

Electronic Supplementary Material (ESI) for RSC Advances.
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Supporting Information

Production of pure potassium salts directly from sea bittern employing tartaric acid as a benign and recyclable K⁺ precipitant

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Section S1. (Figures S1 to S8)

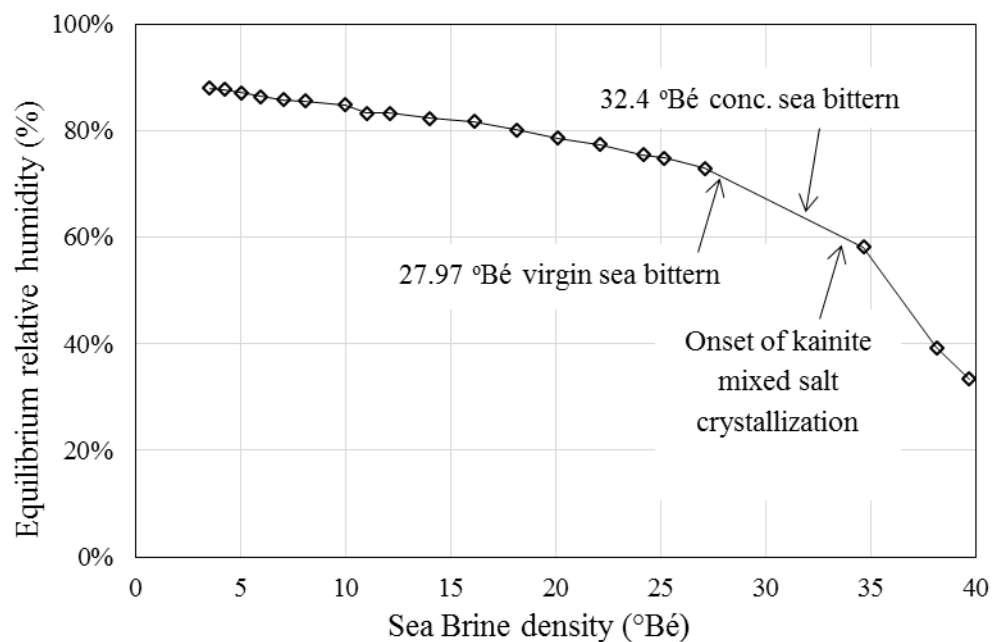


Figure S1. Plot of equilibrium relative humidity (ERH) vs. Baumé density of sea brine based on literature data [$^{\circ}\text{Bé} = 145(1-1/\rho)$, where ρ its specific gravity and $^{\circ}\text{Bé}$ is the density in Baumé scale].¹⁻³ The onset of kainite mixed salt crystallization, essential for recovery through conventional process is indicated. The points are also marked for the virgin and concentrated bittern samples used in the present study.

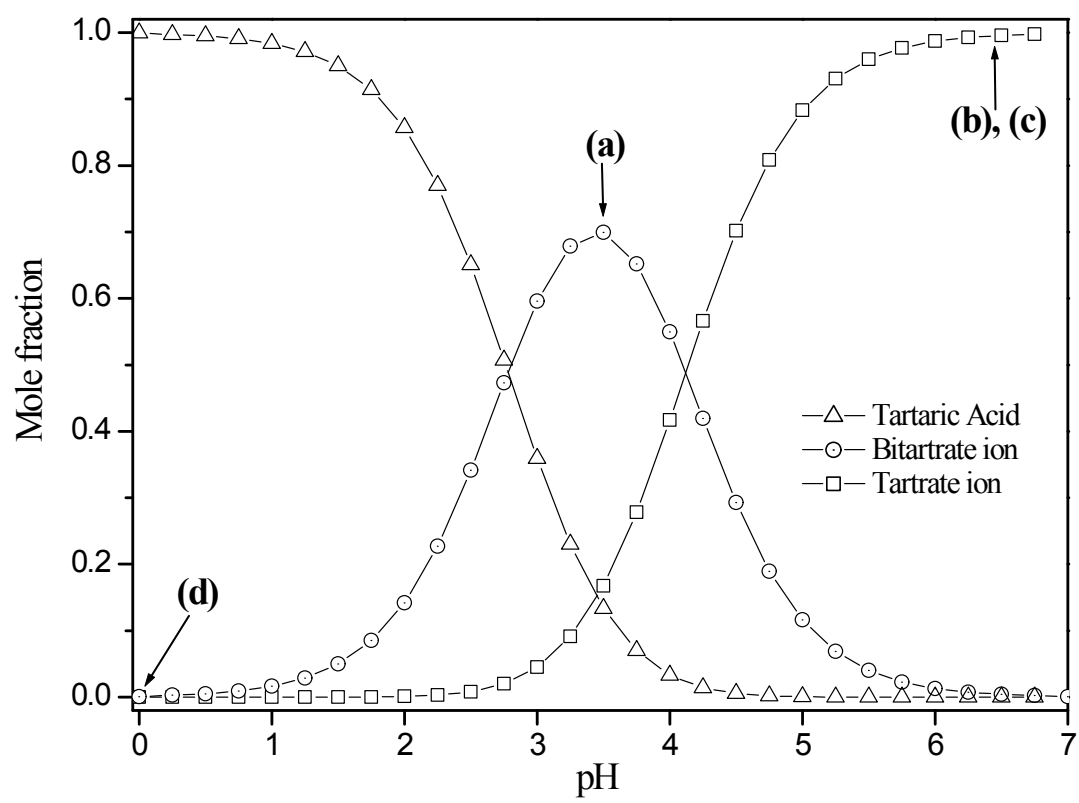


Figure S2. Plot of tartaric acid species distribution as function of pH based on literature data.⁴ Favourable regions for (a) MgT to KHT conversion (b) KHT to MgT conversion, (c) residual tartrate removal as CaT and (d) CaT to H₂T conversion are indicated.

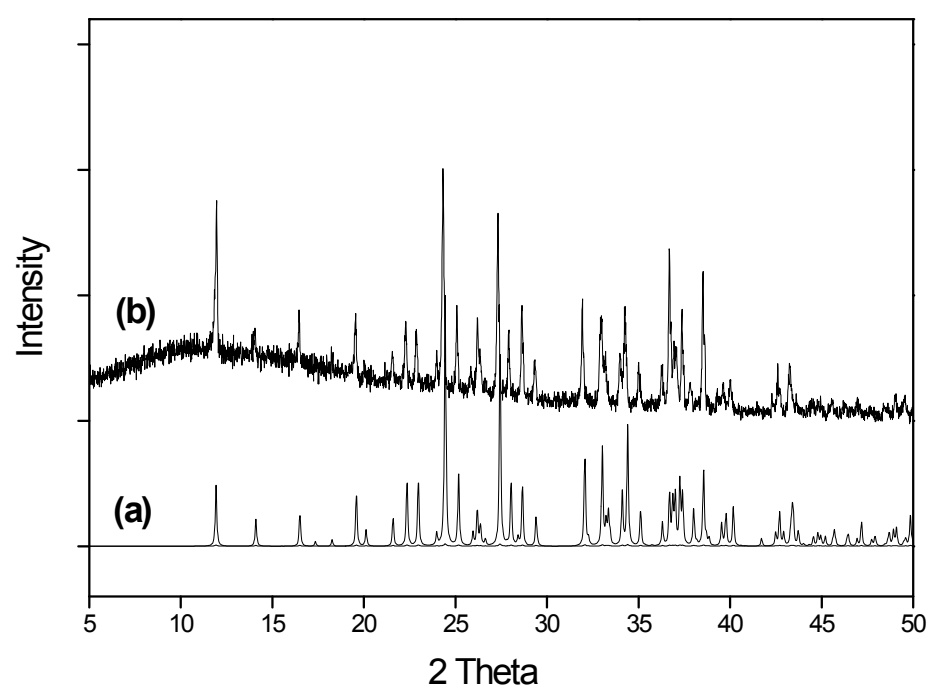


Figure S3. Powder XRD of (a) simulated pattern generated from the single crystal XRD data of DL- KHT (CCDC 236651) and (b) precipitate obtained at pH 3.5 from the experiment of Figure 1A.

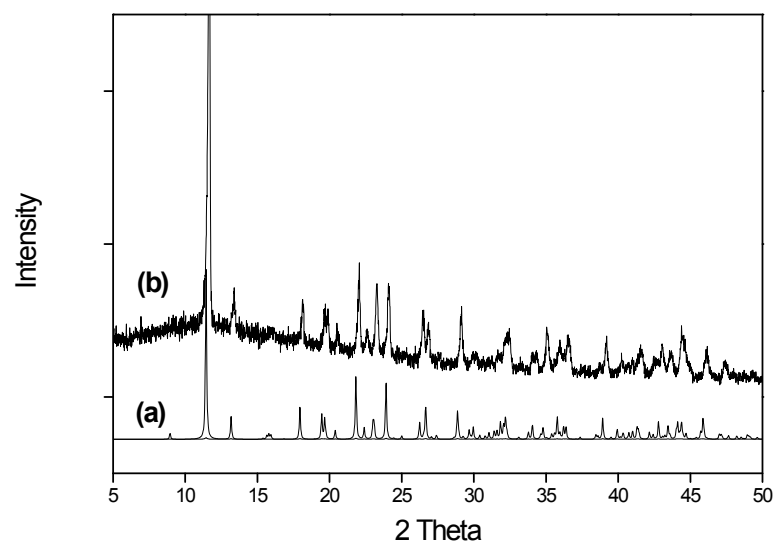


Figure S4. Powder XRD of (a) simulated pattern generated from the single crystal XRD data of DL-calcium tartrate (CCDC 738956)⁵ and (b) precipitate obtained in the experiment of Figure 1B.

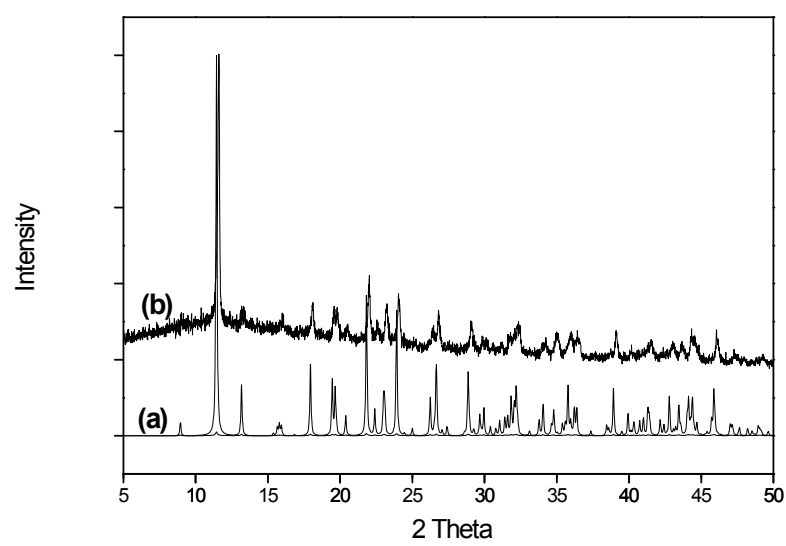


Figure S5. Powder XRD of (a) simulated pattern generated from the single crystal XRD data of DL-calcium tartrate (CCDC 738956)⁵ and (b) precipitate obtained in the experiment of Figure 2A.

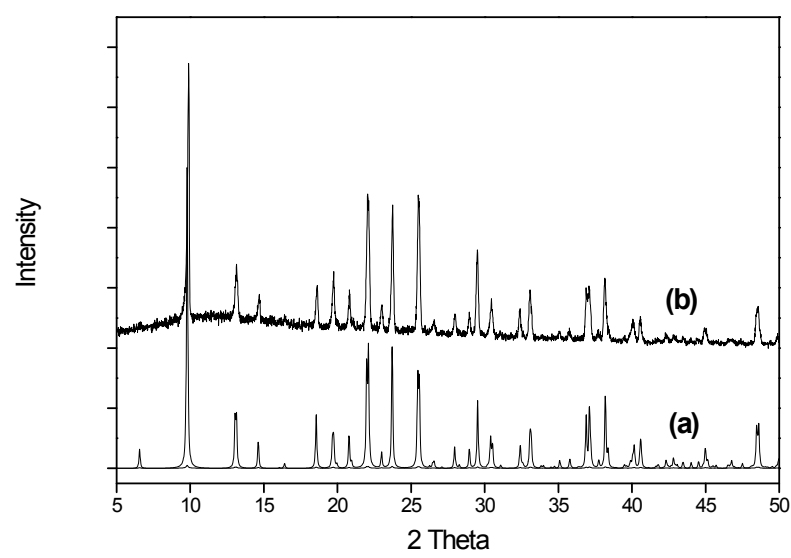


Figure S6. Powder XRD of (a) simulated pattern generated from the single crystal XRD data of DL-magnesium tartrate (CCDC 631939) and (b) precipitate obtained in the experiment of Figure 2B.

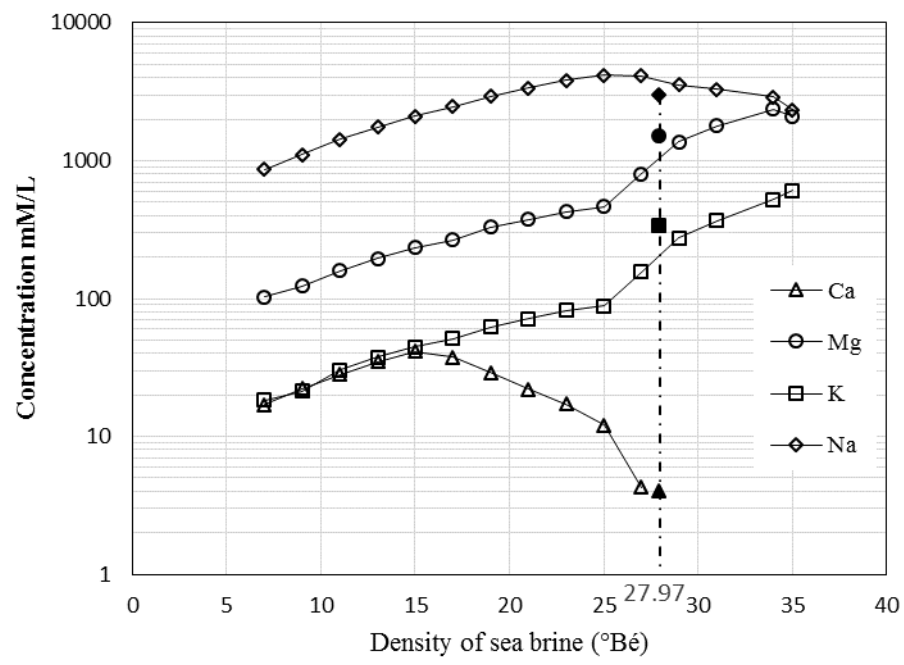


Figure S7. Concentration profiles of major cations in sea brine as a function of Baumé density.⁶ The concentrations of cations in the virgin sea bitter (27.97 °Bé) employed in the present study are superimposed in the plot as the corresponding filled shapes.

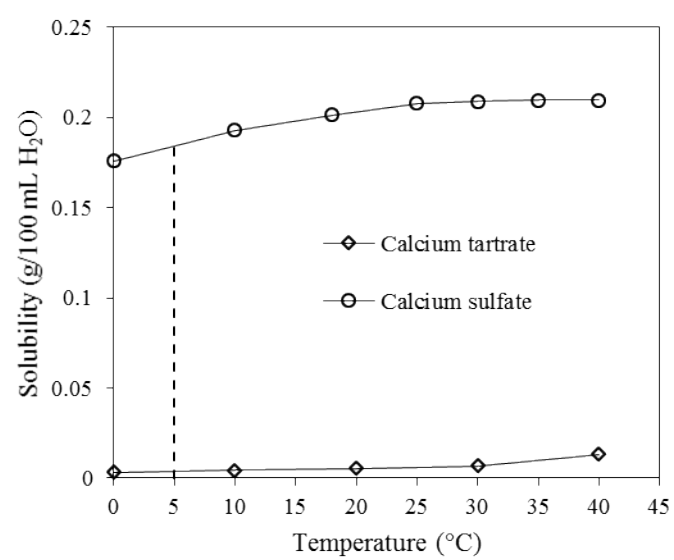


Figure S8. Solubility versus Temperature curves of gypsum and calcium tartrate based on literature data on their solubility characteristics in water.⁷ 5 °C corresponds to the temperature adopted in the present study for recovery of residual tartaric acid in K⁺ depleted bittern through the conversion of CaSO₄ to CaT.

Section S2.

Table S1. Composition of bitters.

<i>Parameter</i>	<i>27.97 °Bé Virgin Bittern^a</i>	<i>32.42 °Bé Concentrated Bittern^b</i>	<i>MgSO₄- depleted Concentrated Bittern^c</i>
Specific gravity	1.239	1.288	1.235
pH	6.8	5.4	6.2
Sodium, as Na ⁺ (% w/v)/ (M)	6.83/ (2.969)	2.60/ (1.13)	2.65/ (1.152)
Potassium, as K ⁺ (% w/v)/ (M)	1.31/ (0.336)	2.47/ (0.633)	2.47/ (0.633)
Magnesium, as Mg ²⁺ (% w/v)/ (M)	3.63/ (1.494)	7.50/ (3.086)	6.7/ (2.757)
Calcium, as Ca ²⁺ (% w/v)/ (M)	0.016/ (0.004)	BDL ^d	BDL ^d
Chloride, as Cl (% w/v)/ (M)	27.48/ (7.741)	20.38/ (5.74)	19.3/ (5.437)
Sulphate, as SO ₄ ²⁻ (% w/v)/ (M)	4.51/ (0.469)	9.00/ (0.9375)	4.85/ (0.505)

^aAs obtained from M/s Tata Chemicals, Mithapur, India; ^b After further concentration of the same bittern; ^cAfter dilution of the concentrated bittern with 10% (v/v) H₂O followed by chilling to separate out Epsom salt; ^dBDL=below detection limit.

Table S2. Comparative data of energy input in the present process and energy input for equivalent products from reference database.

Energy Input for Production based on Developed Process (GJ) ^a		Energy Input from database (GJ) ^{a,b}	
Raw Material ^b		N from KNO ₃	12.47
HNO ₃	9.86	K ₂ O from KNO ₃	7.26
NH ₃	12.52	N from (NH ₄) ₂ SO ₄	14.13
H ₂ SO ₄	1.29	MgSO ₄ from MgSO ₄ ·7H ₂ O	0.94
Process Energy ^c		Total	34.80
Electrical	3.13		
Thermal	11.51		
Total	38.31		

^aBasis: 1 t KNO₃ + 1.47 t (NH₄)₂SO₄ + 0.3 t MgSO₄·7H₂O; ^bCalculations based on Ecoinvent database, v 2.2 and GaBi database (see Table S3); ^cFigures based on 1 t day⁻¹ KNO₃ production (see detailed calculations in Table S4).

Table S3. Illustration of computations using Ecoinvent database, v 2.2 and GaBi database (PE International, Germany) operated with GaBi software, version 6

Sl. No.	Name	Quantity (t)	Per ton energy requirement as per database (GJ/t)	Total energy input (GJ)	Reference	
1	HNO ₃ (60%)	1.0560	9.34	9.86	PE:DE	Obtained through PE GaBi 6 Software-System and databases for Life Cycle Engineering. Stuttgart, Echterdingen
2	NH ₃	0.3440	36.40	12.52	PE:NL	
3	H ₂ SO ₄	0.6100	2.12	1.29	RER Ecoinvent database	
4	N from KNO ₃	0.1386	90.00	12.47	RER Ecoinvent database	
5	K ₂ O from KNO ₃	0.4653	15.60	7.26	RER Ecoinvent database	
6	N from (NH ₄) ₂ SO ₄	0.3120	45.30	14.13	RER Ecoinvent database	
7	MgSO ₄ from MgSO ₄ .7H ₂ O	0.1490	6.28	0.94	RER Ecoinvent database	

Table S4 (A). Process electrical energy requirement

	Particulars	Electrical Energy				
		Connected load KW	Runtime (hr)	Energy consumed (GJ)	Energy Recovery Efficiency	Net Energy Consumption (GJ)
Step-1	Magnesium sulphate recovery					
1/a	Chilling of bittern for magnesium sulphate crystallisation (based on chiller rating of 13 TR as computed from chilling load in Step 1/a in Table S4 (B))	9.1	24	0.79	33%	0.53
1/b	Stirring of slurry	1.5	24	0.13	0%	0.13
1/c	Centrifugal separation	2	24	0.17	0%	0.17
	Total (step-1)					0.83
Step-2	KHT precipitation					
2/a	Stirring of slurry	1.5	24	0.13	0%	0.13
2/b	Centrifugal separation	1.5	24	0.13	0%	0.13
	Total (step-2)					0.26
Step-3	KHT decomposition					
3/a	MgT precipitation	0.5	24	0.04	0%	0.04
3/b	Centrifugal separation	3	24	0.26	0%	0.26
	Total (step-3)					0.3
Step-4	KNO3 crystallisation					
4/a	KNO3 crystallisation	0.5	24	0.04	0%	0.04
4/b	Centrifugal separation	1	24	0.09	0%	0.09
4/c	KNO3 drying	1	24	0.09	0%	0.09
	Total (step-4)					0.22
Step-5	Magnesium hydroxide and magnesium carbonate from magnesium sulphate					
5/a	Reaction with ammonia					
Input-1	Magnesium sulphate					
Input-2	Water					
Input-3	Liquor ammonia (25%)					
	Total	1	24	0.09	0%	0.09
5/b	Centrifugal separation	1	24	0.09	0%	0.09
5/c	Reaction with CO2	1	24	0.09	0%	0.09
5/d	Centrifugal separation	1	24	0.09	0%	0.09

	Total (step-5)					0.36
Step-6	CaT precipitation					
6/a	Stirring of slurry	2	24	0.17	0%	0.17
6/b	Centrifugal separation	1	24	0.09	0%	0.09
	Total (step-6)					0.26
Step-7	CaT digestion					
7/a	Reaction					
Input-1	CaT					
Input-2	H2SO4					
Input-3	Water					
	Total	1	24	0.09	0%	0.09
7/b	Centrifugal separation	1	24	0.09	0%	0.09
	Total (step-7)					0.18
Step-8	Calcium carbonate from gypsum					
8/a	Reaction					
Input-1	Gypsum					
Input-2	Liquor ammonia (25%)					
Input-3	CO2					
Input-4	Water					
	Total	0.5	24	0.04	0%	0.04
8/b	Centrifugal separation	1	24	0.09	0%	0.09
	Total (step-8)					0.13
Step-9	Ammonium Sulphate					
9/a	Evaporation of ammonium sulphate solution					
Input-1	Liquor from MgSO4 section					
Input-2	Liquor from CaSO4 section					
	Total	1	24	0.09	0%	0.09
9/b	Centrifugal separation	1	24	0.09	0%	0.09
9/c	(NH4)2SO4 drying	1.5	24	0.13	0%	0.13
	Total (step-9)					0.31
10	Material handling	10%	of process electrical energy requirement			0.28
	Total energy requirement (1-10)					3.13

Table S4 (B). Process thermal energy requirement^a

	Particulars	Quantity (m3 / t)	Unit	Sp. Gravity	Mass t	Thermal Energy					Energy Recovery Efficiency	Net Energy Consumption (GJ)
						Sp. Heat (cal/gm-°C)	ΔT (°C)	Latent Heat cal/gm	Overage	Energy required (GJ)		
Step-1	Magnesium sulphate recovery											
1/a	Chilling of bittern for magnesium sulphate crystallisation (data used for computation of chiller rating and estimation of electrical energy requirement in Table S4 (A))											
Input-1	Bittern (32.5 °Bé)	21.51	m3	1.288	27.70488							
Input-2	Water	2.151	m3	1	2.151							
	Total				29.85588	0.77	30		33%			
Step-7	CaT digestion											
7/a	Reaction											
Input-1	CaT	0.56	t		0.56							
Input-2	H2SO4	0.24	t		0.24							
Input-3	Water	1.62	m3	1	1.62							
	Total				2.42	1	55		33%	0.74	0%	0.74
7/b	Centrifugal separation											
	Total (step-7)											0.74
Step-9	Ammonium Sulphate											
9/a	Evaporation of ammonium sulphate solution											
Input-1	Liquor from MgSO4 section	5.335805	t		5.335805	0.8125	80	540	33%	13.95		
Input-2	Liquor from CaSO4 section	0.552558	t		0.552558	0.8125	80	540	33%	1.44		
	Total				5.888363	0.8125	80	540	33%	15.39	30%	10.77
9/b	Centrifugal separation											
9/c	(NH4)2SO4 drying											
	Total (step-9)											10.77
10	Material handling											
	Total energy requirement											11.51

^aNumbering of the steps follows the same sequence as in Table S4 (A). Only those steps are shown wherein thermal energy is required.

Section S3. Computation of pH of bittern with added bitartrate

The ionic strength (I) was computed based on eq S1 (C_i = molar concentration and Z_i = ionic charge) and the data for $MgSO_4$ -depleted bittern in Table S1. The value was 10.1 M

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (\text{Eq S1})$$

The proton concentration $[H_3O^+]$ in the bittern with added bitartrate was computed based on eq S3 and considering $pK_{a2} = 4.37$ of tartaric acid. The value was 4.93×10^{-3} M

$$[H_3O^+] = \sqrt{[HT^-] \cdot K_{a2}} \quad (\text{Eq S2})$$

The Davies relationship (eq S3) was used to compute the proton activity coefficient ($\gamma_{[H_3O^+]}$). The value was 14.46.

$$\log \gamma_i = -0.509 Z_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right] \quad (\text{Eq S3})$$

Eq. S4 gave the proton activity ($a_{[H_3O^+]}$), the value being estimated to be 0.0713.

$$a_{[H_3O^+]} = [H_3O^+] \cdot \gamma_{[H_3O^+]} \quad (\text{Eq S4})$$

Finally, $pH = -\log a_{[H_3O^+]} = 1.14$

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