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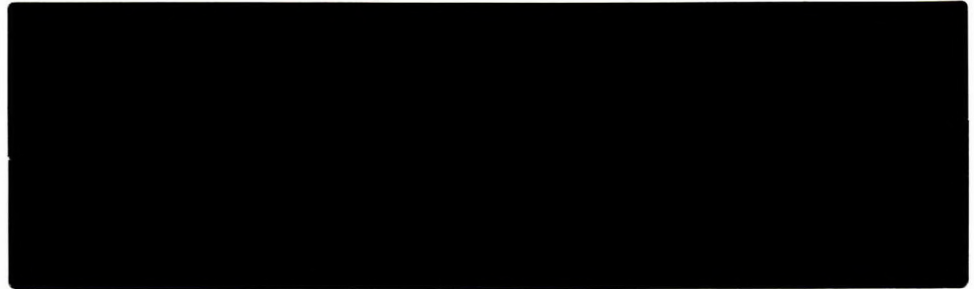
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THE EFFECTS OF CARBONATES ON THE
ACID/BASE DISSOCIATION EQUILIBRIA OF
OIL SANDS TAILINGS POND WATER ORGANIC
SPECIES

C.W. Angle and R. Hewgill

Division Report WRC 92-61 (TR)

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by

C.W. Angle* and R. Hewgill*

ABSTRACT

The dibasic properties of the pond or supernatant waters from the tailings ponds of an oil sands processing operation have been investigated. The carbonate/bicarbonate buffer system which has developed during and after processing was shown in previous studies to promote dispersion of the clays. A method of eliminating this buffer system was tested. From the results, the above buffer system was shown to dominate the surface and water chemistries of the system. Distinguishing the direct responses of the soluble organic species in the system using potentiometry was difficult in this buffered system. Results showed that the pKa of organic and inorganic were coincidental. Elimination of this buffer is possible and leads to a method of investigation of the effects of the soluble organic species alone. Other experiments on the surface chemistry and rheology of a carbonate/bicarbonate depleted system will be pursued.

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EFFETS DES CARBONATES SUR LES ÉQUILIBRES DE DISSOCIATION
ACIDE/BASE DES ESPÈCES ORGANIQUES CONTENUES DANS LES EAUX
DES BASSINS À RÉSIDUS DE SABLES PÉTROLIFÈRES

par

C.W. ANGLE* et R. Hewgill*

RÉSUMÉ

Les propriétés dibasiques des eaux surnageantes des bassins à résidus d'une usine de traitement de sables pétrolifères ont été examinées. Des études antérieures ont montré que le système tampon carbonates/bicarbonates qui a été mis au point pendant et après le traitement favorisait la dispersion des argiles. Une méthode d'élimination de ce système tampon a été mise à l'essai. Les résultats ont révélé que le système tampon susmentionné donne les chimies de surface et de l'eau du système. Il a été difficile dans ce système tampon de distinguer entre les réponses directes des espèces organiques solubles dans le système par potentiométrie. Les résultats ont montré que les pKa des parties organiques et inorganiques coïncidaient. Il est possible d'éliminer ce tampon et d'obtenir une méthode d'examen des effets des seules espèces organiques solubles. D'autres expériences sur la chimie et la rhéologie de surface d'un système épuisé en carbonates/bicarbonates seront menées.

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CONTENTS

	<u>Page</u>
ABSTRACT.	i
RESUME.	ii
INTRODUCTION	1
EXPERIMENTAL.	2
Materials.	2
Methods.	2
RESULTS AND DISCUSSION	3
CONCLUSIONS	6
RECOMMENDATIONS	6
REFERENCES.	7
ACKNOWLEDGEMENTS	7
APPENDIX A	19
APPENDIX B	21

FIGURES

No.

1. Titration of 20 mL of supernatant of sludge from pond 2, Feb 1990, using 0.05M HCl as titrant and purging with high purity nitrogen. 8
2. Titration of 20 mL of supernatant of sludge from pond 2, June 1991, using 0.05M HCl as titrant and purging with high-purity nitrogen. 9
3. Titration of 20 mL of supernatant of sludge from pond 1, June 1991, using 0.05M HCl as titrant and purging with high-purity nitrogen. 10
4. Titration of 15 mL of 0.01M NaHCO₃ with 0.05 M HCl, in nitrogen atmosphere. 11
5. Titration of 19.453 mL of already reacted 0.01M NaHCO₃ of Fig. 4 with 0.05 M NaOH after purging for 10 min.

nitrogen atmosphere. 12

INTRODUCTION

In the Clarke hot water extraction process used for obtaining crude oil from tar sands, sodium hydroxide is added to the oil sands. The sodium hydroxide acts as a solvent for atmospheric carbon dioxides and together with the dolomites and calcites present, forms a very good buffer of carbonates/bicarbonates in the suspensions (1-3). Our previous studies on the sludge clays surface chemistry and electrokinetics established that carbonates played a significant role in creating aggregates when bound to the clay minerals by crystal formation with some of the clay surfaces acting as the nuclei (1). Whether found as siderite or as calcites, carbonates have been found in the petroleum industry to initiate scales deposition in pipes and to create problems in processing at a later stage. Bicarbonates may act as an advantageous buffer for an extraction process, but may contribute to problems for pipelining and tailings treatment process.

It was established that the soluble carbonate/bicarbonate anionic species in the water were specifically adsorbing to the model kaolinite particle edges, thus creating high negative zeta potentials of these particles and hence promoting dispersion, on one hand (2). On the other hand, their acid-base chemistry dominated the chemistry of the other species of the pond water. It was clearly differentiated that the soluble species were interacting with the clays synergistically to produce a-dispersion and with the insoluble species antagonistically to promote aggregation. An interesting paradoxical system resulted. Potentiometric titrations revealed that the dissociation equilibria of this buffer system masked any detection of the effective behaviour of the organic species in the water (2). In this work we decided to further pursue the removal of this buffer system from the pond water and note the actual effects of the other dissociating species present in the pond water. As a consequence of this work we have arrived at a methodology for removal of the bicarbonate buffer system in the pond water. We have also noted

variations in the concentration of these species from water to water. It is expected that the results of this work will allow us to further understand sludge systems as well as provide a methodology of analyzing for stoichiometry of other dissociating species. When pH varies with depth in a pond it is usually a consequence of the extent of the interactions of the clay and other minerals species with the water environment and its buffer system.

EXPERIMENTAL

MATERIALS

Pond waters were obtained from recirculating water, or the water associated with different sludge systems from pond 1 or pond 2. These ponds are identified as the tailings ponds for rejects from the SUNCOR oil sands extraction process. Sludge supernatants were obtained by centrifuging the sludge between 15 000 - 19 000 rpm for 30 minutes using a Ti-19 rotor in a Beckman L8-80 Ultracentrifuge, at 20°C. The supernatants were removed for potentiometric titrations. Titrations were conducted on an automated titration system assembled at CANMET using a Radiometer PHM 84 and ABU 80 autoburette, with software designed for titrating solids and liquids systems at CANMET. Titrants were 0.05M HCl and 0.05M NaOH. Sodium bicarbonate standards (0.01M) were used as the control test sample. Humic acids samples were obtained from Aldrich chemicals. All other reagents were obtained from Fisher Scientific and were ACS grade. All solutions were prepared using Millipore 18-M Ω resistivity water. All titrations were conducted in an inert nitrogen atmosphere.

METHODS

All samples were titrated using the variable equilibration time mode (VET) of the instrument where the equilibrium time was computer controlled. Three sets of experiments were conducted. All

samples were degassed with nitrogen before, during, and after titration to the acidic pH, of 2.5. Back titration to the basic pH 8.5 followed the first titration. The following treatments were performed:

The first batch of various sludge supernatant samples were first titrated to acidic pH and the shapes as well as the stoichiometry of the samples noted.

The second batch was titrated to acidic pH, boiled for 10 minutes in a reflux, then back titrated to basic pH and titrated again to acidic pH (For details see appendix A).

The sodium bicarbonate controls were treated in a similar manner to the first and second batch. Test humic acids were also titrated for comparison of dissociation equilibria.

RESULTS AND DISCUSSIONS

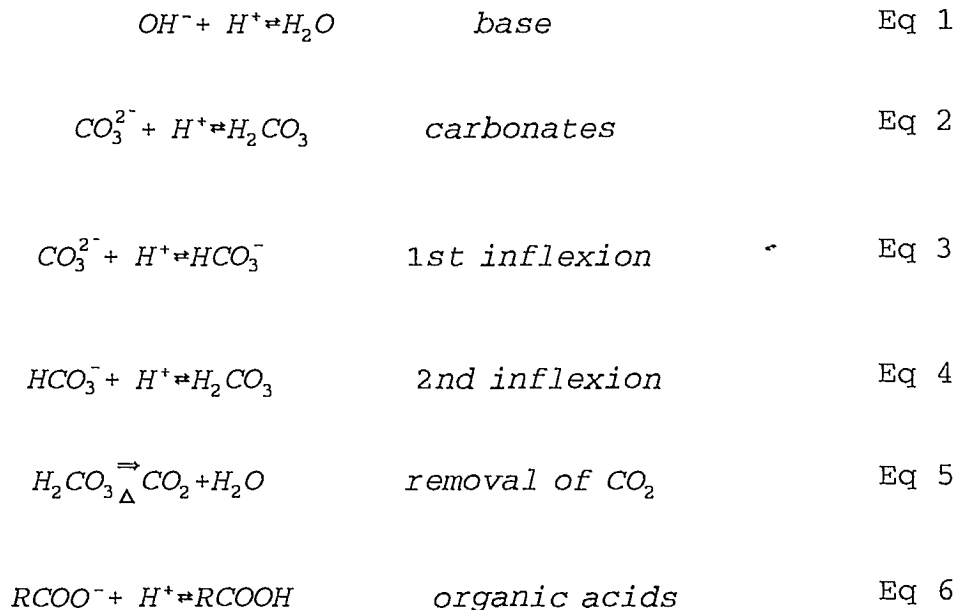
Typical acid titrations of various pond waters are found in Fig. 1, 2, and 3. Here variations in stoichiometry and equilibria are noted from pond to pond, sampled at various times. These samples show that most of the pond supernatant have similar dibasic character. The dibasic properties are coincident with those of the bicarbonates present in the water. Only removal of these bicarbonate species would show the true acid/base character of other soluble species present in the water. These may be surfactants or polymeric humic and fulvic acids indigeneous to the pond water. Potentiometric titrations of solids present in these waters are difficult to resolve as the bicarbonates appear to dominate the reactivity of the other species present (1,2). In order to remove the bicarbonate effects, the first tests were conducted on the standard bicarbonates.

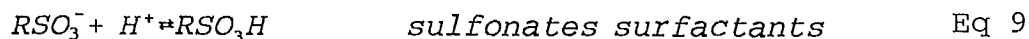
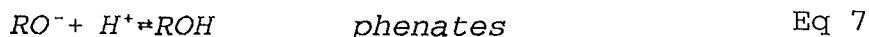
The acid/base character of standard sodium bicarbonates are found in the graphs of Fig. 4, 5, and 6. Figure 4 shows a typical titration curve of 0.01M NaHCO_3 , conducted with 0.05M HCl in an inert N_2 atmosphere. Figure 5 shows the sample of Fig. 4 after back

titration to basic pH, and after extensive purging with inert high-purity nitrogen. Figure 6 shows a back titration of the reacted bicarbonate solution after boiling for 10 minutes and purging for 10 minutes, before base titration up to pH 10. From these curves it is quite clear that removal of trace carbonic acids requires extensive energy which was introduced in the form of heat. Without these treatments trace carbonates are left in the system and their behaviour interferes with detection of the effects of other variables in the data acquired. Purging alone is not enough.

Titrations of the pond water treated similarly to the bicarbonates are shown in the Fig. 7, 8. Figure 7 shows a base titration of a boiled and degassed sample of pond water which was previously titrated to acid pH with 0.05M HCl. Figure 8 shows the acid titration of the pond water which was first acid titrated, but was not boiled for 10 minutes, or purged with high purity nitrogen and retitrated with 0.05M NaOH. Fig. 9 shows the acid retitration of pond water which was acidified, boiled, purged, and then brought back to basic pH.

The following reactions are descriptive of the systems:





Where bicarbonates were titrated first, followed by back titration with base and retitration without boiling and purging, reactions 1-5 hold. Because hydroxide and bicarbonate react to form carbonate, they cannot coexist individually in significant amounts (3). Therefore the majority of the pond waters which have caustic and bicarbonates really are carbonate systems. This was clearly shown by the double inflections.

Equations 6-9 describe the reactions of the organic species. Whereas Eq 6 and 9 describe the organic acids, 7 describes the phenates from polymeric humics, and 8 describes the dissolved mineral species from pH of zero charge down to the acidic region.

The diprotic character of the sample of Fig. 9 is typical of two weak acids. These acids can be derived from one of many reacting species. Possibilities are surface-active agents, and humic/fulvic acids, carboxylates, and phenates. A typical acid titration of standard 100ppm humic acids are shown in Fig.10. From this graph dibasic character is obvious. The pKa appears to correspond with those of the pond waters as well as those of the bicarbonates. Since all bicarbonates are absent, this technique appears useful for determining the stoichiometry of organic acids and surface-active agents found in the pond water.

Interpretations of the interactions of solids with pond waters should be done with caution as the buffering capacity of bicarbonates appears to mask the solids responses (1). We have therefore found a method of eliminating the effects of the bicarbonates in the pond waters. When the pond water is treated by the above techniques (see Appendix A), any behaviour observed from interactions with the solids would only be a result of the organic

species present in the waters. The solids, nevertheless, would contain adsorbed carbonates either as crystals deposited on the clays or as specifically adsorbed carbonates on the clay edges (1).

CONCLUSIONS

1. These bicarbonates have been successfully eliminated the acidic waters and then purging with inert nitrogen.
2. Interpretations of surface dissociation equilibria of solids and liquids in pond waters must be done with extreme caution as the bicarbonates present in the waters appear to mask other effects.
3. Previous practices of purging at the acidic pH with nitrogen only for elimination of CO_2 are shown to be insufficient as more energy is required for CO_2 elimination and a stabilizer is needed to reestablish thermodynamic equilibrium.
4. The pond waters have organic components with definite weakly dibasic character, analogous to humic acids; their effects can be distinguished better after removal of the bicarbonates.

RECOMMENDATIONS

Our next phase of work is to study the exact role of real sludge systems without the bicarbonate buffers. Surface-chemistry, electrokinetics, and rheology will be used to investigate elasticity and structure or floc formation properties in these systems.

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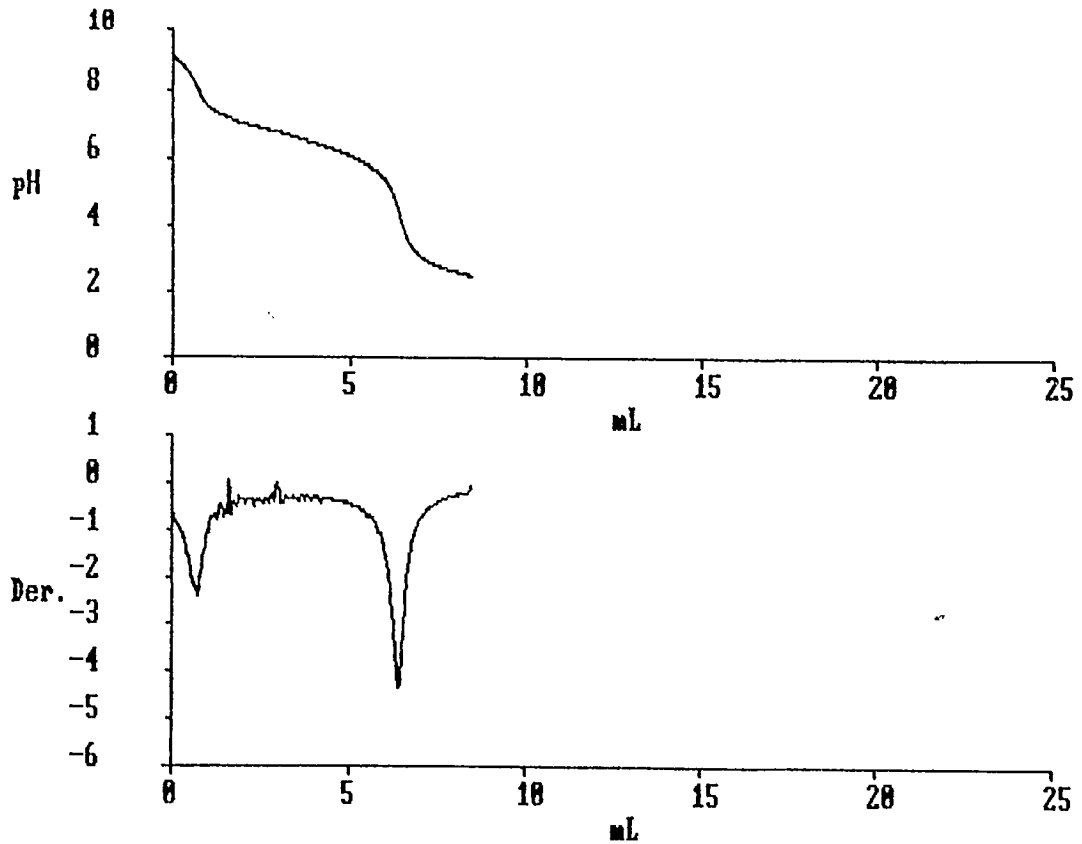


Fig.1 - Titration of 20mL of supernatant of sludge from pond 2, Feb 1990, using 0.05M HCl as titrant and purging with-high purity nitrogen

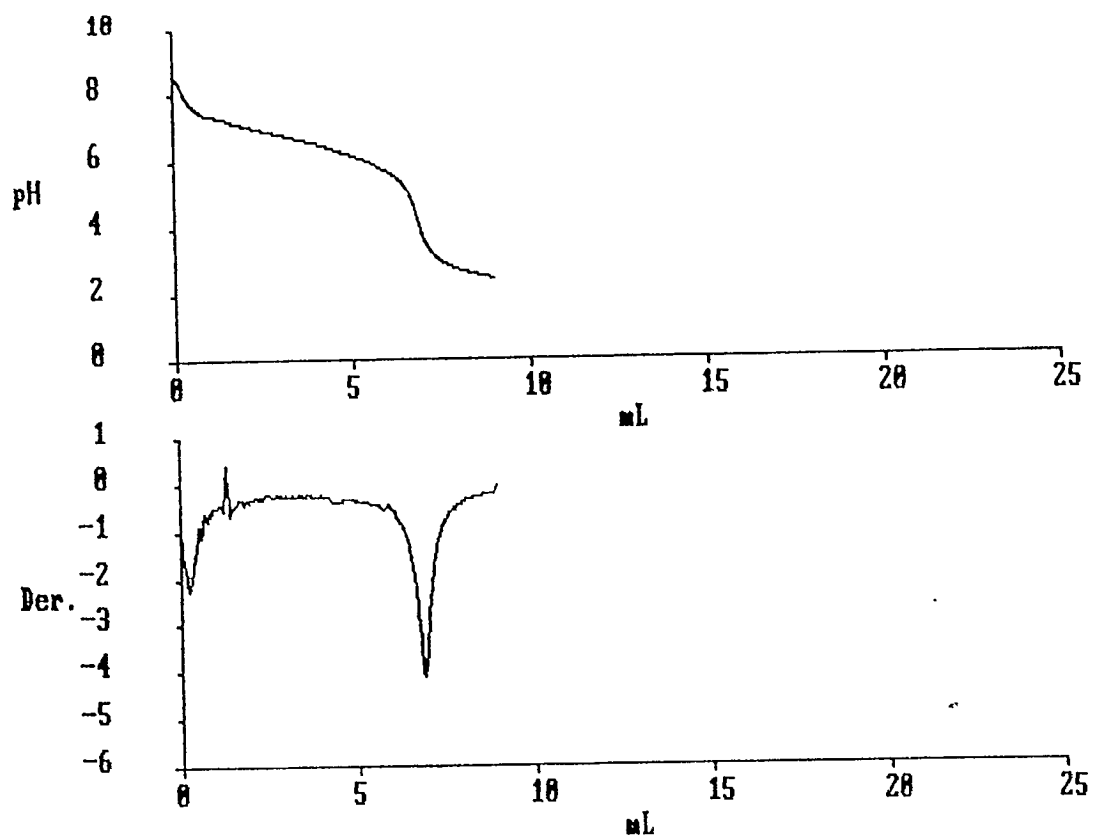


Fig.2 - Titration of 20mL of supernatant of sludge from pond 2, June 1991, using 0.05M HCl as titrant and purging with high-purity nitrogen

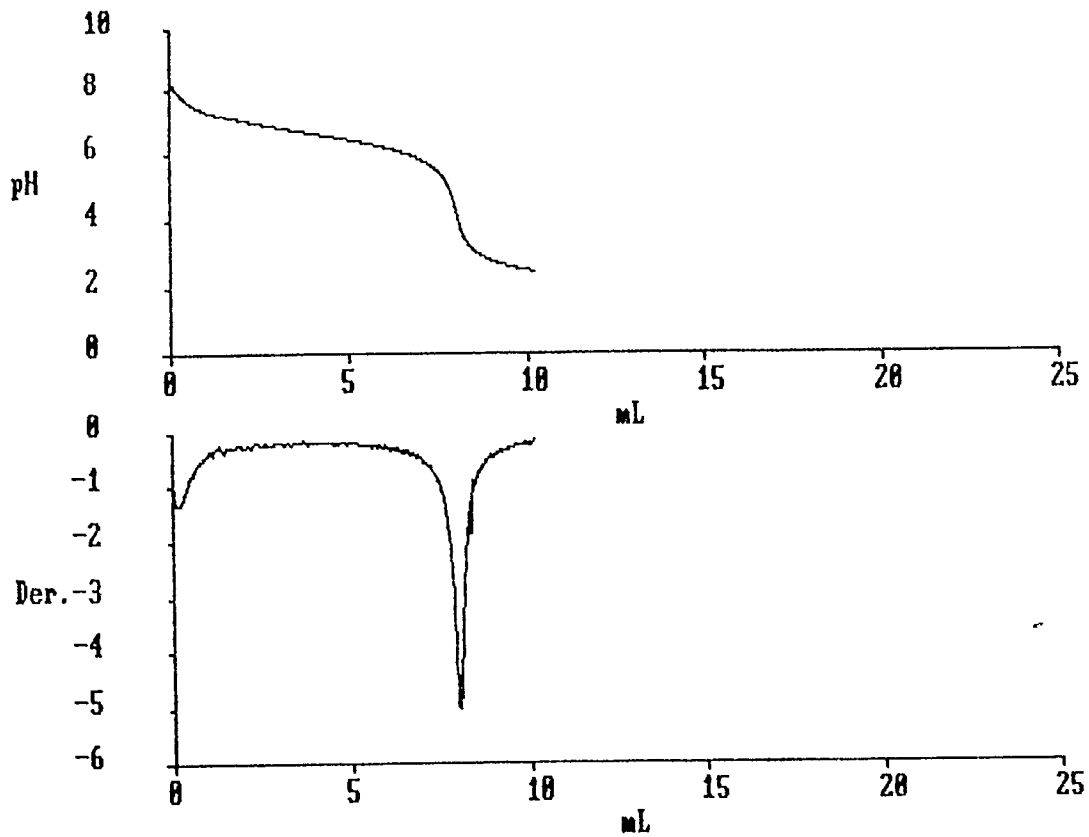


Fig.3 - Titration of 20mL of supernatant of sludge from pond 1, June 1991, using 0.05M HCl as titrant and purging with high-purity nitrogen

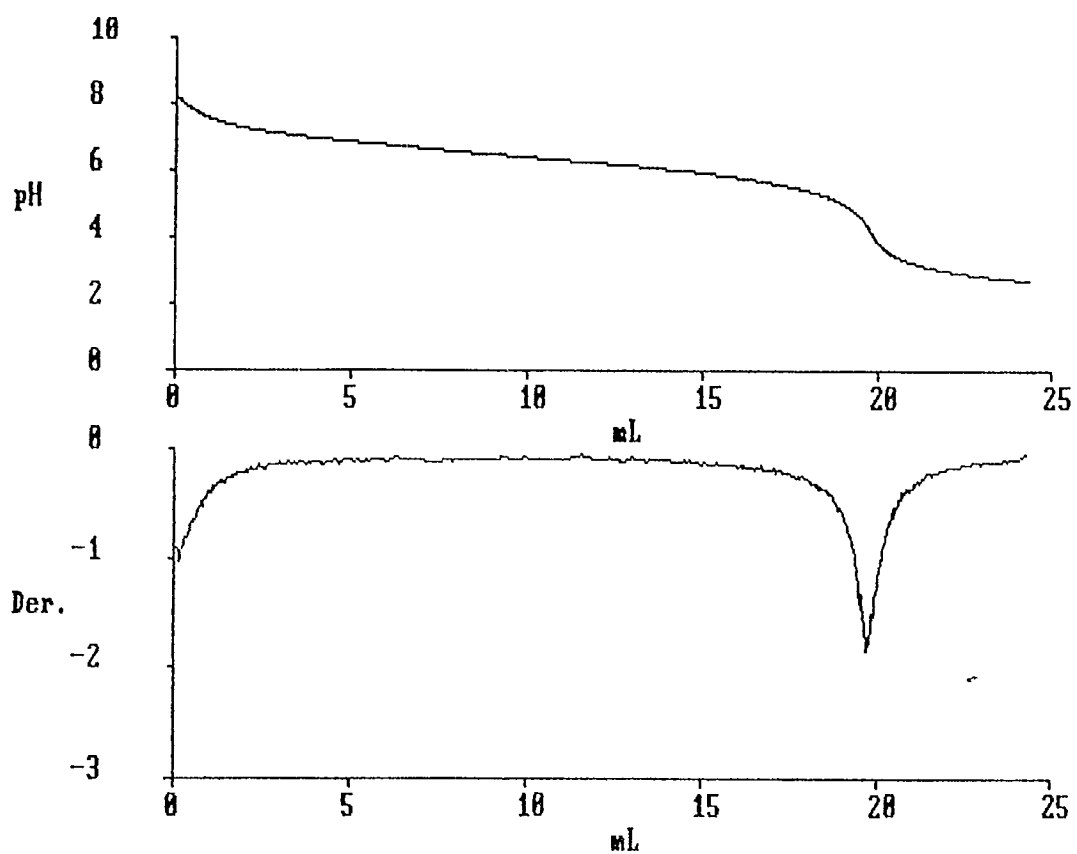


Fig. 4 - Titration of 15 mL of 0.01M NaHCO_3 with 0.05 M HCl , in nitrogen atmosphere

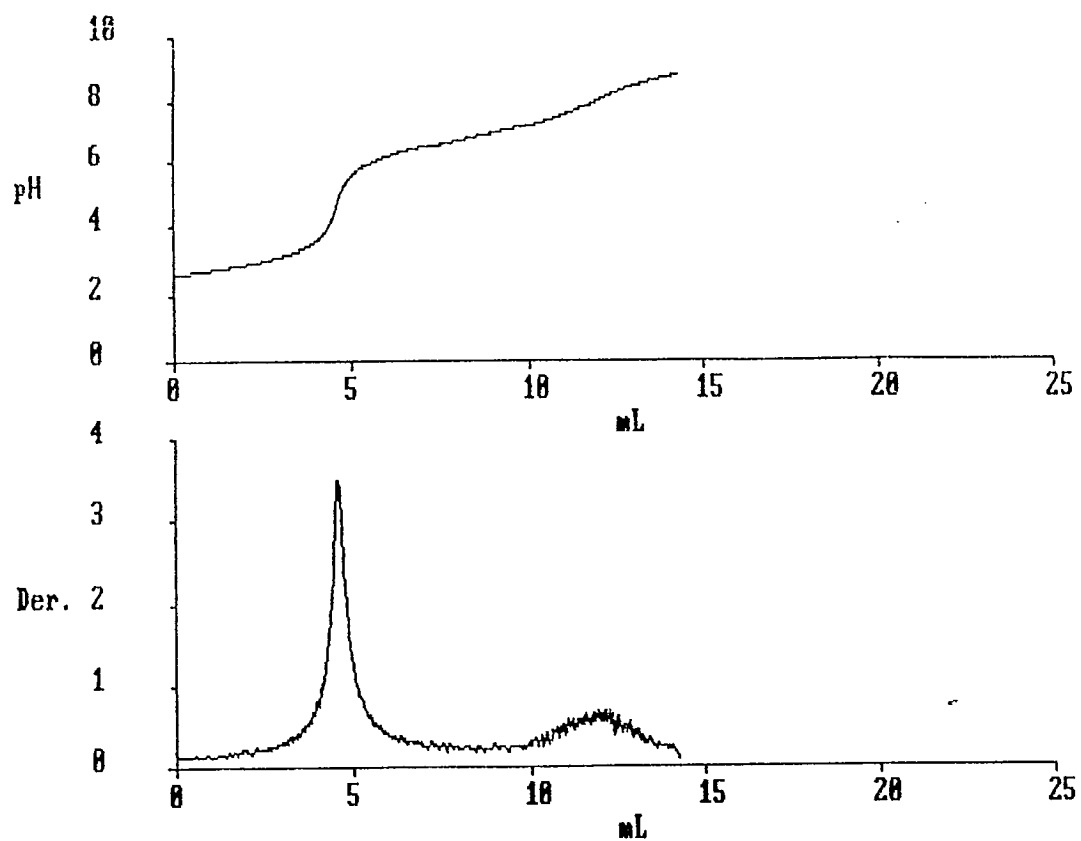


Fig. 5 - Titration of 19.453 mL of already reacted 0.01M NaHCO_3 of Fig. 4 with 0.05 M NaOH after purging for 10 min. nitrogen atmosphere

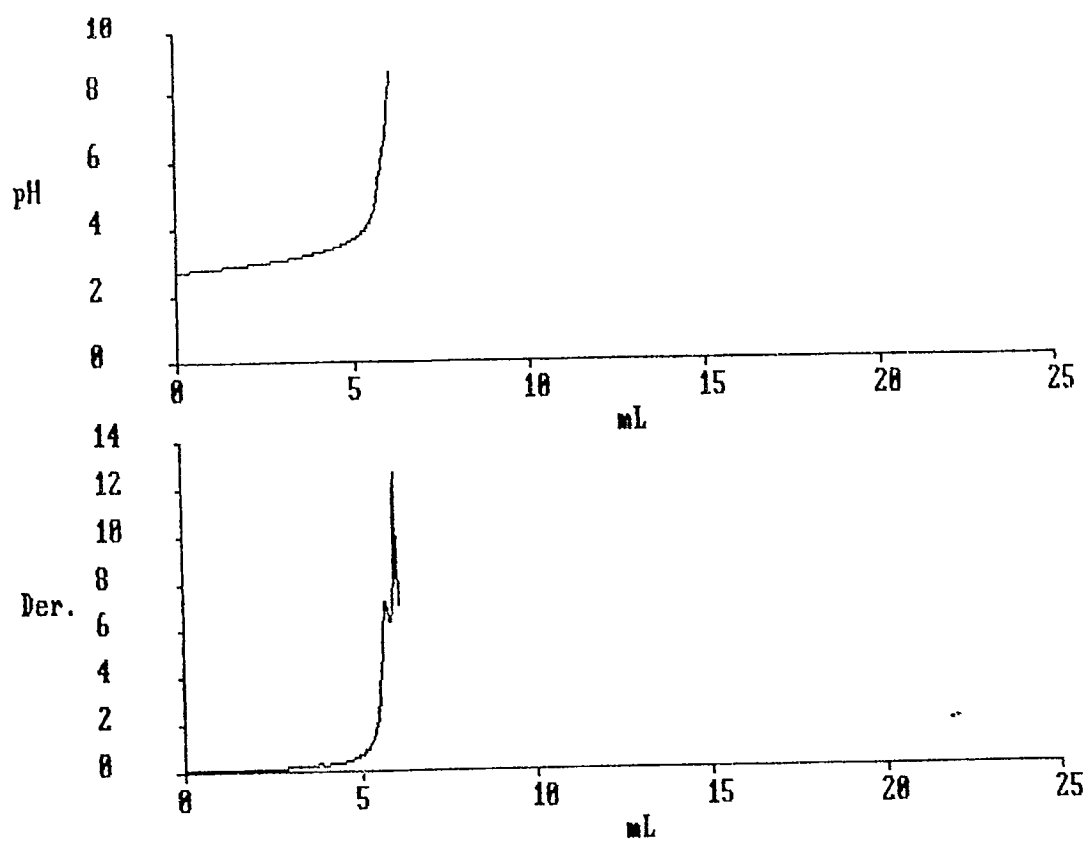


Fig. 6 - Titration of 15.453 mL of already reacted 0.01M NaHCO_3 of Fig. 4 with 0.05 M NaOH after boiling for 10 min then purging for 10 min with nitrogen atmosphere

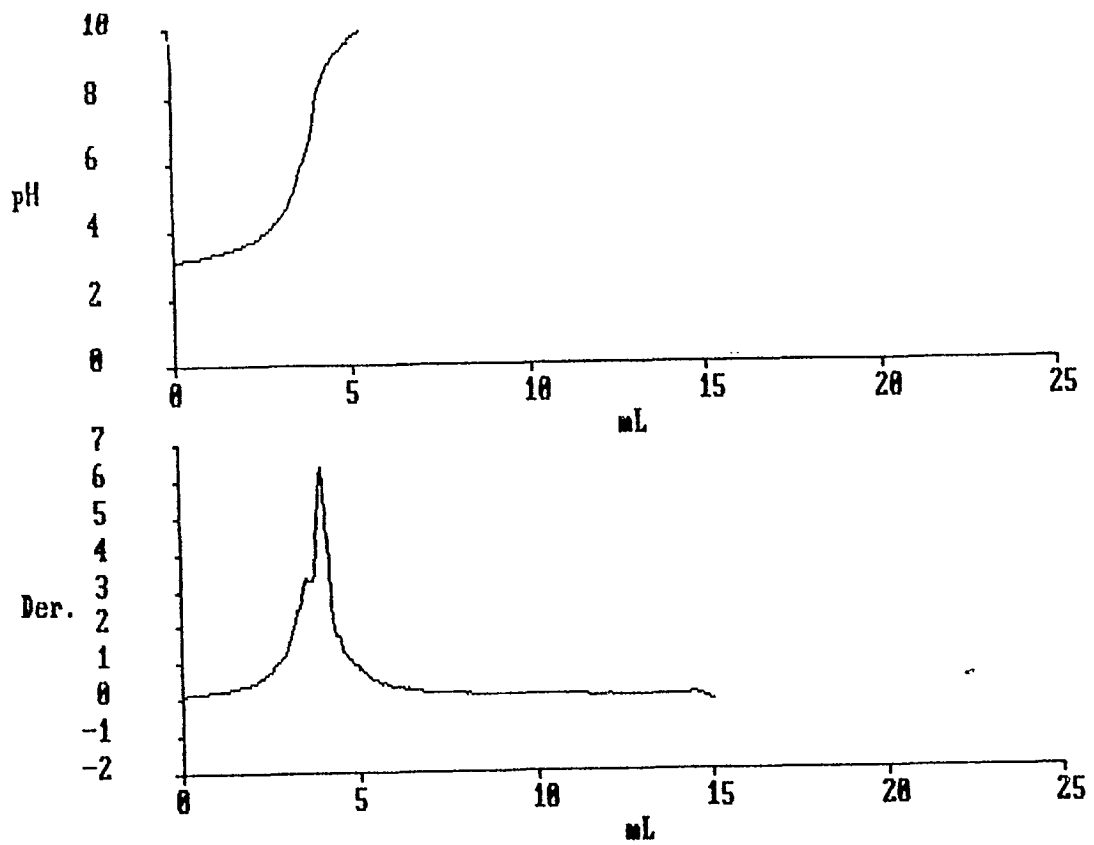


Fig. 7 - Base titration of boiled and purged sample of pond water previously titrated with 0.05M HCl to pH 2.5

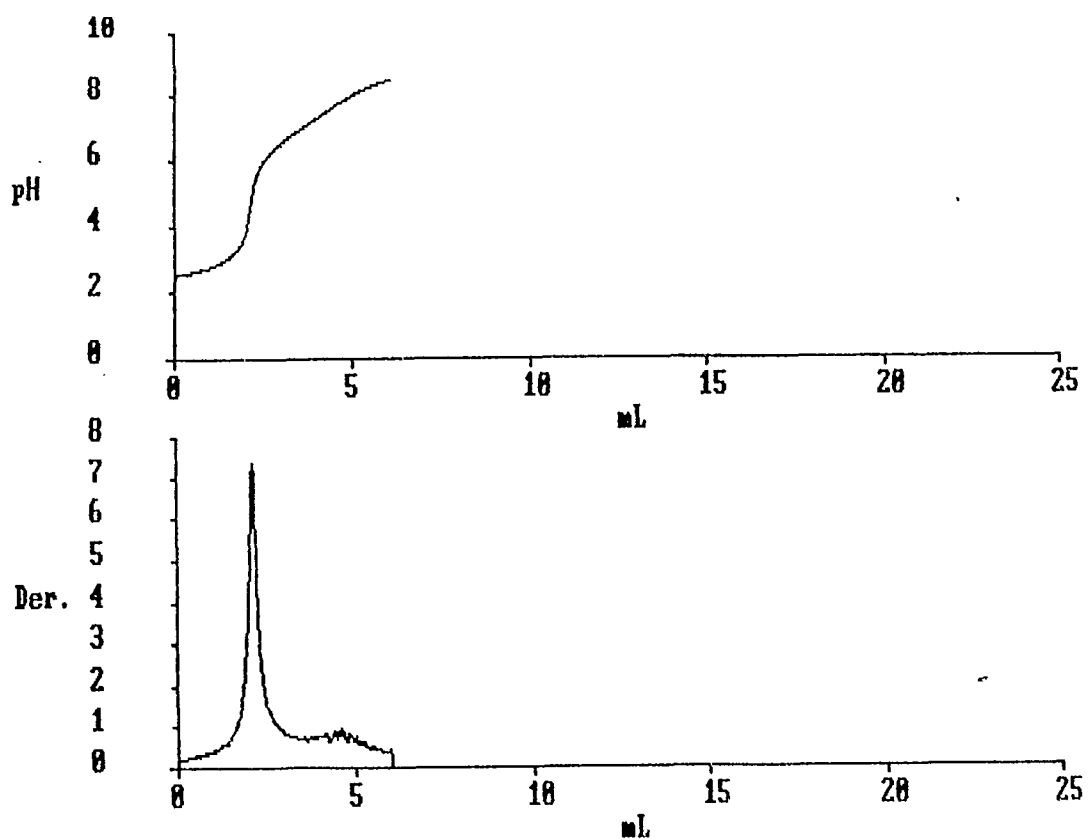


Fig. 8 - Titration of an acidified pond 1 water (20 mL) using 0.049M NaOH (no purging or boiling)

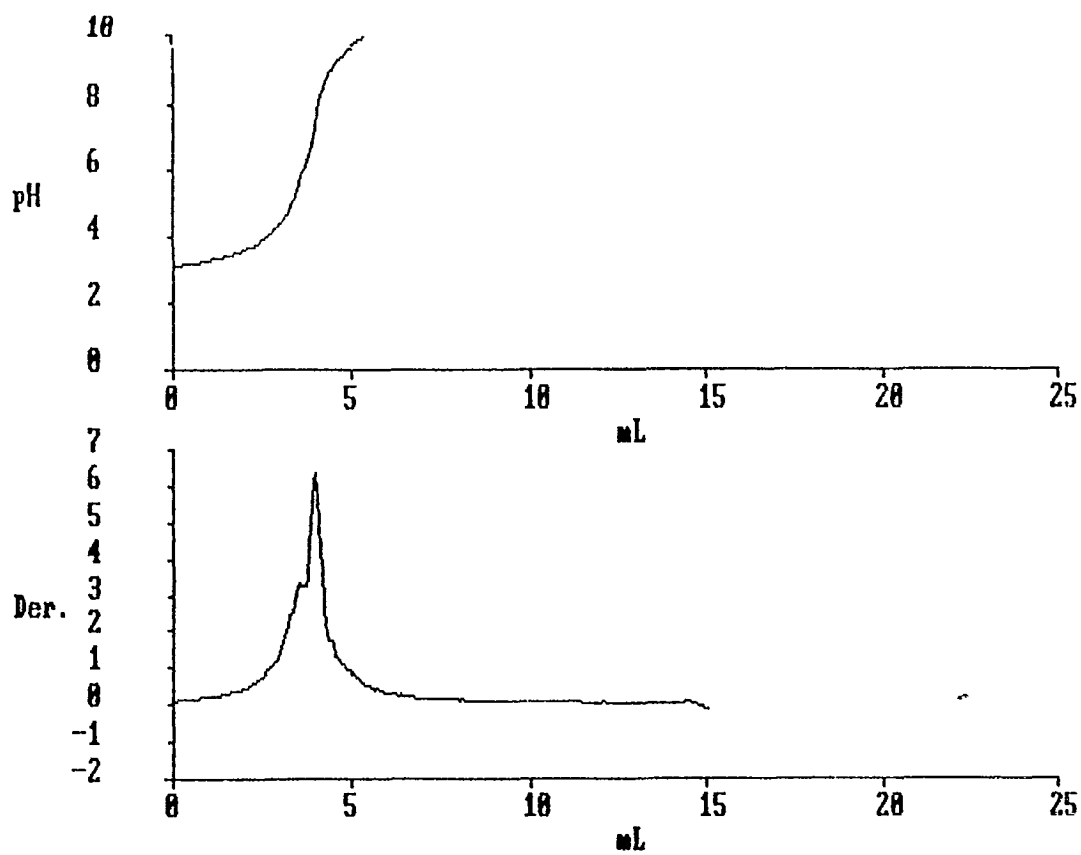


Fig. 9a - Acid titration of boiled and purged sample of pond 1 water which was previously titrated with 0.05M HCl to pH 2.5 and back titrated with 0.05M NaOH to pH 10.2

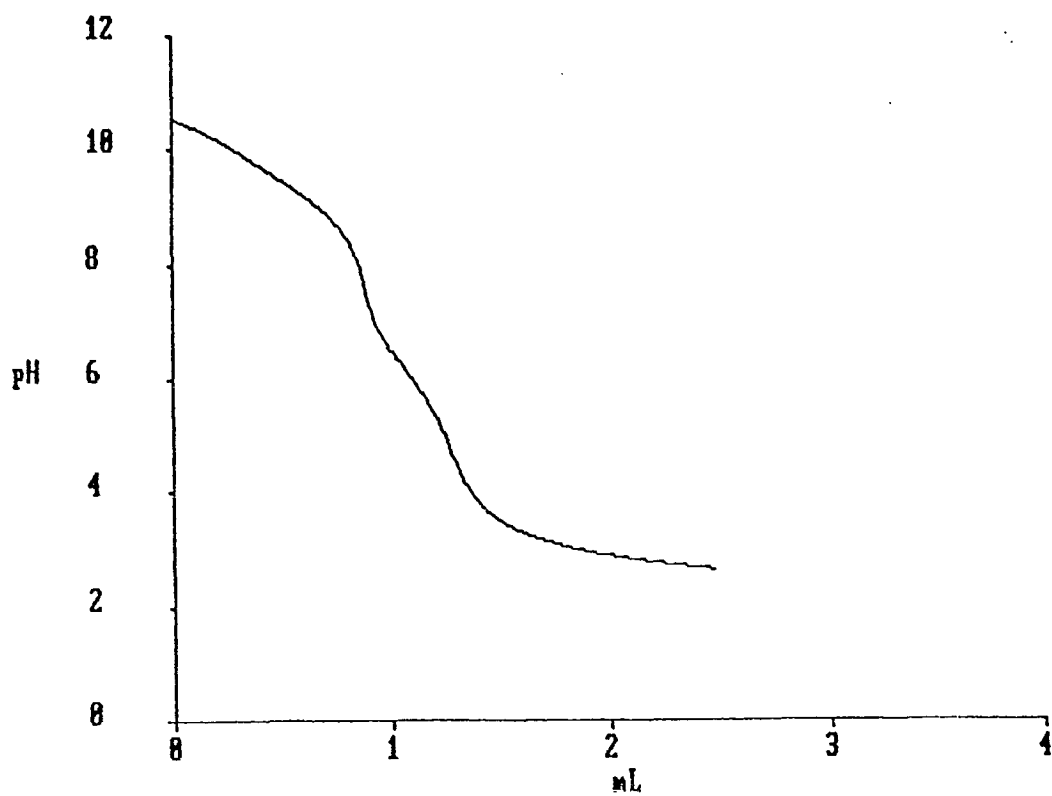


Fig. 9b - Acid titration of sample of Fig. 9a

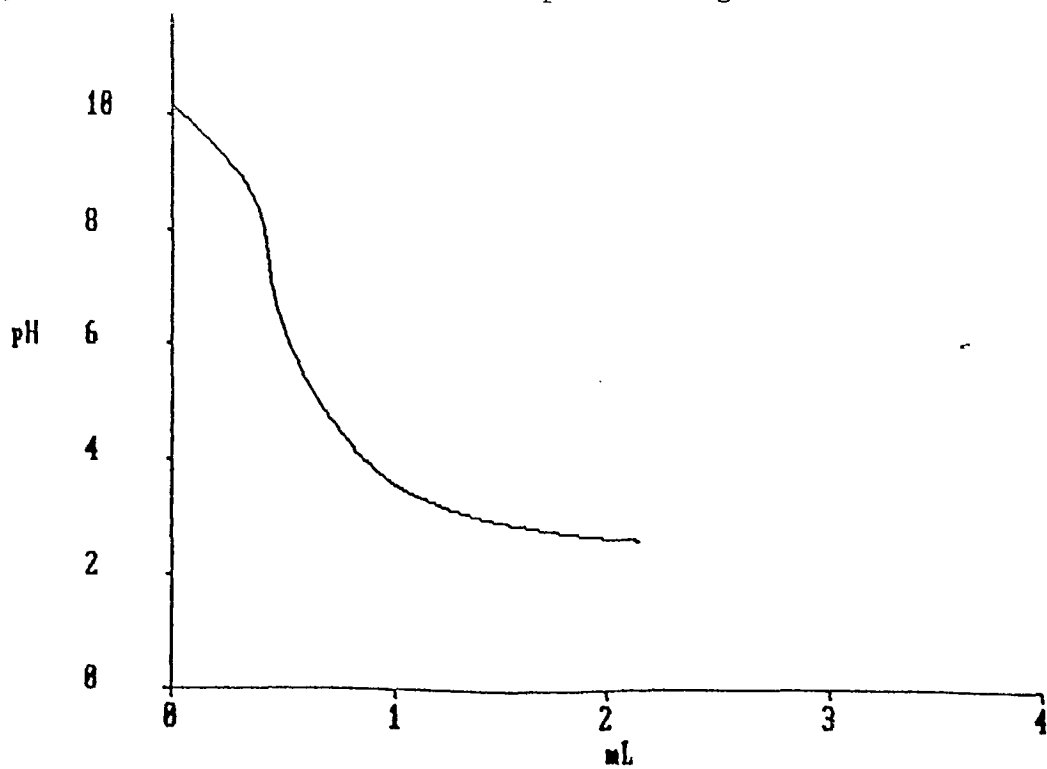


Fig. 9c - Acid titration of another sample of pond water treated as in Fig. 9a

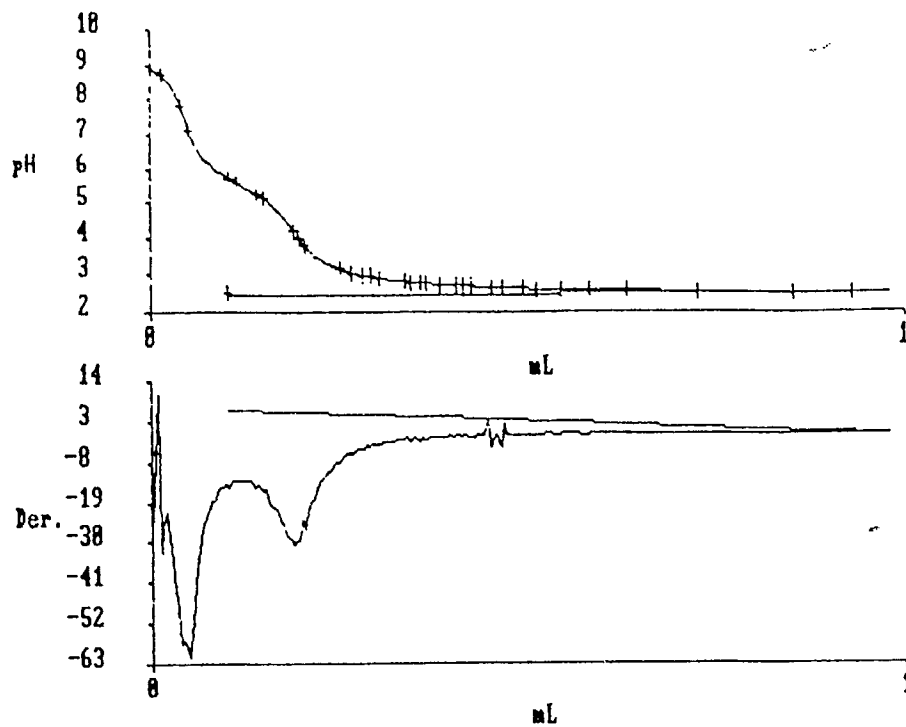


Fig.10.- Acid titration of a typical 100 ppm humic acid solution

A-19

APPENDIX A

APPENDIX A

Procedure for the Elimination of Bicarbonate in a 0.0100M Solution

1. Add 0.0840 g of NaHCO_3 to 100 mL of DIH_2O to produce a 0.0100M solution.
2. Titrate the sample from a pH of approximately 8.3 to $\text{pH}=3.5$ using a Radiometer-Copenhagen PHM 84 Research pH Meter and ABU 80 Autoburette.
3. Boil the sample for 10 minutes; add DIH_2O up to a pre-determined mark.
4. Use the automatic titrator to titrate the sample back up to a basic pH (this should resemble a strong acid/strong base titration).
5. Repeat 4, but go down to an acidic pH; this should also resemble a strong acid/strong base titration.
6. If both 4 and 5 are strong acid/strong base titration curves, the bicarbonate has been successfully eliminated.

B-21

APPENDIX B

APPENDIX B

Procedure for the Elimination of the Bicarbonate Buffer System in the Pond Water

1. Use a 200-mL Erlenmeyer flask, add 100 mL of pond water.
2. Add 33 mL of 0.05000M HCl, using a 15-mL pipette and an Eppendorf pipette (the pH should be approximately 3.5).
3. Add a teflon magnetic stirrer for mixing and to act as a boiling ship. Boil the solution for 10 min (start time when $T=95^{\circ}\text{C}$).
4. Let cool to room temperature.
5. Pour solution to a graduated cylinder of appropriate capacity and add DIH_2O up to the 133-mL mark.
6. Add 8 mL of 0.04847M NaOH using an Eppendorf pipette.
7. Take 20-mL aliquots from the flask and put them in six large titration cups.
8. Before titration, use high-purity N_2 to degas the sample of CO_2 . Degas the sample for 10 min before titration (the N_2 must be introduced into a closed system of pond water and air).
9. Titrate the sample with 0.05000M HCl using the Radiometer-Copenhagen PHM 84 Research pH Meter with an ABU 80 Autoburette.

Note: When the pond water solution is boiled, escaping vapour should be collected using a refluxing apparatus. The solution should also be cooled in this apparatus. This type of apparatus will minimize any change in the concentration of species present in the pond water. Accurate concentrations of the reactant are needed for any quantitative calculations such as pK_a 's.

