Acidity of Rain and Fog: Conceptual Definitions and Practical Measurements of Acidity

Carola Annette Johnson and Laura Sigg*

Abstract: Conceptual definitions are applied to the measurement of acidity and pH. A reliable method is described, and the use of Gran plot titrations as a diagnostic tool in rainwater and fogwater analysis is shown.

The acidity of rainwater is derived from a mixture of strong mineral acids, H_2SO_4, HNO_3, HCl, and a variety of weaker acids including H_2SO_3, HNO_2, H_2CO_3, and organic acids. It is largely controlled by the strong acids present in solution, but also by NH_3 and $CaCO_3$ which neutralise the rainwater to some extent[1].

The measurement of pH and acidity in rain and fog is of great importance in assessing their impact on forests and other ecosystems. Due to the very small concentrations and low ionic strength, pH and acidity measurements are not as trivial as one would assume[2]. Here, we briefly present the experimental methods which we have adapted. In developing our procedures we have been guided by conceptual definitions of acidity and pH.

Usually a pH measurement is carried out by comparing the response of a glass electrode with a standard buffer solution of given pH. This procedure gives rise to large errors due to the difference in ionic strength between buffer and rainwater which induces an additional liquid junction potential, and also causes differences in activity coefficients; in addition contaminaton of samples with the buffer solution is possible[3]. Calibration using a strong acid adjusted to 0.05 M KCl is recommended, the observed potentiometer (pH meter) reading being compared with the $H^{\oplus}$ concentrations. Test solutions are also adjusted to 0.05 M with respect to KCl so that calibration and measurement are carried out in the same ionic medium. This calibration technique leads to a measurement of pH in terms of the hydrogen ion concentration (p^cH) instead of the hydrogen ion activity (p^aH) as determined by buffer calibration[4].

It is necessary to distinguish the acidity due to strong (mineral) acids, the «mineral acidity», which often is nearly the same as the free $H^{\oplus}$ concentration, and the total acidity[5] given by the base neutralising capacity (BNC) of the sum of strong and weak acids. «Gran titrations» have found wide acceptance in the determination of rainwater acidity[6, 7]. The advantage of this technique lies in the fact that the acidity measurement is determined from the base addition, and is independent of electrode calibration. Accurate values of $H^{\oplus}$ concentration are thus obtained.

The Definition of pH and Acidity

The strong acidity, H-Aci, in rainwater is expressed with respect to the reference conditions: H_2O, H_2CO_3, $SO_4^{2\ominus}$, $NO_3^\ominus$, $Cl^\ominus$, $NO_2^\ominus$, $F^\ominus$, $HSO_3^\ominus$, $NH_4^\oplus$, H_4SiO_4, and ΣH_nOrg (organic acids, $pK < 10$).

$$\begin{aligned}\text{H-Aci} = & [H^\oplus] + [HSO_4^\ominus] + [HNO_2] + [HF] \\ & + [H_2SO_3] - [OH^\ominus] - [HCO_3^\ominus] \\ & - 2[CO_3^{2\ominus}] - [NH_3] - [H_3SiO_4^\ominus] \\ & - \Sigma n[Org^{n\ominus}]\end{aligned} \quad (1)$$

Components such as $HSO_4^\ominus$, HNO_2, HF, H_2SO_3, $CO_3^{2\ominus}$, NH_3, and $H_3SiO_4^\ominus$ are in negligible concentrations in a typical rainwater, so equation (1) may be simplified to

$$\text{H-Aci} = [H^\oplus] - [OH^\ominus] - [HCO_3^\ominus] \\ - \Sigma n[Org^{n\ominus}] \quad (2)$$

For most samples H-Aci $\approx [H^\oplus]$, but it must be noted that in samples of low pH ($\lesssim 2.5$) such as one may find in acid fog, concentrations of $HSO_4^\ominus$ and H_2SO_3 may no longer be negligible.

The reference conditions pertaining to the determination of total acidity (Aci$_T$) are: H_2O, $CO_3^{2\ominus}$, $SO_4^{2\ominus}$, $NO_3^\ominus$, $Cl^\ominus$, $NO_2^\ominus$, $F^\ominus$, $SO_3^{2\ominus}$, NH_3, $H_3SiO_4^\ominus$, and $\Sigma Org^{n\ominus}$.

$$\begin{aligned}\text{Aci}_T = & [H^\oplus] + [H_2CO_3] + [HCO_3^\ominus] \\ & + [HSO_3^\ominus] + [NH_4^\oplus] + [H_4SiO_4] \\ & + \Sigma n[H_nOrg] - [OH^\ominus]\end{aligned} \quad (3)$$

For a typical rainwater of pH 4–5 where

the concentrations of $OH^\ominus$, $HCO_3^\ominus$, $CO_3^{2\ominus}$, and of strong organic acids are negligible, the $H^\oplus$ concentration determined from p^cH measurements approximates to H-Aci.

$$\text{H-Aci} \approx [H^\oplus] \approx 10^{-p^cH} \quad (4)$$

Free and Total Acidity Determinations from Gran Plot Titrations

Titration curves obtained from the addition of base to test solutions may be converted to linear Gran functions[8] to ease the determination of equivalent points from which values of acidity are calculated. A typical plot of a rainwater titration containing both weak and strong acids is shown in Figure 1.
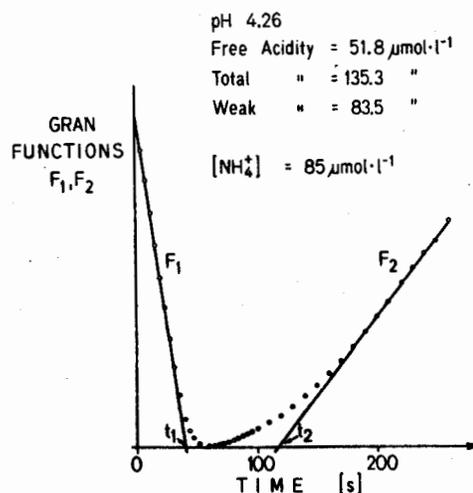

Fig. 1. Gran plot of a rainwater sample (Dübendorf, Nov. 1984): free acidity function F1, and total acidity function F2.

Free Acidity: The function F1 is a mathematical description of the change in free $H^\oplus$ concentration, $[H^\oplus]$, of a solution of initial volume v_0, and initial free hydrogen ion concentration $[H^\oplus]_0$, as a result of base addition. Instead of base addition with a burette, it may be generated coulometrically within the titration vessel. For coulometric generation of base at a current, I, for a time, t, F1 is written as

$$\text{F1} = [H^\oplus]_0\, v - \frac{I \cdot t}{F} = v_0 \cdot 10^{-p^cH} \quad (5)$$

where $F = 96490$ C mol^{-1}

The free acidity may be calculated from the equivalence point determined from the extrapolation of the linear section of F1 vs. t to the x-axis[9]. This operationally excludes weak acids dissociating during titration, such as HCOOH or CH_3COOH, which cause the deviations from linearity of the function. They are thus assumed to be unprotolysed (ΣH_nOrg) for the refer-

* *Correspondence:* Dr. L. Sigg, Dr. C. A. Johnson
EAWAG/Abteilung Chemie
Swiss Federal Institute for Water Resources and Water Pollution Control
Überlandstrasse 133, CH–8600 Dübendorf

ence conditions, applying to description of acidity determined from F1 (equation (1)). Since $CO_{2(aq)}$ is removed prior to titration, and $OH^\ominus$ concentrations are negligible in the linear section of F1, equation (2) may be written as

$$H\text{-Aci} \approx [H^\oplus] - \Sigma n[Org^{n\ominus}] \qquad (6)$$

In most cases, the term $\Sigma n[Org^{n\ominus}]$ is negligible in rainwater resulting in comparable results of free acidity with those determined from p^cH measurements. Organic acids have been found in the range of few $\mu eq\ L^{-1}$ [10]. For a rainwater of p^cH 4 (100 $\mu eq\ L^{-1}$) this will not present such a problem as for a rainwater of p^cH 5 (10 $\mu eq\ L^{-1}$). Fig. 2b and 2c present Gran plot analyses of strong and weak acid mixtures (HCOOH and CH_3COOH) of comparable concentrations. The overestimation of free acidity is clearly illustrated by these examples.

It is therefore advisable to compare free acidity measurements with acidities determined from p^cH measurements, and in addition, to check the slope of F1 which should be equal to $-I \cdot F^{-1}$. A more positive value is an indication that the free acidity determination is too high. (It must be noted however that an error of $+1.2\%$ in E^0 calibration can result in slope error of -18%).

Total Acidity: After a sufficient quantity of base is added, weak acids with pK values < 10 have undergone protolysis, and the concentration of base is proportional to that added. This is described by F2.

$$F2 = \frac{I \cdot t}{F} - Aci_T \cdot v_0 = v_0 \cdot 10^{p^cH} \qquad (7)$$

where Aci_T is the total acidity.

Equation (3) may be simplified to

$$Aci_T \approx [H^\oplus] + [HSO_3^\ominus] + [NH_4^\oplus] + \Sigma n[H_nOrg] \qquad (8)$$

since $OH^\ominus$ (in the original sample) and H_4SiO_4 concentrations are negligible, and $CO_{2(aq)}$ has been removed from solution.

Fig. 2d represents a titration from which $CO_{2(aq)}$ has not been removed. Aqueous CO_2 protolyses to $HCO_3^\ominus$ and then only partially to $CO_3^{2\ominus}$. Titrations are simplified if CO_2 is removed. Bases used for titration are often contaminated with $CO_3^{2\ominus}$. (This problem is avoided by coulometric generation of $OH^\ominus$).

The ammonium ion, though having a relatively high pK value (9.3) is fully included in total acidity measurements (Fig. 2e). The plot is similar to that of the rainwater sample shown in Fig. 1, whose major weak acid component is indeed $NH_4^\oplus$ (85 $\mu eq\ L^{-1}$).

In some samples, other weak acid components may be present in significant concentrations. Metal ions, subject to hydrolysis below pH 10, may be included in titra-
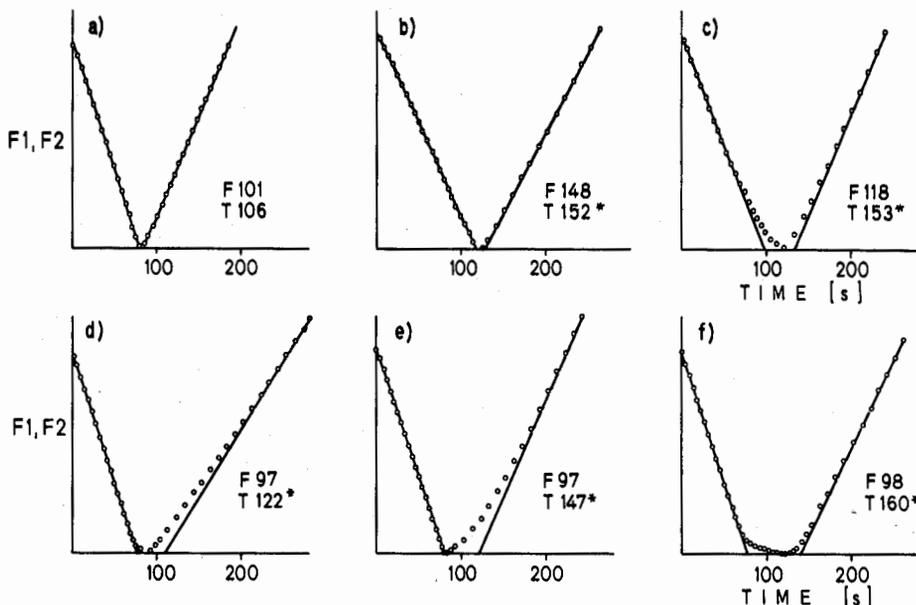

Fig. 2. Gran plot analyses of a) 100 μeq L^{-1} HCl; b) 100 μeq L^{-1} HCl + 50 μeq L^{-1} HCO_2H; c) 100 μeq L^{-1} HCl + 50 μeq L^{-1} CH_3CO_2H; d) 100 μeq L^{-1} HCl, CO_2 not removed; e) 100 μeq L^{-1} HCl + 50 μeq L^{-1} $NH_4^\oplus$; f) 100 μeq L^{-1} HCl + 20 μeq L^{-1} $Al^{3\oplus}$. (* Corrected for weak acid contamination).

tions for total acidity. Aluminium, for example, when titrated from pH4 to 10 will hydrolyse from $Al^{3\oplus}$ to $Al(OH)_3$, consuming 3 μeq L^{-1} of base for every μmol L^{-1} of $Al^{3\oplus}$ (Fig. 2f).

The technique provides accurate results of total acidity in the order of 3 μeq L^{-1} for the standard solutions tested, though accurate values below 10 μeq L^{-1} are difficult to obtain (from experience with rainwater samples). As shown in Figures 2a–2f, the Gran plots are characteristic of the weak acids in solution, and can provide information about dominant acids contributing to the total acidity in a rain- or fogwater sample. Titrations of strong acids (e. g. Fig. 2a) have shown weak acid contamination of the order of 6–10 μeq L^{-1}. It is therefore recommended that such blank tests should be carried out routinely.

The method outlined below involves the calibration of an electrode using a strong acid standard titrated with coulometrically generated $OH^\ominus$. Values of pH are thereby determined on a concentration scale. A recommended procedure for «Gran titration» is also described.

Recommended Procedure[11]

Apparatus: All measurements are carried out in an argon atmosphere using a double walled cell, thermostated at 25°C. A Ross 81–66 combination electrode is employed for potential measurements. For titrations, hydroxide ions are generated coulometrically with Metrohm coulometer, E 211 A, a platinum electrode (0.8 × 1.2 cm), and a coiled silver wire electrode (≈ 10 cm^2). All solution are adjusted to 0.05 M with respect to KCl to avoid errors arising due to liquid junction potential and activity coefficient difference between calibration and test samples.

Calibration: Titration of a standard solution (25 mL, 0.001 M HCl + 0.05 M KCl) is carried out by stepwise coulometric generation of hydroxide ions in the stirred solution at a current, I, of 3 mA for periods of 30 s. After each generation period the potential of the quiescent solution is noted.

From equation (5) we obtain

$$v_0[H^\oplus] = v_0[H^\oplus]_0 - \frac{I \cdot t}{F} \qquad (9)$$

At the equivalence point

$$\frac{t_e \cdot I}{F} = v_0[H^\oplus]_0 \qquad (10)$$

From the Nernst-equation

$$p^cH = -lg[H^\oplus] = \frac{E^0 - E}{k} \qquad (11)$$

where E^0, E and k are the standard and measured potential, and Nernstian slope respectively. Thus

$$v_0 \cdot 10^{(E - E^0)/k} = \frac{I}{F}(t_e - t) \qquad (12)$$

$$v_0 \cdot 10^{E/k} = 10^{E^0/k} \cdot \frac{I}{F}(t_e - t) \qquad (13)$$

A plot of $v_0 \cdot 10^{E/k}$ against t now gives a straight line of slope $10^{-E^0/k} \cdot I/F$ from which E^0 is determined. $[H^\oplus]$ may be calculated and plotted against potential. A value of k is obtained from the slope (equation (11)).

p^cH Measurement: Test samples are transferred to the thermostated vessel, adjusted to 0.05 M with respect to KCl and allowed

to reach 25°C, whilst stirring. The potential, E, of the quiescent solution is determined and the p^cH value determined from equation (11).

Gran Titrations: Test samples are transferred to the tiration vessel, adjusted to 0.05 M with respect to KCl, and p^cH measured. For solutions with $p^cH < 5$, argon gas is passed through for 10 min. Stepwise titration is then carried out until a $p^cH \approx 10.3$ is achieved, making sure to obtain 8–10 potential readings corresponding to $p^cH < 5$. All potential measurements are made in quiescent solutions.

Calculations: Functions F1 and F2 (equations (5) and (7)), modified to $v_0 \cdot 10^{(E-E^0)/k}$ and $v_0 \cdot 10^{(E^0 - E)/k}$ are plotted as a function of coulometric time t. Linear functions (chosen from points corresponding to $p^cH < 5$ for F1 and > 10 for F2 respectively) and x-axis intercepts t_1 and t_2 are calculated by linear regression. From equation (10), the free and total acidities are calculated.

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