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COMPUTERIZATION OF CONDUCTOMETRIC TITRATION

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MANAGEMENT PERSPECTIVE

Significant improvements in the productivity of water quality testing laboratories can be achieved by speeding up some of the routine analysis procedures. This report documents the development of software to use an available microcomputer to obtain the benefits possible through such investment in automation.

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ABSTRACT

A desk-top computer has been programmed to control a sample changer, an autoburette and a conductivity meter so that twenty samples in succession can be titrated rapidly to determine alkalinity. The computer also detects the end-point and computes the total alkalinity from the conductivity response curves. To assist in the confirmation, the curves are shown graphically along with the results. Minimum time is required of the operator while the titrations are in progress.

INTRODUCTION

In the National Water Quality Laboratory, Burlington, Ontario, the titrations for total alkalinity take too long. To correct this, Dr. I. Sekerka of the National Water Research Institute, Burlington, Ontario, developed the conductometric method for determining the end-point of the titrations. In his demonstration, the time required for each titration was reduced about ten-fold.

This development work concluded by automating the method, using a personal computer and commercial instruments. The final system is covered by this report, which reviews the basic technique, describes the instrument connections, denotes the instrument settings and outlines the software. So far, evaluations show that the system is accurate and useful for a wide range of alkaline water samples.

REVIEW OF TECHNIQUE

The conductometric titration method was described by Sekerka and Lechner (1984). Figure 1 depicts a typical trace for Burlington tapwater. 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 mathematics and the core program are described by Ford (1985).

Titration graphs shown in Figure 2 are generated from a variety of natural samples of different concentration ranges. 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.

HARDWARE CONNECTIONS AND SETTINGS

The Radiometer-Copenhagen instruments operate with computers 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. The system hardware is shown in Figure 3.

Figure 4 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 (ABU80) 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 (RS-232) port. It recognizes certain character commands and responds with readings. A null-MODEM corrects the mismatch in the serial 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 4.

The 10 mL burette operates in the ABU80. The unit is left in Manual Mode once the burette is filled. The speed knob is set to 80. It may be set lower for samples with less than 20 ppm alkalinity or set higher for those above 200 ppm. The conductivity meter is left in Manual Mode and the scale set to integer values of conductivity (no decimal values). No front panel settings are required for the sample changer.

The sample size of 40 mL with a 30:10 sample to dilutant volume ratio is found to be optimum for the present setup. The sample is titrated with about 0.01 N sulphuric acid. Sekerka and Lechner (1984) recommended trichloroacetic acid instead of sulphuric acid. However, the present setup will cover more than 85% of the analyses performed at the NWQL. The samples, with alkalinities less than 20 ppm, require diluted titrant (0.002 N sulphuric acid) and those with alkalinities 200 ppm require reduced sample volumes (20 or 10 mL), depending upon the concentrations. The samples with specific conductances greater than 300 microsiemens per centimetre, also require dilution prior to titration.

The 0.01 N sulphuric acid titrant is standardized with 5 mL of 0.02 N sodium carbonate or sodium borate diluted to 40 mL. The 0.002 N titrant is standardized with 1000 microlitres diluted to 40 mL.

Figure 5 shows the typical titration graphs for sodium carbonate and sodium borate standards.

The software takes over when the program "CT" is loaded and the RUN command given.

SOFTWARE OUTLINE

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 6 shows the steps "CT" uses for the process. These include hardware initialization and requests to the operator for information about the titrant, the sample changer 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 7 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 with 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 total alkalinity adds it to the graph then produces a hard copy for the operator to check later. Examples are shown in Figure 2. 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.

RESULTS

Table 1 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 proper selection of titrant normality, sample size and pump speed reduces the number of reruns to about 5 percent. This applies when the source of the sample is known. Without knowledge of the source, the reruns are estimated to be less than 15 percent. Other titration methods have about the same characteristics.

The system produces a four to five-fold increase in the speed of processing. The conductometric method takes 3 minutes per sample compared to the 12-to-15 minutes taken by the potentiometric method. These times include sample retrieval, pipetting, dilution and other procedures.

CONCLUSIONS

As the evaluations near completion, the system appears to have met the requirements of the NWQL for precision and repeatability while speeding up the analyses by a factor of four or five compared to the present system in use.

TABLE 1

CONDUCTOMETRIC TITRATION METHOD

TOTAL ALKALINITY PRECISION RESULTS

AVG. CONC. PPM	NO. OF SAMPLES	STD. DEV.	C. V. %	95% CONF. INTER. PPM
4.83	12	± 0.26	5.3	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

REFERENCES

Sekerka, I. and J. Lechner. 1984. Determination of Alkalinity and Acidity of Water by Conductometric Acid-Base Titration. J. Assoc. Off. Anal. Chem., Vol. 67, No. 5, September, 1984, pp. 893-5.

Ford, J.S. 1985. End-Point Determination for a Chemical Titration Using a Microcomputer. Technical Note, Hydraulics Division, National Water Research Institute, Burlington, Ontario, p. 2.

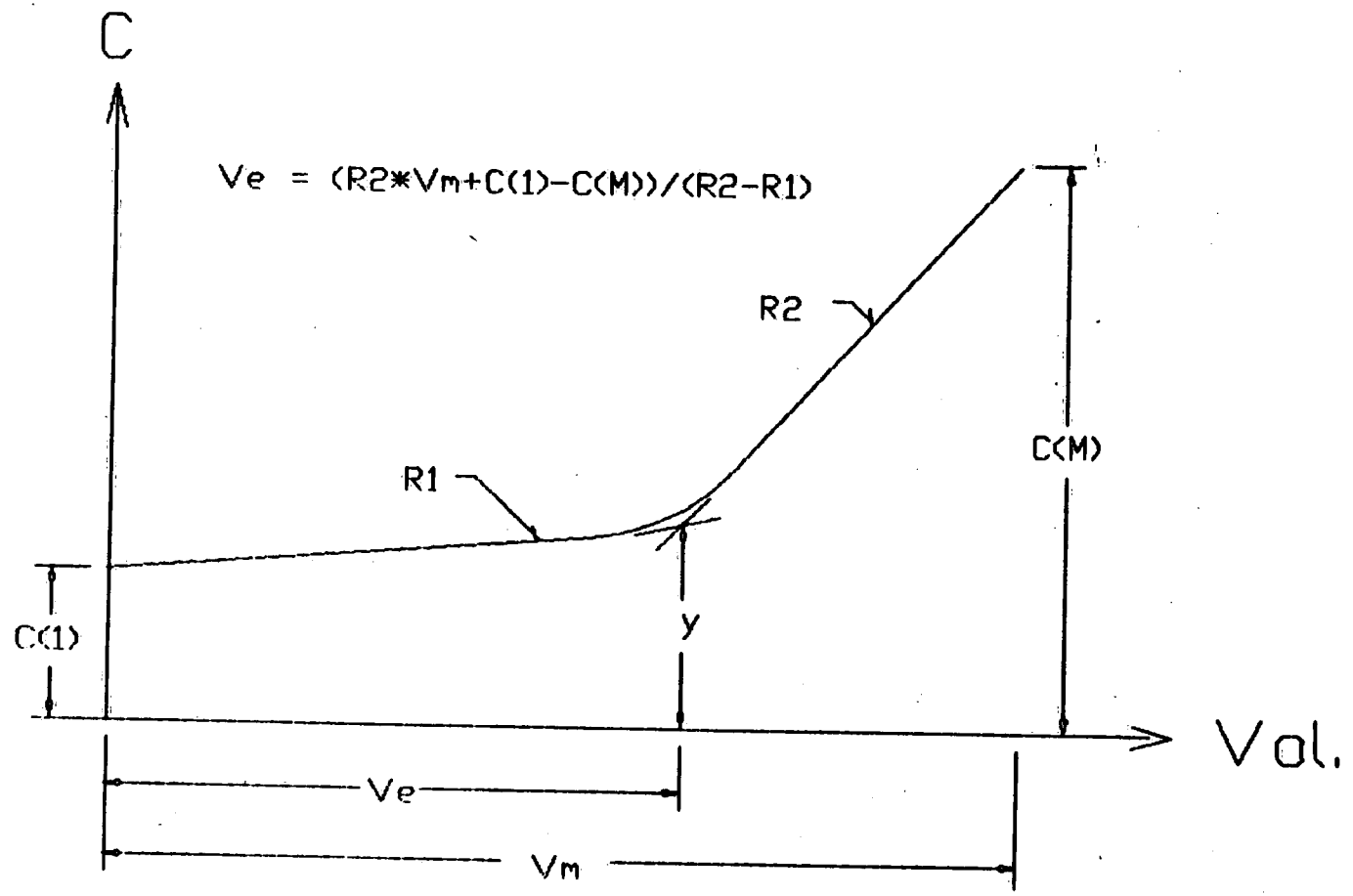
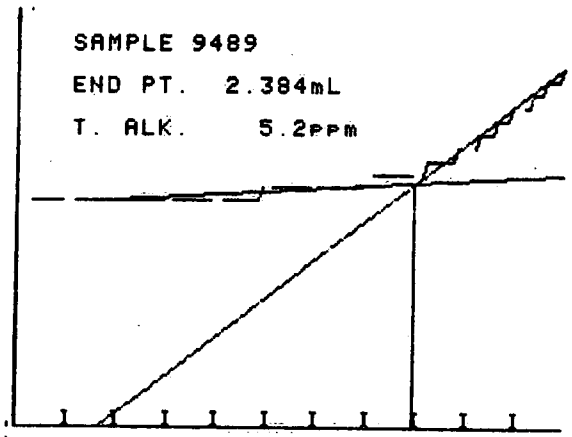
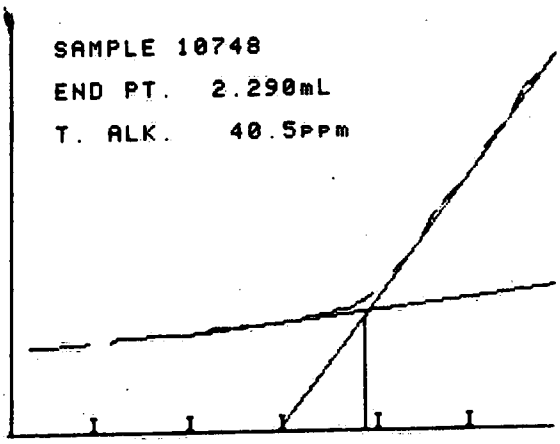


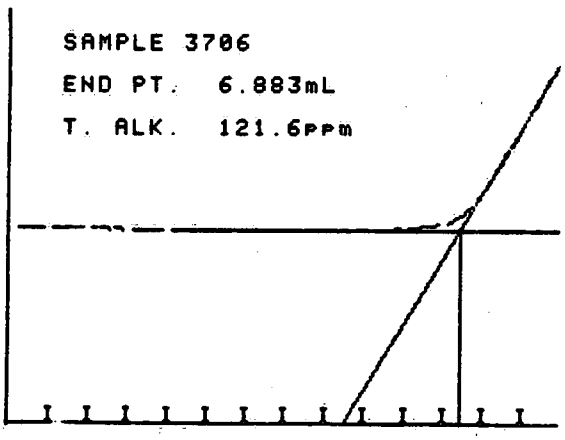
FIG.1 DERIVATION OF END-POINT VOLUME



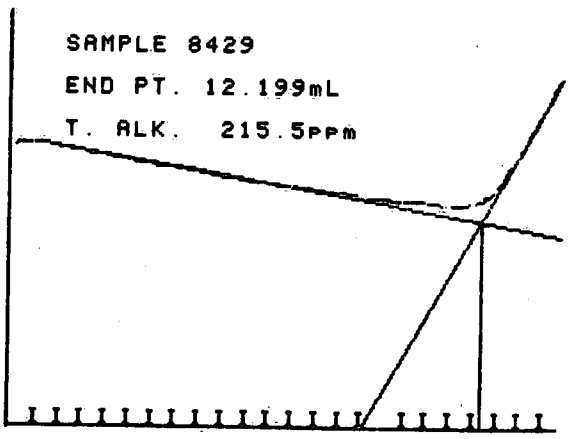
a. NATURAL SAMPLE
<20 ppm



b. NATURAL SAMPLE
20 – 100 ppm



c. NATURAL SAMPLE
100 – 200 ppm



d. NATURAL SAMPLE
>200 ppm

FIG.2 EXAMPLES OF TITRATION CURVES

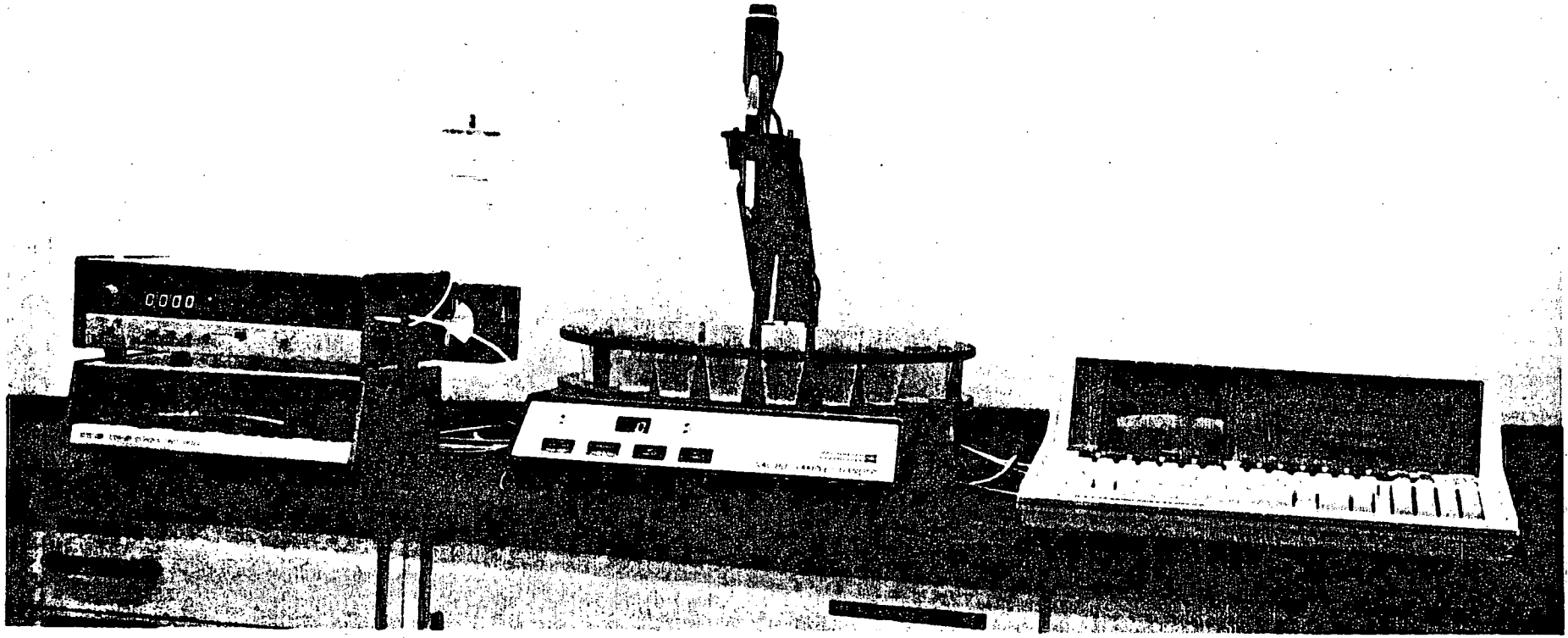


FIG.3 PHOTOGRAPH OF SYSTEM

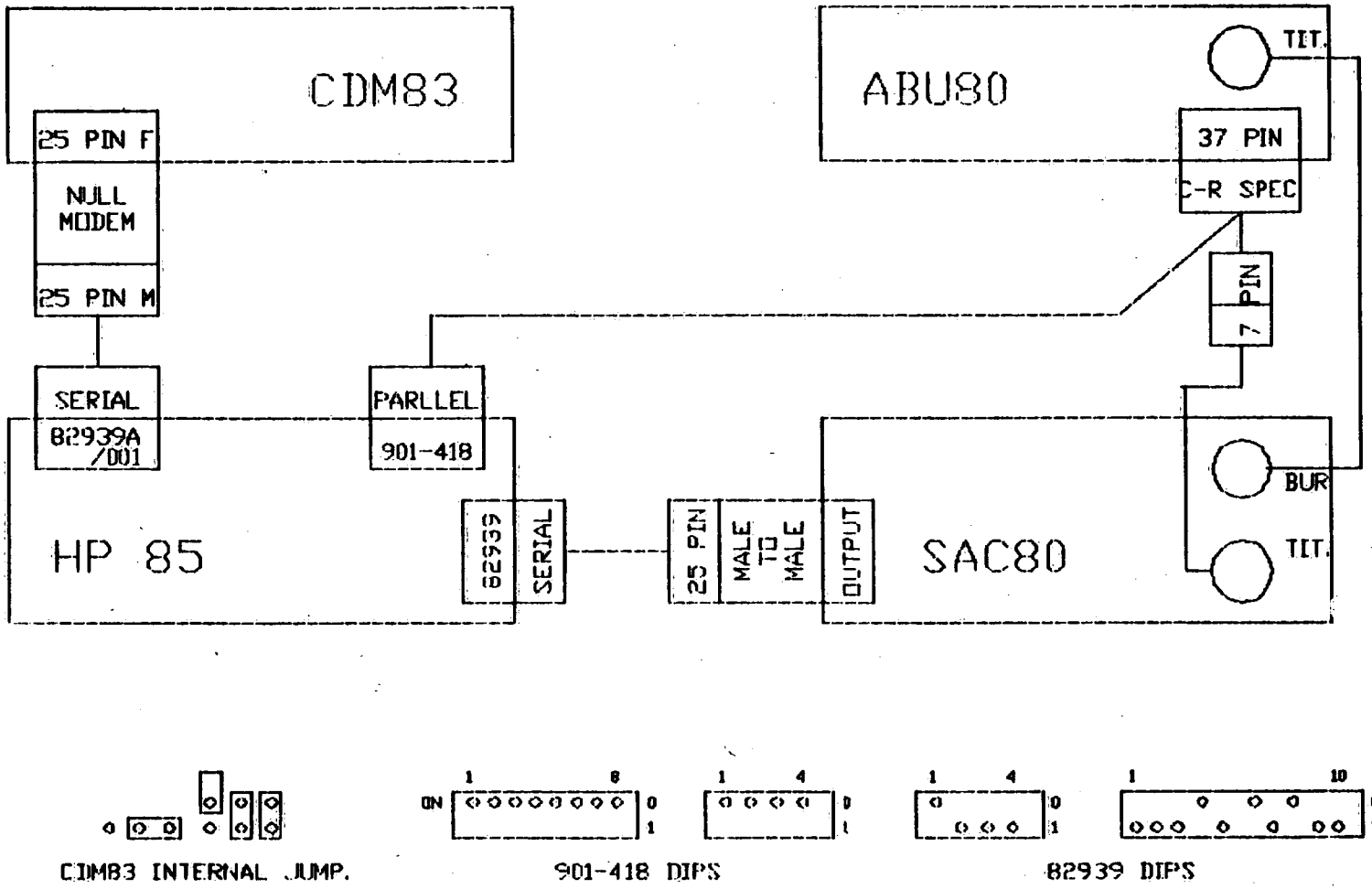
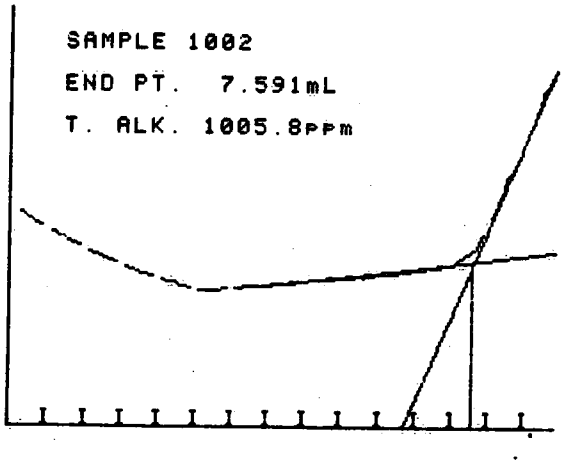
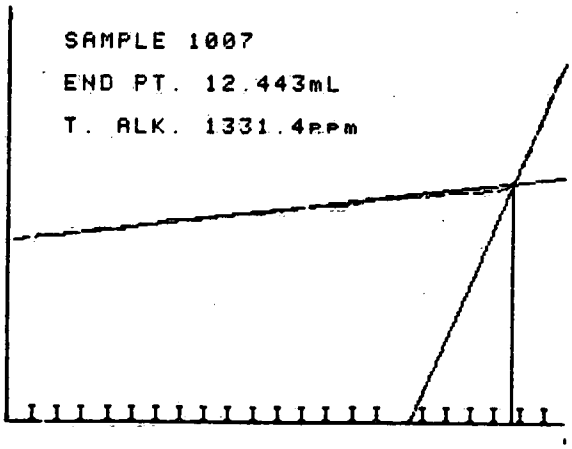


FIG.4 INTERCONNECTION DIAGRAM



a. SODIUM CARBONATE
0.02 N



b. SODIUM BORATE
0.0264 N

FIG.5 STANDARDISATION OF TITRANT

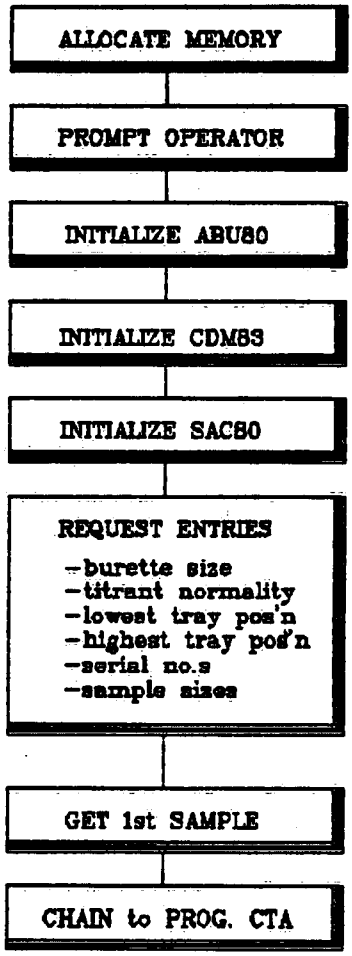


FIG.6 MAIN FLOW DIAGRAM OF PROGRAM "CT"

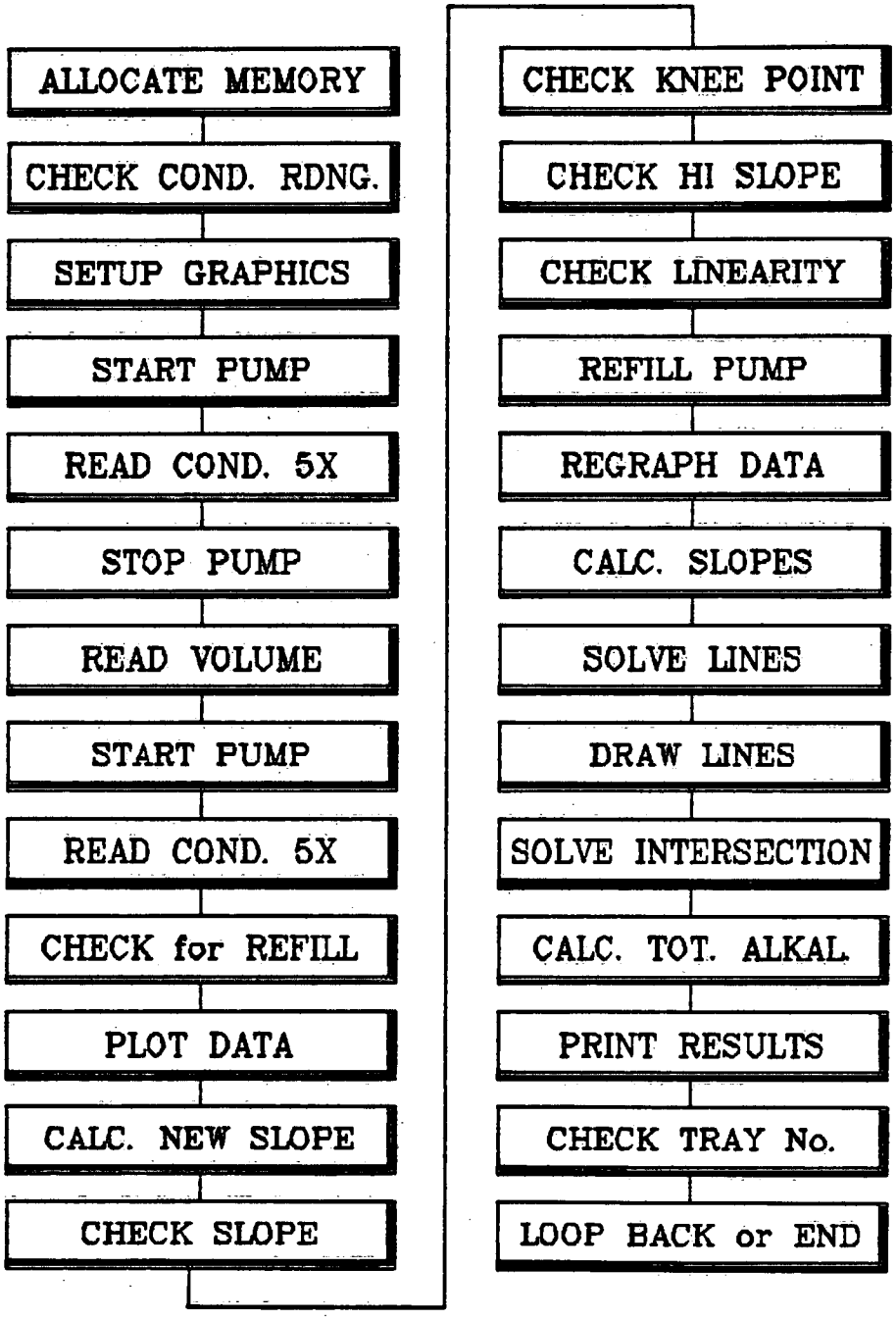


FIG.7 MAIN FLOW DIAGRAM OF PROGRAM "CTA"