

5th meeting of the heads of the laboratories
(17-18 September 2015, Wien)

Problems related to measurements of low values of total alkalinity and pH in dilute samples



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Total alkalinity

In sample 1 low values of alkalinity resulted among the variables affected by the highest percent of data outside the acceptance range.

Following ICP Forests manual, alkalinity measurement is mandatory in deposition samples with $\text{pH} > 5.0$.

In these samples alkalinity is important for the check of the ion balance.

Total alkalinity

Sample 2: pH = 4.42

Alkalinity measurement is not requested

If you perform the titration, you should find that the (first) end point (pH 4.5) has been reached BEFORE starting to add the acid

If you use the Gran method you should find negative alkalinity

ALKALINITY ($\mu\text{eq/l}$)			Sample 1 (Median: 63,0000 = 100% Recovery, Number of labs: 33 passed: 26)			
Parameter	Sample	Labcode	Preparation	Determination	Result	% Recovery
ALKALINITY	1	A39	MB01	DF04	<100	too high LOQ
ALKALINITY	1	F21	MB01	DF06	,1	0,16
ALKALINITY	1	F27	MB01	DF05	42,67	67,73
ALKALINITY	1	F06	MB01	DF04	54	85,71

ALKALINITY	1	A60	MB01	DF05	71,5	113,49
ALKALINITY	1	F08	MB01	DF05	73	115,87
ALKALINITY	1	F07	MB02	DF05	74,7	118,57
ALKALINITY	1	F14	MB01	DF06	75	119,05
ALKALINITY	1	D60	MB01	DF08	81,8	129,84
ALKALINITY	1	D05	MB01	DF06	90	142,86
ALKALINITY	1	D63	MB02	DF04	91,7	145,56
ALKALINITY	1	D39	MB01	DF06	96	152,38
ALKALINITY	1	D06	MB01	DF06	103	163,49
ALKALINITY	1	F24	MB01	DF06	153	242,86

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Error in reporting unit



(note: it is the same unit as in the ICP Forets database!)

Time for stabilization of the electrode too short

ISO 9963-1

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Total alkalinity

Lab	pH	Alkalinity
D60	4.42	19.8 $\mu\text{eq L}^{-1}$
F24	4.63	13 $\mu\text{eq L}^{-1}$
F04	4.70	5 $\mu\text{eq L}^{-1}$
D63	4.83	37 $\mu\text{eq L}^{-1}$

a problem with pH electrode also affecting alkalinity?

ISO 9963-1:1994(E)

trations. Other buffering substances (X) such as ammonia, borate, phosphate, silicate and organic anions may be included in the determination.

$$A_p \approx c(\text{CO}_3^{2-}) - c(\text{CO}_2\text{aq}) + c(\text{OH}^-) - c(\text{H}^+) + c(\text{X})$$

$$A_T \approx 2c(\text{CO}_3^{2-}) + c(\text{HCO}_3^-) + c(\text{OH}^-) - c(\text{H}^+) + c(\text{X})$$

By definition, composite alkalinity is zero for waters which have a pH value of 8,3 or less.


4 Principle

The sample is titrated with standard acid solution to fixed pH endpoint values of 8,3 and 4,5. These endpoints, which are determined visually or potentiometrically, are the selected equivalence points for the determinations of the three principal components: hydrogen carbonate, carbonate and hydroxide. The pH 8,3 endpoint approximates to the equivalent concentrations of carbonate and carbon dioxide and represents the titration of approximately all the hydroxide and half of the carbonate present. The pH 4,5 endpoint approximates the equivalence point for hydrogen ion and hydrogen carbonate and allows for the determination of the total alkalinity of the sample.

NOTE 2 The equivalent point values depend on the ionic strength as well as the concentration of total inorganic carbon and may not always be optimum at the chosen endpoints.

Whilst methyl orange and methyl red have been commonly used in the past as indicators for the determination of total alkalinity, in practice the use of different indicator systems produce slightly different results in alkalinity titrations. For alkalinity determinations in accordance with this part of ISO 9963, the correct bromocresol green-methyl red indicator solution as defined in 5.6 should be used.

One end-point
pH = 4.5



ISO 9963-1:1994(E)

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NOTE 2
strength of
carbon and
endpoints

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Whilst methyl orange and methyl red have been commonly used in the past as indicators for the determination of total alkalinity, in practice the use of different indicator systems produce slightly different results in alkalinity titrations. For alkalinity determinations in accordance with this part of ISO 9963, the correct bromocresol green-methyl red indicator solution as defined in 5.6 should be used.

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.

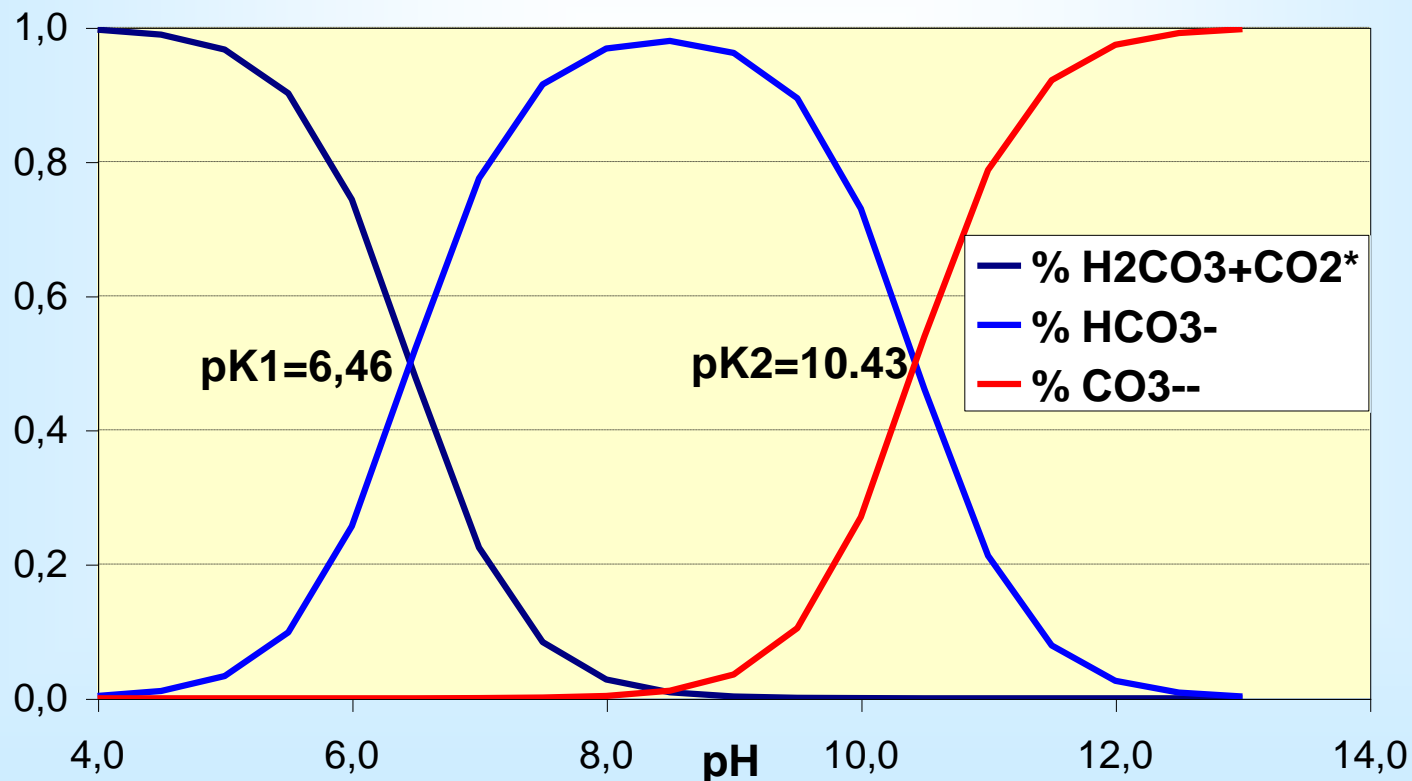
$$\text{TA} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{A}^-_{\text{org}}] + [\text{B}^-_{\text{inorg}}]$$

where concentrations are expressed in eq L^{-1} , A^-_{org} are organic compounds and $\text{B}^-_{\text{inorg}}$ 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 $\text{TA} = [\text{HCO}_3^-]$

Forms of inorganic carbon ($C_t = 1$)



Total alkalinity: methods of analysis

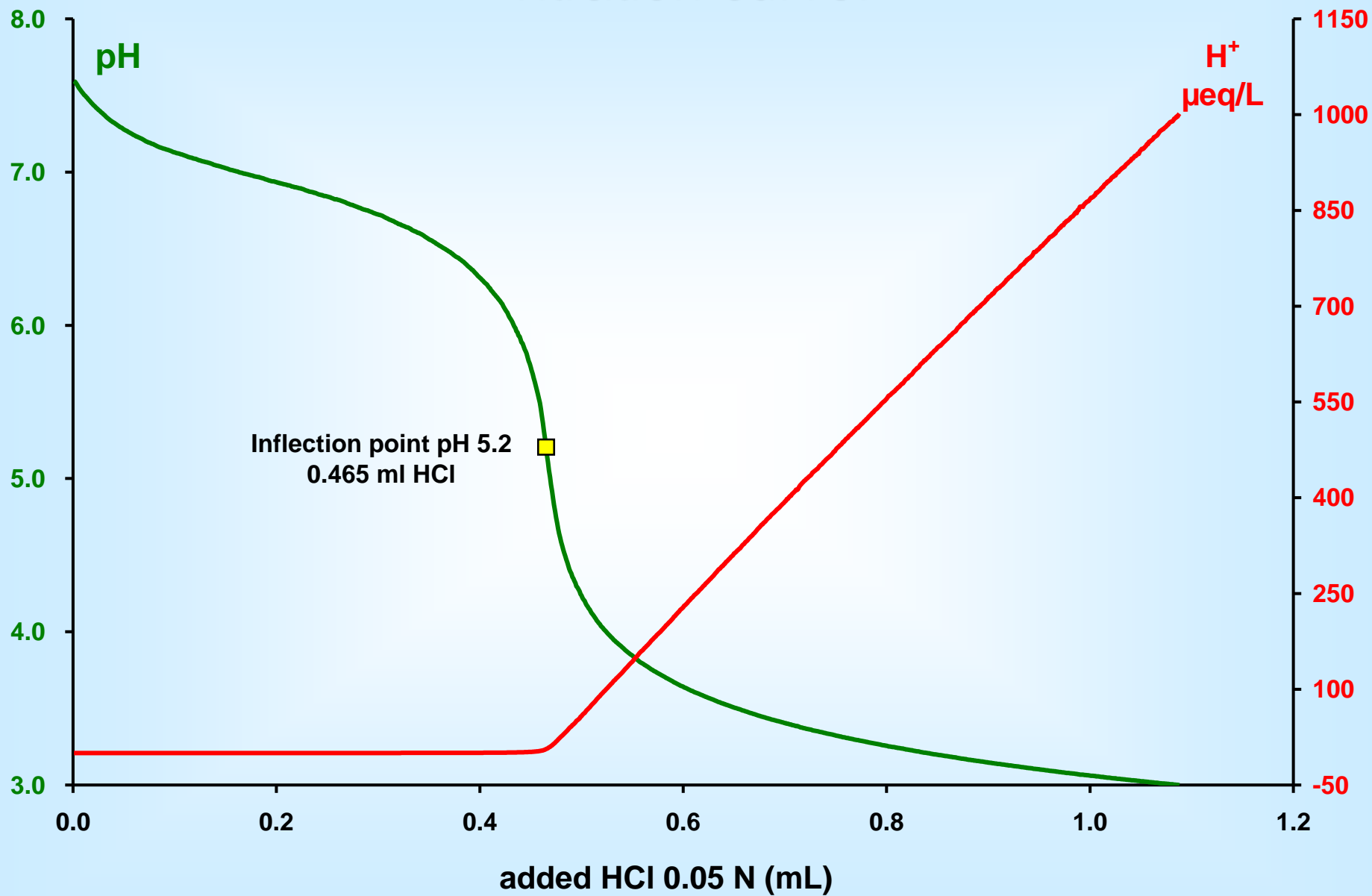
Total alkalinity is determined through an acidimetric titration (it does exist as well a conductometric method).

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:



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:

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

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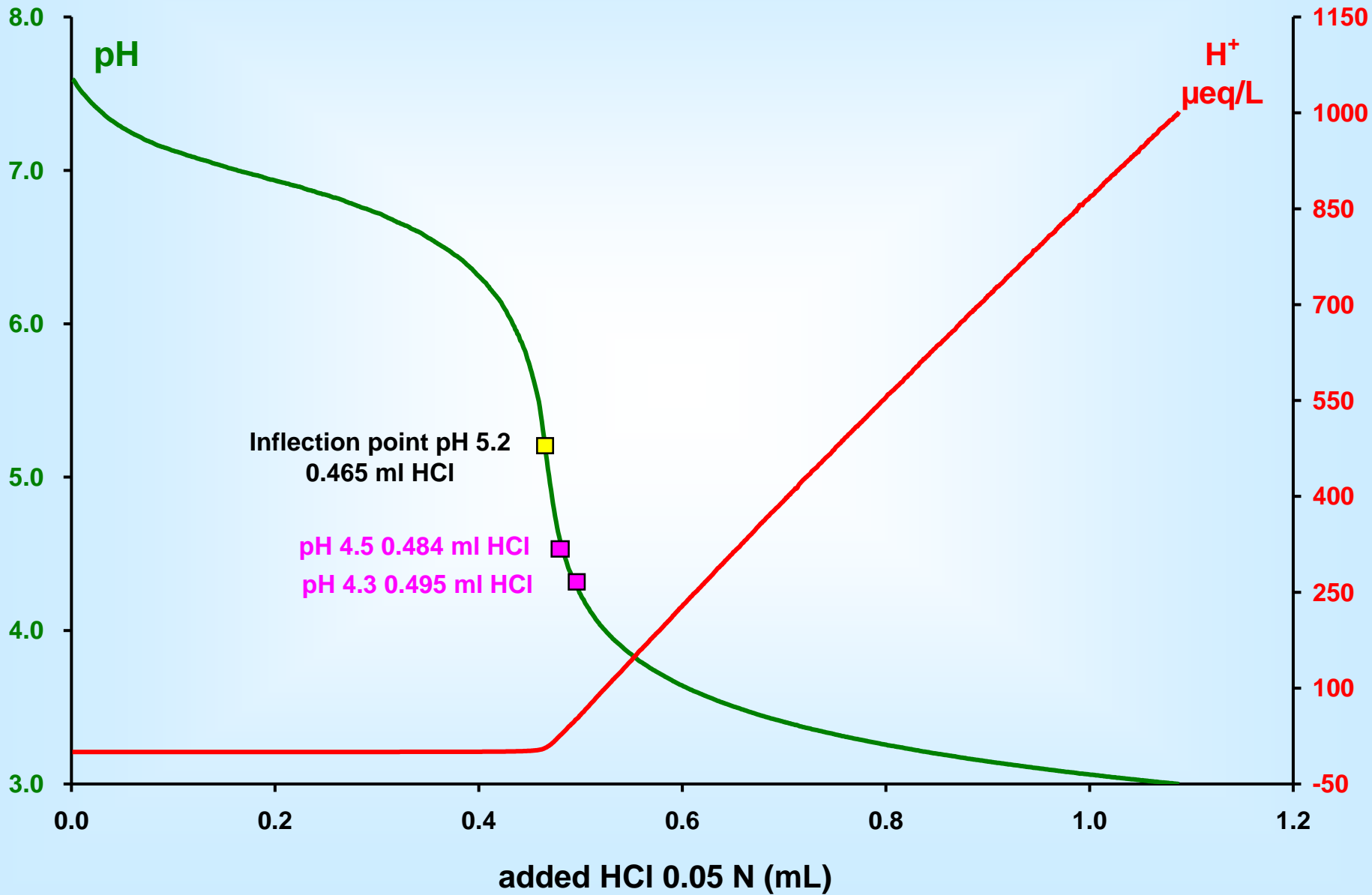
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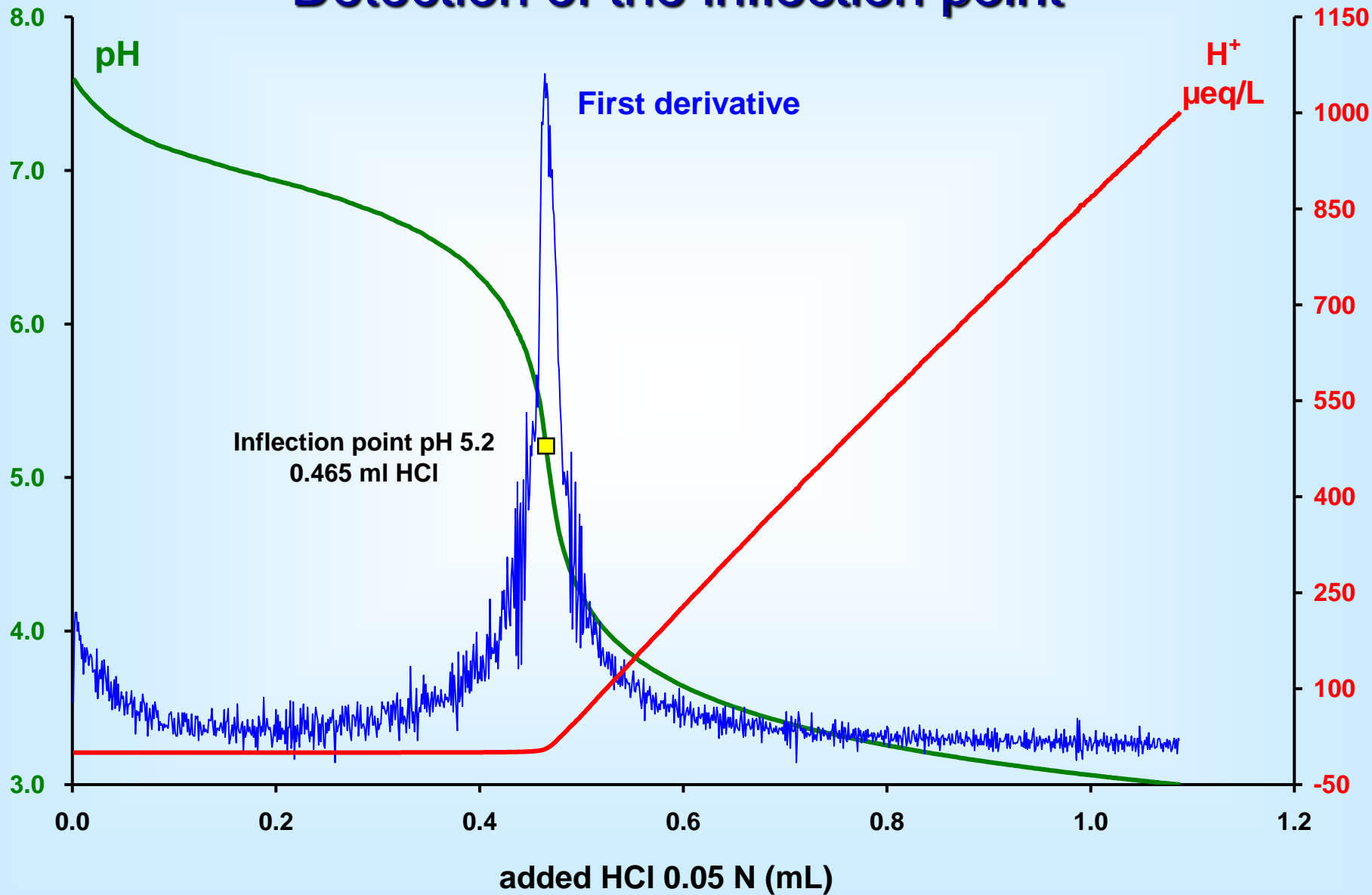
ISO 9963-2

ISO 9963-1

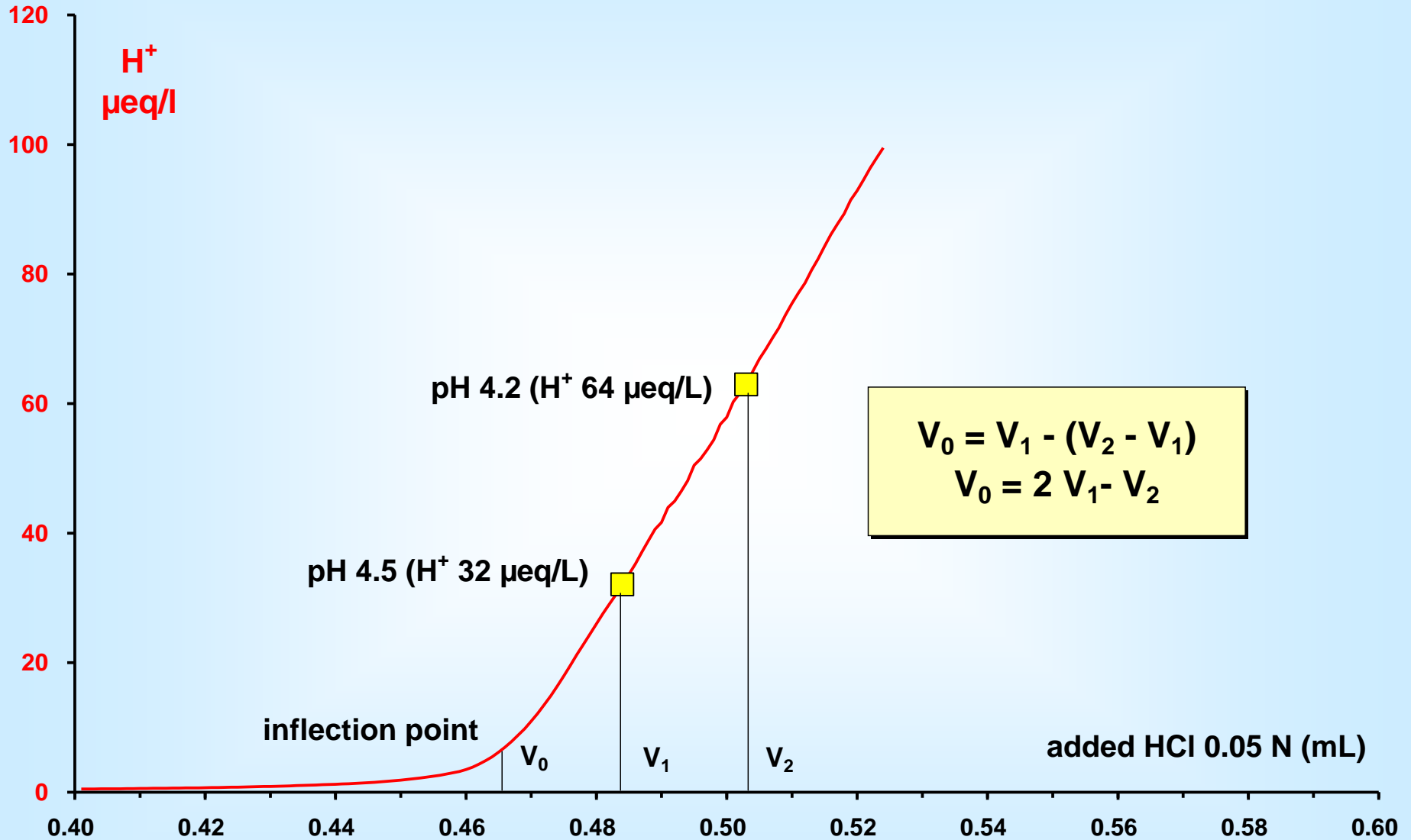
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Detection of the inflection point

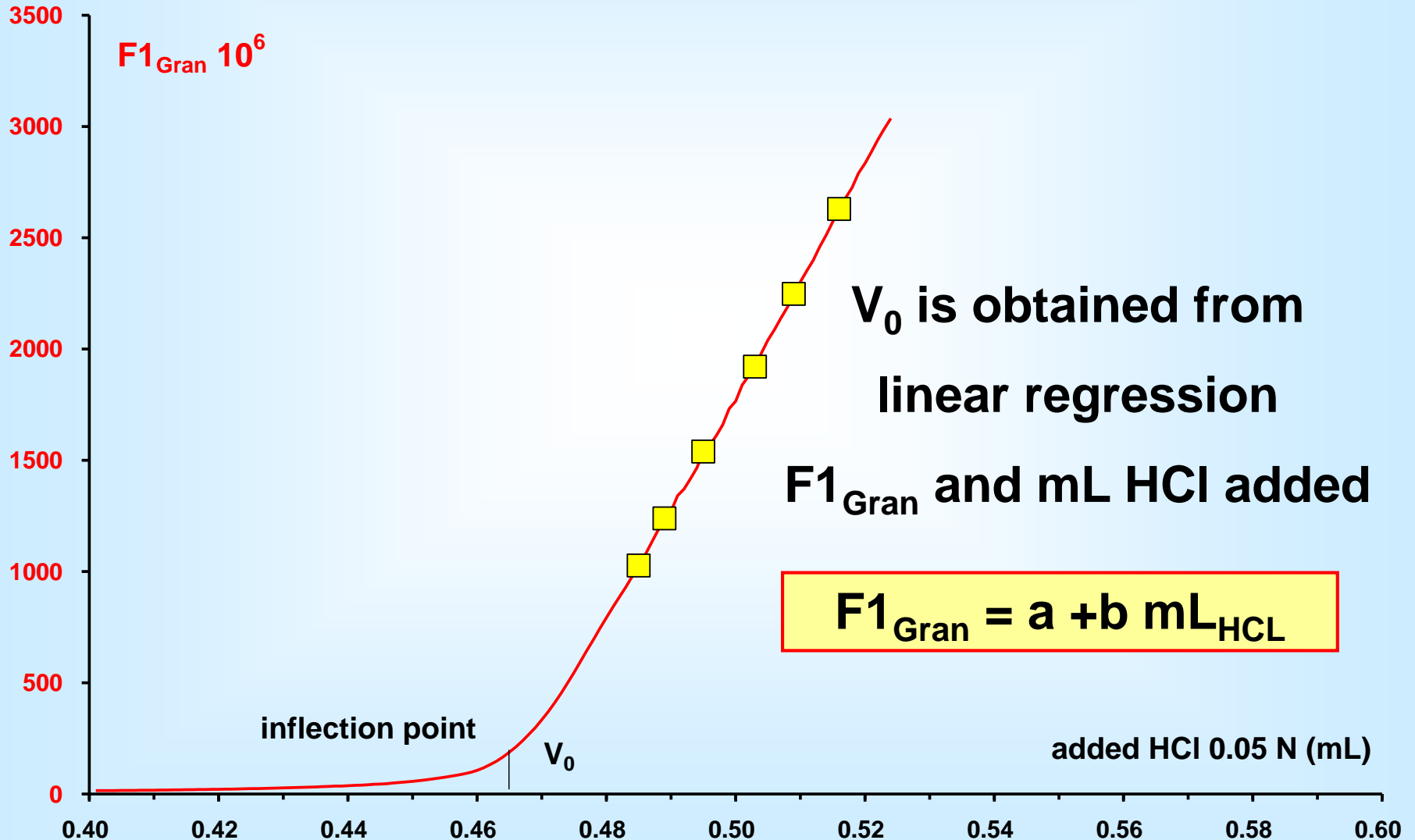


Two end-point titration

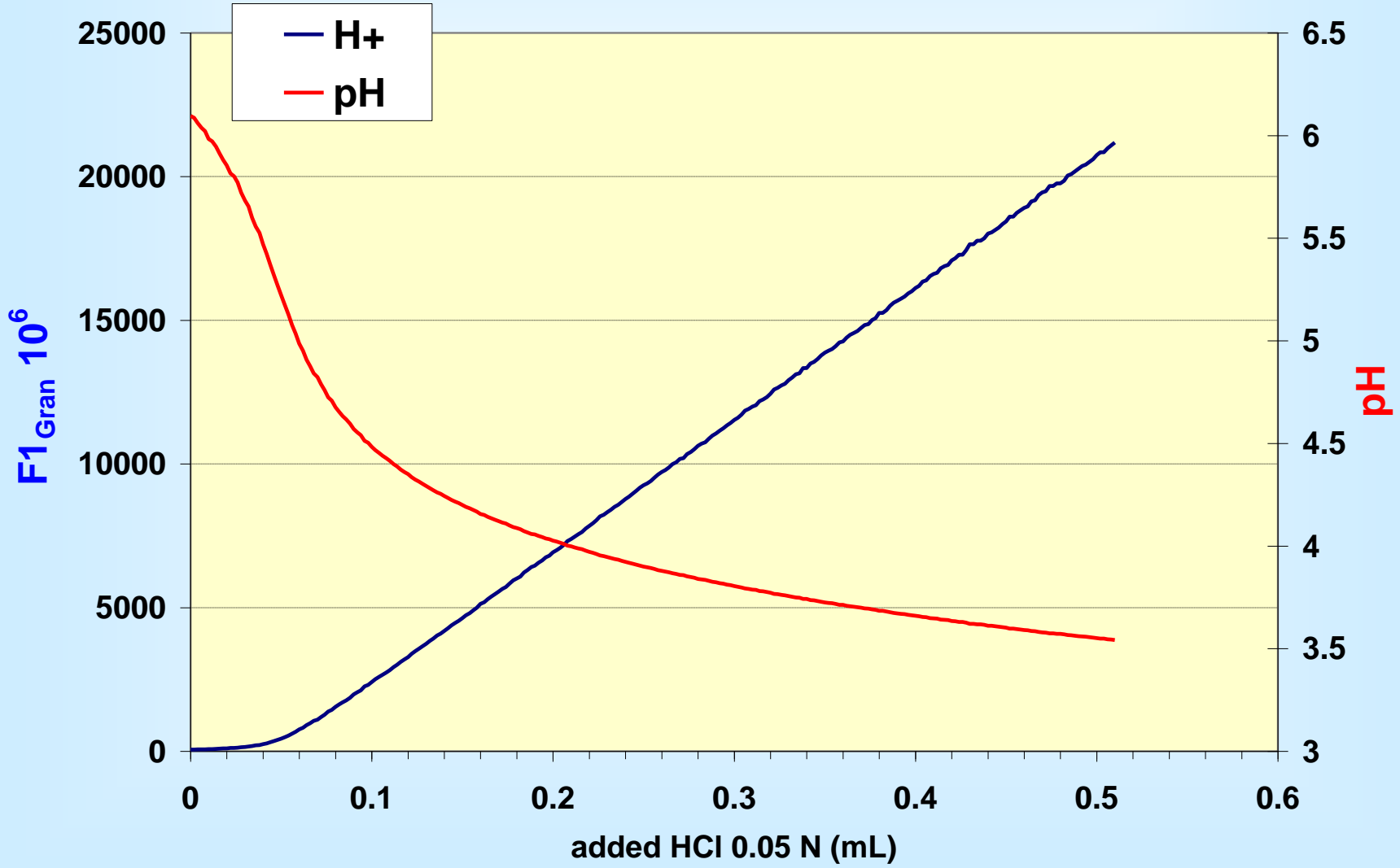


Gran's titration

$$F1_{\text{Gran}} = (\text{mL}_{\text{sample volume}} + \text{mL}_{\text{HCl added}}) 10^{-\text{pH}}$$



Gran's titration



Gran 23 points (range pH 4.4 - 4.16)	32 µeq/L
Gran 200 points (range pH 4.4 - 3.54)	34 µeq/L
Two end-point titration (pH 4.5 – 4.2)	32 µeq/L
One end-point titration (pH 4.5)	68 µeq/L
One end-point titration (pH 4.2)	89 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 ($\Delta\text{pH} = 0.3$ 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.