Acid Release during Brewing

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Introduction

Acids are released into brews from coffee grinds - but, the pH of brews is higher than the measured acid composition in grinds would suggest. Maier (1997) argued that the acids are part neutralised by bases both from the grinds and the brew water. In this poster, this effect is estimated using a model of poly-acid solutions. Experiments measured the kinetics of pH and Titratable Acidity (TA) of coffee brews.

Methods

A modelling tool was developed to predict the pH and TA of solutions of mixtures of weak poly acids, and strong bases. It was used to model coffee brews with literature data for the composition of organic acids in coffee grounds. Experiments were conducted on a *Schaerer Art* espresso coffee machine set to a coarse grind. Aliquots were collected and analysed for TA and pH over time.

$$A^{j-}H + H_2O \xrightarrow{f} H_3^+O + A^{(j+1)-} \qquad \frac{f_{j,j+1}}{b_{j,j+1}} = K_{j,j+1} \qquad K_{j,j+1} = 10^{pKa(j,j+1)}$$

$$A^{j-}H + H_2O \xrightarrow{b} H_3^+O + A^{(j+1)-}$$

For each such reaction, and for all acids present

$$\frac{\partial c_{ai}^j}{\partial t} = -f_{j,j+1}c_{ai}^j + b_{j,j+1} c_h c_{ai}^{j+1} + f_{j-1,j} c_{ai}^{j-1} - b_{j-1,j} c_h c_{ai}^j$$

$$\frac{\partial C_h}{\partial t} = \sum_{ij} + f_{j,j+1}c_{ai}^j - b_{j,j+1}C_h C_{ai}^{j+1}$$

c_{ai}^j : concentration of the jth dissociation state of acid i C_h : concentration of H_3^+O

Iterate the Eqs. to equilibrium $\frac{\partial c_{ai}^j}{\partial t} = 0, \frac{\partial C_h}{\partial t} = 0$ from $C_h(t=0) = 10^{-7}$ and given $C_A(t=0)$

If strong bases are present, neutralisation is done in ascending order of pka until all mols of OH⁻ are used up; the total mols of OH⁻ is set to that of an assumed strong base, the starting concentrations are so adjusted without the addition of H_3^+O

$$A^{j-}H + OH^- \Longleftrightarrow H_2O + A^{(j+1)-}$$

Table 1 data

From Fig. 6 of   Maier (1997)

Acids	MW	pka	Valence (ph 8)	g/kg (of coffee)	mmol/g Acid	mmol/g H_3^+O
Quinic	192	3.4	1	9.6	0.0500	0.0500
Formic	46	3.75	1	2.3	0.0500	0.0500
Acetic	60	4.73	1	6	0.1000	0.1000
Glycolic	76	3.83	1	2.28	0.0300	0.0300
Pyroglutamic	129	3.32	1	0	0.0000	0.0000
Lactic	90	3.89	1	0	0.0000	0.0000
Chlorogenic	343	3.4	1	13.72	0.0400	0.0400
Minor Mono	137.91	4.57	1	1.55	0.0112	0.0112
Minor Dipro	120.25	2.95/4.92	2	0.45	0.0037	0.0075
High Mw	>500	6?	1?	46.5	0.0930	0.0930
Malic	134	3.4/5.05	2	3.35	0.0250	0.0500
Citric	192	3.14/4.77/6.39	3	7.68	0.0400	0.1200
Phosphoric	97	1.96/7.21/12.3	2	2.425	0.0250	0.0500
					0.4680	0.6017

Table 1: Acid data extracted from Maier (1987); it includes mmol of acid per gm of dry coffee grind and the mmol/gm of H_3^+O in a brew if they are fully released into a brew and fully disassociated . Unknowns are the high MW molecules with acid groups, their valences and numbers of groups per molecule, it is first assumed these are mainly COOH groups but with high pK$_a$.

Model

Given a composition of weak poly acids in solution. The model (see left) solves for the equilibrium states and the overall solution pH. Equations for each dissociation reaction are coupled together by the concentration of H_3^+O. The model can include reactions due to strong base co-solutes . Table .1 shows an example of the acid composition reported for a coffee grind.

Results/Discussion.

The pH of coffee brews are in the range 4.5-5.5 ; however, if the composition of Table 1. were fully released into the brew, the pH would be ca. 2.5. (more like Coca-Cola!). Figure 1 shows the model brew the acids are assumed fully extracted along with a strong base quantified as as mmol /gm of coffee. The pH of real brews is found with base levels 3.5 – 5 mmol/gm. This is comparable to the mineral content of coffee Janganyi & Madlala (2000), suggesting *that the coffee itself is the source of much of the neutralising bases.* This level of bases cannot be provided by the water – it would be at pH 11-12 (c.f. 8-9 for the hardest water). A brew prepared with hard, softened and de-ionised water had pH 5.6, 5.5 and 5.4 respectively , confirming the minor role of water hardness.

Experiments:

aliquots were taken at intervals during brewing, for each sample pH and TA was measured. The pH increased from 5.6 to 5.9 over the 25 sec brew . The cumulative TA results are shown in **Fig. 2.** If the composition of acids released was constant with time the ratio TA 6.6 to TA 8.1 would be constant but they are not; Aa explanation of is that at later times the compositions of acids has a higher proportion of slower releasing high MW molecules with high pK$_a$.
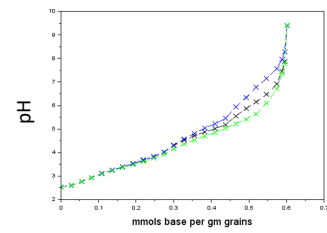

Figure 1. Model of pH of a 6gm grind into a 40ml espresso using the acid mix of Tab. 1 vs a level of a co-solute strong base . The green. black and blue curves are for 0.5, 0.6, 0.7 mg/gm resp. of the high MW molecules .
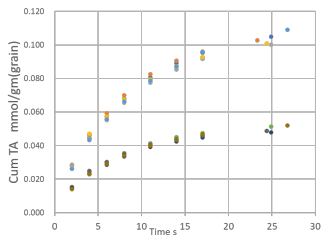

Figure 2. The aliquots were titrated to pH 6.6 (lower curves) and 8.1 (upper curves) and the mmol/gm of titrant added (per gm of coffee grind) cumulated over successive aliquots. Several runs are shown.

Conclusion/Perspectives

A quantitative tool for relating the pH and TA of coffee brews to measured organic acid compositions has been developed . This poster supports the role of neutralisation from the coffee grounds Maier (1977). Experiments and evolutions of conpostionover time. There is a need for data on the role of acid-groups high MW molecules - they could have a key role on brew acidity.

References: Maier, H. G., The acids in Coffee 1987 . *In ASIC(ed.) proceedings 12th conference , France, pg 229.* ; Jaganyi, D., Madlala, S.P., 2000. *J. Sci. Food. Agric.* 80, 85-90.

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