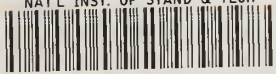


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# Evaluation of Methods Used for the Determination of Acidity in "Acid Rain" Samples

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U.S. DEPARTMENT OF COMMERCE  
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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  $\mu\text{eq}$  of  $\text{H}^+$ /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  $\text{H}_2\text{O}$  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  $\text{CO}_2$  in the sample. If distilled water saturated with air is used as the "blank", the  $\text{CO}_2$  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  $3 \times 10^{-3}$   $\mu\text{eq/g}$  and  $5 \times 10^{-3}$   $\mu\text{eq/g}$  for the two end-point pH's, respectively. The overall root-mean-square error of the results for this titration procedure is  $2 \times 10^{-3}$   $\mu\text{eq/g}$ .

Variation (3) in apparent  $\text{H}^+$  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  $\Delta V$  refers to the standard NaOH solution increment,  $\Delta pH$  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<sub>2</sub>CO<sub>3</sub>) in a mixture by Gran's technique. The results of this phase of the study are summarized in Figure 4. Three samples [deaerated 2·10<sup>-5</sup> mol/kg HCl (A), air-saturated distilled H<sub>2</sub>O used for preparation of the above HCl solutions (B) and air saturated 2·10<sup>-5</sup> 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<sub>2</sub>O 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<sup>-</sup> 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 ( $\text{OH}^-$ ) 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  $\text{CO}_2$  from redissolving in the electrolyte in the course of titration. However, any  $\text{CO}_2$  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  $\text{CO}_2$  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  $\mu\text{eq H}^+$  per gram of solution ( $\mu\text{eq/g}$ ). 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  $\mu\text{eq/g}$  and 0.3  $\mu\text{eq/g}$ , respectively). The closed loop titration of deaerated solution A yielded a value of 49.57  $\mu\text{eq/g}$ , which is only 0.07  $\mu\text{eq/g}$  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  $\mu\text{eq/g}$ . 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  $\text{CO}_2$  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<sub>2</sub>O. 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<sub>2</sub>.

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<sub>2</sub>O 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<sub>2</sub>, then the extrapolated value for carbonic acid is 0.69  $\mu\text{eq H}^+$  per 49 g of distilled H<sub>2</sub>O. Finally, direct determination of carbonic acid in distilled H<sub>2</sub>O yields the value 0.70  $\mu\text{eq H}^+$  per 50 g of distilled H<sub>2</sub>O, confirming the extrapolated value. In view of the fact that difficulties are encountered in maintaining the CO<sub>2</sub> 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  $\text{CO}_2$ . 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  $\text{OH}^-$  at constant volume eliminates the need for dilution corrections; (2) coulometric apparatus are highly amenable to maintaining inert atmospheres, hence excluding atmospheric  $\text{CO}_2$ ; (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  $\text{CO}_2$ . It is recommended that titrations of acidic precipitation be performed on deaerated samples only, to eliminate this source of variability and uncertainty.

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

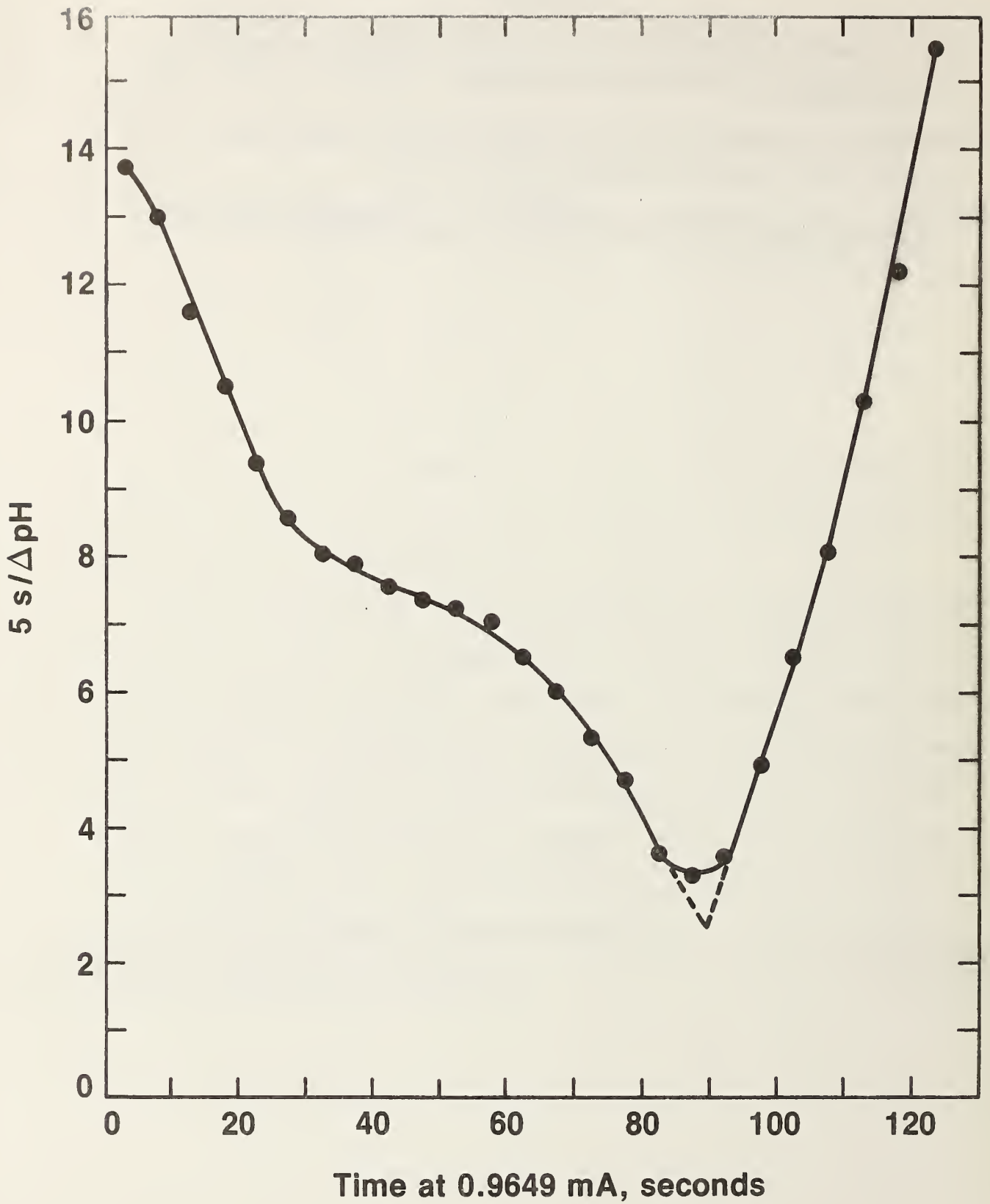


Figure 1. Gran's Plot of Coulometric Titration of  $2 \times 10^{-5}$  mol/kg HCl.



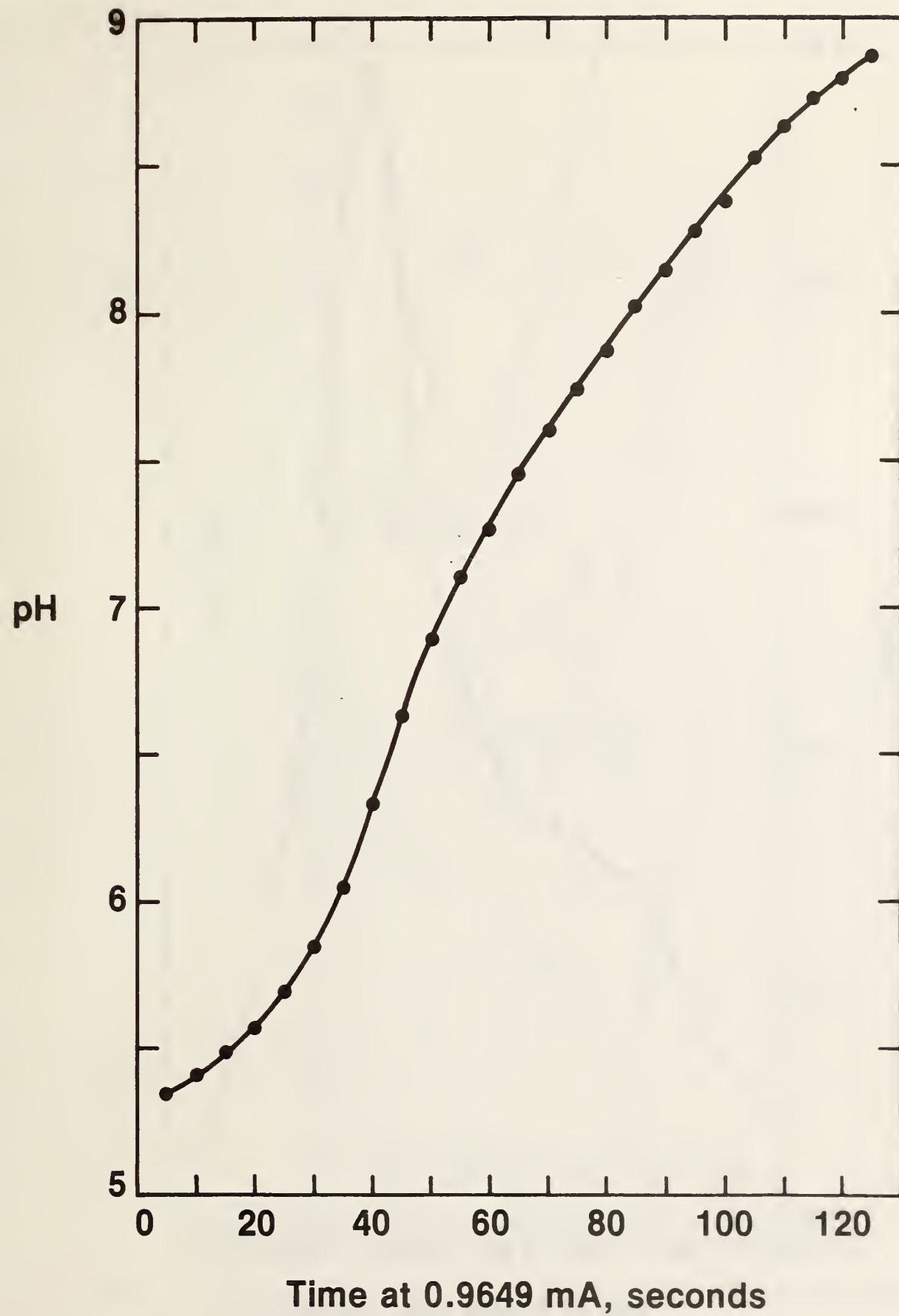


Figure 2. Conventional Plot of Coulometric Titration of  $2 \times 10^{-5}$  mol/kg HCl.

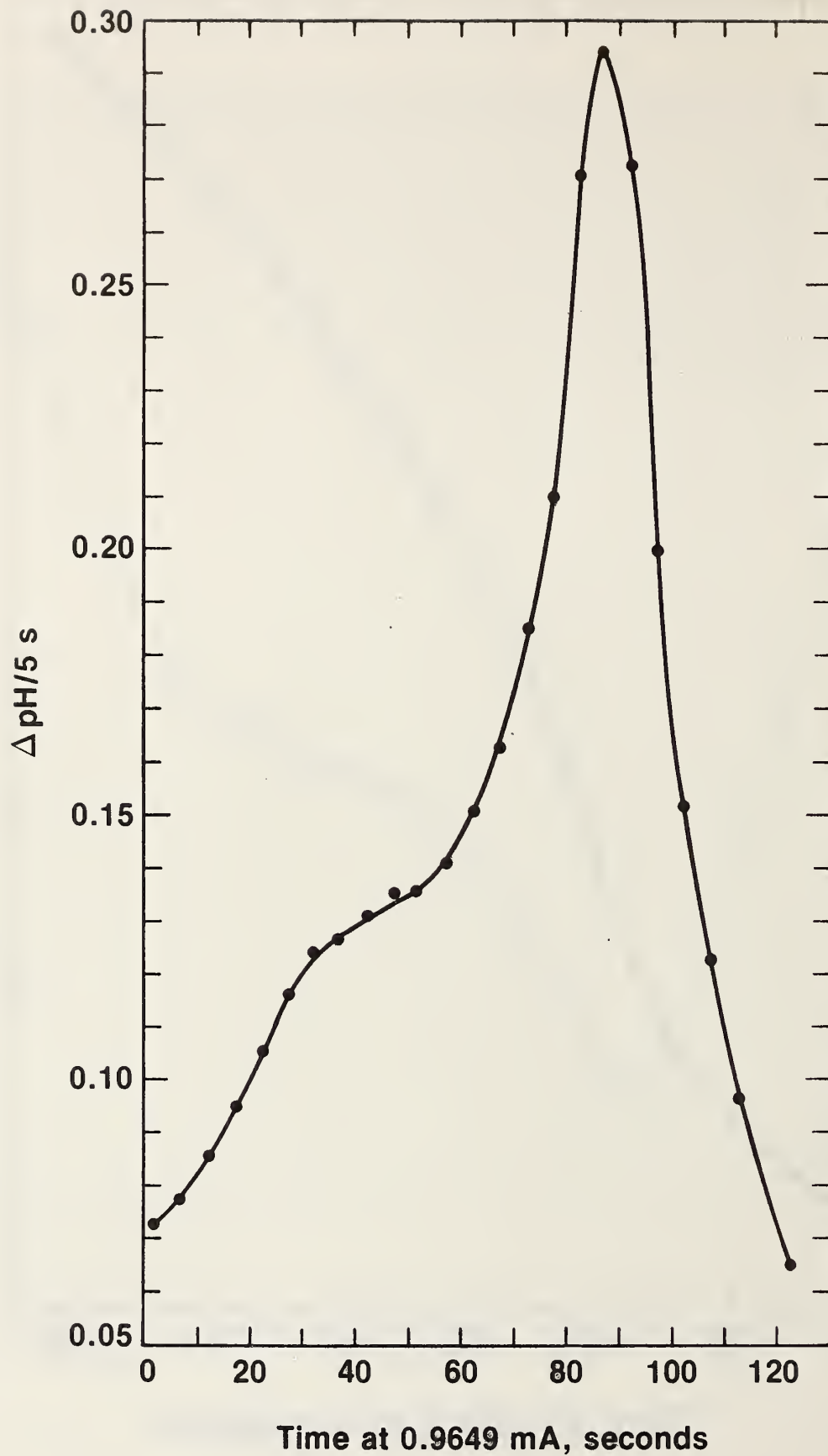
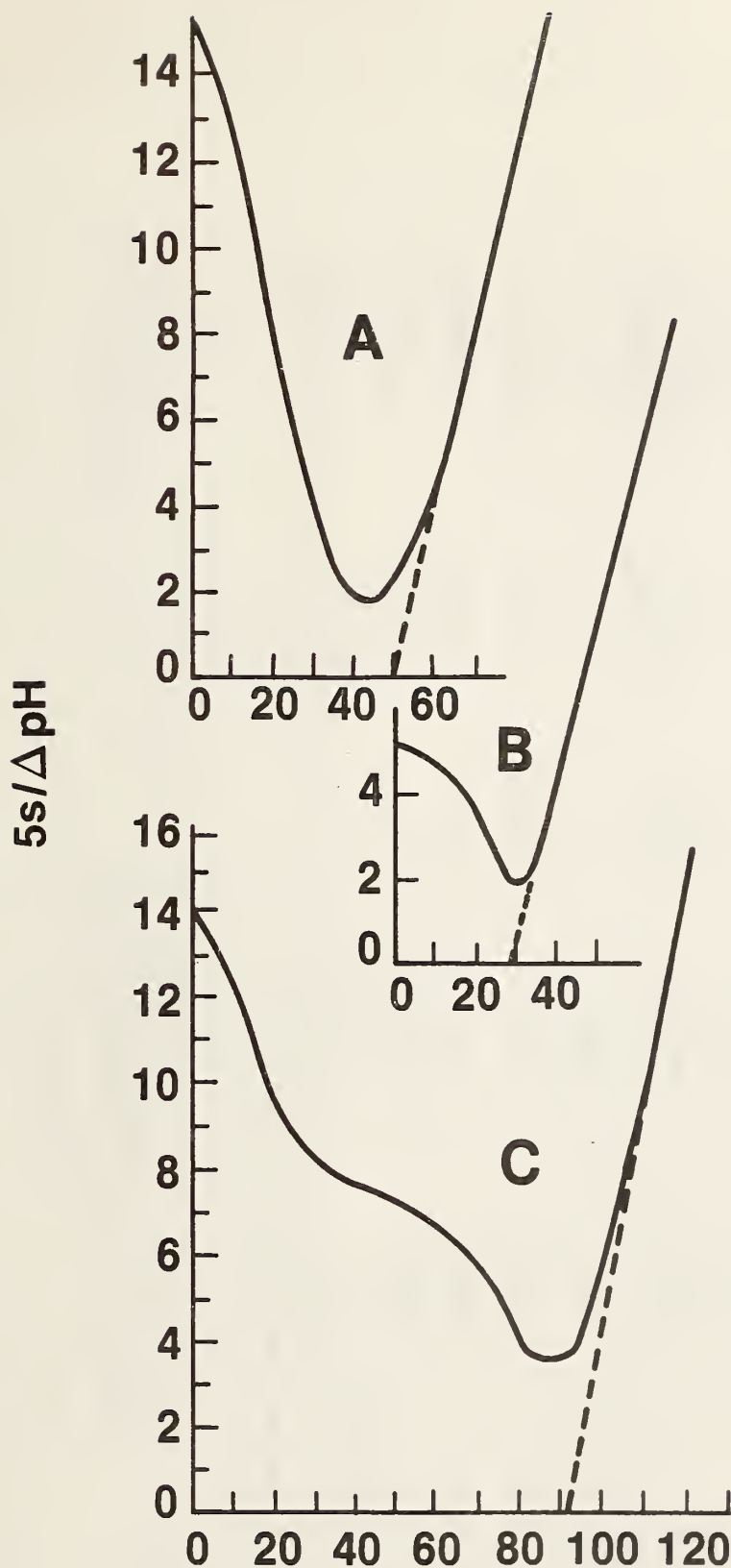


Figure 3. Differential Plot of Coulometric Titration of  $2 \times 10^{-5}$  mol/kg HCl.



### Titration Time at 0.9649 mA, seconds

Figure 4. Determination of Acidity by Coulometric Titration Using Gran's Plot Technique.

A - 24g sample of  $2 \times 10^{-5}$  mol/kg HCl, deaerated with argon;

B - 24g sample of air saturated distilled,  $H_2O$ ;

C - 24g sample of air saturated  $2 \times 10^{-5}$  mol/kg HCl.

Table I. Gravimetric Titrations of HCl Solutions,  
Using 0.9989  $\mu\text{eq/g}$  NaOH

Concentration of $\text{H}^+$ , $\mu\text{eq/g}$ Soln						
End-Point pH	Soln 1 0.0201 $\mu\text{eq/g}$ HCl	Soln 2 0.2001 $\mu\text{eq/g}$ HCl	Soln 3 Distilled $\text{H}_2\text{O}$	Soln 1 Corrected for Blank	Soln 2 Corrected for Blank	Soln 3 Corrected for Blank
6.4	0.021	0.202	---	0.021	0.202	0.202
7.0	0.028	0.210	0.009	0.019	0.201	0.201
8.0	0.036	0.218	0.014	0.022	0.204	0.204
9.2 (phenolphthalein)	0.051	0.230	0.025	0.026	0.205	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

Solution	Concentration of H <sup>+</sup> , $\mu\text{eq/g}$ soln			
	Closed Loop (pH 8.1 in Sodium Citrate)		Gran's Plot ( $\Delta V/\Delta\text{pH}$ )	
	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  $s = 0.08 \mu\text{eq/g}$   
Pooled standard deviation for samples B to E  $s = 0.006 \mu\text{eq/g}$

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

Results are in  $\mu\text{eq H}^+/\text{g}$  of Original Concentrate

Sample No.	Solution No.	<u>Deaerated with Argon</u>			$\Delta$
		Concentrate Sample	Diluted (50:1) Sample		
1	3000	14.99	15.00	+0.01	
2	2000	5.05	4.94	-0.11	
3	1000	2.53	2.46	-0.07	
<u>Not Deaerated</u>					
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 <sub>2</sub> O	0.014	0.70	+0.69	

Pooled standard deviation is 0.03  $\mu\text{eq H}^+/\text{g}$  soln.



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<b>10. SUPPLEMENTARY NOTES</b>  <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
<b>11. ABSTRACT</b> <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i>  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.			
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