Non-suppressed ion chromatography-tandem electrospray mass spectrometry using a short column for simultaneous analysis of dichloroacetic acid, trichloroacetic acid, and bromate: Aqueous ammonia as the eluent additive

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This supporting information contains 2 texts, 3 tables, and 1 figure with 8 pages.

Text S1

(1) Calculation of ${}^{s}_{s}pK_a$

At high proportions of acetonitrile, the "apparent" pK_a values of DCAA and TCAA in acetonitrile-water solvent (${}^{s}_{s}pK_a$) increase significantly from the pK_a values of the same compounds in water (${}^{w}_{w}pK_a$), because acetonitrile is a poor hydrogen bond donor, with weak solvation of H^+ relative to water [1,2].

In the water-acetonitrile solvent mixtures, the relationship between ${}^{s}_{s}pK_a$ and ${}^{w}_{w}pK_a$ is described by ***Eq. (S1)***. The slope (${}^{a}_{s}$) and intercept (${}^{b}_{s}$) values vary with the changes in acetonitrile proportions, and can be calculated using ***Eq. (S2)*** and ***Eq. (S3)***, where a_1, a_2, a_3, a_4, b_1, b_2, b_3 and b_4 are fitting parameters as reported by Espinosa et al. [1] The ${}^{a}_{s}$ and ${}^{b}_{s}$ data in **Table S2** for amines and aliphatic carboxylic acids were calculated using ***Eq. (S2)*** and ***Eq. (S3)***.

$${}^{s}_{s}pK_a = a_{sw}{}^{w}_{w}pK_a + b_s \quad \textbf{(Eq. S1)}$$

$$a_s = \frac{1 + a_1 * v_{ACN} + a_2 * v_{ACN}^2}{1 + a_3 * v_{ACN} + a_4 * v_{ACN}^2} \quad \textbf{(Eq. S2)}$$

$$b_s = \frac{b_1 * v_{ACN} + b_2 * v_{ACN}^2}{1 + b_3 * v_{ACN} + b_4 * v_{ACN}^2} \quad \textbf{(Eq. S3)}$$

The ${}^{s}_{s}pK_a$ values of ammonia, DCAA, and TCAA for varying proportions of acetonitrile in mobile phase were calculated from **Eq. S1**, and are summarized in **Table S2**.

(2) Calculation of mobile phase pH

The pH values of mobile phases with different aqueous/acetonitrile proportions were calculated from charge balance and acid-base equilibrium expressions as per ***Eq. (S4)*** and ***Eq. (S5)*.** The calculated pH values are summarized in **Table S2**.

$$[OH^-] = [H^+] + [NH_4^+] \quad \textbf{(Eq. S4)}$$

$$0 = 10^{-pH} + [ammonia]_{mobile\ phase} * 1/\left(1 + 10^{pH - pK_a}\right) - 10^{pH - 14} \quad \textbf{(Eq. S5)}$$

(3) Calculation of logK_{ow}*

The logK_{ow} values represent the octanol/water partition coefficients of the HAAs' undissociated forms, as opposed to their dissociated forms. In aqueous mobile phases with pH >12, HAAs are ~100% dissociated. However, as the proportion of acetonitrile in the mobile phase is increased, the extent of deprotonation is decreased – on account of the aforementioned increase in ${}^{s}_{s}pK_a$ for the HAAs with increasing acetonitrile proportion. The proportion of the HAAs present in their undissociated form, α, therefore increases with increasing acetonitrile proportion for a given pH, according to ***Eq. (S6)***,

$$\alpha = \frac{1}{(1 + 10^{pH - {}^{s}_{s}pK_a})} \quad \textbf{(Eq. S6)}$$

where α is the proportion of the HAAs present in their undissociated form.

Noting again that the logK_{ow} values correspond to the undissociated forms of each HAA, and assuming that the dissociated (anionic) forms of the HAAs exhibit comparably negligible values of logK_{ow}, the values of "apparent" logK_{ow}* (equivalent to the log-scale distribution ratio, D_{ow} = $[HA]_{o,tot}/([HA]_w+[A^-]_w)$) for a given HAA can be approximated at particular pH values as per ***Eq. (S7)***. [3]

$$logK^{*}_{ow} = \log(\alpha \times K_{ow}) = log\alpha + logK_{ow} \quad \textbf{(Eq. S7)}$$

The values of logα and logK_{ow}* determined for DCAA and TCAA at different acetonitrile proportions are summarized in **Table S2**.

Text S2

Limits of detection (LODs) were calculated as standard deviation (SD) × Student's t value for a 99% confidence level with n − 1 = 7° of freedom, and limits of quantification (LOQs) were calculated as 3 × LODs, this method was referenced the work from L.A. Currie [4].

Reference:

[1] Espinosa S., Bosch E., Rosés M. Retention of ionizable compounds in high-performance liquid chromatography: 14. Acid–base pK values in acetonitrile–water mobile phases. Journal of Chromatography A. 2002, 964: 55-66.

[2] Rossini, E., Bochevarov, A. D., Knapp, E. W. Empirical Conversion of pKa Values between Different Solvents and Interpretation of the Parameters: Application to Water, Acetonitrile, Dimethyl Sulfoxide, and Methanol. Acs Omega. 2018, 3:1653-1662.

[3] Schwarzenbach RPG, P. M.; Imboden, D. M. Environmental Organic Chemistry. Hoboken, NJ: John Wiley & Sons, Inc., 2003.

[4] Currie L. A. Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC Recommendations 1995). Anal. Chim. Acta. 1999, 391(2):105-126.

Table S1. Optimized MRM parameters for DCAA, TCAA, and bromate

DBPs	Precursor ion		Product ion		Collision energy (volts)	Collision cell exit potential (volts)	Declustering potential (volts)	Entrance potential (volts)
	m/z	Transition	*m/z*	Transition				
DCAA	126.8	$[M\text{-}H]^-$	82.9	$[M\text{-}COOH]^-$	-13	-11	-20	-12
TCAA	116.8	$[M\text{-}COOH]^-$	34.8	$[^{35}Cl]^-$	-19	-16	-20	-10
BrO_3^-	128.7	$[^{81}BrO_3]^-$	112.8	$[^{81}BrO_2]^-$	-29	-14	-60	-9

Table S2. The ${}^{s}_{s}pK_a$ / logα / log$K_{ow}{}^{*}$ values of ammonia / HAAs, and pH values of mobile phase versus proportion of acetonitrile as Solvent B in mobile phase (with aqueous ammonia as Solvent A comprising the remaining %)

Acetonitrile proportion			75%		85%	95%
Ammonia conc. (M) in Solvent A		0.02	0.1	0.4	0.4	0.4
a_s of amines			1.074		1.061	0.964
b_s of amines			-0.513		0.483	2.014
${}^{s}_{s}pK_a$ of ammonia			9.46		10.34	10.97
Ammonia conc. (M) in mobile phase		0.005	0.025	0.100	0.060	0.020
Calculated pH of mobile phase		10.56	10.92	11.23	11.55	11.59
a_s of aliphatic carboxylic acids			1.342		1.482	1.790
b_s of aliphatic carboxylic acids			2.028		3.342	6.529
${}^{s}_{s}pK_a$	DCAA		3.72		5.21	8.79
	TCAA		2.71		4.10	7.44
logα	DCAA	-6.48	-7.20	-7.51	-6.34	-2.81
	TCAA	-7.85	-8.21	-8.52	-7.45	-4.15
log$K_{ow}{}^{*}$	DCAA	-5.92	-6.28	-6.59	-5.42	-1.89
	TCAA	-6.52	-6.88	-7.19	-6.12	-2.82

Table S3. Linearity of standard solution calibration curves

	Calibration Linear range(μg/L)	correlation coefficient
DCAA	0.5-100	0.9956
TCAA	0.5-100	0.9978
BrO_3^-	0.5-100	0.9990

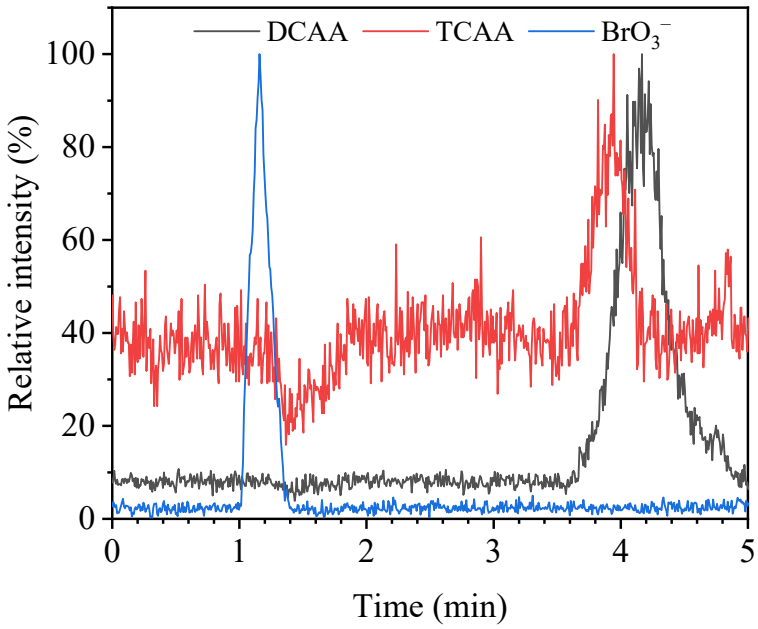

Fig. S1. Extracted ion chromatograms of DCAA (10 μg/L), TCAA (10 μg/L), and BrO_3^- (5 μg/L) in the mixed standards using 25% pure water + 75% acetonitrile as the mobile phases in an isocratic elution mode, with elution from Dionex Ionpac AG18 column (2 mm × 50 mm).