NWRI CONTRIBUTION 88-103

DETERMINATION OF ACID NEUTRALIZING CAPACITY OF WATER AND RELATED PROBLEMS

by

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October 1988

MANAGEMENT PERSPECTIVE

This paper describes the determination of acid neutralizing capacity of water. The method is based on conductometric acid-base titration. It is fully automated and computer controlled The system meets the requirement of NWQL for precision and repeatability while speeding up the analysis by a factor of five. It has simple instrumentation and operation and covers the required concentration range with adequate sensitivity. The method eliminates the problems of analysis of complex samples. Several conceptual and terminological problems related to the determination of acid neutralizing capacity of water are discussed.

Dr. J. Lawrence
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PERSPECTIVE DE GESTION

Ce rapport fait état de la détermination de potentiel de neutralisation de l'acide de l'eau. La méthode est basée sur le titrage conductométrique acide-base. Il s'agit d'une méthode entièrement automatisée et contrôlée par ordinateur. Le système répond aux exigences du LNQE en matière de précision et de répétition et accélère en outre l'analyse par un facteur de cinq. La méthode ne nécessite qu'une instrumentation simple, est facile à utiliser et couvre la gamme de concentrations exigée avec une sensibilité convenable. Elle élimine les problèmes posés par l'analyse d'échantillons complexes. Plusieurs problèmes théoriques et terminologiques reliés à la détermination du potentiel de neutralisation de l'acide de l'eau sont analysés.

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ABSTRACT

Acid neutralizing capacity of water is a parameter of great importance for studies of aquatic ecosystems. In this paper several conceptual and terminological problems related to the determination of acid neutralizing capacity of water are discussed. The determination of acid neutralizing capacity by using automated conductometric acid-base titration is described. Performance is evaluated and compared with performance of the potentiometric titration. Conductometric titration is simple, fast, sensitive (detection limit 0.1 ppm) and accurate. Relative standard deviation of the determination increased from about 1% at high levels to about 10% at 0.1 ppm level. The complete system of automation using a desk top computer to control a sample changer, an autoburette and a conductivity meter is described. The computer functions also as a data handling device.

RÉSUMÉ

Le potentiel de neutralisation de l'acide de l'eau est un paramètre très important dans les études des écosystèmes aquatiques. Dans ce rapport, plusieurs problèmes théoriques et terminologiques reliés à la détermination de ce potentiel sont analysés. La détermination du potentiel de neutralisation de l'acide à l'aide du titrage automatisé conductométrique acide-base est décrite. La performance de la méthode est évaluée et comparée à celle du titrage potentiométrique. Le titrage conductométrique est simple, rapide, sensible (limite de détection de 0.1 ppm) et précis. L'écart-type relatif de la détermination augmente d'environ 1 % aux teneurs élevées et d'environ 10 % à 0.1 ppm. L'ensemble du système d'automatisation, qui fait appel à un ordinateur de bureau pour contrôler le changeur d'échantillon, une autoburette et un appareil de mesure de la conductivité, est décrit. L'ordinateur peut également assurer le traitement des données.

1.0 INTRODUCTION

Extensive research is now being conducted to study the effect of acidic precipitation on aquatic ecosystems. Total alkalinity and acidity of the water are two parameters of great importance in the investigation of this problem (1). Alkalinity of water is defined as the capacity to neutralize the equivalent sum of all acids; acidity is the capacity to neutralize the equivalent sum of all bases. In other words, alkalinity is the sum of the concentration of proton acceptors, whereas acidity is the sum of the concentration of proton donors (2).

Classically, alkalinity and acidity in water are determined by acid-base titration with solutions of H_2SO and NaOH. The equivalence points are detected by colorimetric indicator or by potentiometry with pH glass electrode. Results are reported in ppm or mg/L, expressed as $CaCO_3$ (3).

Several operational errors in the analytical determination of alkalinity and acidity are discussed in the literature (2). A major problem is definition of the titration end points. Titration using colorimetric indicators is inadequate because errors can occur in the visual detection of the end point color change. Potentiometric titration using a "total fixed end point" introduces a relative error in analysis of low alkalinity water because of uncertainty of the pH value at the end point. In water of low alkalinity or acidity, end point recognition must be very precise to obtain meaningful results. In addition, precision and accuracy of traditional techniques are not adequate.

A potentiometric titration procedure developed by Gran (4) and Larson and Henley (5) and discussed by Thomas and Lynch (6) mathematically linearizes a buffered portion of the titration curve before and after the equivalence point to characterize equivalence points. This technique improves the accuracy of the determination with respect to locating the end point. However, the basis of the technique is the actual response of the pH glass electrode which has problems of frequent and tedious calibration and slow response in the presence of other

constituents of alkalinity (borate, silicate, phosphate, weak organic acids). Furthermore, the technique is associated with systematic errors; computer programs have been published to alleviate this problem (7). Several indirect methods reported to quantitate acidity have some fundamental limitations and are not recommended (8).

The first purpose of this paper it to discuss some of the problematic aspects of the alkalinity determination. In the second part the automated conductometric titration is described and evaluated.

There are several terminological discrepancies in existence.

1. Considering the definition of alkalinity and acidity (viz. above) and in accord with W. Summ and J.J. Morgan (8) the terms of Acid (or Base) Neutralizing Capacity (ANC or BNC) are more descriptive and less misleading than commonly used terms of acidity and alkalinity. The term ANC (acid neutralizing capacity) will be used throughout this paper.
2. The frequently used term "Gran Titration" is misleading. It is a potentiometric titration using Gran's plot (concentration vs mL of titrant added). It differs from the potentiometric titration only in the way the data are manipulated.
3. Recently, a term "Gran alkalinity" has been introduced. It is ANC measured by potentiometric titration using Gran's plot and does not have any technical justification.
4. The data of "negative alkalinity and/or acidity" are being reported. In most cases these parameters are generated by improper interpretation of titration data.

2.0 TECHNICAL CONSIDERATION

2.1 Acid-Base Titration Monitored by pH Glass Electrode and Gran's Plot

The pH electrode is an ion selective electrode specific for hydrogen ion. It responds logarithmically to the activity of hydrogen ion. The course of the potentiometric acid-base titration monitored by

pH electrode and plotted in a conventional manner gives a sinusoidal curve A in Fig. 1. For reasons mentioned above, there are difficulties in the location of the equivalence point when using this conventional plot. Advantages credited to Gran's plot can be derived from curve B in Figure 1. It is only necessary to obtain a few points to define a straight line, and it is easy to identify the equivalence point by extrapolating the lines to the horizontal axis. Since it is not necessary to keep points in the region of the equivalence point - "the sluggish response" of the electrode is no longer a problem. The equivalence point can be located even for curves which are almost unrecognizable as titration curves when plotted in the conventional manner. Finally, readings in the straight lines regions are more stable and can be obtained quickly.

In order to draw the linear titration curves, it is necessary to convert the observed pH (mV) values to concentrations. For this conversion the following equation applies:

$$F = \left(\frac{v_s + v_t}{v_s} \right) 10^{-"pH"} \qquad (1)$$

where F is a number related to concentration (H^+), ($v_s + v_t/vs$) is corrected volume and "pH" is log $[H_o^+]$ - log $[H^+]$. In this form, the results are independent of any pH or activity conventions. Assuming that the values of pH (using a pH glass electrode in conjunction with a reference electrode) can be measured with a relative standard deviation of 1% (very optimistic assumption) then computed values of F have an RSD of ≈ 10%. As the example, pH 500 ± 1% gives the relative values of F ranging from 112 to 89 (+12; -11%). Figure 2 illustrates this situation. The relative values of F translate to 7% of relative standard deviation of the titrant volume and consequently to 7% RSD as ppm of $CaCO_3$.

These are the theoretical conclusions based on the 1% RSD of the pH measurement. It is obvious that even this optimistic example (more realistic value of pH RSD is 2%) is not very satisfactory in respect to the precision of the equivalence point identification by Gran's plot. Furthermore, the claim that the "sluggish and slow response" of the electrode in the vicinity of the equivalence point is eliminated is very optimistic. To obtain meaningful data, the titration has to proceed at the speed corresponding to the electrode time response even in the case of Gran's plot. Ignoring this, leads to the distortion of the second part of the curve (after the equivalence point) and therefore to incorrect or uncertain location of the end-point.

There are several terminological flaws which do not affect the technical merit but should be corrected. There is no such paremters as "Gran alkalinity". The scope of the method is the measurement of pH and total alkalinity (acid neutralizing capacity). The term of "Gran alkalinity" is misleading. Alkalinity is measured by a potentiometric acid-base titration in both cases. The difference is in the data manipulation. "Total alkalinity" method employs traditional (conventional) plot of pH versus titrant volume, whereas "Gran alkalinity" refers Gran's plot technique of calculating the equivalence point using a simplified version of the equation for linearizing a logarithmic value of pH as it is registered by the pH glass electrode.

2.2 Negative Alkalinity

Recently a suprising parameter of "Negative alkalinity" has been reported. It is our opinion that such a parameter does not exist. Alkalinity, or better ANC is a parameter based on the presence of species reacting with hydrogen ion. If these species are not present, ANC is zero. Samples having "negative alkalinity" actually are samples having acidity only. An explanation of why these negative values are

being reported can be derived from the analysis of potentiometric curves. Two examples of potentiometric titration curves are given in Figure 3. The A curve is the plot of sinusoidal potentiometric titration curves and the A_1 curve is Gran's plot of the same titration. The first two curves are not titration curves at all. They monitor the change of pH electrode potential by increasing concentration of hydrogen ion. There is no equivalence point in existence. Where there is no equivalence point, there is no titrate present and titration is not possible. As it is demonstrated by the graph (Gran's plot of B), linear lines can be projected to intersect horizontal axis beyond the point of zero volume of titrant and therefore considered (wrongly) as negative value of titrate (alkalinity).

The absurdity of this can be illustrated on the example of other titrations. Let us assume an argentometric potentiometric titration of chloride. If the same situation existed, no one would report "negative concentration of chloride". The analyst would either report nondetectable chloride or, better still, he would titrate the sample with chloride and determine the content of silver ion in the sample.

3.0 CONDUCTOMETRIC TITRATION

It is well recognized that conductometric titration may be applied where potentiometric methods fail to give dependable results, for example, the direct titration of weak acids by weak bases, and the displacement titrations of salts and moderately weak acids or bases by strong acids or bases. These types of titrations include determinations of ANC. If conductivity instead of pH is followed during titration, the plot against increments of titrant is defined by straight lines whose intersection defines the end point. Only six points are required for such a plot. In contrast to potentiometric titration, readings near the end point have no significance. The effects of dissociation, hydrolysis, and solubility of the reaction products are negligible.

A major advantage of conductivity is easy location of the end point regardless of the actual pH at which it occurs (12).

3.1 Reagents

All chemicals used in the measurement were analytical reagent grade. Stock solutions were analyzed by appropriate analytical methods. Synthetic sample solutions were prepared by serial dilution of stock solution. The titrant solutions 0.1 and 0.01 M H_2SO_4 were standardized with tris(Hydroxymethyl)aminomethane and anhydrous sodium carbonate. Titrant solutions were prepared fresh daily and kept under nitrogen atmosphere. To minimize changes in sample volume, 0.01 M titrant solutions were used for low levels and 0.1 M solutions for high levels of ANC.

3.2 Apparatus

Potentiometric titrations were carried out in the conventional manner by using a Radiometer automatic titration system (Parts ABU13, PHM64, TT60, TTA60, and REC61) and Radiometer pH glass and reference electrodes. An automatic conductometric titrator consisted of a YS132 digital conductance meter and two Radiometer ABU13 burettes coupled to a Radiometer REC61-RIA112 recorder. All titrations were carried out at constant temperature (22 ± 0.2°C). Potentiometric and conductometric titrations were conducted simultaneously in one titration vessel.

3.3 Procedure

The electode assembly (pH glass, reference, and conductivity cell) was immersed in 100.0 mL sample in a 150 mL beaker. The standard solution of titrant was dispensed from a 2.5 mL automatic burette, and the values of pH and relative conductivity registered automatically. It was not necessary to convert relative conductivity readings to absolute values.

To test possible CO_2 loss during the alkalinity titration, CO_2 content of a synthetic sample at pH 4 was monitored by a CO_2 gas-sensing electrode. No measurable CO_2 change occurred during the first 60 s. A 5% CO_2 loss was registered after 5 min. Because the duration of the titration is less than 60 s, there is no serious problem of distorted results.

Preliminary titrations of synthetic samples containing various constituents of alkalinity including organic compounds (beef extract, phthalate, humic, fulvic, lactic, acetic and formic acids) showed the superiority of conductometric titration over potentiometry. Potentiometric titration produced distorted curves and indistinct end points. Response of the pH electrode was slow; a single titration required up to 30 min. Conductometric titrations gave better shaped titration curves with well defined points of inflection and were accomplished in 1 min.

To evaluate precision and detection limit of the conductometric titration, 10 replicate analyses were performed on 10 synthetic alkalinity and acidity samples. Samples were prepared from a stock solution of sodium carbonate containing 1% each of borate, silicate, phosphate, acetate, citrate, and phosphoric acid. The initial conductivity was adjusted to 300 µS by addition of KCl solution. The results, summarized in Table 1, demonstrate a 10% relative error in the 1-10 ppm concentration range and about 1% in the 20-200 ppm range. The useful detection limit was 0.1 ppm $CaCO_3$. Relative standard deviations range from 15% (low levels) to 1% (high levels).

Natural water samples were selected, collected, and prepared by the Quality Assurance Project of the National Water Research Institute for the "Interlaboratory Quality Control Study" (12).The criterion for the selection was to use samples with a variety of composition, concentration, and background matrices. Six laboratories of the Water Quality Branch across Canada analyzed eight natural samples from various regions for ANC by using their standard methods.

Table 2 compares the results of the potentiometric titrations with those of conductometric titrations. In summary, conductometry is superior to potentiometry with respect to accuracy and precision. An easy and simple identification of the end point in conductometric titration contributes to its improved performance. The proposed method has simple instrumentation and operation. It covers the required concentration range and has adequate sensitivity. Even complex samples containing various contributory components of ACN can be reproducibly analyzed.

4.0 COMPUTER CONTROLLED TITRATION

The development work continued by automating the method using a personal computer and commercial instruments. Figure 4 depicts a typical trace for Burlington tap water. The conductivity readings of the sample are plotted along the vertical axis and the total volume of titrant added to the sample is along the horizontal axis. As titrant is added to the water, the conductivity rises linearly at a low rate. Near the end-point, the rate of rise increases. Beyond the end-point, the conductivity rises linearly at a high rate. The automation process finds the two linear portions and calculates the point of intersection of their extensions. This determines the volume of titrant used to reach the end-point. The computer program recognizes the differences and calculates the correct end-point volume of titrant. The computer also controls the sample changer, the autoburette and the conductivity meter.

4.1 Hardware Connections and Settings

The Radiometer-Copenhagen instruments operate with computer through communications ports. For the computations and control, in this instance, a Hewlett-Packard Model HP-85 was readily available so it was

used instead of a more modern microcomputer. Its compact design and built-in printer offer an advantage.

Figure 5 shows how the units are connected to operate as a system. The HP-85 must have the Advanced programming ROM, two Serial Interfaces and a special parallel interface provided by Radiometer-Copenhagen. The computer controls the sample changer (SAC80) through a serial (RS-232) link using the telecommunications protocol (ACK/NACK). A male-to-male adaptor corrects the mismatch of cables. The computer controls the autoburette (AU80) with coded signals on parallel wires. The ABU80 also interacts with the sample changer through special cables provided by the manufacturer. The conductivity meter (CDM83) communicates with the computer through a serial (SO-232) port. It recognizes certain character commands and responds with readings. A null-MODEM corrects the mismatch in the aerial port. The communications interfaces must be set up with internal jumpers or dual-in-line switches. The settings are shown at the bottom of Figure 5.

Figure 4 shows the geometry in solving for the time that the burette was turned on until the titration end-point was reached, t. The simultaneous equations for slope:

$$R2 = (C(M)\ 0\ y)/(V_m - V_e) \quad (2)$$

$$R1 = (y - C(1))/V_e \quad (3)$$

can be reduced to

$$V_e = (R2*V_m + C(1) - C(M))/R2 - R1) \quad (4)$$

where
- R1 is the slope of the first line, µS/cm • mL
- R2 is the slope of the second line, µs/cm • mL
- C(M) is the reading of the cell at the end, µs/cm
- C(1) is the reading of the cell at the beginning, µs/cm
- V_m is the total volume of titrant added, mL
- V_e is the volume added to the equivalence point, mL
- y is the ordinate value at the equivalance point, V.

The computer first logs the data from the beginning of titration to the time the burette is turned off by averaging a burst of ten readings from the conductivity meter every half second. From these data C(1) to C(M) are known. The volume of titrant added is reported by the autoburette after each addition. The readings are processed to find the mean slopes using the equation:

$$S(N) = (e(M+8) + C(M+7) + C(M+6) + C(M+5) - C(M+4) - C(M+3) - C(M+2) - C(M+1))/16*T, \quad (5)$$

where S(N) is the Nth slope V/s

C(M+8) is the M+8th reading from the cell, V

•

•

•

C(M+1) is the M+1th reading from the cell, V.

T is the time between readings from the conductivity meter, s

This approximation of the slope has to be adequately insensitive to noise in the conductivity signal, caused by the rate of mixing in the sample cup, because the titation is stopped once the difference in slopes is small enough beyond the major change in slope. If the noise is too great, the process continues too long. The knee point is determined by the zone where the slope increases markedly above the earlier slopes. The knee point is an important location for computing the intersecting lines which determine the end point. The values of the slopes, the knee point volume, knee point conductivity, the total volume and the final conductivity are used to compute the end point volume. The results are shown graphically for a series of natural examples in Figure 7.

The software was written in HP BASIC, one of the variants of the original BASIC programming language. The program was too large for

the available memory (32 kilobytes), so it operates in two parts called "CT" and "CTA". Figure 8 shows the steps "CT" uses for the process. These include hardware initialization and requests to the operator for information about the titrant, the sample change pattern and the samples themselves. To save time, the program branches to shorter formats for data entry if the sample numbers are in sequence or the sample size is the same for all entries. This can reduce the number of entries from forty to four. When complete, "CT" automatically loads and runs "CTA".

Figure 9 indicates the main sequence of "CTA" once the titrations begin. The program gathers readings from the conductivity meter while controlling the burette. It does several checks and branches according to the rate of change of the conductivity meter readings. The incoming data are plotted as they arrive. If the final rate of change is linear, the titration ends and the burette is refilled. Some samples require more than one full burette to complete the titration. This is taken care of automatically. When the titration is done, the data are replotted including the two lines that correspond to the linear sections. The intersection is indicated by a line that extends to the horizontal axis. This gives the operator a quick, visual confirmation that the final result is reasonable. The program computes the end-point and the ANC, adds it to the graph and then produces a hard copy for the operator to check later. Examples are shown in Figure 10. If the next tray number is beyond the designated last position, the program ends. Otherwise, it commands the SAC80 to rinse the probe and move in the next sample. The next tray is processed similarly except a program "CTC" is loaded and used instead of "CT". This saves repeating the hardware initializations.

Table 3 shows the results of the current evaluations. Because the tests show that the precision and repeatability are adequate to meet the NWQL standards, the authorization to use the system routinely is expected quite soon.

The system produces a five-fold increase in the speed of sample processing. The conductometric method takes three minutes per sample compared to the 15 minutes taken by the potentiometric method. These times include sample retrieval, pipetting, dilution and other procedures.

5.0 CONCLUSIONS

As the evaluations are completed, the system has met the requirements of the NWQL for precision and repeatability while speeding up the analyses by a factor of five compared to the present system in use. The conductometry is superior to potentiometry with respect to accuracy and precision. An easy and simple identification of the end point on conductometric titration contributes to its improved performance. The proposed method has simple instrumentation and operation. It covers the required concentration range and has adequate sensitivity. Even complex samples containing various contributory components of ANC can be reproducibly analyzed at the sampling rate of 30 s/titration.

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TABLE 1

ANC Analysis of Synthetic Samples (ppm $CaCO_3$)

Sample	Nominal Total Alkalinity	Mean	Rel. SD, %	Rel. Error, %
1	210.0	210.5	1.1	0.25
2	105.0	104.1	1.2	0.86
3	52.0	51.0	2.9	1.0
4	21.0	20.5	2.9	2.4
5	1.5	10.4	2.9	1.0
6	5.3	5.4	3.7	1.9
7	2.1	2.0	5.0	4.8
8	1.1	1.0	5.0	10.0
9	0.5	0.55	9.1	9.1
10	0.1	0.12	15.3	20.0

TABLE 2

Comparison of Potentiometric and Conductometric Titrations of ANC*

Sample	$CaCO_3$ added, ppm	Mean $CaCO_3$ found**, ppm	RSD**, %	Rel. Error**, %	Rec.** %
1	1.5	1.4(1.4)	67(10)	7.3(4.0)	93(93)
2	10.0	10.4(10.2)	12.6(4.7)	4.0(2.0)	104(102)
3	12.6	12.5(12.6)	10.3(1.8)	0.8(0.0)	87(100)
4	45.0	44.0(44.3)	1.7(1.4)	3.9(3.1)	98(98)
5	150.0	149.4(148.9)	2.0(1.6)	1.3(0.9)	99(99)
6	299.0	292.6(296.6)	1.1(0.7)	2.3(1.0)	97(99)

* Results are based on nine replicate analyses

** Values in parentheses are results of conductometric titrations

TABLE 3

Automated Conductometric Titration of ANC

Avg. Conc. ppm $CaCO_3$	No. of Samples	Std. Dev.	RSD	95% Conf. Inter. ppm
4.83	12	±0.26	5.4	4.57 - 5.35
9.4	10	±0.05	0.53	9.3 - 9.5
40.9	13	±0.17	0.42	40.56 - 41.24
122.0	13	±0.28	0.23	121.44 - 122.56
214.5	15	±0.45	0.21	213.6 - 215.4

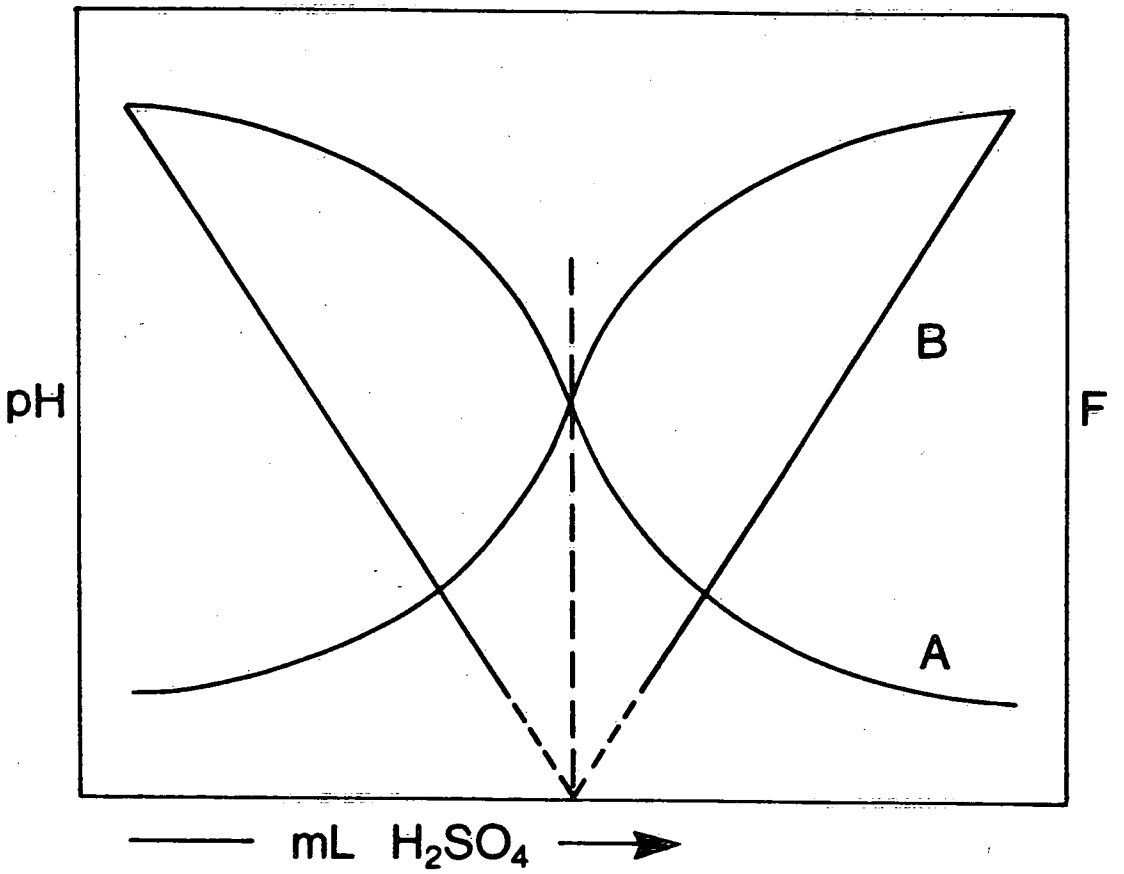


Figure 1. Conventional (A) and Gran's (B) plots of Acid-Base Titration

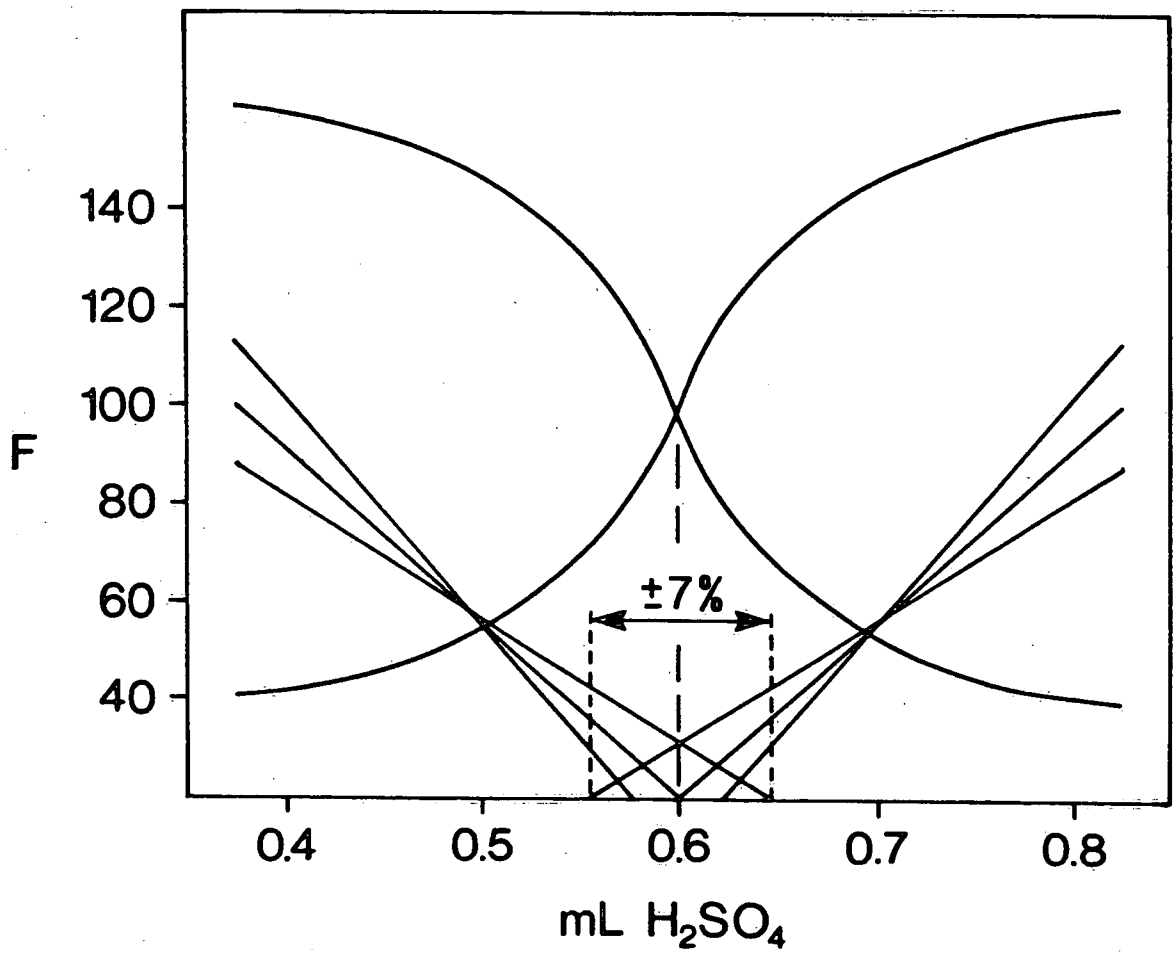


Figure 2. Precision of Gran's Plot

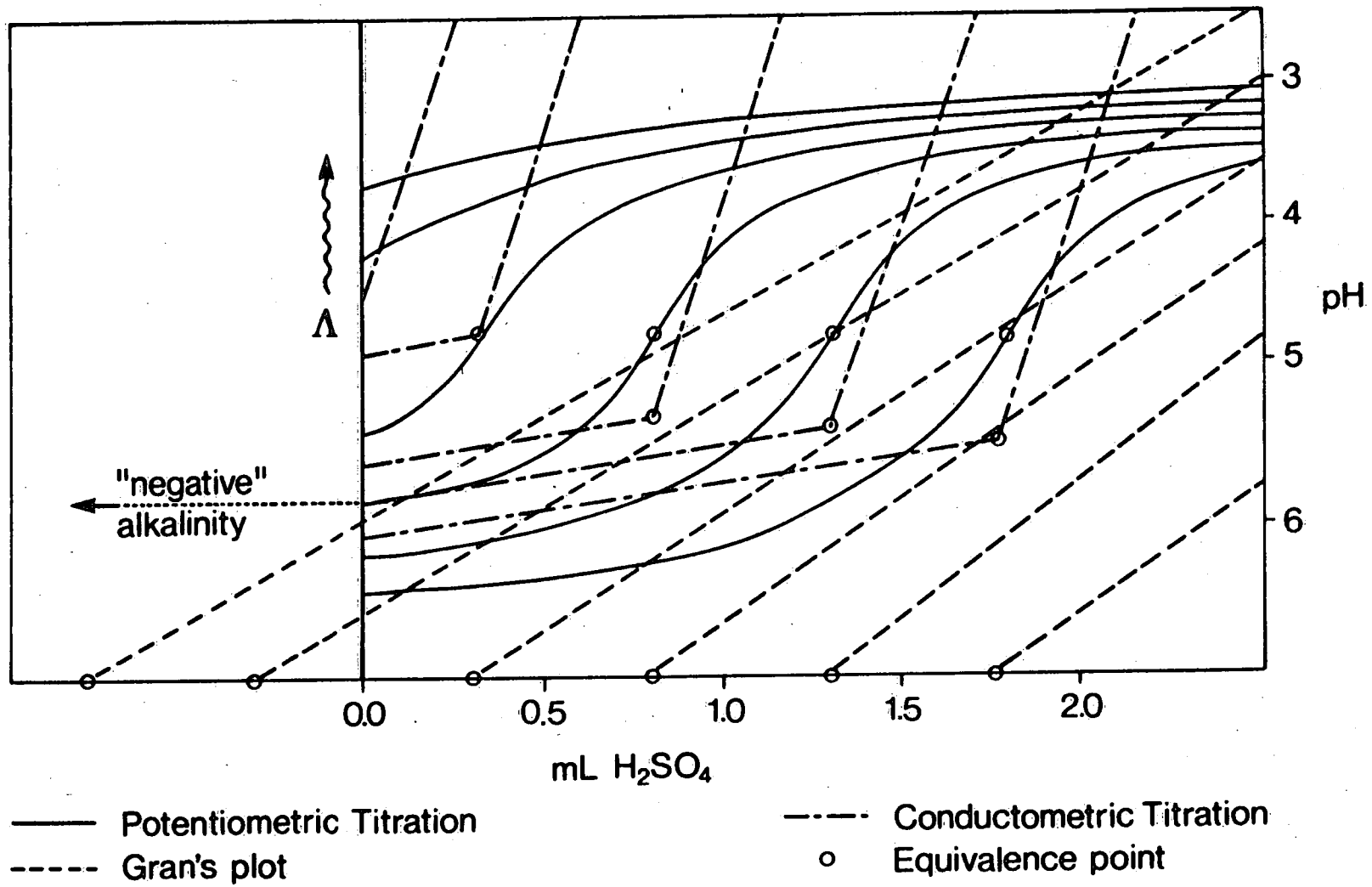


Figure 3. Comparison of Potentiometric, Gran's plot and Conductometric Titrations

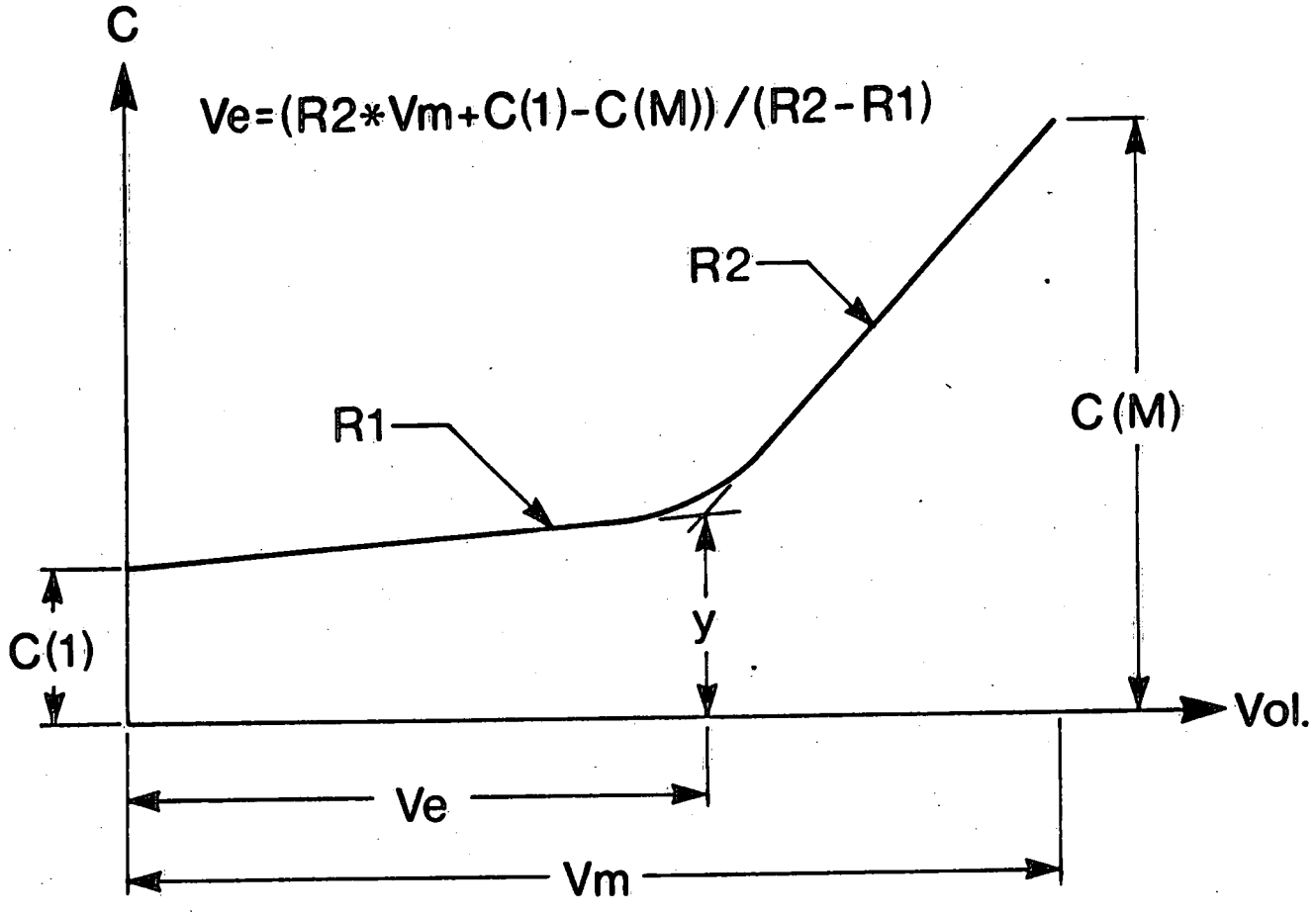


Figure 4. Derivation of End-Point Volume

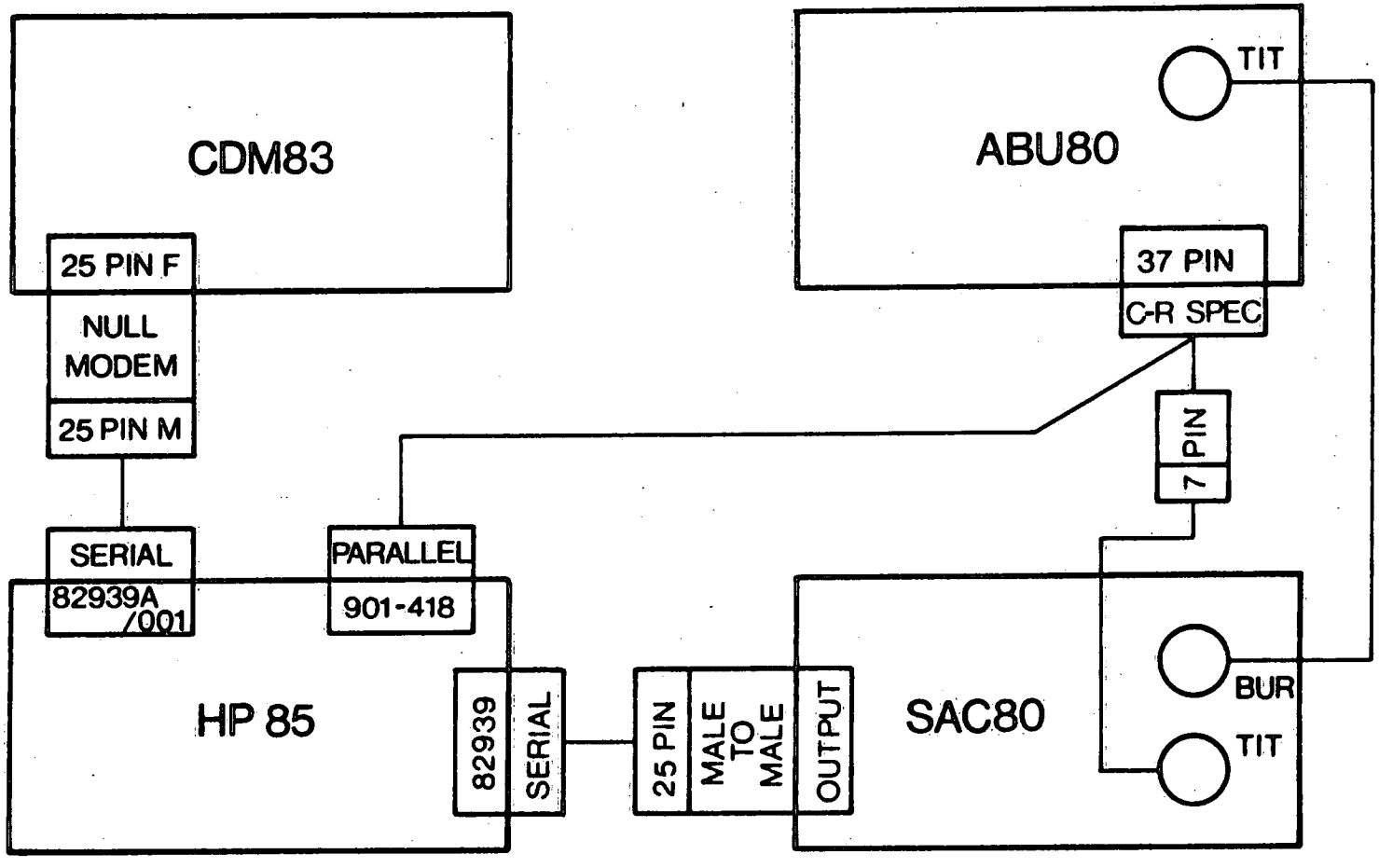
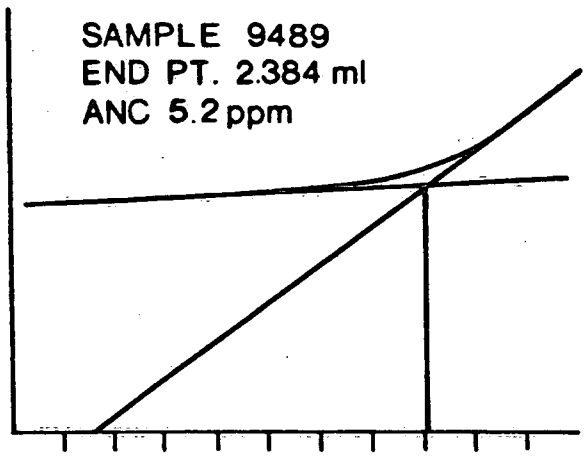
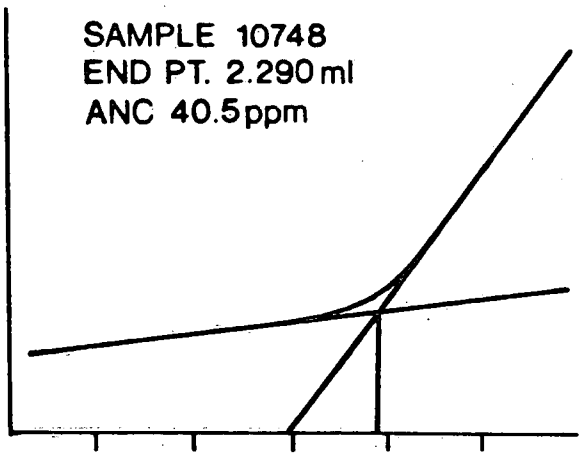


Figure 5. Interconnection Diagram



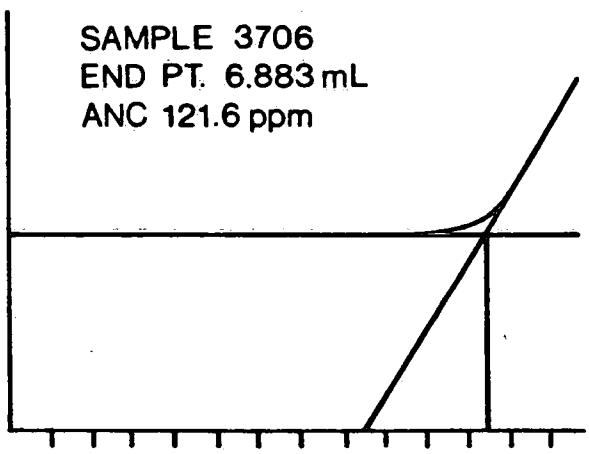
a. NATURAL SAMPLE

<20 ppm



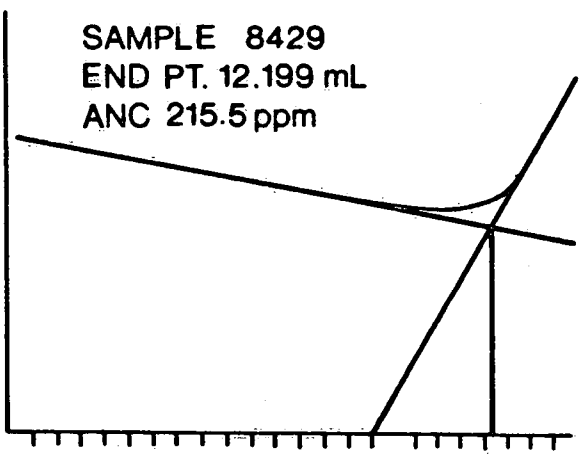
b. NATURAL SAMPLE

20-100 ppm



c. NATURAL SAMPLE

100-200 ppm



d. NATURAL SAMPLE

>200 ppm

Figure 7. Examples of Titration Curves

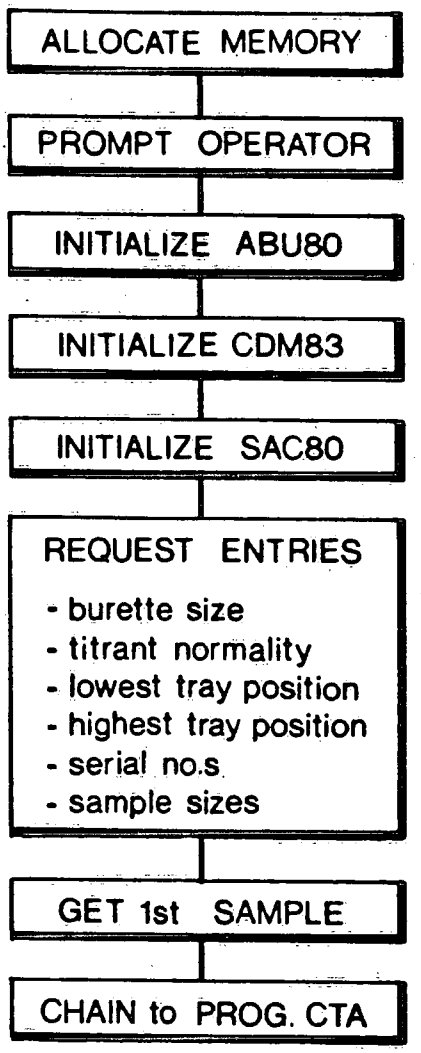


Figure 8. Main Flow Diagram of Program "CT"

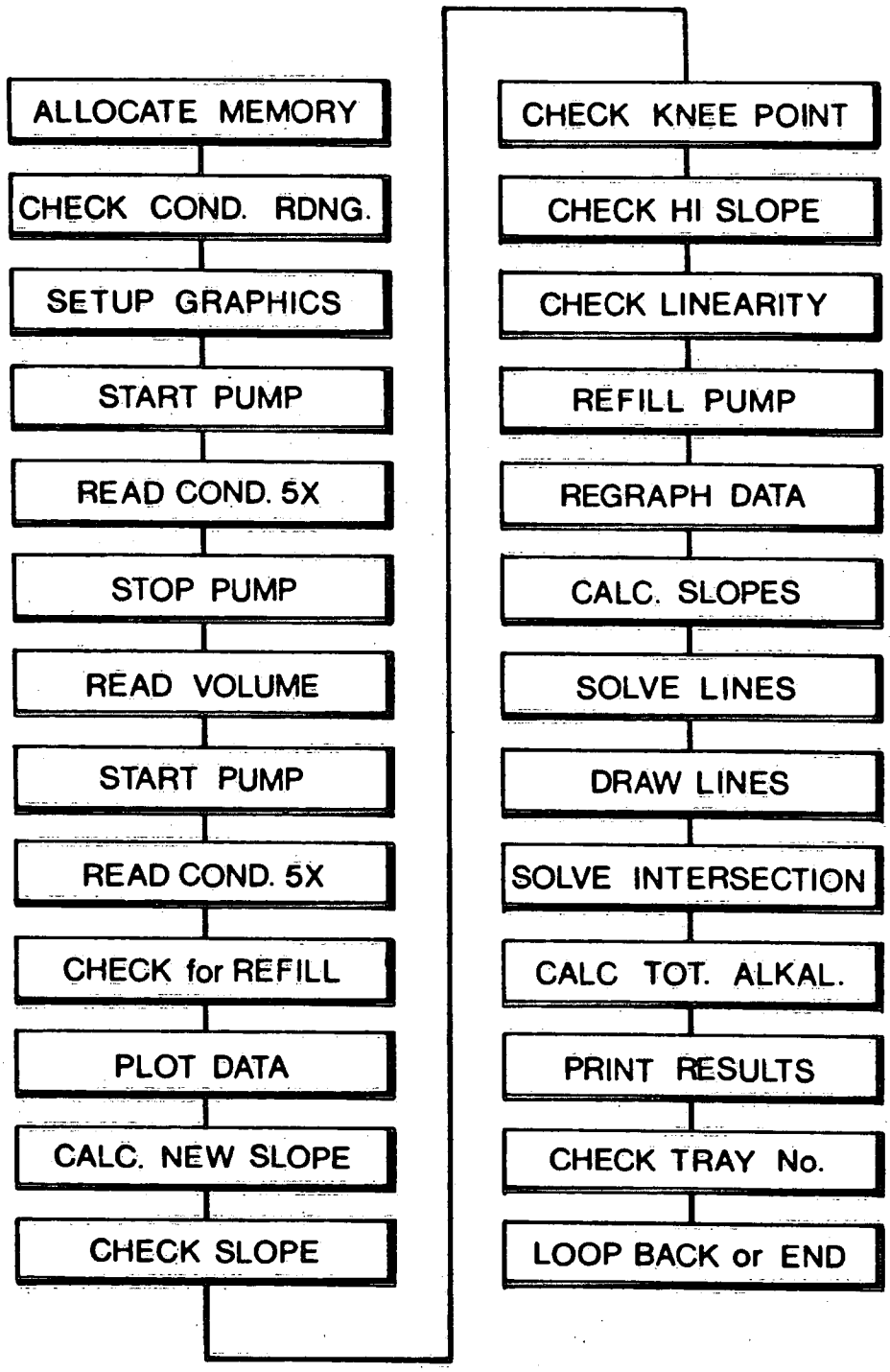


Figure 9. Main Flow Diagram of Program "CTA"