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Measurements of low values of total alkalinity

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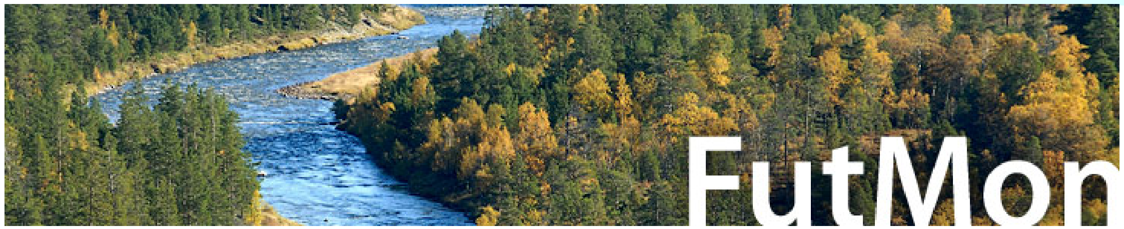
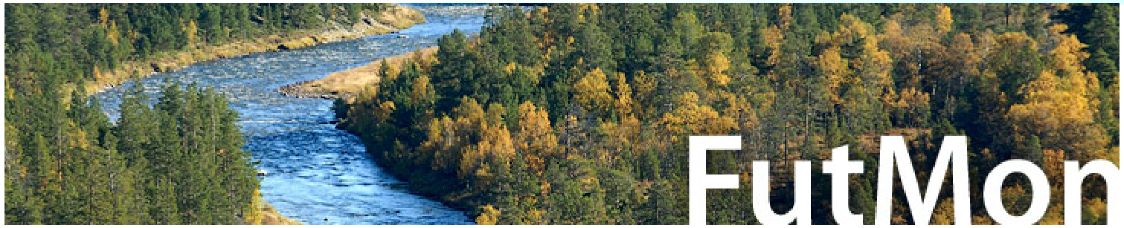


Total alkalinity: definition

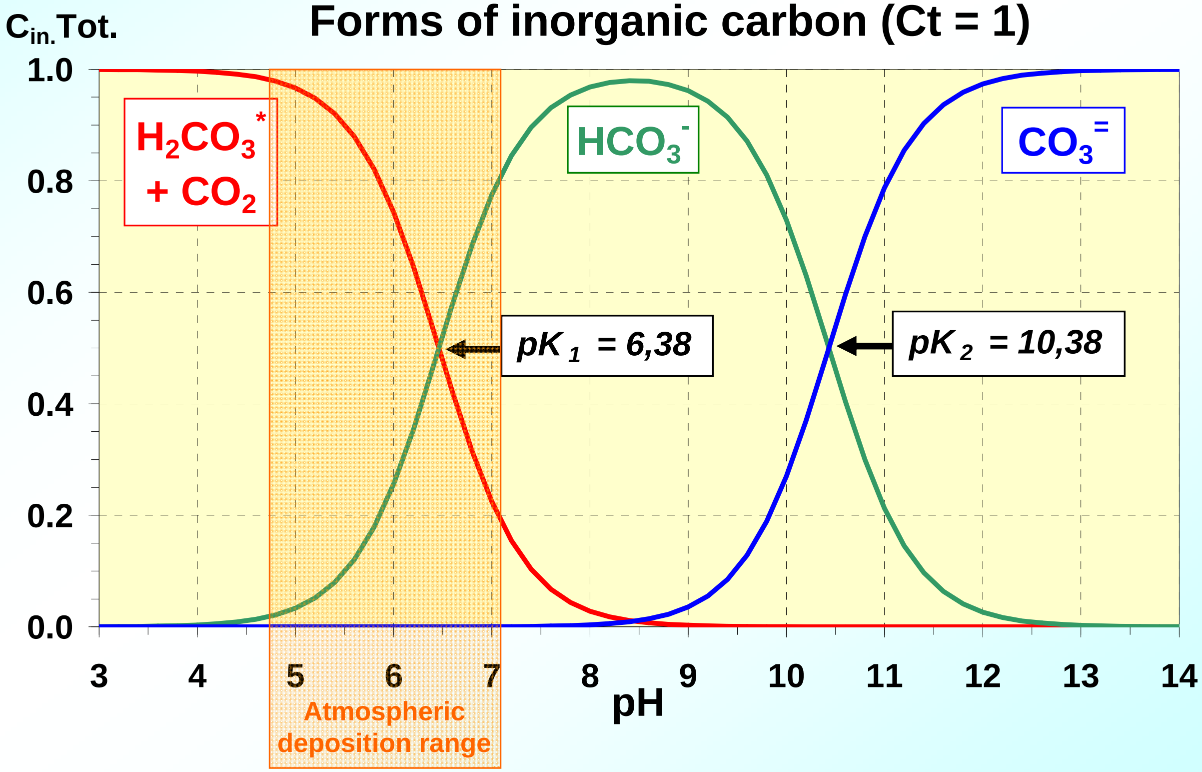
- Water alkalinity is its acid-neutralising capacity. It is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.
- It is the sum of all the titrable bases.

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

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 freshwater and in atmospheric deposition alkalinity is mainly dependent on the inorganic carbon equilibrium. In the pH range of atmospheric deposition (4.7-7.2) 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:

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

Acidimetric titration of alkalinity

Determination of the equivalent point by:

Indicators:

Different indicators change color at different pH!

Potentiometry:

- One end-point (pH 4.5, 4.3, ….)
- Detection of the inflection point
- Two end-points (normally differing by 0.3 pH units 4.5-4.2)
- Gran's titration

The best methods!

Indicators

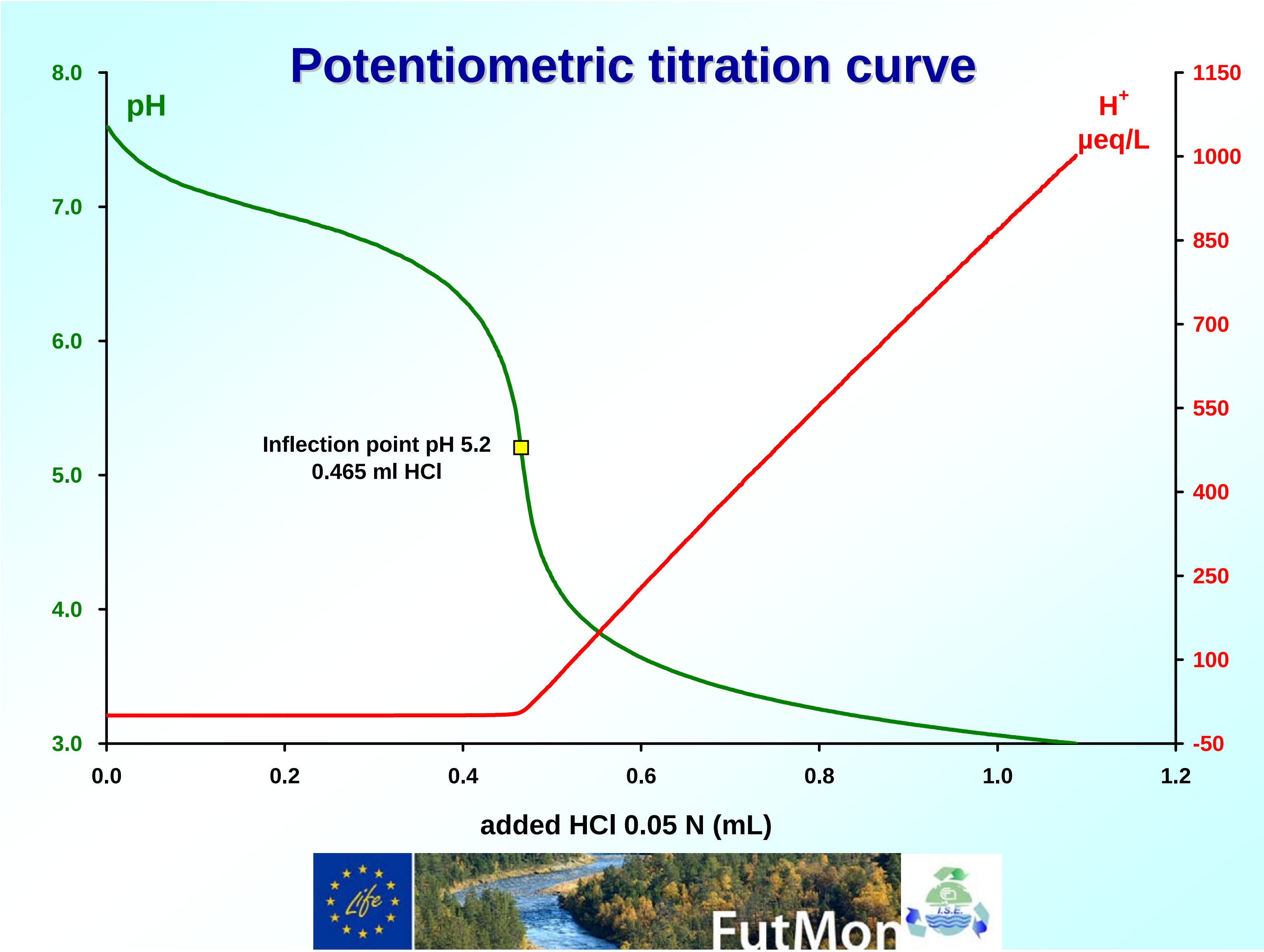
	pH range	
Methyl orange	**3.0 - 4.4**	**red-yellow**
Bromophenol blue	**3.0 - 4.6**	**yellow-blue**
Methyl red	**4.2 - 6.2**	**red - yellow**
Bromocresol green	**3.8 - 5.4**	**yellow-blue**

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.


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

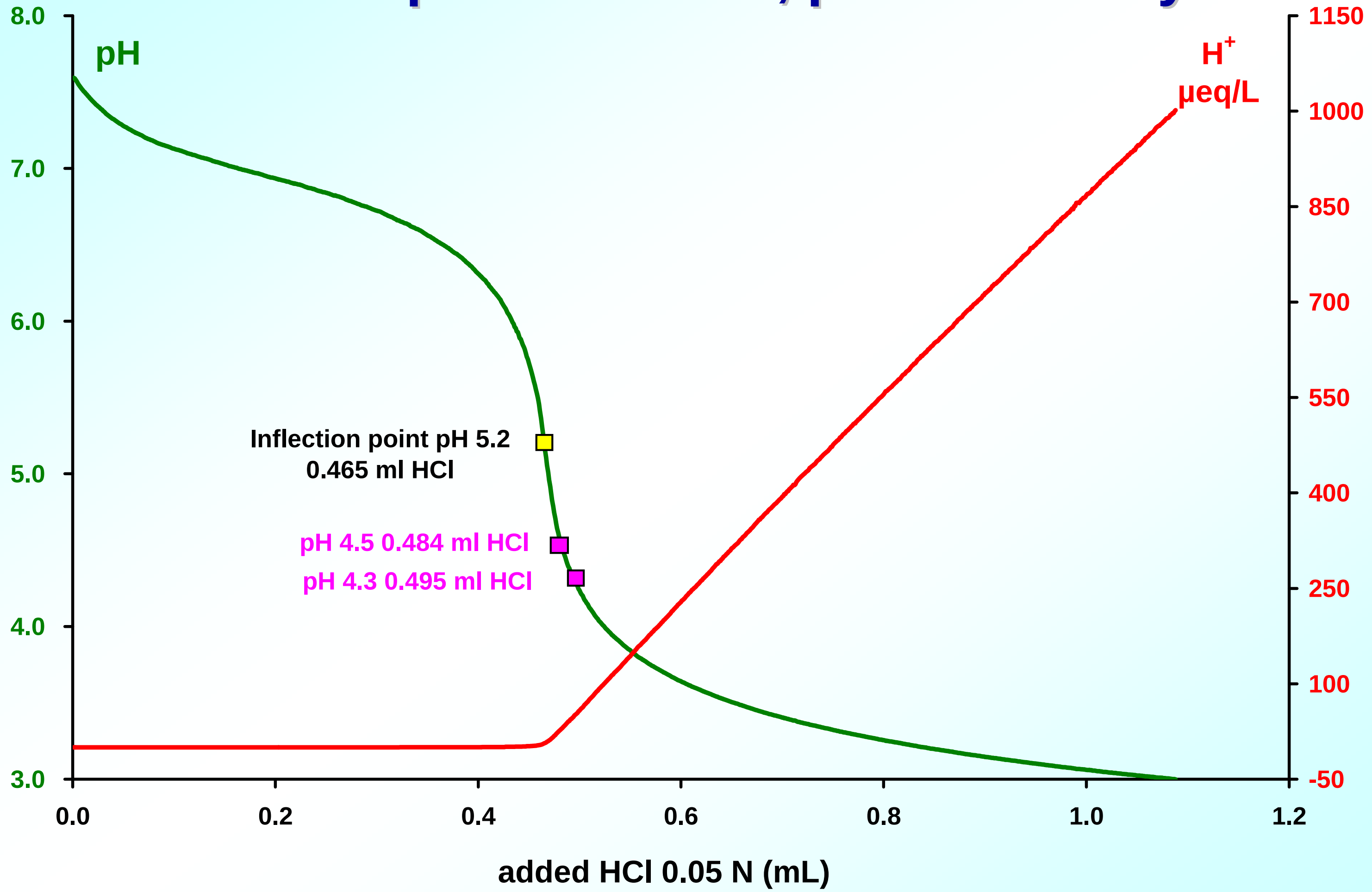
One end point titration, potentiometry. Correction of alkalinity values

	pH	H^+ conc.	Correction to be applied to the alkalinity concentration
Real equivalent point	**5.4-5.7**	**2-3 μeq L^{-1}**	**--**
One end point to	**4.5**	**32 μeq L^{-1}**	**~29 μeq L^{-1}**
One end point to	**4.3**	**50 μeq L^{-1}**	**~47 μeq L^{-1}**

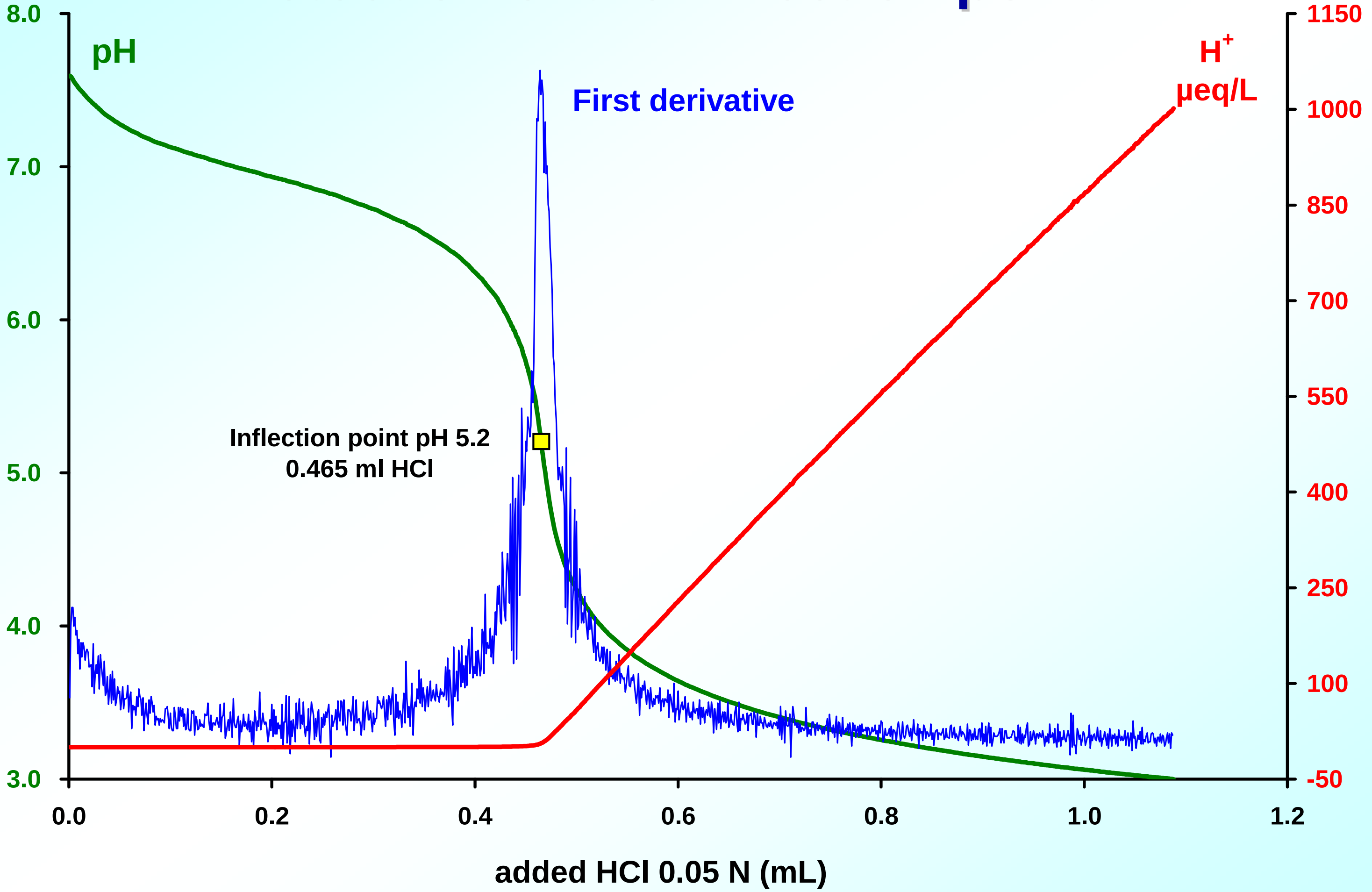
Henriksen (1982) correction for one end point (pH = 4.5) titration:

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

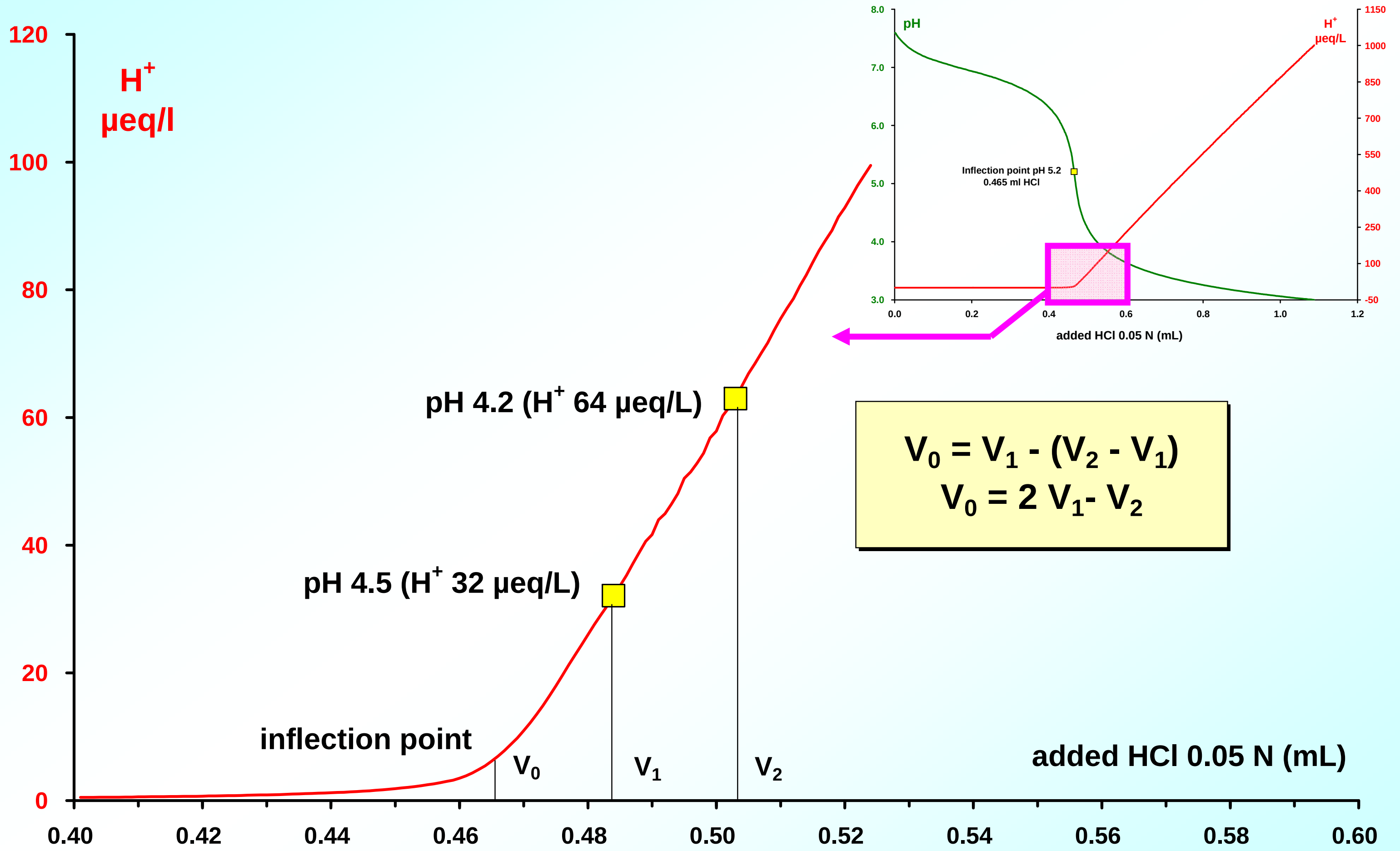
One end point titration, potentiometry.



Detection of the inflection point



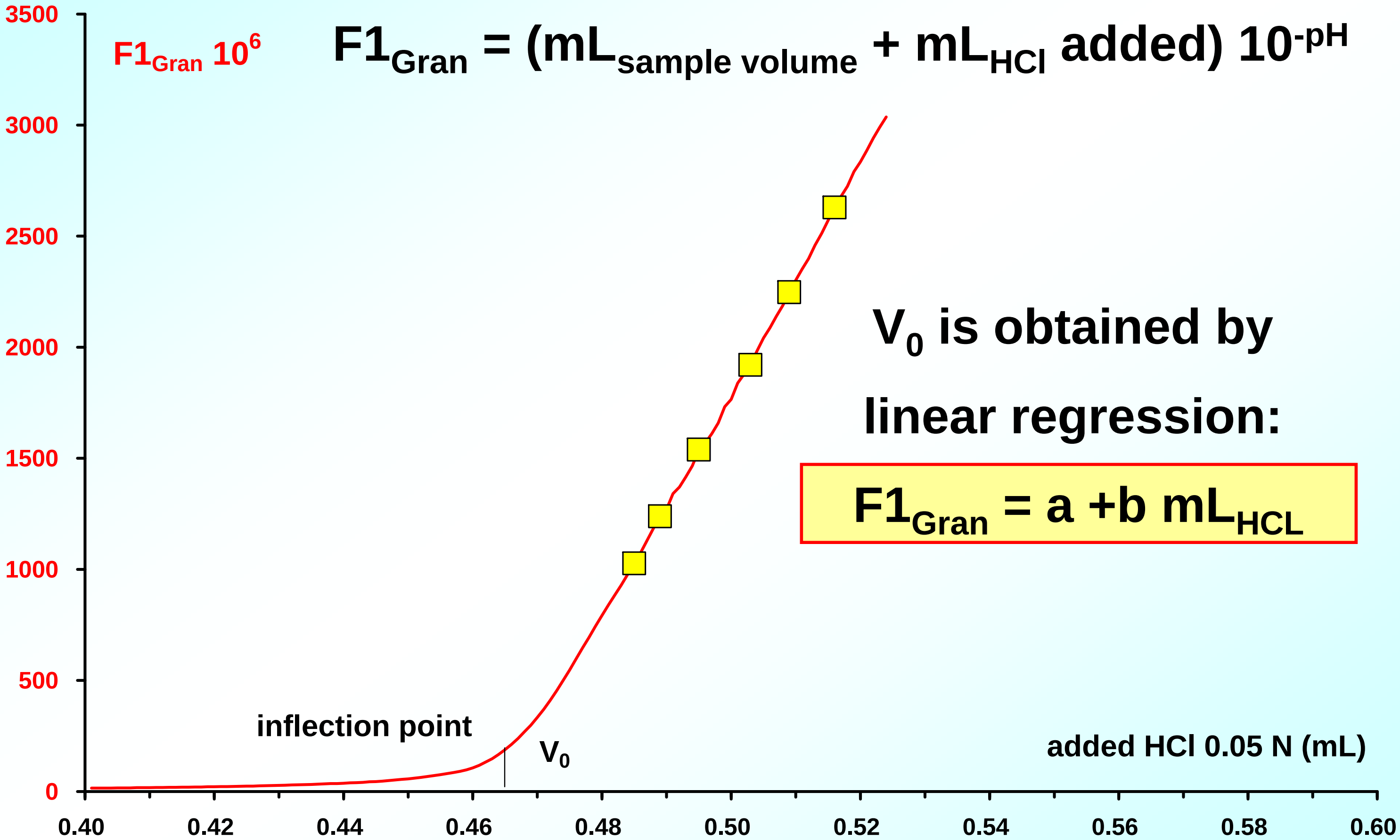
Two end-point titration



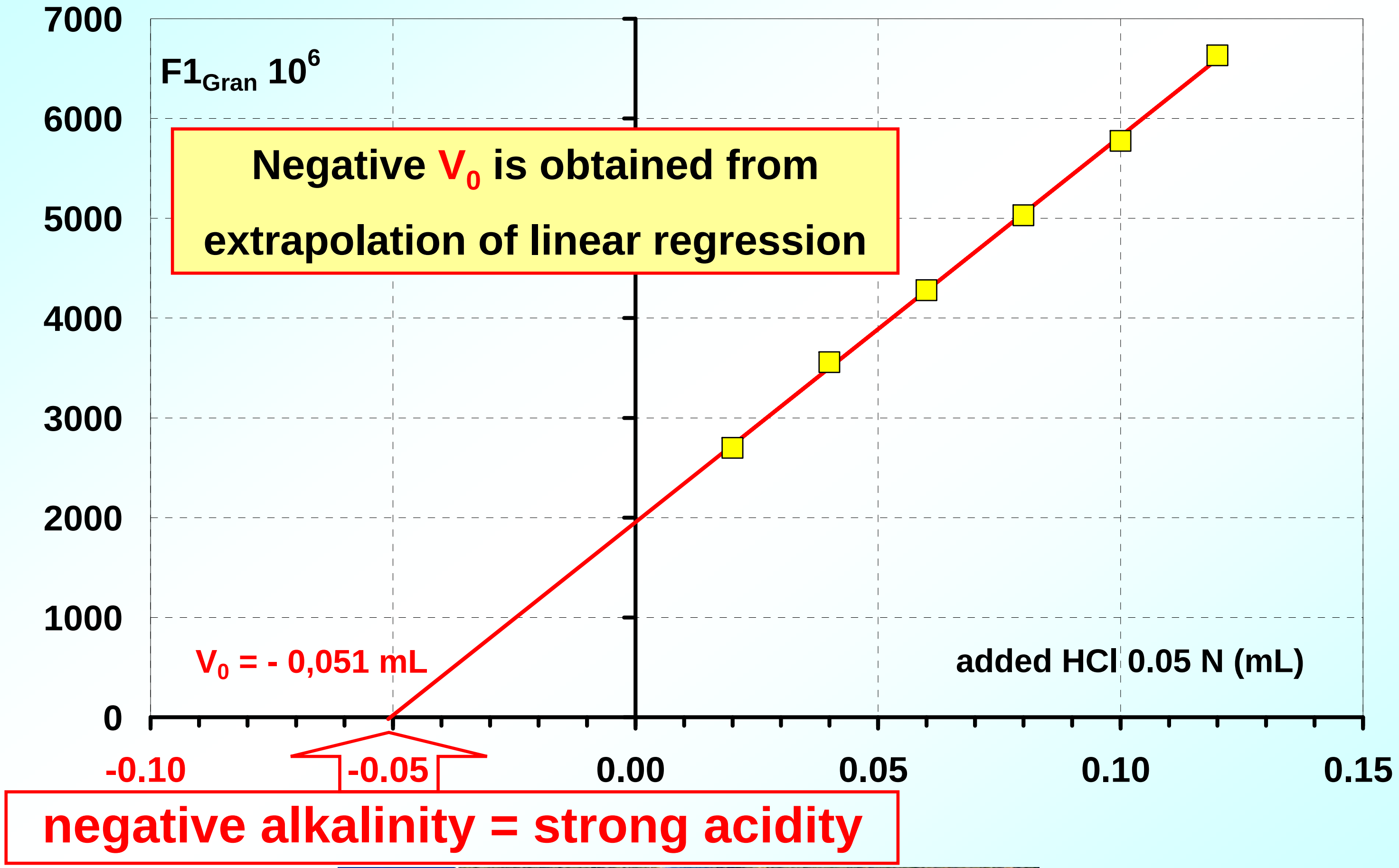
$$V_0 = V_1 - (V_2 - V_1)$$

$$V_0 = 2\,V_1 - V_2$$

Gran’s titration for sample with pH>5



Gran’s titration for sample with pH<5



Conclusions for general aspects

The measurement of low values of alkalinity are reliable if:

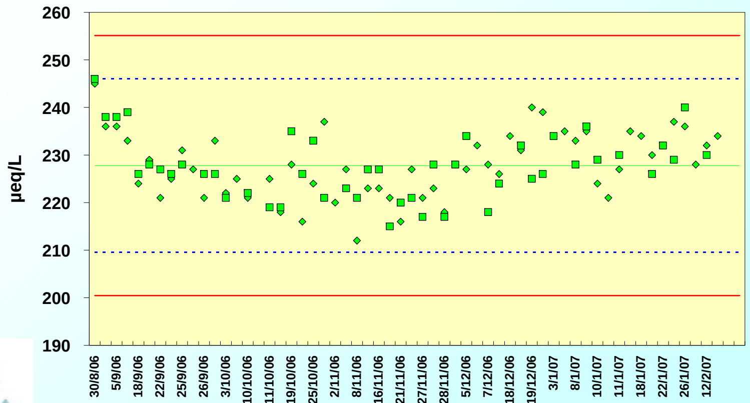
1) the following analytical methods are used:

- 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 electrodes and titrator;
- periodic calibration of the titrant acid (HCl 0.01 or 0.05 N);
- use of quality control charts.

Example for $NaHCO_3$ standard solution



Calculation example for WRT2009, sample SYN 6

Methods:

- two end point titration (ΔpH = 0.3 u. e.g. **4.500-4.200**);
- Gran with linear regression (5 points)
- titration at pH 4.5 and correction for the extra acid added.

Conditions and data:

- Sample volume titrated: 40.43 mL
- Titrant HCl 0.04996 N

Formulae:

- H^+ (µeq/L) = $10^{-pH} \times 10^6$
- $F1_{Gran} = (mL_{sample\ volume} + mL_{HCl})\ 10^{-pH}$

mL_{HCl}	pH	H^+ µeq/L	$F1_{Gran}\ 10^3$
0.088	**4.500**	31.6	
0.100	4.349	44.8	1.8
0.110	4.252	56.0	2.3
0.116	**4.200**	63.1	
0.120	4.170	67.6	2.7
0.130	4.103	78.9	3.2
0.140	4.046	89.9	3.6

Calculation example for WRT2009 sample SYN 6

- Two end point titration (pH **4.5 and 4.2**);

  pH 4.5 $V_1 = 0.088$ mL

  pH 4.2 $V_2 = 0.116$ mL

  $V_0 = 2V_1 - V_2$

  $V_0 = 2 \times 0.088 - 0.116$

  $V_0 = 0.0600$ mL

- Gran with linear regression (5 points)

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

  V_0 is obtained by linear regression: ⇨

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

  $a = -2.78$ $b = 46$

  $$V_0 = \frac{F1_{Gran} - a}{b} = \frac{-a}{b} = \frac{2.78}{46}$$

  $V_0 = 0.0604$ mL

Results for example WRT2009 sample SYN 6

$$\text{Alkalinity } (\mu eq / L) = \frac{\text{mL } V_0 \times N_{HCl} \times 10^6}{\text{mL sample volume titrated}}$$

Method used	V_0 mL	Alkalinity µeq/L
Two end-point titration (pH 4.5 – 4.2)	0.0600	**74.1**
Gran 5 points (range pH 4.4 - 4.0)	0.0604	**74.8**
One end-point titration (pH 4.5) with Henriksen (1982) correction	0.088	**82.4**
One end-point titration (pH 4.5) with correction -32 µeq/L	0.088	**76.7**

Sample volume titrated: 40.43 mL
Titrant HCl: 0.04996 N

Calculation example to standardize the titrant acid HCl 0.05 N concentration

- Dry at 250°C and weigh 1.0599 g Na_2CO_3 to 1000 mL volumetric flask (sol. A = 20 meq/L)
- Standard solutions preparation:

  100 µeq/L = 5000 µL sol. A to 1000 mL volumetric flask

  200 µeq/L = 5000 µL sol. A to 500 mL volumetric flask

  500 µeq/L = 25 mL sol. A to 1000 mL volumetric flask

- Titrate the standards like the samples, compare and calculate the new HCl titrant concentrations:

Standard µeq/L	Results µeq/L	HCl Normality
100	97	0.05155
200	196	0.05102
500	489	0.05112
The average is the new HCl concentration		**0.05123**

$$0.05102 = \frac{200}{196} \times 0.05$$

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