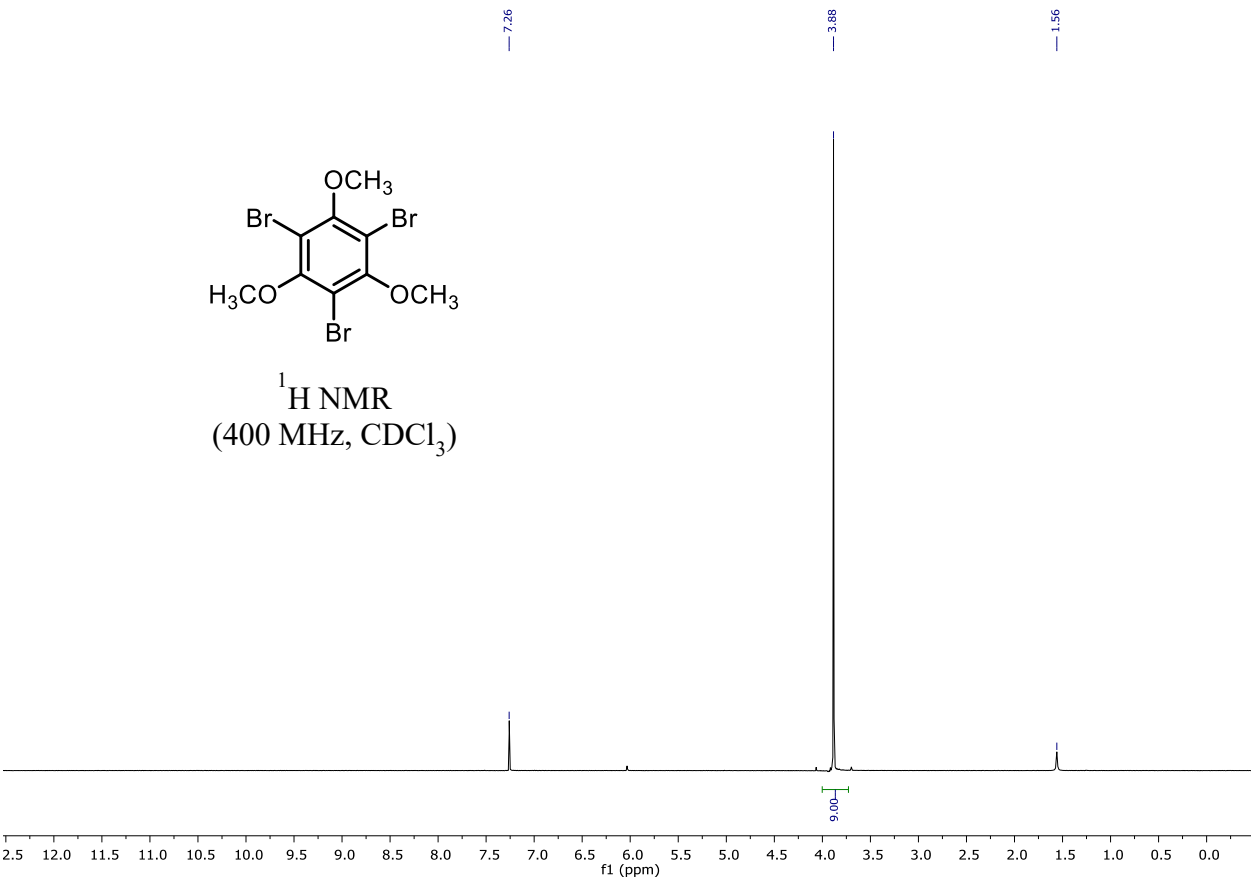


Figure S1. ^{1}H NMR spectrum of 1,3,5-tribromo-2,4,6-trimethoxybenzene.

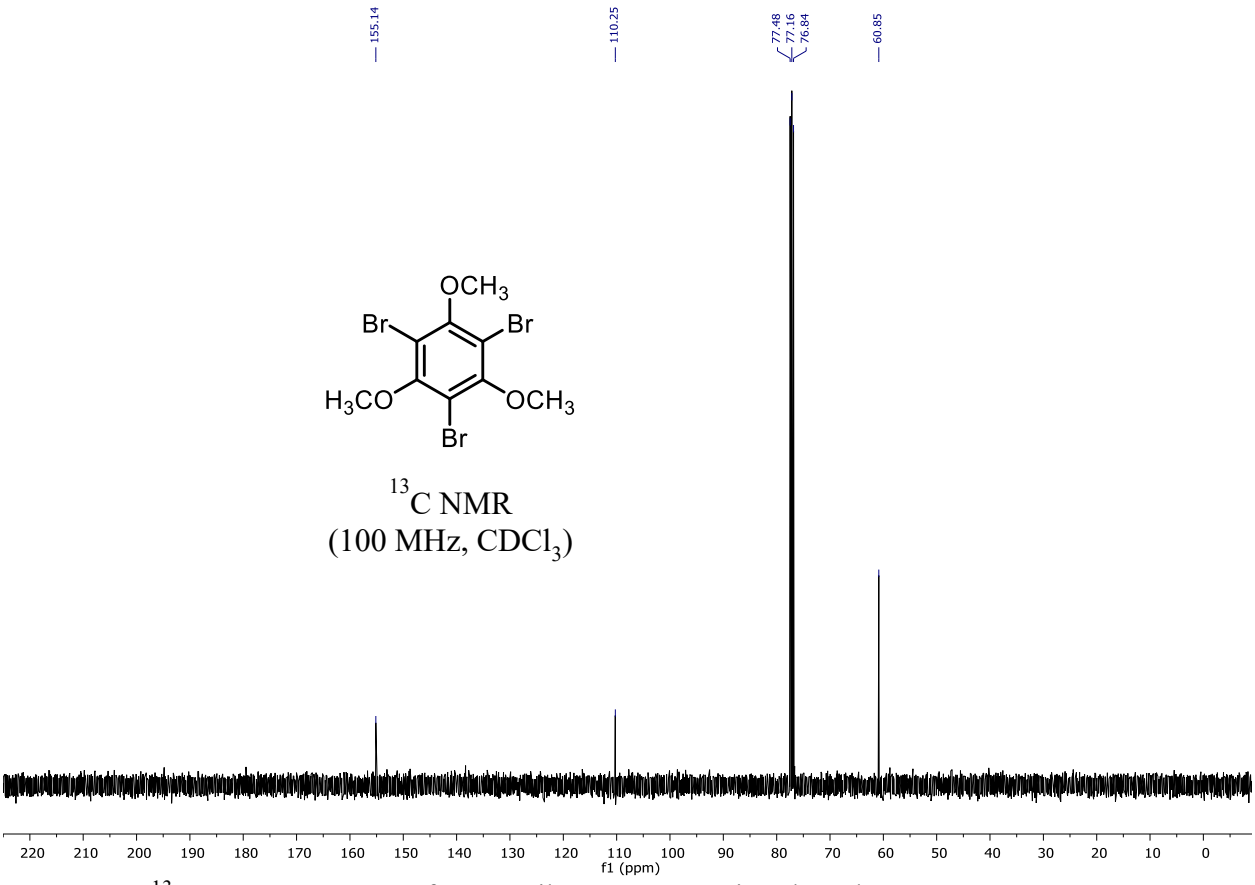
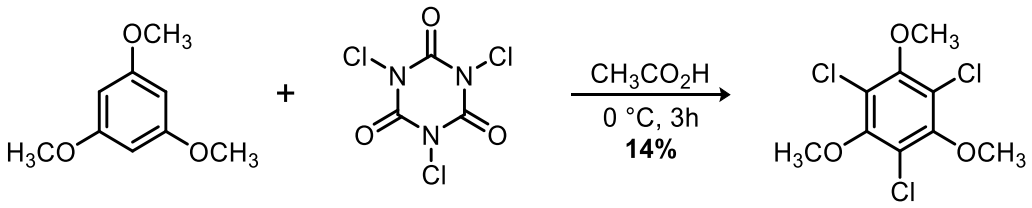


Figure S2. ^{13}C NMR spectrum of 1,3,5-tribromo-2,4,6-trimethoxybenzene.

Synthesis of 1,3,5-trichloro-2,4,6-trimethoxybenzene



To a 50 mL round bottom flask equipped with a magnetic stirring bar was added a solution of 1,3,5-trimethyoxybenzene (1.00 g, 5.95 mmol, 1.00 eq.) in 12 mL of ethyl acetate. This solution was cooled to 0 °C in an ice bath, and neat acetic acid (588 μL, 10.3 mmol, 1.73 eq.) was added via autopipette. A solution of trichloroisocyanuric acid (1.65 g, 7.09 mmol, 1.19 eq.) in 6 mL of ethyl acetate was then added dropwise over the course of 15 minutes. After addition was complete, the reaction mixture was stirred at 0 °C for 3 hours before it was quenched with 1 mL of 10% aqueous sodium sulfite solution. The reaction mixture was diluted with water, aqueous sodium hydroxide solution (1 M), and additional ethyl acetate and transferred to a separatory funnel. After separation of the layers, the organic phase was washed with two additional portions of aqueous sodium hydroxide solution (1 M) before drying over anhydrous sodium sulfate. The drying agent was removed by filtration, and the solvent was removed under reduced pressure to give 1.53 g (95%) of the crude product as a light yellow solid. This material was recrystallized twice from absolute ethanol and dried under high vacuum to afford the pure product as a white solid (220 mg, 14%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 61.1, 120.7, 152.4.

This synthesis was based on a procedure reported by Daraie *et al*.[3]

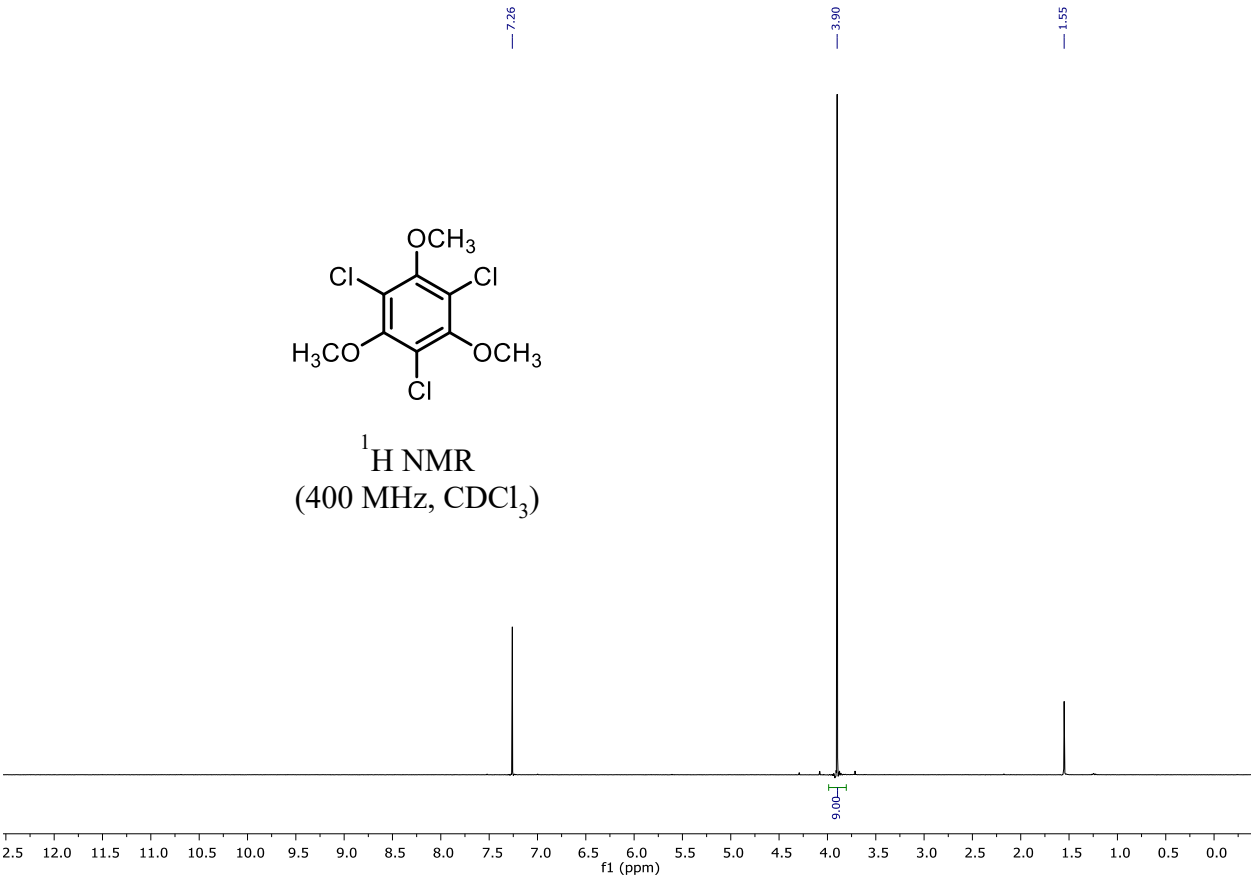


Figure S3. ^{1}H NMR spectrum of 1,3,5-trichloro-2,4,6-trimethoxybenzene.

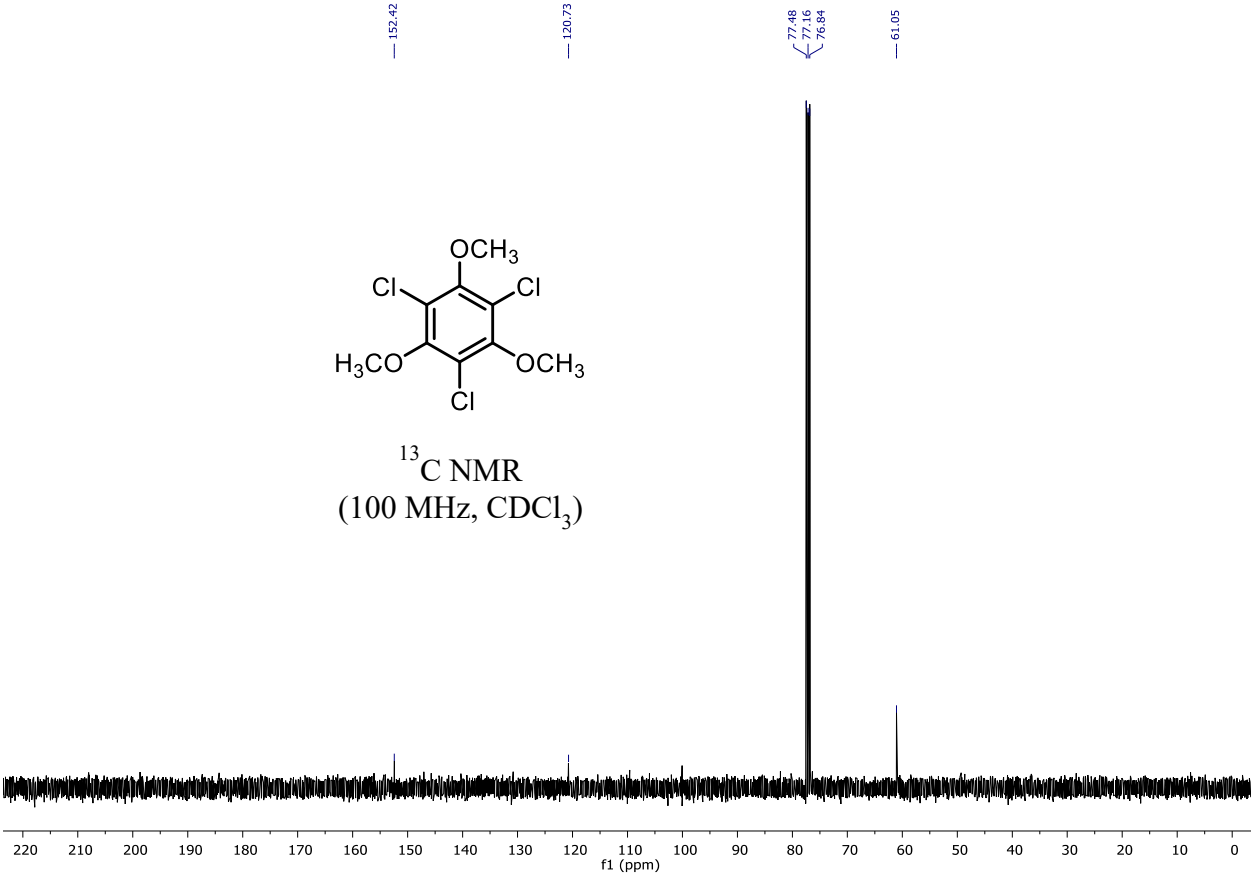


Figure S4. ^{13}C NMR spectrum of 1,3,5-trichloro-2,4,6-trimethoxybenzene.

Additional experimental methods

Determination of a Beer's Law constant (ε) of hypochlorite ion. Sodium hypochlorite stock solutions (~6% w/w) were standardized using iodometric titrimetry according to standard methods.[4] An aliquot of this solution (100 μL) was diluted in 40 mL of a sodium hydroxide solution (10 mM, pH > 11). The wavelength monitored by the spectrophotometer for hypochlorite ion was 295 nm (λ_{max}). The standardized hypochlorite concentration and the absorbance of this solution measured at 295 nm (21 ± 1 °C) were substituted into the Beer-Lambert's Law equation to yield an experimentally determined value of $\varepsilon_{OCl^-} = 365.8\ M^{-1}\ cm^{-1}$ (%RSD = 0.2%).

Mass balance considerations. In addition to generating Cl-TMB and Br-TMB, when TMB is not added in sufficient excess of the total free halogen concentration, Cl-TMB and Br-TMB could undergo subsequent halogenation to give dihalogenated products, including 1,3-dichloro-2,4,6-trimethoxybenzene (diCl-TMB), 1,3-dibromo-2,4,6-trimethoxybenzene (diBr-TMB), and 1-bromo-3-chloro-2,4,6-trimethoxybenzene (BrCl-TMB). When formation of dihalogenated products of TMB is non-negligible, mass balances corresponding to TMB, residual free chlorine, and residual free bromine can be computed as:

$$[\text{TMB}]_{\text{tot}} = [\text{TMB}] + [\text{Cl-TMB}] + [\text{diCl-TMB}] + [\text{Br-TMB}] + [\text{diBr-TMB}] + [\text{BrCl-TMB}] \quad \text{(S1)}$$

$$[\text{HOCl}]_{\text{res}} = [\text{Cl-TMB}] + 2[\text{diCl-TMB}] + [\text{BrCl-TMB}] \quad \text{(S2)}$$

$$[\text{HOBr}]_{\text{res}} = [\text{Br-TMB}] + 2[\text{diBr-TMB}] + [\text{BrCl-TMB}] \quad \text{(S3)}$$

Chlorine or bromine substitution onto TMB is anticipated to decrease the reactivity of the products toward further halogenation due to (1) the decreased number of ring positions available for substitution and (2) the propensity of chlorine and bromine to deactivate aromatic systems toward electrophilic aromatic substitution.[5] Hence, reactions of free halogens with dihalogenated forms of TMB are likely to be slow, particularly when TMB is present in excess of the initial free halogen concentration (as was always the case herein). Nevertheless, the method described herein is capable of quantifying TMB as well as its mono-, di-, and selected trihalogenated products, including 1,3,5-trichloro-2,4,6-trimethoxybenzene (triCl-TMB) and 1,3,5-tribromo-2,4,6-trimethoxybenzene (triBr-TMB).

GC-MS method details. Toluene samples (1.0 μL) containing TMB and its halogenated products were analyzed on an Agilent 7890A GC interfaced with an Agilent 5975C MS. An Agilent DB-35MS UI column (30 m, 0.250 mm inner diameter, 0.25 μm film thickness) was used to effect separations for most experiments; selected experiments were performed using an Agilent DB-5MS column (30 m, 0.250 mm inner diameter, 0.25 μm film thickness). For both columns, the GC inlet was set to 260 °C and operated in splitless mode. The total column flow was constant at 1.0 mL min^{-1}. The oven temperature program included an initial temperature of 70 °C (0.5 min hold), ramp at 20 °C min^{-1} to 190 °C (no hold time), ramp at 10 °C min^{-1} to 290 °C (no hold time); the total analysis time was 16.5 min. The transfer line was fixed at 280 °C. Retention times and ions quantified in selected ion monitoring mode for each analyte are shown in **Table S2**. An example GC-MS chromatogram is shown in **Figure S5**.

Table S2. GC-MS selected ion monitoring (SIM) method details for analysis of TMB and its halogenated products

Analyte	SIM Group	Retention Time (min)[a]	Quantitation Ion (m/z)	Monitoring Ion (m/z)	Extraction Efficiency
2-chlorobenzonitrile (internal standard)[b]	A	5.62	137 $M^{+\bullet}$	102 $(M - Cl)^+$	not determined[c]
1,3,5-trimethoxybenzene (TMB)[b]	B	7.21	168 $M^{+\bullet}$	137 $(M - OCH_3)^+$	103%
1-chloro-2,4,6-trimethoxybenzene (Cl-TMB)[b]	C	9.18	202 $M^{+\bullet}$	204 $M^{+\bullet}$ (^{37}Cl)	104%
1,3,5-trichloro-2,4,6-trimethoxybenzene (triCl-TMB)	D	9.61	270 $M^{+\bullet}$	272 $M^{+\bullet}$ (^{37}Cl)	92%
1,3-dichloro-2,4,6-trimethoxybenzene (diCl-TMB)[b]	E	10.04[d]	236 $M^{+\bullet}$	238 $M^{+\bullet}$ (^{37}Cl)	99%
1-bromo-2,4,6-trimethoxybenzene (Br-TMB)[b]			246 $M^{+\bullet}$	248 $M^{+\bullet}$ (^{81}Br)	95%
1-bromo-3-chloro-2,4,6-trimethoxy-benzene (BrCl-TMB)[b]	F	10.96	282 $M^{+\bullet}$ (^{35}Cl, ^{81}Br)	280 $M^{+\bullet}$ (^{35}Cl, ^{79}Br)	111%
1,3-dibromo-2,4,6-trimethoxybenzene (diBr-TMB)[b]	G	11.93	326 $M^{+\bullet}$ (^{79}Br, ^{81}Br)	324 $M^{+\bullet}$ (^{79}Br, ^{79}Br)	112%
1,3,5,-tribromo-2,4,6-trimethoxybenzene (triBr-TMB)	H	12.56	404 $M^{+\bullet}$ (^{81}Br)	406 $M^{+\bullet}$ (^{81}Br, ^{81}Br)	71%

[a] Retention times correspond to experiments performed on an Agilent DB35-MS UI column (30 m, 0.250 mm inner diameter, 0.25 μm film thickness).

[b] Method parameters and extraction efficiencies of these analytes were previously reported.[1]

[c] Raw peak areas of analytes were normalized to the peak area of the internal standard before the concentrations of the analytes were computed from linear regressions of external calibration standards. The extraction efficiency of the internal standard was not determined as it was not used in our computations.

[d] diCl-TMB and Br-TMB co-eluted at 10.03 min; the quantitation and monitoring ions of diCl-TMB and Br-TMB were different, which permitted quantitation of both analytes in SIM mode despite incomplete chromatographic separation. Baseline resolution of diCl-TMB and Br-TMB were, however, achieved in selected experiments performed using an Agilent DB5-MS column (30 m, 0.250 mm inner diameter, 0.25 μm film thickness); see example chromatograms below.

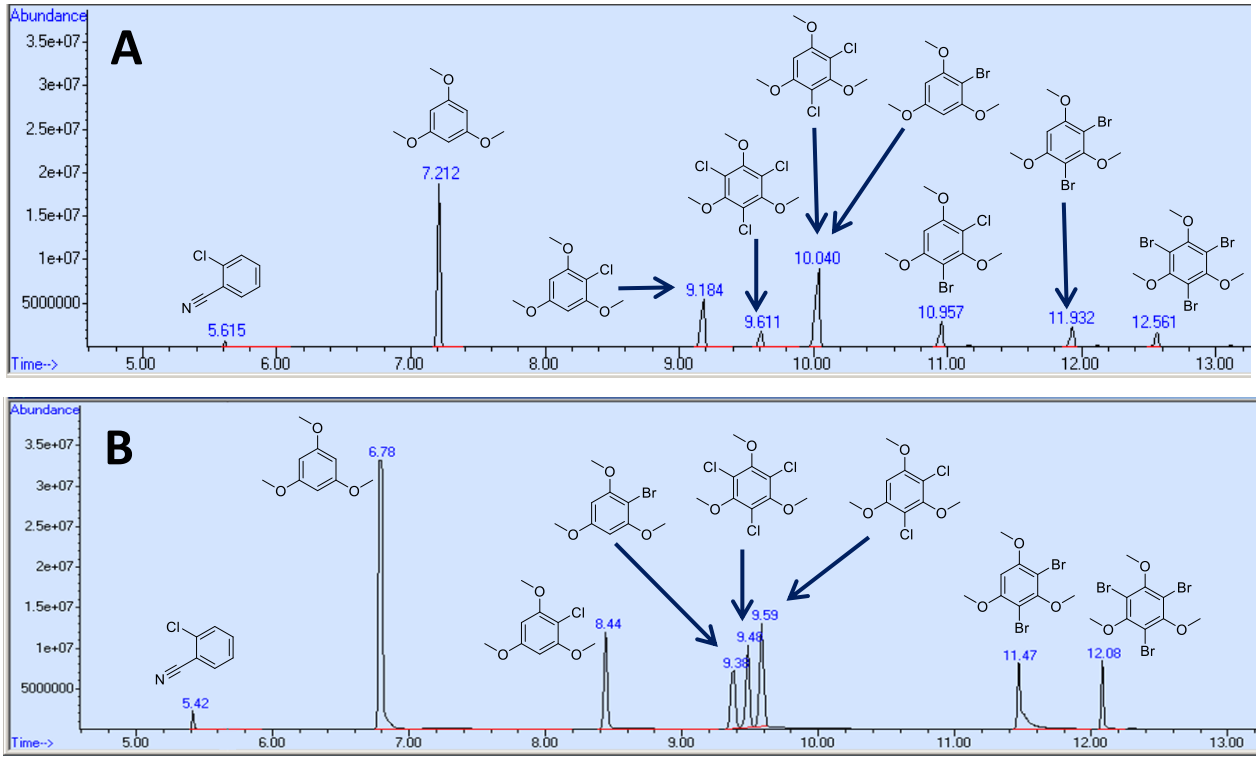


Figure S5. GC-MS selected ion monitoring chromatogram of 1,3,5-trimethoxybenzene (TMB) and its chlorinated and brominated analogues obtained on an Agilent (**A**) DB-35MS and (**B**) DB-5MS column (see p. S9 for additional column details). 2-Chlorobenzonitrile served as the internal standard; the retention time of BrCl-TMB was not determined on the DB-5MS column.

HPLC method details for TMB, 2,6-dichlorophenol (DCP), and their halogenated products. Samples (injection volume = 10 µL) were separated using an Agilent Poroshell 120 EC-C18 column (50 mm length, 2.1 mm inner diameter, and 2.7 µm particle size) and isocratic elution with a mobile phase (0.500 mL/min) consisting of either (1) 68 vol% 18 MΩ·cm water and 32 vol% acetonitrile or (2) 64 vol% 18 MΩ·cm water and 36 vol% acetonitrile. Mobile phase composition 1 was employed for TMB and its halogenated products; mobile phase composition 2 was employed for DCP and its halogenated products. The wavelengths monitored by the diode array detector for signal quantitation were 266 nm (TMB), 271 nm (Cl-TMB, Br-TMB), and 240 nm (DCP and its halogenated products). The elution times of TMB, Cl-TMB, Br-TMB were 2.59, 3.54, and 4.28 min, respectively. The elution times of DCP, 2,4,6-trichlorophenol, and 4-bromo-2,6-dichlorophenol were 1.32, 2.99, and 3.51 min, respectively. The total run time was 5.00 min. Example HPLC chromatograms are shown in **Figure S6**.

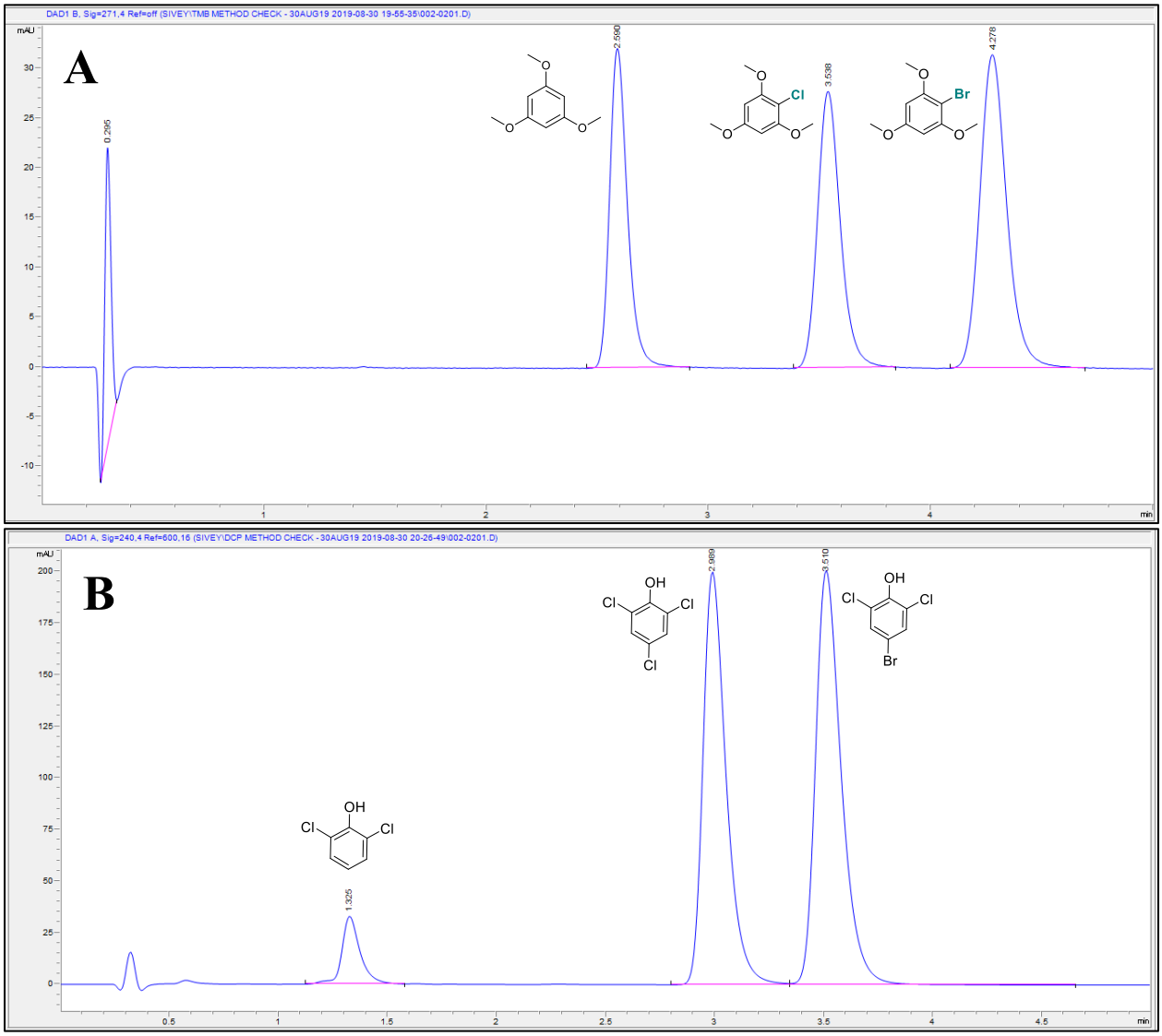


Figure S6. HPLC chromatogram of a solution containing (**A**) TMB, Cl-TMB, and Br-TMB or (**B**) DCP, 2,4,6-trichlorophenol, and 4-bromo-2,6-dichlorophenol.

Determination of water quality metrics. The pH of synthetic aqueous solutions and natural waters was measured using a double-junction combination electrode (accumet^{TM} Fisher) with automatic temperature compensation. The pH electrode was calibrated daily using certified buffer solutions with nominal pH values of 4.01, 7.00, and 10.01. Concentrations of chloride ion and bromide ion were determined using a combination chloride ion-selective electrode (ISE, Thermo Scientific Orion) and a combination bromide ISE (accumet^{TM} Fisher). ISEs were calibrated daily using solutions prepared from crystalline NaCl (99.999%) and NaBr (99.5%). Dissolved organic carbon was measured via a total carbon analyzer (Shimadzu TOC-V_{CSH}) for pre-filtered samples (0.2 μm nylon syringe filter). Ultraviolet (UV) absorbance measurements were obtained using quartz cuvettes (1.00-cm pathlength) and an Agilent Cary 60 UV-visible spectrophotometer.

Chemical characteristics of surface water samples

Table S3. Summary table of water quality metrics of natural water sources.

Water Source	pH	$[Cl^-]$ (mM)	$[Br^-]$ (μM)	$[Cl^-]/[Br^-]$	[DOC] (mg L^{-1})	$SUVA_{254}$ (L mg^{-1} cm^{-1})[a]	$CDOM_{440}$ (m^{-1})[b]
Chesapeake Bay	7.77	187	892	210	4.94	0.011	0.564
Atlantic Ocean	7.88	513	2318	221	4.03	0.0062	0.070
Susquehanna River	7.76	0.477	1.80	265	5.36	0.013	0.330
Loch Raven Reservoir	8.31	1.32	4.52	291	5.14	0.0085	0.198

[a] Specific UV absorbance at 254 nm, $SUVA_{254} = \frac{A_{254nm}}{b \cdot [DOC]}$, where A_{254nm} = absorbance at 254 nm, b = pathlength (cm), and [DOC] = concentration of dissolved organic carbon (mg L^{-1}).

[b] Colored dissolved organic matter, $CDOM_{440} = \frac{A_{440nm}}{b}$, where $A_{440\,nm}$ = absorbance at 440 nm.

Analysis of chlorinated drinking water samples

Table S4. Sampling locations and free chlorine residuals quantified in drinking water samples.

Sampling Location[a]	Date (Month/Day/Year)	Free Chlorine Residual ± 95 % Confidence Interval	
		μM	mg/L as Cl_2
Drinking Fountain, Smith Hall, Floor 5	8 Nov 2016	10 ± 2	0.71 ± 0.14
Bathroom Sink, Smith Hall, Floor 5	9 Jan 2017	3 ± 4	0.2 ± 0.3
Drinking Fountain, University Union, Floor 2	8 Nov 2016	15 ± 2	1.07 ± 0.14
	10 Nov 2016	16 ± 2	1.14 ± 0.14
	16 Dec 2016	17 ± 1	1.21 ± 0.07
	9 Jan 2017	10 ± 3	0.7 ± 0.3

[a] All sampling locations are from Towson University (Towson, Maryland, USA). Refer to main text (Section 2.3) for more details on sampling locations and procedures.

Reagents for bromide impurity tests

Table S5. Identities and initial concentrations of reagents tested for bromide impurities.

Reagent	Initial Concentration (mol L^{-1})	Reagent	Initial Concentration (mol L^{-1})
NaCl (99.999%)	1.0	HNO_3	1.2
NaCl (99.0%)	1.0	HCl (Fisher Scientific)	0.97
NaCl (pool salt)	1.2	HCl (Fisher Chemical)	0.97
NaCl (table salt)[a]	1.0	HCl (J.T. Baker)	0.97
$NaNO_3$	1.0	NaOH	1.4
NH_4Cl	0.31	$FeCl_3$ (anhydrous)	0.55
$Na_2B_4O_7 \cdot 10\ H_2O$	0.50	$FeCl_3 \cdot 6\ H_2O$	0.52
Na_2HPO_4	0.50	$FeCl_3 \cdot 6\ H_2O$ (desiccated)	0.55
$NaHCO_3$ (extra pure)	0.50	$FeCl_3 \cdot 6\ H_2O$ (lump)	0.55
$NaHCO_3$ (ACS reagent)	0.50	$AlCl_3$ (anhydrous)	0.55

[a] Also contains calcium silicate as an anticaking agent (amount not specified by manufacturer)

Analytical metrics for TMB

Table S6. Method detection limits (MDL), method quantitation limits (MQL), and instrument upper limits of linearity (LOL) of TMB by HPLC and GC-MS.

Method	Analyte	MDL	MQL	LOL	Slope $\left(\frac{\text{peak area}}{\mu g\ L^{-1}\ as\ Cl_2}\right)$
		µM	µM	µM	
HPLC	TMB	7	20	700	1.340 ± 0.014
GC-MS	TMB	1.5	5	240	870 ± 180

[a] MDL (3s/m) and MQL (10s/m) values account for preconcentration (e.g., associated with liquid-liquid extraction prior to GC-MS analysis) and extraction efficiencies (Table S2).

Comparison of TMB and DPD free halogen quantitation

Table S7. Summary of paired Student's t test results between DPD and TMB GC-MS methods for pool water.[a]

Sample #	Total Free Halogen Concentration (µM)			Significantly Different at 95% Confidence Level?
	DPD method	TMB method	Difference	
1	26.07	25.14	0.93	No (p-value = 0.996)
	25.87	24.61	1.26	
	25.79	27.96	–2.17	
2	27.56	27.81	–0.25	No (p-value = 0.156)
	28.40	31.71	–3.31	
	27.86	31.51	–3.65	
3	28.31	27.75	0.56	No (p-value = 0.108)
	28.92	27.59	1.33	
	28.39	27.95	0.44	
4	29.24	27.88	1.36	No (p-value = 0.213)
	29.30	28.23	1.07	
	29.32	29.39	–0.08	

[a] Pool water samples were collected from an indoor swimming pool in Baltimore County, Maryland, USA; p-values are two-tailed.

Control experiments associated with background salt interference studies

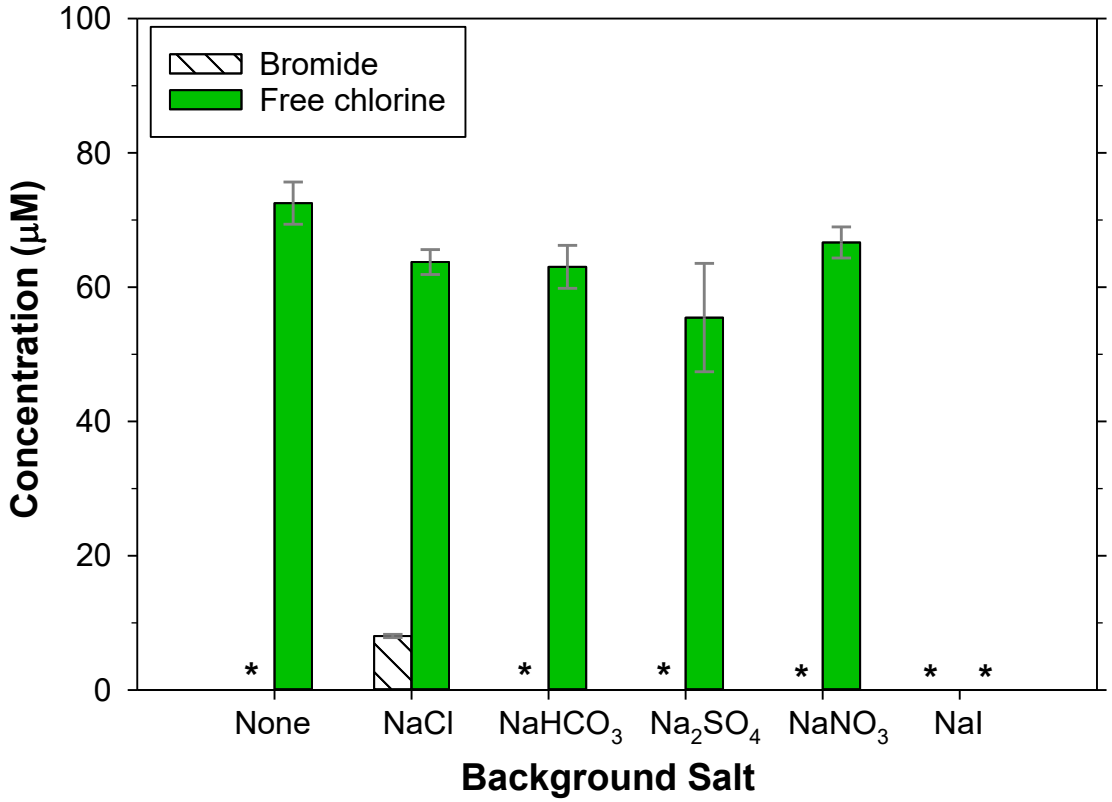


Figure S7. Influence of background salts on quantification of bromide and total free chlorine via derivatization with TMB to give Br-TMB and Cl-TMB. Conditions: No added NaBr, [background salt]$_o$ = 1.00 M (excepting NaI, which was added at 0.200 mM as NaI•2H$_2$O), [NaOCl]$_o$ = 0.100 M. Experimental conditions are summarized in Table 1 (main text). Free chlorine calculated as [Cl-TMB] + [Br-TMB] (eq 5, main text). Error bars denote 95% confidence intervals. Asterisks (*) denote not detected.

Free chlorine recovery from background salt interference studies

For background salt interference studies performed in the absence of added NaBr (**Figure S7**), free chlorine recoveries ranged from 55% to 73%. A similar range of free chlorine recoveries (56% – 76%) were observed for analogous experiments performed in the presence of 30 μM NaBr (**Figure 1**, main text). Across all background salt experiments (**Table 1**), mass balances on TMB ($[TMB]_{tot} = [TMB] + [Cl\text{-}TMB] + [Br\text{-}TMB]$) ranged from 89% to 99% (average ± 95% confidence interval = 94% ± 6%). The incomplete recovery of free chlorine, concurrent with TMB mass balances not significantly different from 100%, is consistent with kinetic limitations on the rate of TMB chlorination (but not bromination). All of the background salt solutions (**Table 1**) are moderately alkaline, with pH values calculated by Visual MINTEQ[6] in the range of 8.5 – 8.8.

These solution conditions can be used to estimate half-lives associated with TMB halogenation by free chlorine and by free bromine based on published rate constants.[1,7] The calculated half-lives for chlorination ranged from 1 to 4 min (average = 3 min). The calculated half-lives for bromination were all < 1 s. TMB-quenched samples were permitted to react with free chlorine/bromine for ~5 min prior to performing liquid-liquid extractions, which is consistent with theoretical free chlorine recoveries ranging from 56% to 98% and bromide recoveries of approximately 100%. While the objective of these experiments was quantitation of bromide, if complete recovery of free chlorine is desired, longer incubation times (prior to extraction) can be employed and/or the solution pH can be decreased 6 – 7, noting that (at near-neutral pH) reactions of TMB with free chlorine increase with decreasing pH.[7] Examples of specific conditions amenable to complete recovery of free chlorine (and free bromine) are described in Lau et al.[1]

References

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