2nd Workshop on QA/QC in Analysis
Combined meeting of the Expert Panel on Deposition and Working Group on Soil Solution
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Problems related to measurements of low values of total alkalinity

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Total alkalinity

In WRT1 and in most of the intercomparison exercises, low values of alkalinity resulted among the variables affected by the highest errors

Following ICP Forests manual, alkalinity measurement is mandatory in deposition samples with pH>5.0.
In this samples alkalinity is important for the check of the ion balance.

Total alkalinity: definition

- Alkalinity of a water is its acid-neutralising capacity. It is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

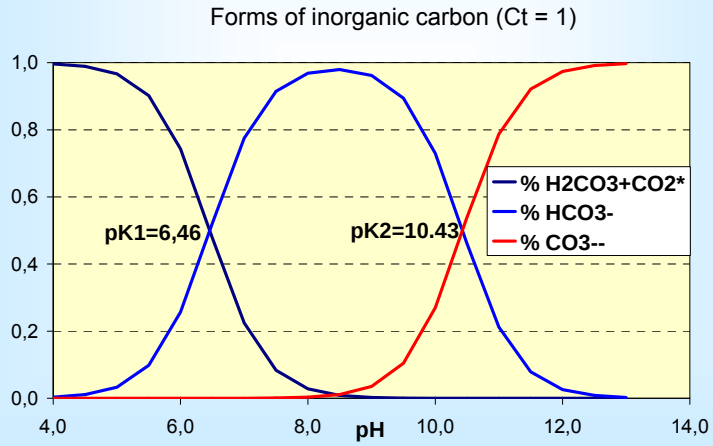
- It is the sum of all the titratable bases.

$$TA = [HCO_3^-] + [CO_3^=] + [OH^-] - [H^+] + [A^-_{org}] + [B^-_{inorg}]$$

where concentrations are expressed in eq L^{-1}, A^-_{org} are organic compounds and B^-_{inorg} are inorganic bases which may accept protons (borate, phosphate, silicate, etc)

In most of the freshwater and in atmospheric deposition alkalinity is mainly dependent on the inorganic carbon equilibrium.

In the pH range of atmospheric deposition (5.0-7.5) the prevailing form of inorganic carbon are $H_2CO_3^*$ and HCO_3^-; so it is normally assumed that TA= $[HCO_3^-]$



Total alkalinity: methods of analysis

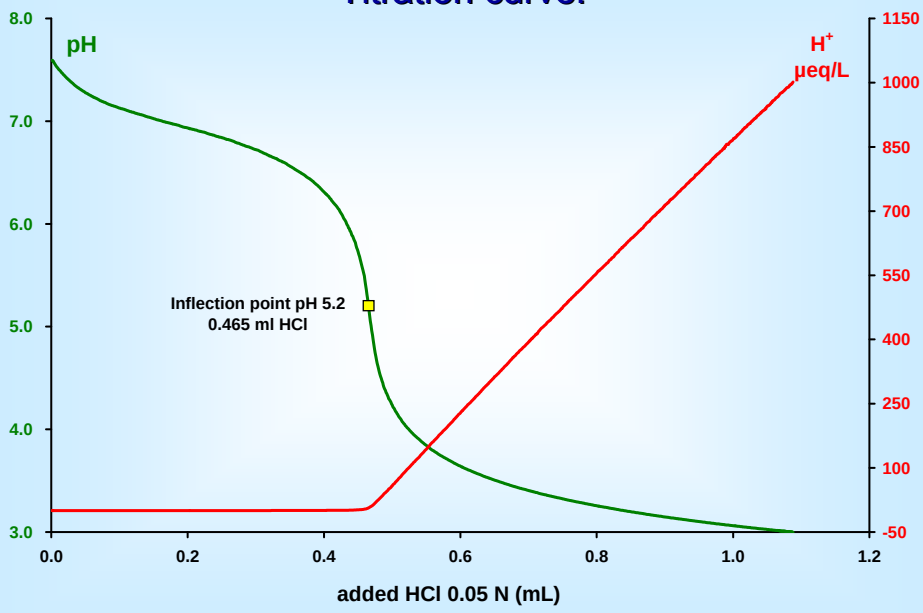
Total alkalinity is determined through an acidimetric titration (it does exist as well a conductometric method).

The measured value may vary significantly with the analytical technique used and with the selected end-point.

The problem is the detection of the equivalence point of the titration, i.e. the condition:

$$[H^+] = [\ HCO_3^-\ ]$$

Titration curve.



Acidimetric titration of alkalinity

Determination of the equivalent point by:

Indicators:

Different indicators change color at different pH!

Potentiometry:

- One end-point (pH 4.3, 4.5, ….)
- Detection of the inflection point
- Two end-points (normally differing by 0.3 pH units)
- Gran's titration

Indicators

	pH range	
Methyl orange	**3.0 - 4.4**	red-yellow
Bromophenol blue	**3.0 - 4.6**	yellow-blue
Methyl red	**4.2 - 6.2**	red - yellow
Bromocresol green	**3.8 - 5.4**	yellow-blue

Disadvantages: high error associated due to:

1) Not coincidence between the pH range of variation of colour and pH range of the equivalence point (5.4-5.6);

2) range of pH of the colour change;

3) different sensitivity of the operator to detect the colour change.

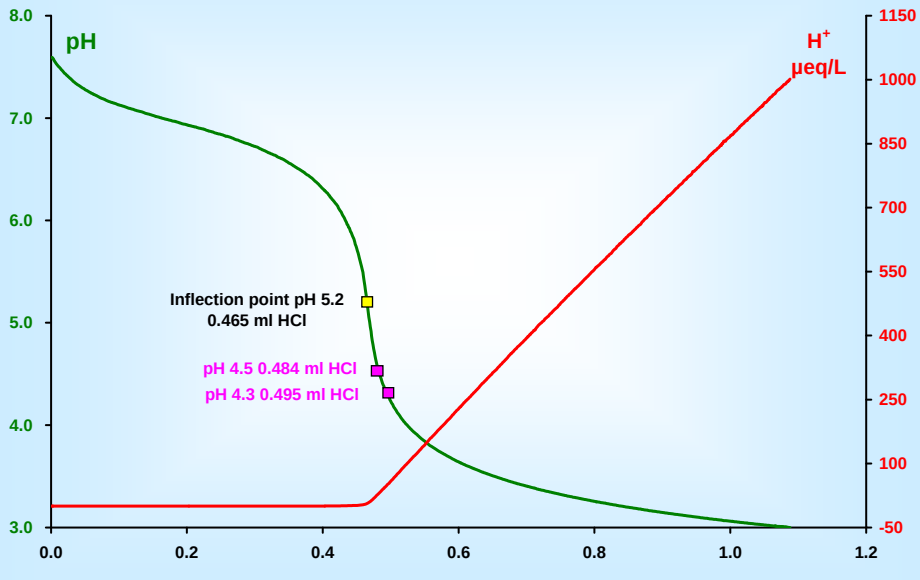
One end point titration, potentiometry. Correction of alkalinity values

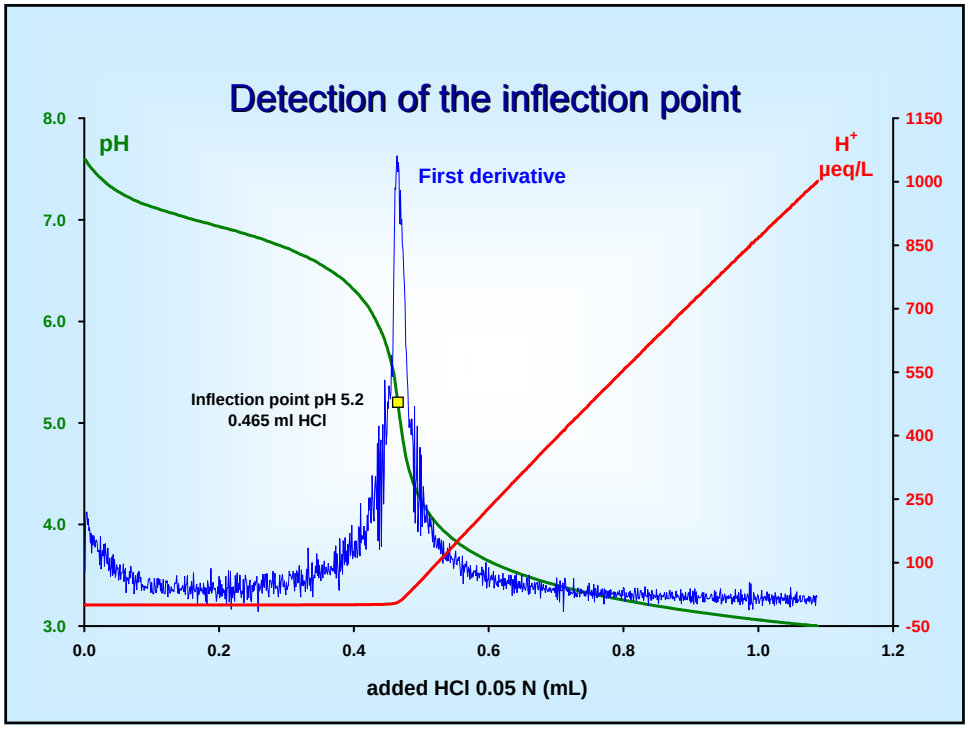
	pH	H^+ conc.	Correction to be applied to the alkalinity concentration
Real equivalent point	5.4-5.7	2-3 µeq/L	--
One end point to	4.5	32 µeq/L	29 µeq/L
One end point to	4.3	50 µeq/L	47 µeq/L

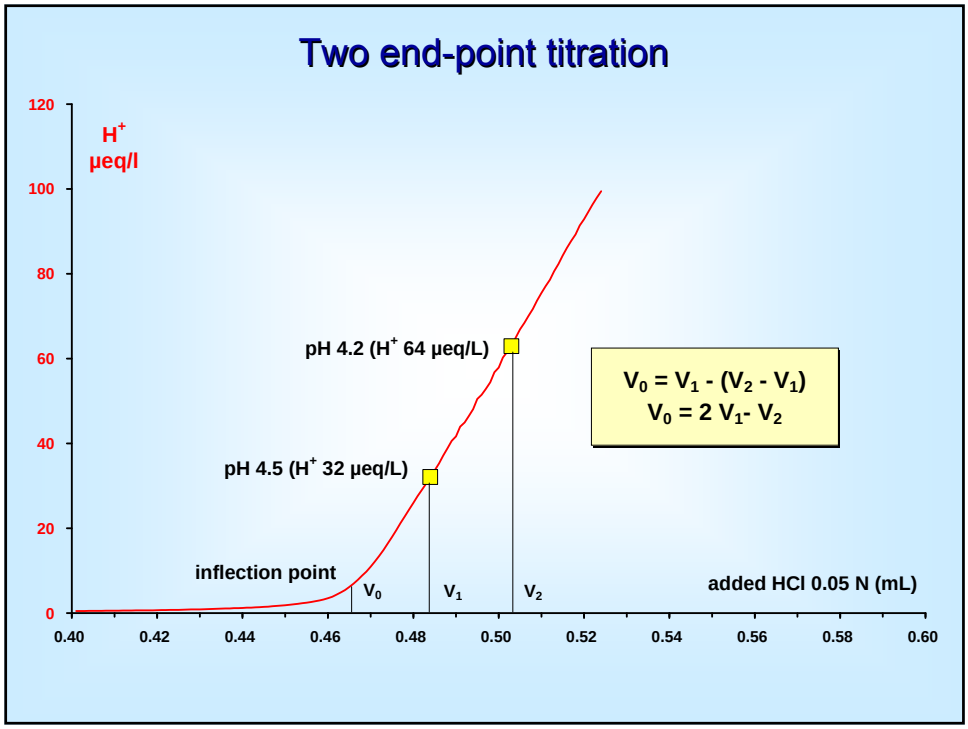
Henriksen (1982) correction:

$TA\ (\mu eq/L) = (TA_{4.5} - 32) + 0.646\ (TA_{4.5}-32)^{0.5}$

One end point titration, potentiometry.

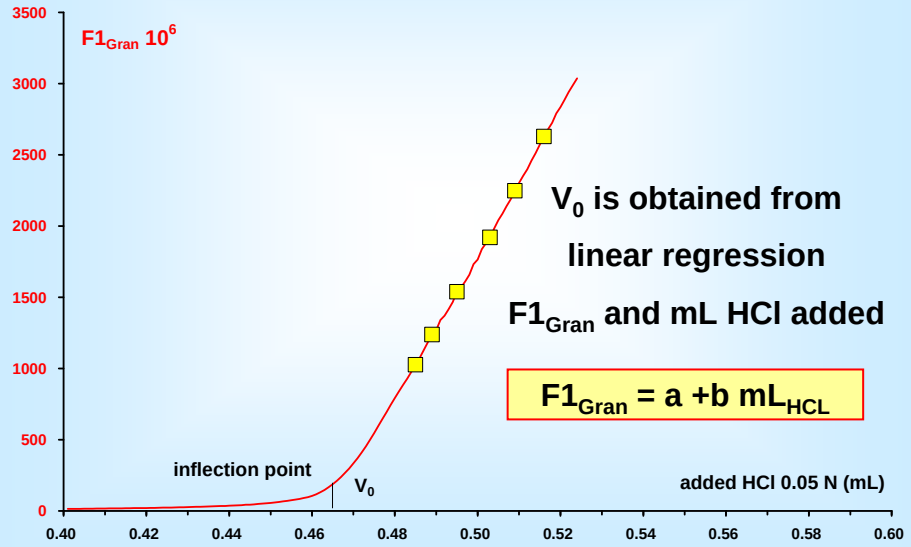



Detection of the inflection point
pH
First derivative
H+ µeq/L
Inflection point pH 5.2
0.465 ml HCl
8.0
7.0
6.0
5.0
4.0
3.0
1150
1000
850
700
550
400
250
100
-50
0.0
0.2
0.4
0.6
0.8
1.0
1.2
added HCl 0.05 N (mL)


Two end-point titration
H+ µeq/l
120
100
80
60
40
20
0
pH 4.2 (H+ 64 µeq/L)
pH 4.5 (H+ 32 µeq/L)
inflection point
V0
V1
V2
V0 = V1 - (V2 - V1)
V0 = 2 V1- V2
added HCl 0.05 N (mL)
0.40
0.42
0.44
0.46
0.48
0.50
0.52
0.54
0.56
0.58
0.60

Gran's titration

$F1_{Gran} = (mL_{sample\ volume} + ml_{HCl}\ added)\ 10^{-pH}$

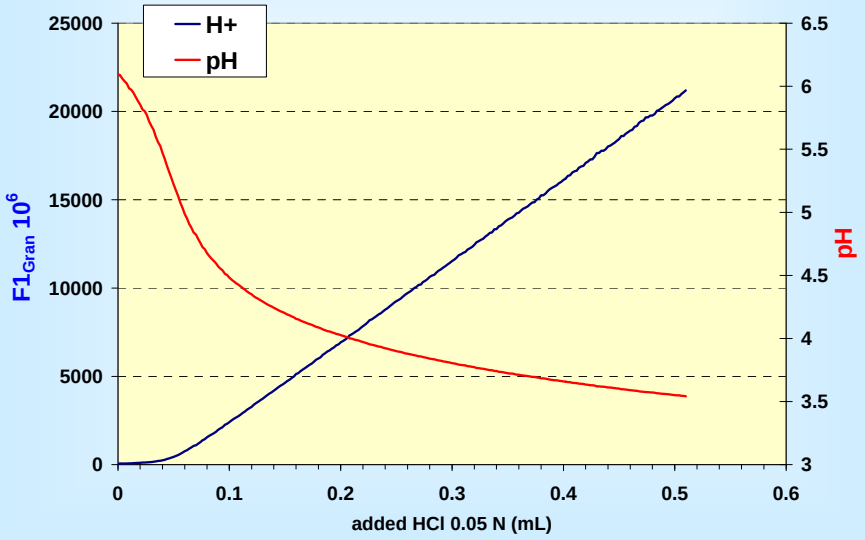


V_0 is obtained from linear regression $F1_{Gran}$ and mL HCl added

$F1_{Gran} = a + b\ mL_{HCL}$

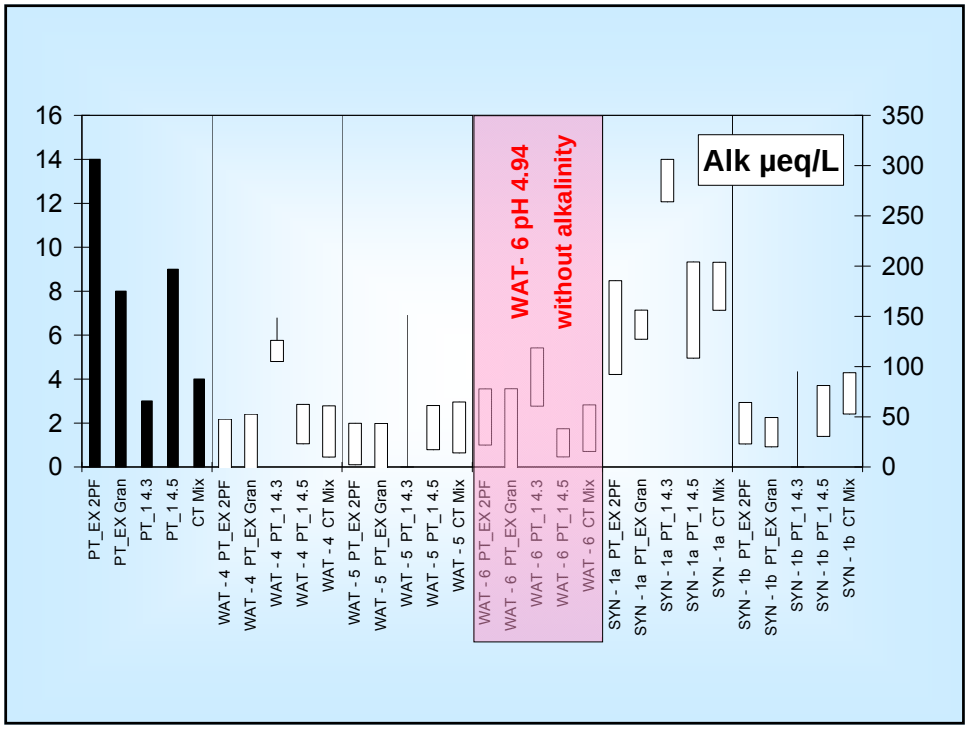
Gran's titration

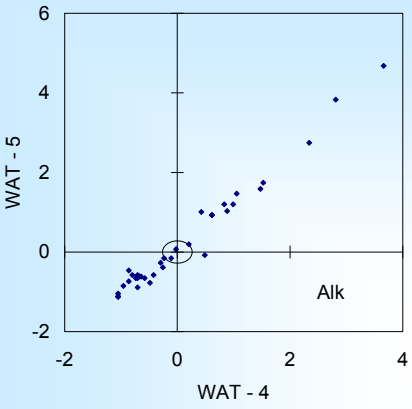
Sample SYN-1b median values 39 µeq/L



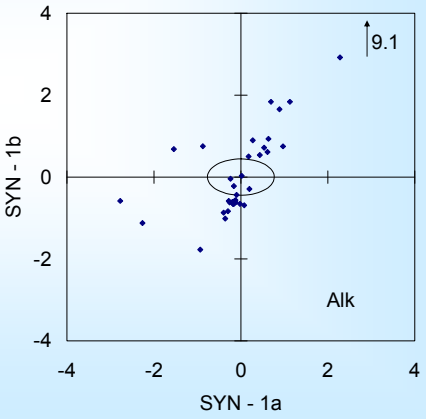
Sample SYN-1b median values 39 µeq/L

Gran 23 points (range pH 4.4 - 4.16)	0.0324 µeq/L
Gran 200 points (range pH 4.4 - 3.54)	0.0340 µeq/L
Two end-point titration (pH 4.5 – 4.2)	0.0319 µeq/L
One end-point titration (pH 4.5)	0.068 µeq/L
One end-point titration (pH 4.2)	0.089 µeq/L

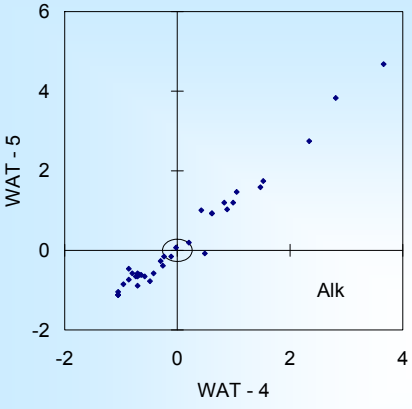




Alkalinity ring	25 %
WAT - 4 (µeq /L)	26
WAT - 5	21
SYN - 1a	149
SYN - 1b	39



No. of labs	39
No. measures	148
Within target (25 %)	52
No. outliers	4



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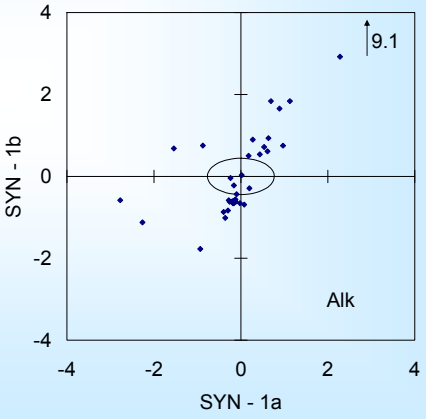

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Two laboratories measured alkalinity in the samples WAT-1, WAT-3, WAT-7, with median pH 4.2, 3.9 and 4.2 respectively.

Fifteen laboratories measured alkalinity in sample WAT-6 (pH 4.94±0.11), with results ranging between 8 and 110 µeq/L , mean 41 µeq/L, median 30 µeq/L

Conclusions

The measurement of low values of alkalinity are reliable if:

1) the following analytical methods are used:

- Gran titration;
- two end point titration (ΔpH = 0.3 u. e.g. 4.5-4.2);
- titration at pH 4.5 and correction for the extra acid added.

2) the ordinary AQC are adopted, e.g.:

- ordinary maintenance of titrator and electrodes;
- periodic calibration of the titrant acid;
- use of quality control charts.

Conclusions

A chemical variable is normally identified by:
name of the variable, unit of measurement, numerical value:
calcium, mg L^{-1} , 0.25

In some case it is important to specify the analytical method used:
total alkalinity, µeq L^{-1}, 26
(one end-point (4.5) acidimetric titration).

In the case of alkalinity this is of the main importance because of the relevant differences existing among the different analytical methods used.

Alkalinity values stored in the ICPF European database, as well as other chemical variables, should be perfectly comparable.

This is the goal.