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Trihaloforms in Humic Acid Reactions by GC-MS

Purpose

In this experiment, trihaloforms in humic acid reaction mixtures were determined by GC-MS and concentrations analyzed. Internal standard 2-bromo-1-chloropropane ($ClCH_2CHBrCH_3$) was used for GC calibration, and 1000 ppm standard containing four trihalomethanes ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$) was used to determine extraction efficiency.

Data and Procedure

We added 100 mL Humic Acid solution (TOC = 0.25 g carbon/L) to five 250 mL Erlenmeyer flasks and transferred 1, 2, 3, 4, 5 mL of the 2.5 g/L KBr into five flasks. Additional 5 mL of bleach was transferred to each with 30 minute string so that approximate molar ratios of Br:Cl:TOC by weights are (1) 0.01:1.93:1, (2) 0.02:1.93:1, (3) 0.03:1.93:1, (4) 0.04:1.93:1, (5) 0.05:1.93:1 respectively for five humic acid solutions. After quenching by 1 g of hydroxylamine hydrochloride and 1g of sodium bisulfite, haloforms in 25 mL aliquots were extracted by 10.0 mL pentane. 100 µL of 1000 ppm standard in 25.0 mL deionized water and 10.0 mL pentane was prepared as extraction mixture; 20 µL internal standard was added to 2.0 mL aliquots of pentane layers transferred in each mixture for GC-MS analysis; standards mixture with 10 ppm of four trihaloforms and internal standard was also analyzed for calibration, as shown in Tables 1-7. The peaks elute in the following order: [1] $CHCl_3$, [2] $CHBrCl_2$, [3] $ClCH_2CHBrCH_3$, [4] $CHBr_2Cl$, [5] $CHBr_3$, which correspond to peak numbers, with their retention times, peak height, corrected area, and % area of total.

Table 1: 10 ppm standard

Peak #	R.T. min	Peak Height	Corr. Area	% of total
1	2.086	82909	2234934	35.246%
2	2.687	58471	1329684	20.969%
3	3.398	34546	709983	11.197%
4	3.597	51620	1005542	15.858%
5	4.779	43598	762122	12.019%

Table 2: Extraction

Peak #	R.T. min	Peak Height	Corr. Area	% of total
1	2.080	33434	1024179	26.776%
2	2.682	37285	933218	24.398%
3	3.394	22286	465586	12.172%
4	3.593	37114	762408	19.933%
5	4.778	29122	507165	13.259%

Table 3: Br mixture #1

Peak #	R.T. min	Peak Height	Corr. Area	% of total
1	2.079	28252	884662	31.854%
2	2.681	30059	776939	27.975%
3	3.393	24203	509907	18.360%
4	3.593	19630	402103	14.478%
5	4.777	2188	39033	1.405%

Table 4: Br mixture #2

Peak #	R.T. min	Peak Height	Corr. Area	% of total
1	2.088	20901	520224	15.945%
2	2.690	41128	851787	26.108%
3	3.401	23720	433497	13.287%
4	3.601	54802	981110	30.072%
5	4.781	15706	258308	7.917%

Table 5: Br mixture #3

Peak #	R.T. min	Peak Height	Corr. Area	% of total
1	2.077	18964	448620	7.051%
2	2.681	50412	1299737	20.428%
3	3.393	26860	592114	9.306%
4	3.593	98287	2203069	34.626%
5	4.775	75790	1424236	22.385%

Table 6: Br mixture #4

Peak #	R.T. min	Peak Height	Corr. Area	% of total
1	2.065	9947	226713	2.678%
2	2.659	42975	1244889	14.704%
3	3.380	38484	819078	9.675%
4	3.580	133483	2839446	33.538%
5	4.768	163296	2921220	34.504%

Table 7: Br mixture #5

Peak #	R.T. min	Peak Height	Corr. Area	% of total
1	2.082	7068	214467	4.197%
2	2.684	24950	652809	12.776%
3	3.395	22110	470430	9.206%
4	3.595	72889	1523082	29.807%
5	4.777	113454	2027774	39.684%

Calculations and Results

(a) Response factors (F) for each compound with respect to the internal standard is given by Equation (1)

$$F = \frac{A_c \,/\, C_c}{A_{IS} \,/\, C_{IS}}$$

where A_c and C_c are the area and the concentration for a give compound, and A_{IS} and C_{IS} are the area and the concentration for the internal standard ($ClCH_2CHBrCH_3$). For the standard solution containing 10 ppm of chloroform and 10 ppm of internal standard, the peak areas are 2234934 and 709983 units respectively, and the response factor is

$$F = \frac{(2234934/10)}{(709983/10)} = 3.15$$

The response factors of other compounds are calculated as shown in Table 8.

Table 8: Response Factors from 10ppm Standard

Compound	Response Factor (F)	Concentration (ppm)	Corr. Area
$CHCl_3$	3.15	10	2234934
$CHBrCl_2$	1.87	10	1329684
$ClCH_2CHBrCH_3$	1.00	10	709983
$CHBr_2Cl$	1.42	10	1005542
$CHBr_3$	1.07	10	762122

Extraction efficiency (EE) is calculated by comparing the area ratios of each trihaloforms (X) to the internal standard (IS) from the extracted deionized water sample to the same ratios from the 100 ppm standard, as given by Equation (2)

$$EE = \frac{(A_X/A_{IS})_{extract}}{(A_X/A_{IS})_{standard}}$$

The peak areas of chloroform and the internal standard in extraction are found to be 1024179 and 465586, and the area generated from 10 ppm chloroform and internal standard are 2234934 and 709983 as previously given in Table 8. The extraction efficiency is shown:

$$EE_{CHCl_3} = \frac{(1024179/465586)}{(2234934\ /709983\ )} = 0.70$$

The extraction efficiencies are shown in Table 9.

Table 9: Extraction Efficiencies

Compound	E.E.	Corr. Area
$CHCl_3$	0.70	1024179
$CHBrCl_2$	1.07	933218
$ClCH_2CHBrCH_3$	1.00	465586
$CHBr_2Cl$	1.16	762408
$CHBr_3$	1.01	507165

(b) The concentration of the unknown by rearranging Equation (1) gives us Equation (3)

$$C_c = \frac{C_{IS}\, A_c}{F_c\, A_{IS}}$$

The corrected concentration of each compound [X] is given by Equation (4)

$$[X] = \frac{[X]_p [V]_p / [V]_{aq}}{EE_X}$$

where $[X]_p$ and $[V]_p$ are the concentrations of the haloform in the pentane extract and the volume of pentane used respectively, and $[V]_{aq}$ is the volume of the water extracted, and EE_X is the extraction efficiency.

For example, a chromatogram obtained from 25.0 mL of a reaction mixture extracted with 10.0 mL of pentane resulted in peak areas for chloroform and the internal standard (10 ppm) of 884662 and 509907 units respectively. The concentration of chloroform in pentane extract (F =3.15, first bromide level) is given by

$$C_c = \frac{(10\ \text{ppm})(884662)}{(3.15)(509907)} = 5.51\ \text{ppm}$$

The actual concentration in aqueous mixture is then given by

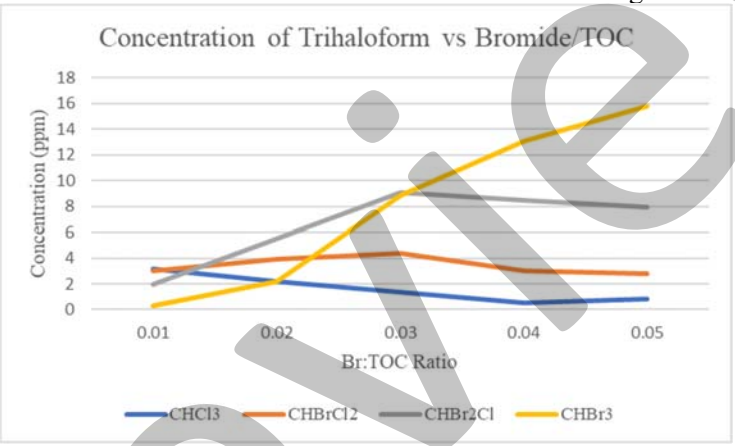
$$[CHCl_3] = \frac{5.51\ \text{ppm}\ (10.0\ \text{mL}/25.0\text{mL})}{0.70} = 3.15\ \text{ppm}\ (\mu\text{g/mL})$$

The calculated concentrations in other bromide levels and other compounds are shown in Table 10.

Table 10: Calculated concentrations in pentane extract and aqueous solutions

Concentration (ppm)	Br #1		Br #2		Br #3		Br #4		Br #5	
Compound	Extract	Aqueous	Extract	Aqueous	Extract	Aqueous	Extract	Aqueous	Extract	Aqueous
$CHCl_3$	5.51	3.15	3.81	2.18	2.41	1.38	0.88	0.50	1.45	0.83
$CHBrCl_2$	8.14	3.04	10.49	3.92	11.72	4.38	8.12	3.03	7.41	2.77
$CHBr_2Cl$	5.57	1.93	15.98	5.53	26.27	9.09	24.48	8.47	22.86	7.91
$CHBr_3$	0.71	0.28	5.55	2.19	22.41	8.83	33.22	13.10	40.16	15.83

(c) the plot of concentration of each trihaloform vs. the bromide:TOC ratio is given as Plot 1.



Conclusion

We successfully finished the experiment and conclude that the response factors for four trihaloforms $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$ are 3.15, 1.87, 1.42, and 1.07 respectively; the extraction efficiencies are 0.70, 1.07, 1.16, and 1.01 respectively.

Questions

(1) Answers is shown in Table 11:

Table 11: Answers to Question 1

m/z	Ions detected
77	$CH_2CHCH_3{}^{35}Cl^{+\cdot}$
83	$CH^{35}Cl_2{}^{+\cdot}$
129	$CH^{81}Br^{35}Cl^{+\cdot}$
173	$CH^{79}Br^{81}Br^{+\cdot}$

(2) Adding 0.1 L of Humic Acid (0.25 g TOC/L), thus mol TOC $= \frac{\left(0.25\ \text{g}\frac{\text{TOC}}{\text{L}}\right)(0.1\text{L})}{12\text{g/mol C}} = 2.083\times10^{-3}$ mol

0.001 L of KBr (2.5g/L), mol Br $= \frac{(2.5\ \text{g/L})(0.001\text{L})}{119\text{g/mol KBr}} = 2.101\times10^{-5}$ mol

5 mL of 6%(m/v) NaClO, mol Cl $= \frac{(6\%)(5\text{mL})}{74.44\text{g/mol NaClO}} = 4.030\times10^{-3}$ mol

In the same solution, Molar ratio Br:Cl:TOC = $2.101\times10^{-5}: 4.030\times10^{-3}: 2.083\times10^{-3} = 0.01: 1.93: 1$.