Effect of settings on the result of a pH-stat titration: soil acidity and lime requirement estimated

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For investigation of proton transfer reactions in soils pH-stat titration is an appropriate method. But the experimental conditions have significant effect on the results of reaction kinetic measurements: even on constant temperature the other settings (e.g. target pH, supporting electrolyte conc. and type) may cause important changes in the reaction parameters.

The aim of this work was to find the best titration settings for measurement of soil acidity and based on this an exact lime requirement calculation.

Titration at a given pH level was achieved with an equipment and software combination built for this purpose (Czinkota et al. 2002). The pH of continuously stirred soil suspension is regularly measured with a pH-selective electrode that is connected to a computer. The software on the computer compares the incoming pH values in predefined time intervals with a predefined pH limit value. If the measured pH value is lower than the limit pH value, the computer sends a signal to an automatic burette, which adds basic solution to the soil suspension.

Two pH values were tested in pH-stat titrations: 8.2 and 6.5.
The pH = 8.2 was chosen because this is the pH around the dissolving lime particles in soil and this is the pH of the extractant that is used for the measurement of hydrolytic acidity (Pearson – Adams, 1967; Kappen, 1929), which is the basis of lime requirement calculations in Hungary and some other countries.
The pH = 6.5 is the practical target value of liming on field.
Application of N_2 atmosphere was tested for the exclusion of the effect of dissolving CO_2, which increases the amount of added base solution.
Two salt solutions were applied. These solutions were used for keeping constant ionic strength. The 1 M KCl is widely accepted as a conductor salt for solution pH measurement, or as a cation exchanger in case of soils. The 0.01 M $CaCl_2$ is an extractant solution for measurement of plant available cations, suggested by Houba et al. (1986).

The amount of added base solution (KOH) without the application of N_2 atmosphere was investigated in function of background solution (1 M KCl, 0.01 M $CaCl_2$) and target pH (8.2, 6.5) (Figure 1).
Titrations to pH 6.5 required half as much alkali as titrations to pH 8.2. The 0.01 M $CaCl_2$ solution is also suitable for background solution but base consumption values slightly differ from those with 1M KCl.
From agronomic view acidity values measured at pH = 6.5 are probably more suitable for estimation of lime requirement than those at pH = 8.2. For the investigation of this hypothesis field experiments had been set up.
The pH = 6.5 value allows to titrate the soil acidity in connection with air because at this pH the effect of dissolving CO_2 from air is neglectable.
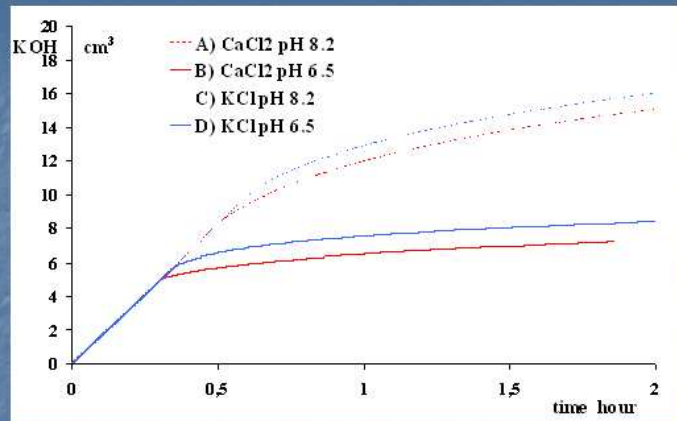
Figure 1. The added 0.1 M KOH solution in function of time.
A) background: 0.01 M $CaCl_2$, pH = 8.2;   B) background: 0.01 M $CaCl_2$, pH = 6.5.
C) background: 1 M KCl, pH = 8.2;   D) background: 1 M KCl, pH = 6.5;
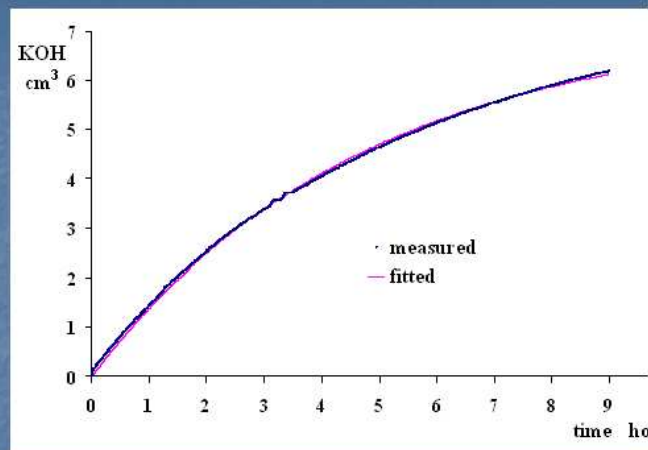

Figure 2. The added 0.1 M KOH solution in function of time – titration of 1M KCl solution without soil to pH = 8.2.

The effect of CO_2 can be described with the following equations:
$$CO_2 + H_2O = H_2CO_3 \qquad H_2CO_3 + KOH = KHCO_3 + H_2O$$
This means that the added alkali solution reacts not only with the protons from soil acidity but indirectly with the CO_2 dissolving from air. That is why the results of titrations in N_2 atmosphere differ significantly from those measured in air.

The background solutions (1 M KCl, 0.01 M $CaCl_2$) without soil were also titrated with 0.1 M KOH. The base consumption values can be seen on Figure 2. The model of first order kinetic reaction fits well on measured data.
With MINTEQ model the change of HCO_3^- and CO_3^{2-} concentration in 1 M KCl and 0.01 M $CaCl_2$ solutions equilibrium with air was calculated in function of pH.
The relation for HCO_3^- can be seen on figure 3. Figure 3. shows that at pH = 6.5 the effect of CO_2 can be neglectable compared to the values calculated at pH = 8.2.
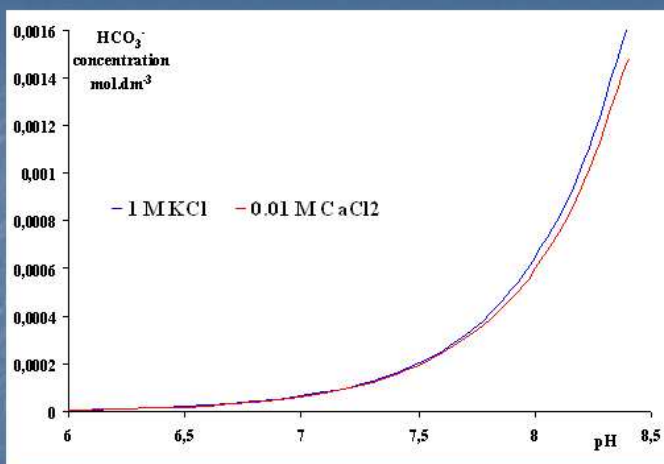

Figure 3. The HCO_3^- concentration in function of pH in 1 M KCl and 0.01 M $CaCl_2$ solutions equilibrium with air (calculated with MINTEQ model).