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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

Introduction

The existing methodologies for the determination of acidity of atmospheric precipitation samples were reviewed by us earlier [1]. The purpose of this work is to establish the performance characteristics of a number of these methods under conditions which exist in a single laboratory. Such a test should provide a valid method intercomparison, free from laboratory-to-laboratory variations. Furthermore, in this test, the same solutions were used in all intercomparison measurements, and therefore, any difference in the results could not be attributed to the compositional differences in samples.

Experimental Part

Several different titration procedures were evaluated with respect to their applicability to the determination of acid concentration (acidity) of dilute solutions of a strong acid (HCl). The concentrations of these samples were in the range of interest for acid rain studies. The following is the list of methodology variations employed:

(1) Titration with 10^{-3} mol/kg NaOH, using phenolphthalein as indicator,

(2) Titration with 10^{-3} mol/kg NaOH, using a pH meter and pre-determined end-point pH's,

(3) Titration with 10^{-3} mol/kg NaOH, using the Gran plot technique for end-point detection [2],

(4) Coulometric titration using the Gran plot technique,

(5) Coulometric closed loop titration to pH 8.1 in the electrolyte containing 0.1 mol/kg KCl and 10 mg sodium citrate per 100 mL [3].

Methodologies (1) and (2) were tested using two HCl solutions prepared gravimetrically from the coulometrically standardized 1 mol/kg stock solution containing 0.0201 and 0.2001 μeq of H^+/g of solution, respectively. The results of these analyses are summarized in Table I.

In Table I, column 1 lists three titration end-point pH values, measured using a combination electrode and a pH meter, and a fourth value (pH=9.2) determined with phenolphthalein indicator. The raw titration data for solutions 1 and 2 are listed in columns 2 and 3, respectively. Column 4 gives the apparent acidity of distilled water, determined to the corresponding end-point pH's. By taking the data for distilled H_2O as the "blanks" and applying these respective corrections to the data in columns 2 and 3, the data in columns 5 and 6 are obtained.

It is quite apparent from these data (columns 2 and 3) that titrations with sodium hydroxide solution will yield different results for acidities depending on the pH selected for the end-point if no "blank" correction is applied, with recovery ranging from 100% for pH 6.4 to the maximum of 254% for pH 9.2. This is due primarily to the dissolved CO_2 in the sample. If distilled water saturated with air is used as the "blank", the CO_2 titer is factored out of the final result. Nevertheless, even after the "blank" correction, some residual error still remains for samples titrated to pH 8.0 and 9.2. The magnitude of this error is $3x10^{-3}$ μeq/g and $5x10^{-3}$ μeq/g for the two end-point pH's, respectively. The overall root-mean-square error of the results for this titration procedure is $2x10^{-3}$ μeq/g.

Variation (3) in apparent H^+ concentration as a result of titrating the acid with 10^{-3} mol/kg NaOH and employing Gran's method for establishing the end-point of titration was studied on a limited basis. The Gran's plot method, which requires incremental delivery of reagent and measurement of pH after each delivery, is very tedious and difficult to implement, unless it is automated. The primary difficulty lies in the ability to control precisely the size of small reagent increments. When the increments are not of exactly the same size, the graphed function of $\Delta V/\Delta pH$ as a function of V is not very smooth (where ΔV refers to the standard NaOH solution increment, ΔpH is the pH change resulting from the addition of the reagent increment, and V is the amount of reagent added which corresponds to the particular $\Delta V/\Delta pH$). On the basis of three titrations, the recovery of acid was 104% with a standard deviation of 11%.

A far more productive procedure is the fourth method listed above, which entails use of a Gran's plot technique for the end-point determination combined with coulometric in-situ generation of reagent (base) at constant current. By selecting an appropriate value of the current, one can 'fine-tune' the system so that the time increments for reagent generation are precisely controlled, e.g., 5 seconds. In fact, the procedure is so easily adaptable to point-by-point incremental measurements that one can easily discern two different segments of the titration curve: one for the titration of a strong acid and the second for the titration of the weak carbonic acid, present in the sample due to the absorbed atmospheric CO_2. This is shown in Figure 1, which illustrates a Gran's plot of the titration of a 24 g sample of $2 \cdot 10^{-5}$ mol/kg HCl. Two distinct inflections are apparent.

For the purposes of intercomparison, two other sets of the same titration data are plotted on a nearly identical scale. Figure 2 contains a conventional acidimetric titration graph of pH as a function of coulometrically added titrant, expressed in seconds. Also, Figure 3 shows a differential titration graph of $\Delta pH/s$ as a function of added titrant. Both the differential plot and the Gran's plot reveal quite vividly the two inflections. The conventional plot of pH vs titration time in Figure 2, on the other hand, is far less sensitive. It was of interest to establish if it were feasible to separate graphically, and determine quantitatively, the two dissimilar acids (HCl and H_2CO_3) in a mixture by Gran's technique. The results of this phase of the study are summarized in Figure 4. Three samples [deaerated $2 \cdot 10^{-5}$ mol/kg HCl (A), air-saturated distilled H_2O used for preparation of the above HCl solutions (B) and air saturated $2 \cdot 10^{-5}$ mol/kg HCl (C)] were coulometrically titrated at 0.9649 mA. At this titration current, the rate of reagent delivery is 0.01 μeq/s. The calculated value of the end-point for the 24 g sample of HCl corresponds to 49.2 s, and the titer obtained for deaerated HCl sample (A) is nearly the same (50 s). The end-point for air-saturated H_2O sample (B) is 28 s. Thus, on the basis of the additivity of titers, one would expect to find the titer for the air-saturated sample of HCl to be 78 s. Unfortunately, as seen on graph C, this is not the case. The titer is 92 s. Therefore, a positive bias of about 18% is encountered for this particular end-point evaluation of the sum of the two acids. It is also quite apparent that the quantitative graphic separation of the two acids in a mixture is quite impossible. Hence -- some indication of the presence of the two acids in the mixture is there but quantitation is not possible. This situation may be of some concern to those who determine acidity of rain samples.

The fifth method, coulometric closed loop titration, consists of the following: 20 mL of electrolyte containing 0.1 mol/L KCl and 1 mg/L potassium citrate is delivered into a coulometric titration cell, deaerated by purging with argon and pretitrated by coulometric generation of OH^- to pH 8.1. Subsequently, a sample of unknown solution (e.g., 2g) is weighed into the coulometric cell with the pretitrated electrolyte and purged with argon. The generation of titrant (OH^-) is resumed until the pretitration pH value is restored. The number of coulombs required to return the system to the pH of the pretitrated electrolyte corresponds to the titer of the sample.

An intercomparison of the results of closed loop titrations with Gran's plot procedure is presented in Table II. The data reported in columns 2 and 4 were obtained with an argon atmosphere maintained over the electrolyte during the titration. This procedure precludes atmospheric CO_2 from redissolving in the electrolyte in the course of titration. However, any CO_2 in the sample solution is not excluded by this procedure, and thus it becomes part of the titer. The data in columns 3 and 5 were obtained with solutions subjected to continuous argon purge. Thus virtually all of the CO_2 should have been expelled in this procedure, and only nonvolatile acids would contribute to the titer.

In Table II, solution A was 0.0500 mol/kg potassium acid phthalate, pH 4 buffer, prepared from SRM 185f. Its concentration corresponds to 49.50 μeq H^+ per gram of solution (μeg/g). The determined titer for samples which were not deaerated, both in the case of closed loop and Gran's plot, was significantly higher than the calculated value (by 0.25 μeq/g and 0.3 μeq/g, respectively). The closed loop titration of deaerated solution A yielded a value of 49.57 μeq/g, which is only 0.07 μeq/g higher than the computed value. This difference is well within the uncertainty of the measurements on this solution. The Gran plot procedure yielded a value of 49.3 μeq/g. Again a significant reduction in the titer resulted from deaeration with argon. Similar behavior was observed for strong acid samples B, C, D, and E in Table III. As a final step of this study, it was of interest to establish the contribution of CO_2 to the determined acidity of rain-like samples. For this purpose, three solution concentrates of acid-precipitation research material prepared by the U.S. Environmental Protection Agency were used (1000, 2000, and 3000 series). The samples of the investigated solutions were weighed into a coulometric cell containing a deaerated solution of KCl (1 mol/L), which was initially pretitrated to pH = 7.0. The samples were either taken as the concentrates directly from the original bottles, or were diluted 1:50 by weight with distilled, deionized H_2O. After sample delivery, the cell contents were either titrated immediately or were deaerated by purging the solution with argon gas for ten minutes. An argon atmosphere was maintained over all solutions while in the titration cell to prevent reabsorption of CO_2.

The titrations were performed "cyclically", i.e., by measuring the time necessary to return the system to the starting pH (7.0) while electrogenerating titrant in the solution. The data obtained are summarized in Table III. The following conclusions may be drawn. First, samples deaerated with argon (first three entries in Table III) show no significant difference (Column 5) in the determined acidity using either concentrated or (1:50) diluted samples. This clearly shows that after deaeration the distilled H_2O introduces no additional acid/base modifications to the samples. Secondly, materials which were not deaerated exhibit significant differences between diluted and undiluted samples. If one attributes this difference to the dissolved CO_2, then the extrapolated value for carbonic acid is 0.69 μeq H^+ per 49 g of distilled H_2O. Finally, direct determination of carbonic acid in distilled H_2O yields the value 0.70 μeq H^+ per 50 g of distilled H_2O, confirming the extrapolated value. In view of the fact that difficulties are encountered in maintaining the CO_2 concentration invariant, deaeration of solutions for acidity determinations is recommended.

Conclusions

Most accurate and precise determination of acidity by any method requires deaeration of samples prior to titration to remove the dissolved CO_2. Five methods for the determination of acidity of acid solutions of low concentration (down to 10^{-5} mol/kg) were investigated. Four of the methods provide satisfactory results. Method (3), Gran's plot end-point detection using 10^{-3} mol/kg NaOH, in a conventional titration suffers from the inability to reproduce the size of reagent increments, which is essential for this method. Automated titration systems could remedy this deficiency. "Closed loop" titration procedures are most convenient, where applicable.

Resolution of the two segments of a titration curve, in a reliable and quantitative manner, into strong acid and carbonic acid components does not appear feasible, even when using Gran's plot method.

Coulometric delivery of titrant is recommended as a reference method for the following reasons: (1) in-situ generation of OH^- at constant volume eliminates the need for dilution corrections; (2) coulometric apparatus are highly amenable to maintaining inert atmospheres, hence excluding atmospheric CO_2; (3) aliquot delivery of titrant can be easily controlled. All of the titration procedures are biased in a positive direction by the presence of dissolved atmospheric CO_2. It is recommended that titrations of acidic precipitation be performed on deaerated samples only, to eliminate this source of variability and uncertainty.

REFERENCES

[1] Marinenko, G. and Koch, W. F., "A Critical Review of Measurement Practices for the Determination of pH and Acidity of Atmospheric Precipitation," Environment International (accepted for publication, August 1984).

[2] Gran, G. "Determination of Equivalence Point in Potentiometric Titrations," Acta Chem. Scan. 4. 559-577 (1950).

[3] Koch, W. F., Marinenko, G. and Stolz, J. W., Simulated Precipitation Reference Materials, IV, NBSIR 82-2481, October 1982.

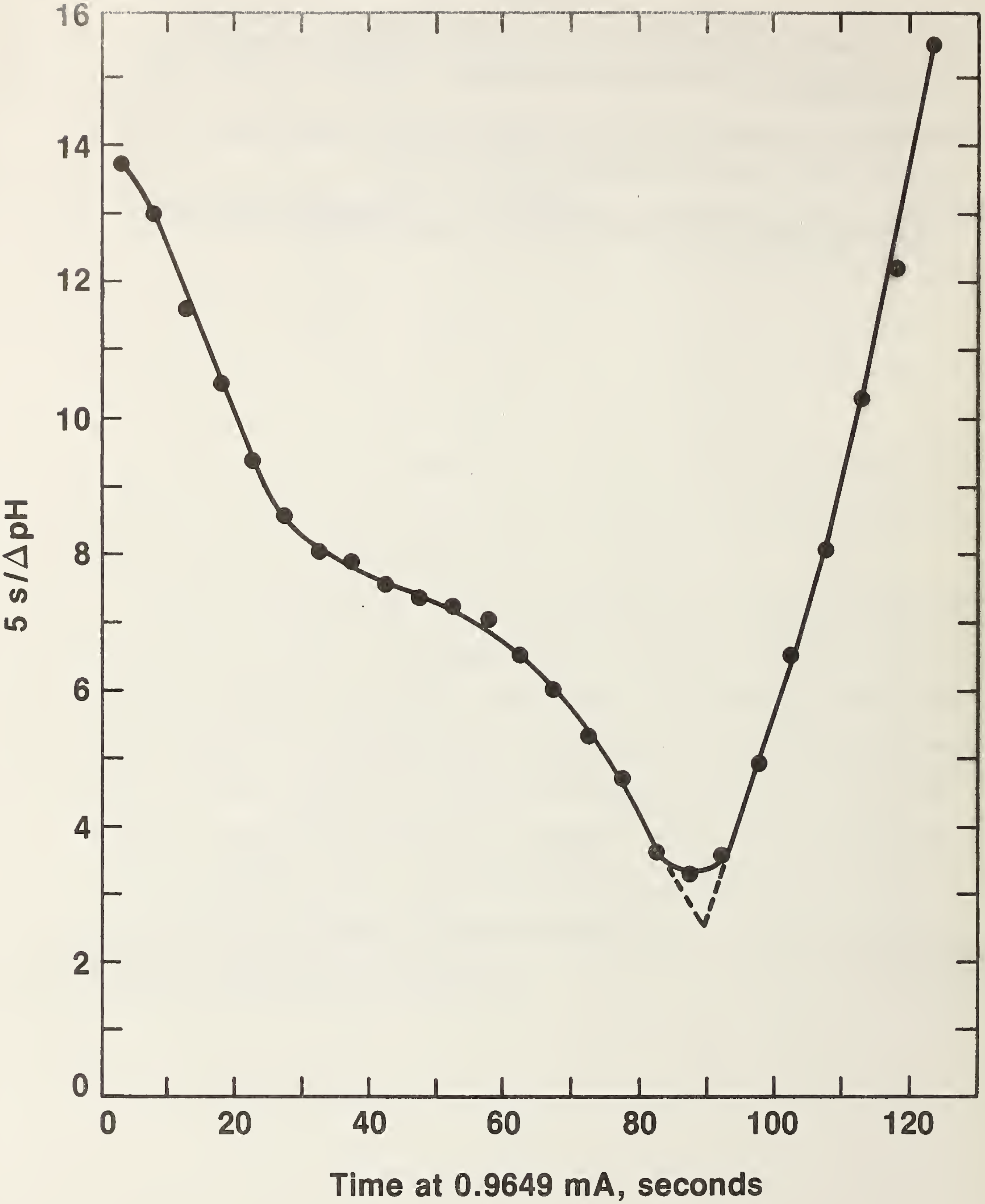

Figure 1. Gran's Plot of Coulometric Titration of 2×10^{-5} mol/kg HCl.

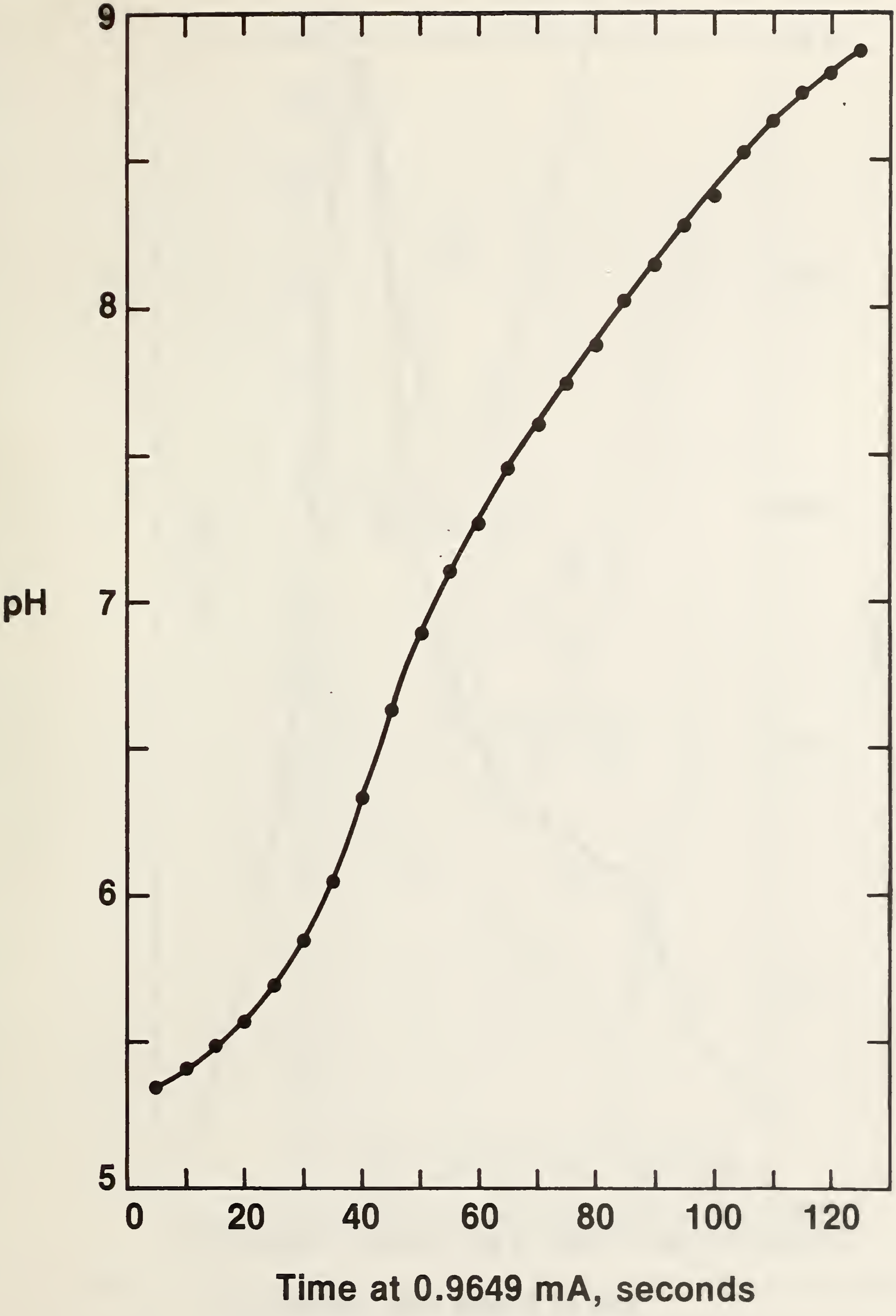

Figure 2. Conventional Plot of Coulometric Titration of 2×10^{-5} mol/kg HCl.

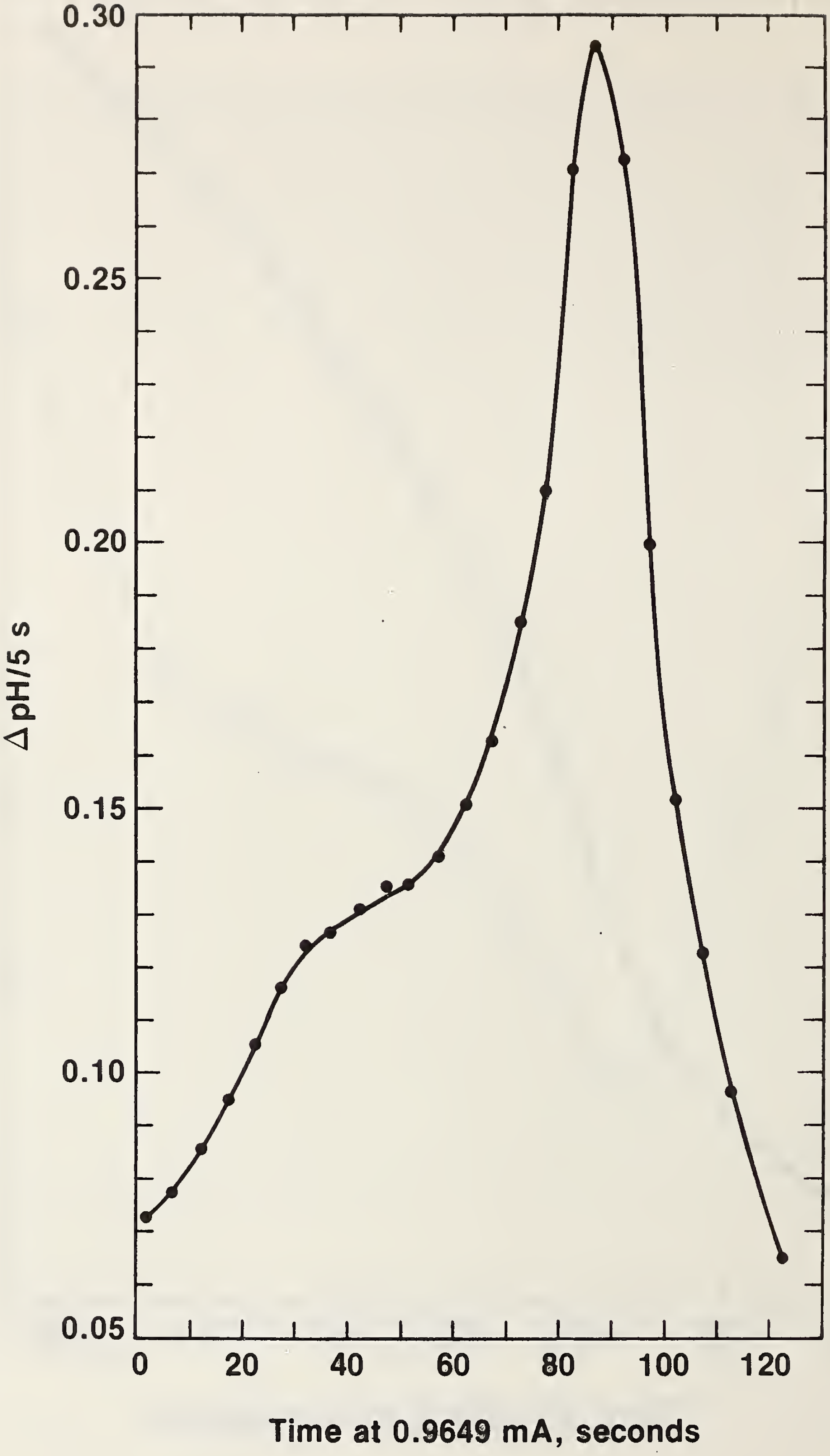

Figure 3. Differential Plot of Coulometric Titration of 2×10^{-5} mol/kg HCl.

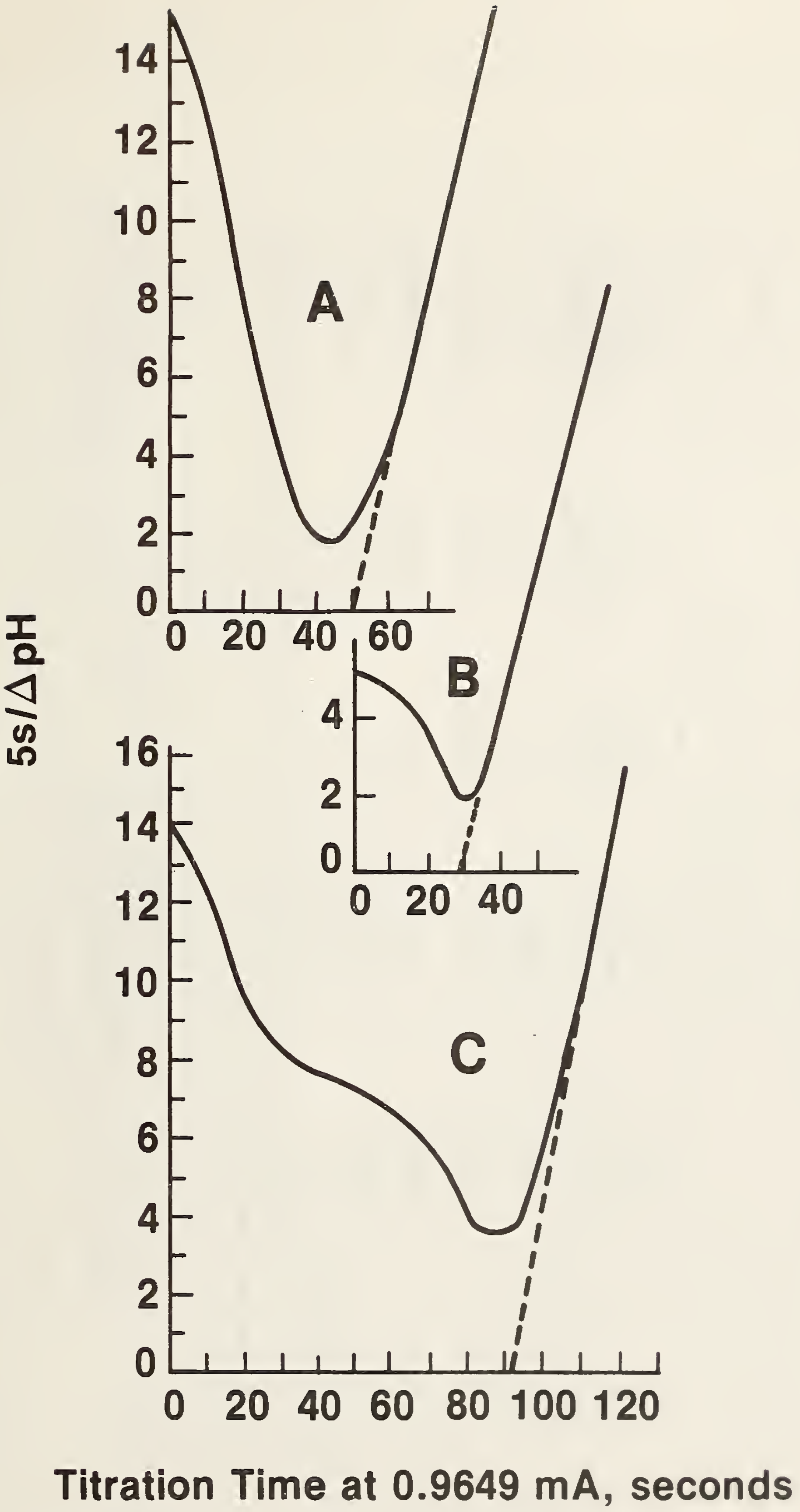

Figure 4. Determination of Acidity by Coulometric Titration Using Gran's Plot Technique.
A - 24g sample of $2x10^{-5}$ mol/kg HCl, deaerated with argon;
B - 24g sample of air saturated distilled, H_2O;
C - 24g sample of air saturated $2x10^{-5}$ mol/kg HCl.

Table I. Gravimetric Titrations of HCl Solutions, Using 0.9989 μeq/g NaOH

End-Point pH	Concentration of H^+, μeq/g Soln				
	Soln 1 0.0201 μeq/g HCl	Soln 2 0.2001 μeq/g HCl	Soln 3 Distilled H_2O	Soln 1 Corrected for Blank	Soln 2 Corrected for Blank
6.4	0.021	0.202	---	0.021	0.202
7.0	0.028	0.210	0.009	0.019	0.201
8.0	0.036	0.218	0.014	0.022	0.204
9.2 (phenolphthalein)	0.051	0.230	0.025	0.026	0.205

Pooled standard deviation s = 0.002.

Table II. Acidity Determinations of Five Solutions by the Coulometric Closed Loop Titration and Gran's Plot Techniques

	Concentration of H^+, μeq/g soln			
	Closed Loop (pH 8.1 in Sodium Citrate)		Gran's Plot ($\Delta V/\Delta pH$)	
Solution	Argon Shield	Complete Deaeration with Argon	Argon Shield	Complete Deaeration with Argon
A	49.75	49.57	49.8	49.3
B	0.212	0.207	0.215	0.209
C	0.057	0.055	0.060	0.046
D	0.091	0.084	0.075	0.076
E	0.199	0.176	0.196	0.185

Pooled standard deviation for sample A s = 0.08 μeq/g
Pooled standard deviation for samples B to E s = 0.006 μeq/g

Table III. Comparison of the Results for Diluted (1:50) and Undiluted "Acid Rain" Reference Solutions

Results are in μeq H^+/g of Original Concentrate

Deaerated with Argon

Sample No.	Solution No.	Concentrate Sample	Diluted (50:1) Sample	Δ
1	3000	14.99	15.00	+0.01
2	2000	5.05	4.94	-0.11
3	1000	2.53	2.46	-0.07
		Not Deaerated		
4	3000	15.07	15.45	+0.38
5	2000	5.10	5.64	+0.54
6	1000	2.56	3.13	+0.57
7	H_2O	0.014	0.70	+0.69

Pooled standard deviation is 0.03 μeq H^+/g soln.

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Five methods for the determination of acidity of acid solutions of low concentration (down to 10^{-5} mol/kg) were investigated. Four of the methods provide satisfactory results. Method (3), Gran's plot end-point detection using 10^{-3}m NaOH titrant, suffers from the inability to control exactly the size of reagent increments, which is essential for this method. Automated titration systems could remedy this deficiency. "Closed loop" titration procedures are most convenient.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

acid rain; acidimetric method evaluation; acidimetry; acidity; closed loop titration end-point determination

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