

Dissociation of weak acids during Gran plot free acidity titrations

By STEVEN E. LINDBERG and JAN M. COE, *Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA* and WILLIAM A. HOFFMAN, *Department of Chemistry, Denison University, Granville, Ohio 43023, USA*

(Manuscript received August 22; in final form December 30, 1983)

ABSTRACT

A comparison of weak and free acid concentrations measured by base titration and hydrogen ion activities determined by direct pH measurement is described for several of our data sets for rain collected above and below a forest canopy in the eastern United States. These data illustrate the influence of weak acid dissociation during titration and the possible effect of activity coefficients on calculated free acid concentrations.

1. Introduction and methodology

Gran (1952) plot techniques are widely used to determine the acid content of natural water samples. The pKa values of particular weak acids have also been determined using these methods (Lee and Brosset, 1978; Seymour et al., 1977). Precautions involved in using these techniques have appeared in the literature (e.g., Burden and Euler, 1975) and have been discussed in particular detail by Brosset and Ferm (1978), Lee and Brosset (1978), and Keene et al. (1983). As reported earlier, we have used Gran functions derived from the initial base consumption and the excess base addition portions of titration curves to determine strong acid (as free H⁺) and total acid content of precipitation samples (Hoffman et al., 1980).

The technique involves plotting calculated Gran function values on the ordinate of an X-Y plot against the respective values of added base on the abscissa (as described in Fig. 1). This is followed by extrapolation of the initial linear region of the plot to the abscissa. In practice, this point of intersection (A, Fig. 1) is taken as the point of equivalence for the acid content variously referred to as free or strong acidity. Because the acid concentration determined from the initial linear region of the Gran plot includes all sources of free

H⁺ from completely and partially dissociated acids, the term free acidity is more accurate. The intersection of the final linear region of the plot (B, Fig. 1) is taken as the point of equivalence for the total acid content of the sample (e.g., Keene et al., 1983), and the difference between these values is

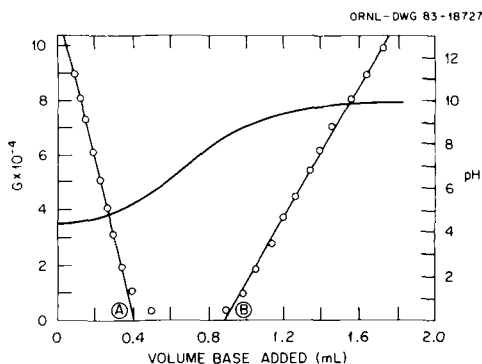


Fig. 1. Titration curve and associated Gran plot of the free acid function (intercept A) and the total acid function (intercept B). The Gran function used to generate this plot is: $G = (V_0 + V_1) \cdot 10^{(pH_1 - k)}$, where V_0 = initial sample volume, V_1 = volume of base added (in our case, the base = 0.003 M NaOH), pH_1 = pH value after base addition, and k = midpoint pH in titration curve.

often reported as the weak acid concentration or the undissociated acid content.

In a simple system, these procedures work quite well and can be used to identify pK_a values of a constituent weak acid. However, field samples of natural precipitation rarely contain a single conjugate acid-base system, and seldom are the acids present identified before a titration. We present here a brief discussion of the application of these methods to precipitation samples recently collected in the southeastern United States as an example of some specific problems caused by weak acid dissociation during the free acid portion of the titration. These samples were collected as wetfall-only on an event basis above (incident rain) and below (throughfall) the deciduous forest canopy at Walker Branch Watershed in eastern Tennessee during 1981 and 1982. Sample collection and detailed titration methods have been published (Hoffman et al., 1980; Lindberg, 1982).

2. Results and discussion

The majority of precipitation samples we have collected above and below the forest canopy exhibit pH values of 4 to 5, a range in which both strong mineral acids and partially dissociated weak organic and inorganic acids contribute to free acidity. The problem with titration analysis of such samples arises when the pK_a values of the weak acids present are of the same magnitude as the initial sample pH. When weak acids are present which only partially dissociate at the initial pH of the sample, a Gran plot analysis of the initial portion of a base titration curve will give a line segment leading to an erroneous free acid concentration value. This has been termed the weak base error by Driscoll and Bisogni (1982) and has been further described by Brosset (1976). The free H^+ in such a system will be controlled by the conjugate acid-base pair buffer that rations the extent to which the hydrogen ion is released to the titrating base. In contrast, the conjugate base of a strong mineral acid is so weak that it does not hinder the availability of H^+ in the system.

For example, at pH 4, a weak acid of $pK_a = 6$ is initially <1% dissociated. As the sample is titrated with a strong base from pH 4 to 5, a relatively small portion (~10%) of the weak acid dissociates to produce free H^+ . Because the initial base con-

sumption portion of the titration curve (roughly the first 1 unit of pH change) is used in the Gran plot to determine free acidity (Lee and Brosset, 1978), the dissociating weak acid will have little influence on the results. However, for a sample initially at pH 5, the $pK_a = 6$ weak acid is ~10% dissociated, but it increases to 50% dissociated at pH 6. Depending on the initial weak acid concentration and pK_a , this dissociation during the early stage of titration can lead to considerable overestimation of the free acidity originally present.

Our earlier data showed that measured pH values converted to corresponding hydrogen ion activities correlated well with strong acid concentrations derived from titrations of samples with initial pH values ≤ 4.5 (Hoffman et al., 1980). Above this pH, anomalies occur because the Gran plot slope may correspond to those weak acids in the system that are dissociating under the impact of initial base addition (i.e., during titration; Lee and Brosset, 1978). Fig. 2 illustrates some of our recent data on the comparison between free H^+ determined from Gran plot titrations and calculated from initial sample pH values for various precipitation samples. The following points are significant.

(i) For samples above pH ~4.5, titrations consistently and increasingly overestimate the free acid content inferred from pH, as indicated by the increased deviation from the 1:1 line below a field H^+ concentration of $\sim 30 \mu\text{eq L}^{-1}$;

(ii) Nearly all values fall on or above the 1:1 line, which indicates that free acidity by titration exceeds free H^+ activity determined from the field pH for many samples;

(iii) The difference is generally less for incident rain samples (solid circles) than for throughfall samples.

There are three possible explanations for the observation that free acid concentrations estimated by titration generally exceed those determined from field pH values: pH drift during sample storage, activity coefficient effects, and a varying degree of weak acid dissociation during the free acid titration. A consistent upward drift in pH values during sample storage between determining field pH and initiating titration would partially explain the trend. The mean ratio of hydrogen ion activities calculated from pH measurements in the field and at the laboratory (as field/lab) is 1.1 for those values of field $H^+ > 32 \mu\text{eq L}^{-1}$ (pH < 4.5). For the full

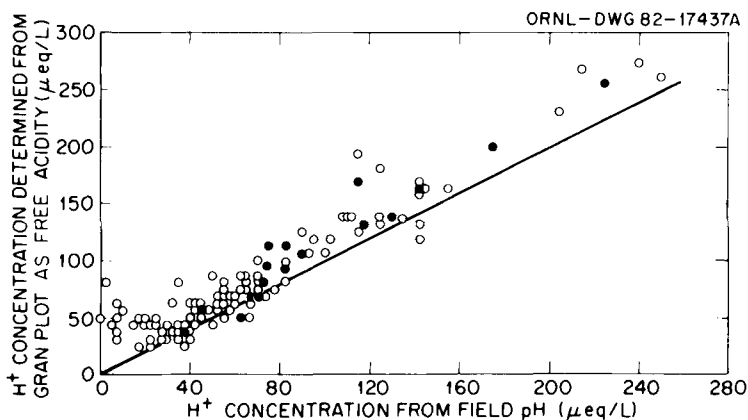


Fig. 2. Relationship between H^+ concentration as free acidity calculated from Gran plot titration and from field pH. The data represent incident precipitation collected above the forest canopy (closed circles) and throughfall collected below an oak forest canopy (open circles) during the summer of 1981. Linear regression parameters for the data are given in Table 1 (the bold line represents the 1:1 relationship). Note that in this context, "field" pH represents an analysis of pH using standard electrode methods on a freshly collected sample returned to the laboratory and allowed to reach room temperature.

data set ($n = 193$) the correlation coefficient between field and laboratory values of H^+ determined from pH measurements is 0.90, with a regression slope of 0.99 and an intercept of 0.57 (coefficients not significantly different from the expected 1:1 line with a zero intercept; $P > 0.05$). While significant upward drifts in pH can occur for long-term stored samples (Peden and Skowron, 1978), our field and laboratory pH values are generally determined on the same day.

Although a certain amount of upward drift in pH (as suggested by the +0.57 intercept term) may explain some portion of the discrepancy, another explanation is that the glass electrode measures hydrogen ion activity (a_{H^+}) while titrations determine the solution acid concentration (m_{H^+}). Recalling that $a = \gamma m$, where γ is the activity coefficient and m the concentration, it is clear that $a < m$, when $\gamma < 1$. Because the ionic strength of a solution is the primary factor influencing the activity coefficient, an increasing total ion concentration begins to decrease the activity coefficient as indicated by the extended Debye-Hückel approximation. Activity coefficients begin to depart from 1 as total ion concentrations approach $100 \mu\text{eq L}^{-1}$, a value common for precipitation samples in the eastern United States (Dana and Rothert, 1983).

Further classification of the complete data set in Fig. 2 by season of collection and type of sample (see Table 1) indicates the influence of free and weak acid concentrations on the differences between titration and field pH estimates of free acidity. For combined rain and throughfall data, winter and summer samples differ slightly in mean free H^+ activity ($\mu\text{eq L}^{-1}$) determined from field pH (73 winter versus 70 summer) but differ significantly in undissociated weak acid concentration (65 and 84, respectively). The combined summer samples exhibit higher weak acid concentrations and yield a mean difference between titration and pH free acidity values measurably higher than the difference for winter samples (a difference of 16 versus $3 \mu\text{eq L}^{-1}$). For throughfall samples, the difference is larger than that for rain samples (a difference of 28 versus $9 \mu\text{eq L}^{-1}$) for combined seasons. Compared with rain, throughfall samples exhibit higher concentrations of weak acidity and lower concentrations of free acidity, both of which would be expected to enhance the difference between H^+ values determined by titration and by field pH measurements. Linear regression analyses of H^+ determined from Gran plots as free acidity (the dependent variable) versus H^+ determined from field pH measurements (e.g., Fig. 2) indicate no significant deviation of the data from the

Table 1. Free and weak acidity characteristics of several data subsets collected during 1981–1982

Data set	N	Acidity ($\mu\text{eq H}^+ \text{L}^{-1}$)				Regression analysis	
		By titration		From field* pH	Difference (free-field)	slope	intercept
		free	weak				
all samples	193	81 ± 3†	77 ± 4	71 ± 3	11 ± 1	1.01	13††
all pH ≤ 4.5	158	91 ± 4	74 ± 4	82 ± 3	9 ± 1	1.07	3.5
all pH > 4.5	35	39 ± 3	89 ± 12	18 ± 1	20 ± 4	-0.61††	50††
winter events	70	74 ± 4	65 ± 5	73 ± 4	3 ± 2	0.98	4.2
summer events§	123	85 ± 5	84 ± 5	70 ± 5	16 ± 2	0.98	17††
rain	35	91 ± 9	47 ± 5	80 ± 7	9 ± 4	1.03	7.3
throughfall	28	66 ± 7	130 ± 16	40 ± 7	28 ± 4	1.02	31††

Regressions are between acidity values determined by titration (dependent variable) and by field pH measurements. Fig. 2 illustrates this relationship for the sample set of summer events.

* In this context, "field" pH represents an analysis of pH using standard electrode methods on a freshly collected sample returned to the laboratory and allowed to reach room temperature.

† Mean ± standard error.

†† Signifies an intercept significantly greater than 0 ($P < 0.01$) or slope significantly different from 1 ($P < 0.01$).

§ This data set is plotted in Fig. 2.

|| Precipitation collected beneath a white oak canopy (*Quercus alba*).

expected 1:1 line through the origin for winter samples, for rain samples, and for all samples of field pH ≤ 4.5. However, there are significant deviations of the regression intercepts from 0 and/or of the slopes from 1 for the other data sets in Table 1, most notably for the samples of field pH > 4.5.

3. Conclusions and implications

Standard Gran plot procedures to determine the free acid content of samples address only peripherally the questions regarding undissociated weak acids that may be present. Methods of addressing the problem of weak acid dissociation during titration and of identifying acid pK values by titration have been published. Addition of a standard strong acid to a sample prior to the base titration and Gran plot analysis has been suggested as a means of measuring free and total acidity as well as the weak acid contribution to the free acidity. However, the influence of this added acid (e.g., HClO_4 as suggested by Lee and Brosset (1978)) on the oxidation of dissolved organic acids in the sample must be determined. A further modification of this method involves an initial

titration of the sample with a standard acid to measure the weak acid influence on free acidity, followed by the standard base titration and Gran plot analysis, thus considerably increasing the sample analysis time.

Determination of the individual pK_a values of the weak acids in the sample may be attempted using a coulometric procedure (Liberti et al., 1972) or by detailed linearization of the titration curve (Seymour et al., 1977). However, because individual line segments for specific weak acids are often difficult to resolve (Seymour et al., 1977), it is still useful to obtain the estimation of total acidity from the Gran plot line segment associated with the excess base plateau (point B in Fig. 1). Subtracting the free acid end point from the total acid end point gives a base equivalency corresponding to the various weak acids which were undissociated at the original sample pH. Some indication of the effect of the weak acids dissociated during the titration on the Gran plot free acidity estimate can be seen by comparison of the Gran plot free acid value with that calculated from the initial sample pH as shown in Fig. 2 and Table 1. For samples showing a significant discrepancy, the weak acid estimate can be revised using the free acidity determined from the initial sample pH (e.g., revised weak acidity =

(total acidity from Gran plot) – (free acidity from sample pH)). This will result in an increase in the calculated weak acid content of the samples.

It has been our experience that the problem of strong acidity overestimates caused by weak acid dissociation during early stages of a titration is generally limited to throughfall samples (Table 1). The problem apparently also occurs for remote site precipitation samples low in mineral acid content but containing weak organic acids (as reported by Keene et al., (1983)), and presumably also for waters having percolated through soil organic horizons. However, samples of incident precipitation collected at sites in eastern Tennessee are either sufficiently low in pH or exhibit levels of weak acids low enough to minimize the differences (Table 1). We suspect this is true for rain event samples collected over much of the mid- and northeastern United States.

Routine determination of the difference between H^+ determined by field pH and Gran plot titration methods may have some value in itself. Currently, we are investigating the relationship between this difference, the cation/anion balance, and the organic acid anion content of several throughfall samples. Throughfall has often been reported to exhibit a measurable anion deficit that may be attributed to an unanalyzed organic anion. We consider the ΔH^+ value discussed above to represent a measure of the "readily dissociated" weak

acid in a sample. If this weak acid is present as an acid salt of a polyprotic acid (e.g. potassium acid oxalate, KHC_2O_4), one might expect a positive correlation between the anion deficit and the calculated H^+ difference. Such a relationship has been reported for precipitation collected at remote, background sites (Keene et al., 1983). Analysis of the specific organic acid anions in these samples will provide the information needed to calculate the dissociated weak acid contribution to the measured free acidity. In addition, these data will be useful in the identification of the sources of weak acids in throughfall and in further describing the interactions between incoming rain acidity and the forest canopy (Hoffman et al., 1980).

4. Acknowledgments

We thank S. Herbes, G. Lovett, and R. Turner for helpful discussions and assistance in sample collection and analysis. The suggestions of the unidentified referees are also appreciated. This research was sponsored in part by the Electric Power Research Institute under contract RP1907-1 and in part by the Office of Health and Environmental Research, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation. Publication No. 2266, Environmental Sciences Division, ORNL.

REFERENCES

- Brosset, C. 1976. A method of measuring airborne acidity: its application for the determining of acid content on long-distance transported particles and in drainage water from spruces. *Water Air Soil Pollut.* 6, 259–275.
- Brosset, C. and Ferm, M. 1978. Man-made airborne acidity and its determination. *Atmos. Environ.* 12, 909–916.
- Burden, S. L. and Euler, D. E. 1975. Titration errors inherent in using Gran plots. *Anal. Chem.* 47, 793–797.
- Dana, M. T. and Rothert, J. E. 1983. The MAP3S Precipitation Chemistry Network: Fifth periodic summary report. PNL 4599, Richland, Washington: Pacific Northwest Laboratory.
- Driscoll, C. T. and Bisogni, J. J. 1982. Weak acid/base systems in dilute acidified lakes and streams of the Adirondack region of New York State. Contribution No. 8. Syracuse, New York: Upstate Freshwater Institute.
- Gran, G. 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst (London)* 77, 661–671.
- Hoffman, W. A., Lindberg, S. E. and Turner, R. R. 1980. Precipitation acidity: The role of the forest canopy in acid exchange. *J. Environ. Qual.* 9, 95–100.
- Keene, W. C., Galloway, J. N. and Holden, J. D. 1983. Measurement of weak organic acidity in precipitation from remote areas of the world. *J. Geophys. Res.* 88, 5122–5130.
- Lee, Y. and Brosset, C. 1978. The slope of Gran's plot: a useful function in the examination of precipitation, the water-soluble part of airborne particles, and lake water. *Water Air Soil Pollut.* 10, 457–469.
- Liberti, A., Possanzini, M. and Vicedomini, M. 1972. The determination of the non-volatile acidity of

- rainwater by a coulometric procedure. *Analyst* 97, 352–356.
- Lindberg, S. E. 1982. Factors influencing trace metal, sulfate, and hydrogen ion concentrations in rain. *Atmos. Environ.* 16, 1701–1709.
- Peden, M. E. and Skowron, L. M. 1978. Ionic stability of precipitation samples. *Atmos. Environ.* 12, 2343–2349.
- Seymour, M. D., Clayton, J. W. and Fernando, Q. 1977. Determination of pKa values of acid compounds in atmospheric condensates by linearization of segmented titration curves. *Anal. Chem.* 49, 1429–1432.