Determination of the titratable acidity, alkalinity and carboxylate content of aqueous samples by ^{1}H NMR

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We present a set of methods that allow the titratable acidity, alkalinity and carboxylate content of aqueous samples to be determined by ^{1}H NMR spectroscopy. The methods require smaller sample volumes and provide far greater chemical insight than conventional potentiometric or conductometric approaches.

https://uk.hach.com/titration-systems/titralab-at1000-kf1000-series/family

Conventional titrations

- Large sample volumes > 10 mL (0.1 g)
- No detailed chemical information
- Expensive for one-off measurements

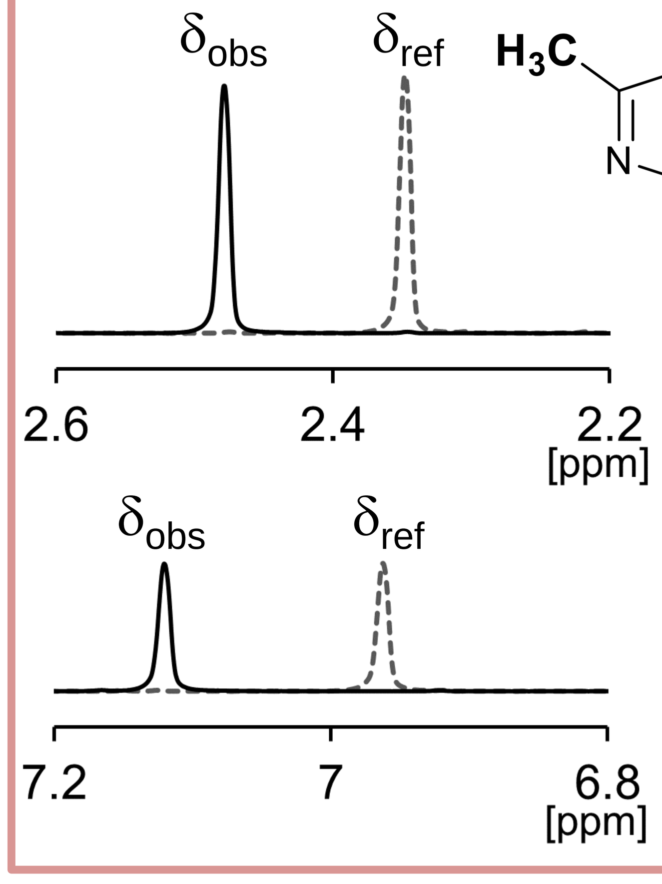
VS

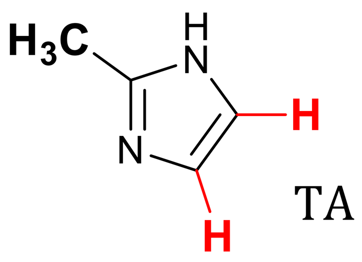
^{1}H NMR

- Small sample volumes < 0.6 mL (6 mg)
- Abundance of chemical information
- Used routinely as part of sample characterisation

Titratable acidity (TA) by ^{1}H NMR

Measure ^{1}H chemical shifts of indicator compound in presence (δ_{obs}) and absence (δ_{ref}) of aliquot of acidic sample





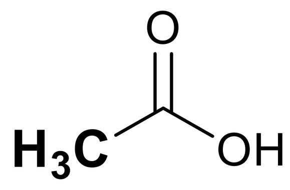
$$\mathrm{TA} = [\mathrm{Ind}]_{\mathrm{total}}\left(\frac{\delta_{obs}-\delta_{ref}}{\delta_H-\delta_L}\right)+\left(\frac{\delta_H-\delta_{ref}}{\delta_{ref}-\delta_L}\right)10^{\mathrm{p}K_a-\mathrm{p}K_w}$$

Sample	δ_{obs}/ppm	pH	TA/mM
Reference	2.3483	9.90	0.18±0.19
	6.9627	9.87	0.20±0.16
HCl 10.0±0.1 mM	2.4789	7.99	10.20±0.30
	7.1206	7.98	10.30±0.27
Apple squash (9.91±0.30 mM)	2.4806	7.98	10.28±0.30
	7.1224	7.97	10.42±0.28

Accurate to 3% with < 20 µL of juice sample

Alkalinity by ^{1}H NMR

Acetic acid reacts quantitatively with base, e.g. HCO_3^- in tap water.



$$\mathrm{Alkalinity} = [\mathrm{Ac}]_{\mathrm{total}}\left(\frac{\delta_H-\delta_{obs}}{\delta_H-\delta_L}\right)-\left(\frac{\delta_{obs}-\delta_L}{\delta_H-\delta_{obs}}\right)10^{-\mathrm{p}K_a}$$

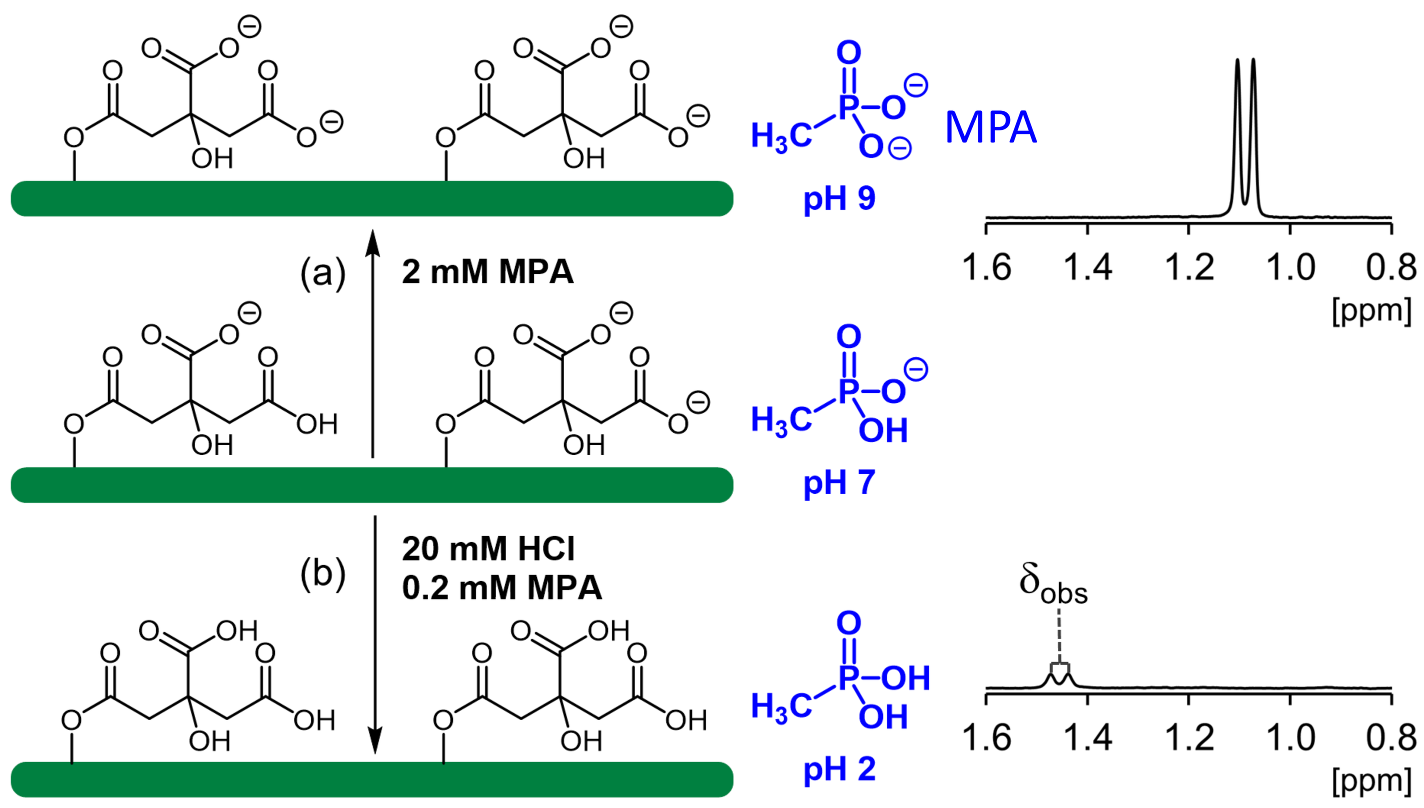
Sample	δ_{obs}/ppm (AcOH)	pH	mg $CaCO_3$/L (NMR)	mg $CaCO_3$/L (Potentiometric)
Tap water	1.9798	4.87	239±6	241±7
Brita® filtered	2.0634	3.82	38±6	30±1
Milli-Q 18.2 MΩ.cm	2.0728	3.51	7±9	-

Excellent agreement with potentiometric titration and Anglian Water quality report (234 mg $CaCO_3$/L)

Carboxylate content of nanomaterials

The carboxylate content of nanomaterials determines their pH and ion-responsive self-assembly behaviour. Conductometric titrations require large quantities of material (0.1 g) that may not be available.[1] In contrast, our method requires less than 6 mg of material per measurement and any degradation of the sample can be readily detected.

1. Foster *et al.* Chem. Soc. Rev. 2018, 47, 2609



$$[\mathrm{COO}] = [\mathrm{HCl}]\left[1-\frac{(\delta_H-\delta_{ref})}{(\delta_{ref}-\delta_L)}\frac{(\delta_L-\delta_{obs})}{(\delta_{obs}-\delta_H)}\right]$$

Sample	[COO]/mM	TA/mM	[Acid]/mM*
Citrate CNC	3.47±0.30	0.16±0.02	1.62±0.08
Malate CNC	2.69±0.31	0.09±0.02	2.78±0.14
Na_2 fumarate	3.87±0.30	-	-

*Total concentration of citrate or malate determined by alkaline hydrolysis of cellulose esters

pH 9

pH 2

Measure residual acidity (a) and deprotonated carboxylate content (b) of 1 wt% neutral dispersions of carboxylic acid functionalised cellulose nanocrystals (CNC) from ^{1}H shift of phosphonate pH reporter.

- [COO] determined by NMR within 10% of value measured by alkaline hydrolysis
- Method reveals mono-esterification of citric and malic acid to CNC
- Aggregation of CNC at low pH can be linked to protonation of carboxylate groups

Conclusions: The titratable acidity, alkalinity and carboxylate contents of aqueous samples can be determined by ^{1}H NMR with an accuracy comparable to conventional titrations but with far lower sample volumes and greater chemical insight. Our methods may be integrated as part of the routine analysis of samples by ^{1}H NMR.

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