

NWRI CONTRIBUTION 88-68

**DETERMINATION OF ALKALINITY OF WATER
BY FLOW INJECTION ANALYSIS WITH
CONDUCTOMETRIC DETECTION**

by

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May 1988

MANAGEMENT PERSPECTIVE

This report describes a new method which eliminates some problems experienced by existing methods.

Reliable alkalinity measurements are essential for studying the effect of acidic precipitation on aquatic ecosystems. Existing analytical methods for alkalinity are satisfactory for medium hard and hard waters but have serious deficiencies in low alkalinity waters such as soft surface water and precipitation. The described method for the determination of alkalinity is simple, sensitive, fast, reliable and eliminates many of the limitations of existing methods. It will be a significant benefit to the Canadian LRTAP program.

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Director
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PERSPECTIVE GESTION

Ce rapport décrit une nouvelle méthode de détermination de l'alcalinité de l'eau dont l'exécution n'est pas affectée par certains des problèmes inhérents aux méthodes existantes.

Pour étudier l'effet des précipitations acides sur l'écosystème aquatique, il est essentiel que les mesures de l'alcalinité soient fiables. Les méthodes d'analyse existantes permettant de mesurer ce paramètre sont satisfaisantes en ce qui touche les eaux dures et moyennement dures, mais elles sont très inefficaces dans le cas des eaux de faible alcalinité, comme les eaux douces de surface et les eaux de précipitations. La méthode décrite est simple, précise et fiable; en outre, elle peut être exécutée rapidement, sans être affectée par nombre des problèmes inhérents aux méthodes existantes. Elle procurera donc d'importants avantages dans l'exécution du programme canadien d'étude du transport à distance des polluants atmosphériques.

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ABSTRACT

This paper describes the determination of total alkalinity of natural water by Flow Injection analysis using conductometric detection. The sample is injected into a stream of sulphuric acid solution and resulting changes of conductivity are related to the parameter of interest. The performance of the method is evaluated and compared to the performance of potentiometric and conductometric titrations. Automated FIA method is simple, fast (90 samples/h), sensitive (detection limit of 0.1 ppm CaCO_3 and accurate (RSD 1% in the 20-200 ppm CaCO_3 range). Samples containing various contributory components (borate, silicate, phosphate, organics) can be reproducibly analyzed.

Key Word: Alkalinity, Water, FIA, Conductivity

RÉSUMÉ

Ce rapport décrit l'analyse par injection dans une solution en mouvement, fondée sur la détection conductimétrique, pour la détermination de l'alcalinité totale de l'eau naturelle. L'échantillon est injecté dans une solution d'acide sulfurique en mouvement et les variations de la conductivité qui en résultent sont reliées au paramètre considéré. On détermine l'efficacité de la méthode et on la compare à celle du titrage potentiométrique et du titrage conductimétrique. La méthode d'injection automatique dans une solution est simple, rapide (traitement de 90 échantillons par heure), précise (écart-type relatif de 1 % dans la plage de 20 à 200 ppm de CaCO_3) et est caractérisée par une grande sensibilité (seuil de détection de 0,1 ppm de CaCO_3). De plus, l'analyse d'échantillons contenant différentes composantes (borates, silicates, phosphates et matières organiques) peut être reproduite.

Mots-clés : alcalinité, analyse, conductivité, eau

1.0 INTRODUCTION

Total alkalinity of water is a parameter of great importance in the investigation of the effect of acidic precipitation in aquatic ecosystems¹. The term 'alkalinity' as used in this paper is defined as the capacity of the water to neutralize the equivalent sum of all acids. In other words, alkalinity is the sum of the concentration of proton acceptors². On a routine basis, alkalinity in water is determined by acid-based titrations with H_2SO_4 solution. The end-points are detected by the colorimetric indicator or by potentiometry, employing the pH glass electrode. The results are reported in ppm or mg/L expressed as $CoCO_3$ ³. Several operational errors in the analytical determination of alkalinity are discussed in the literature². A major problem is definition of the titration end-points. Titration using colorimetric indicator should be abandoned because errors can occur in the visual detection of the end-point color change. Potentiometric titration employing "total fixed end-point" introduces a relative error in analysis of low alkalinity water due to the uncertain value of the pH at the end-point. In water of low alkalinity end-point recognition must be very precise to obtain meaningful results. With regard to data precision and accuracy, application of traditional techniques is not adequate. A potentiometric titration procedure developed by Gran⁴, and Larson and Henley⁵, and discussed by Thomas⁶, mathematically linearizes a buffered portion of the titration curve before and after the equivalence point to characterize equivalent points. This technique improves the accuracy of the determination in respect of locating the end-point. However, it is based on the actual response of the pH glass electrode which requires frequent and tedious calibration and is slow to respond in the presence of other constituents of alkalinity (borate, silicate, phosphate, weak organic acids). Furthermore, the technique is associated with systematic errors although computer programs have been published to alleviate the problem⁷. Several indirect methods reported to quantitate alkalinity have some fundamental limitations and are not recommended⁸.

Very good results by conductometric acid-based titration of alkalinity and acidity have been reported^{9,10}. Flow Injection Analysis (FIA) is a continuous flow analysis utilizing an unsegmented reagent stream, into which reproducible volumes of sample are injected. It yields a fast, precise, accurate and extremely versatile system that is simple to operate and has been successfully applied to many analytical procedures^{11,12}.

In this report, the conductometric detector incorporated into the Flow Injection Analysis system is evaluated for determining total alkalinity in natural waters.

2.0 EXPERIMENTAL

2.1 Reagents

All chemicals used were of analytical reagent grade. The stock solutions were standardized by appropriate standard analytical methods. Synthetic and calibration solutions were prepared by serial dilution of stock solutions using ultra-pure water. The solution of sulphuric acid was kept under nitrogen atmosphere.

2.2 Apparatus

The FIA system consisted of a Tecator 5020 Analyzer and 5007 FIA Star sample changer, a dual valve injector (Rheodyne six port injecting valves with pneumatic actuators and a XANADU programmable timer. Two YSI 32 digital conductance meters in conjunction with a Philips 8252A two line recorder were used for monitoring. Teflon tubing (0.8 mm I.D.) was used for the transmission lines and reaction coils. GORE-TEX microporous Teflon tubing was installed in front of the detectors to remove gas bubbles. The conductometric detector comprised two platinum-platinized wires (0.2 mm diameter) fitted into Teflon housing. The overall geometry of the two parallel flow systems was kept as identical as possible. A block scheme of the system is given in

Figure 1. The design of the detector is shown in Figure 2. The most convenient flow rate was found to be 5 mL/min. Injected volume of the sample was 200 μ L. The sampling rate used in the performance tests was 90 samples per hour.

3.0 DISCUSSION

The conductivity change in the reactant stream (H_2SO_4) due to the sample injection, is the result of two factors. The first is the contribution of the natural conductivity of the sample after mixing and dilution. The second is the change of the conductivity generated by the acid-base reaction resulting in the decrease of the hydrogen ion concentration.

There exist two possibilities for treating this system. The first is to reverse the FIA system and inject the reagent (H_2SO_4) into a constantly flowing stream of the sample. This allows the relative conductivity of the sample to be measured and compute the values of alkalinity according to the following equation:

$$A_{SA} = A_{ST} \left[1 - \frac{P_{SA}}{P} - \Lambda_{SA} \left(\frac{1 - \frac{P_{\Lambda M}}{P_M}}{\Lambda_M} \right) \right]$$

Where

A_{SA}	is the acidity or alkalinity of the sample
A_{ST}	is the acidity or alkalinity of the standard
P_{SA}	is the peak height of the reagent injection into the sample
P_M	is the peak height of the reagent injection into distilled water
$P_{\Lambda M}$	is the peak height of the reagent injection into the high conductivity standard
Λ_{SA}	is the relative conductivity of the sample
Λ_M	is the relative conductivity of high standard

There are several disadvantages incorporated in this system. It significantly slows down the sample rate. The procedure of the calibration becomes complicated. It requires calibration in respect to conductivity and in respect to alkalinity. For this reason, the second alternative as described below was considered to be more convenient for practical application. This procedure involves a simultaneous injection of equal volumes of the sample into parallel streams of reagent and conductivity standard (KCL solution). The conductivities of reagent and standard are adjusted to equal value of 500 μ S. After each dual injection, two peaks are recorded. The peak corresponding to the conductivity channel represents the change of the conductivity by dilution. The peak of the reagent channel corresponds to the change of the conductivity caused by dilution as well as by the acid-base reaction. The difference of the two peak heights relates directly to the alkalinity of the sample. Another way of managing this two-peak system is to connect the outputs of both conductivity meters to one channel of the recorder with reverse polarity. In this case the resulting peaks correspond to the alkalinity only. One problem is that exact timing is required to avoid distortion of the peak signals and consequently inaccurate results.

All performance tests were conducted via the dual channel peak recording system. Because the response of the sensors to the conductivity changes is linear, the calibration procedure of the method is very simple. Three point calibration curves using three standard solutions of known alkalinity values prove to be adequate.

4.0 RESULTS

To evaluate precision and detection limit of the conductometric FIA system, ten replicate analyses were performed on ten synthetic alkalinity samples. Samples were prepared from a stock solution of sodium carbonate containing 1% of borate silicate, phosphate, acetate and citrate. The results demonstrated a standard deviation of 0.2 ppm

CaCO₃ in the concentration range of 1 to 10 ppm and 0.5 ppm in 20-200 ppm range. Useful detection limit was 0.1 ppm CaCO₃. Relative standard deviations ranged from 10% (low levels) to 1% (high levels).

Natural water samples were selected, collected and prepared by Quality Assurance and Methods Section of NWRI for their Interlaboratory Quality Control Study¹³. The criterion for the selection was to use samples with a variety of composition, concentration and background matrices. Six laboratories of Water Quality Branch across Canada performed analyses of eight natural samples from various regions for total alkalinity using their standard methods. Comparison of the results is summarized in Table 1.

The proposed method is simple, sensitive, fast, reliable and eliminates the problems of the end-point location. It covers the required concentration range and has adequate sensitivity. Even complex samples containing various contributory components can be reproducibly analyzed at the sampling rate of 90 samples/h.

REFERENCES

1. Jeffries, D.S. and Zimmerman, A.P. 1980. Can. J. Fish. Aquat. Sci. 37, 901-902.
2. Faust, S.D. and Aly, O.M. 1981. Chemistry of Natural Waters. Ann Arbor Science, Publishers.
3. The Determination of Alkalinity and Acidity in Water. 1981. Methods for the Examination of Waters and Associated Material, London, Her Majesty's Stationery Office, England.
4. Gran, G. 1952. Analyst 77, 61-668.
5. Larson, T.E. and Henley, L. 1965. Anal. Chem. 17, 851-856.
6. Thomas, J.F. and Lynch, J.J. 1960. J. Amer. Water Works Assoc., 52, 255-263.
7. Hanson, I. and Jaqner, D. 1973. Anal. Chim. Acta, 65, 363-373.
8. Liljestrand, H.M. and Morgan, J.J. 1979. Telus 31, 421-431.

9. Bertenshow, M.P. 1977. Anal. Chim. Acta, 91, 339-343.
10. Sekerka, I. and Lechner, J.F. 1984. J. Assoc. Off. Anal. Chem., 67, 893-895.
11. Ranger, C.B. 1981. Anal. Chem. 53, 20A.
12. Ruzicka, J. and Hansen, E.H. Flow Injection Analysis (Wiley-Interscience, New York, 1981).
13. Cheam, V. 1981. Special Interlaboratory Study, 09-AMD-T-6-81-VC, Department of the Environment, Water Quality Branch, Burlington, Ontario, Canada.

TABLE 1

Natural Water Samples Analysis

Sample Number	Interlaboratory Results Potentiometric Titration ppm CaCO_3	Conductometric Titration ppm CaCO_3	Conductometric FIA ppm CaCO_3
1	-0.05 \pm 0.2	0.8 \pm 0.2	0.7 \pm 0.1
2	-0.7 \pm 0.3	0.3 \pm 0.1	0.3 \pm 0.1
3	-0.8 \pm 0.4	0.4 \pm 0.1	0.5 \pm 0.1
4	1.6 \pm 0.6	2.5 \pm 0.2	2.6 \pm 0.1
5	6.0 \pm 2.3	6.7 \pm 0.2	6.6 \pm 0.2
6	4.4 \pm 1.3	6.9 \pm 0.2	6.8 \pm 0.2
7	11.9 \pm 4.9	15 \pm 0.3	15.0 \pm 0.2
8	30.2 \pm 9.5	39.7 \pm 0.4	39.5 \pm 0.2

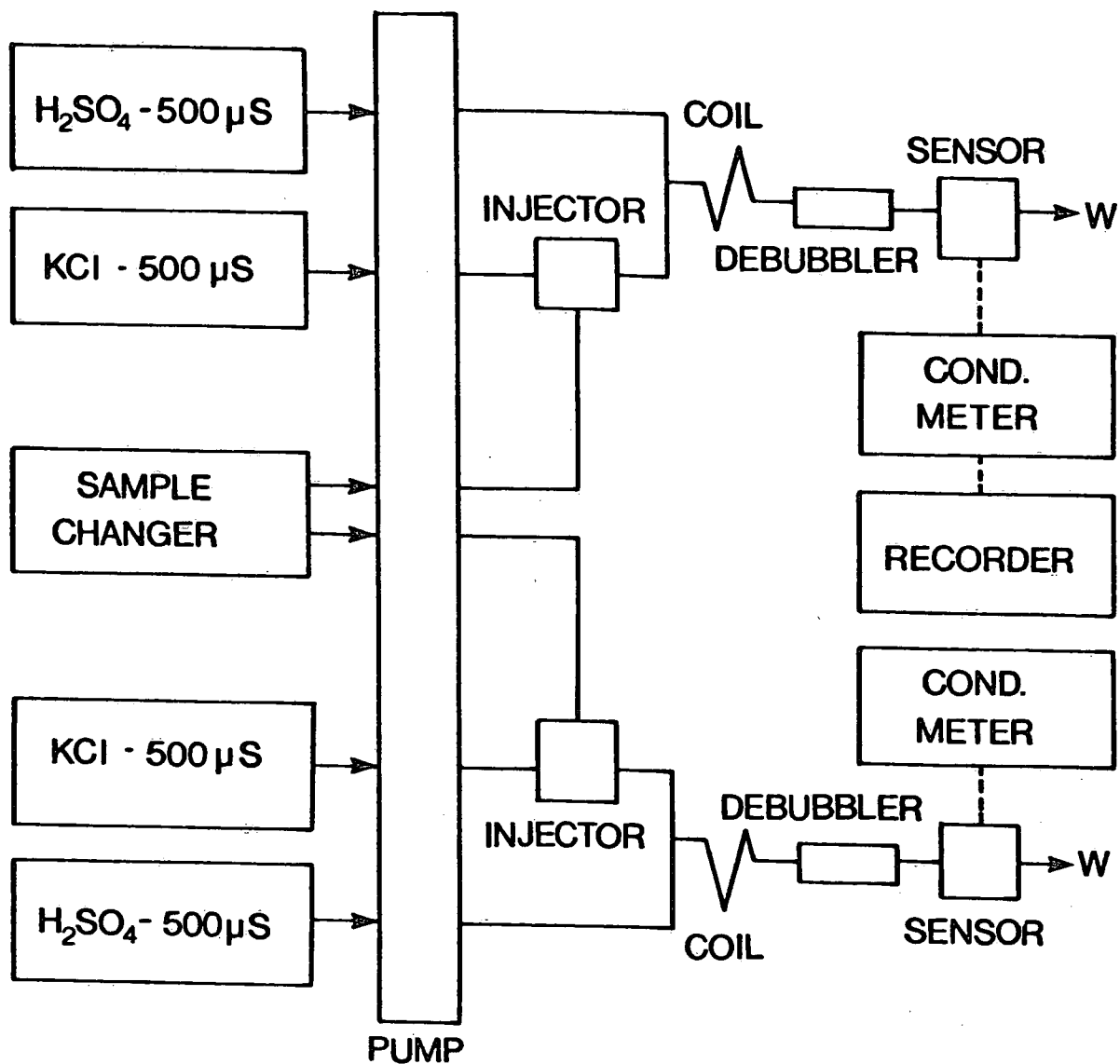


Figure 1. General Set-Up and Flow Scheme

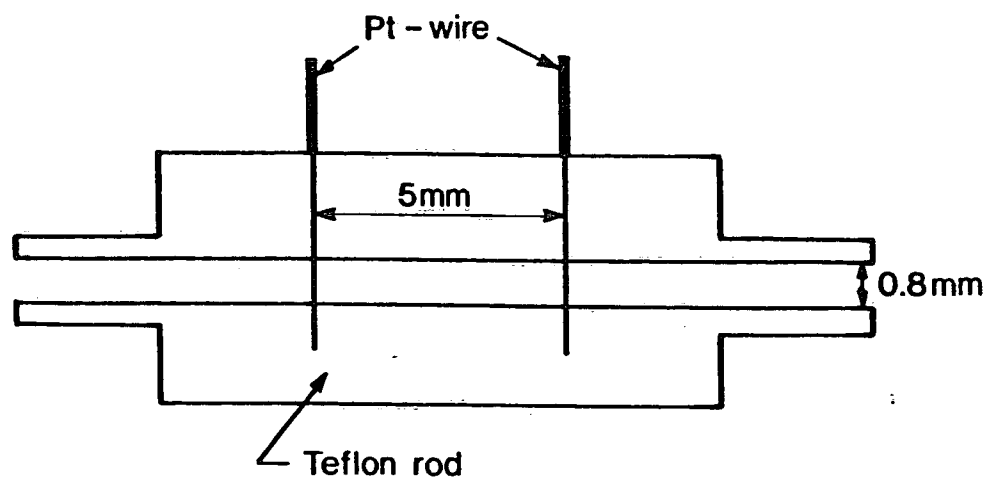


Figure 2. Conductivity Sensor