The Automated Simultaneous Measurement of Electrical Conductance and pH of Surface and Ground Water Samples in a Routine Water Analysis Laboratory

L. H. W. VERHOEF AND S. A. ENGELBRECHT
[HYDROLOGICAL RESEARCH INSTITUTE, DEPARTMENT OF WATER AFFAIRS,
PRIVATE BAG X313, PRETORIA]

Abstract

A dual channel automated system, based on the use of an air-segmented continuous flow stream, was developed for the simultaneous measurement of electrical conductance and pH from one relatively small sample. Results obtained furnished conclusive proof that a single technician can perform both measurements rapidly and with good precision and accuracy. The automated system has other inherent advantages particularly as regards data acquisition and for checking the correctness of results.

Introduction

The pH and electrical conductance of every water sample received at the Hydrological Research Institute are measured manually, using commercially available instruments fitted with immersion type electrodes and measuring cells. The electrical conductance value obtained is used in the computer program for data acquisition to provide an indication of the correctness of the chemical analyses performed on the sample (American Public Health Association, 1971). The computer calculates the relationship between the electrical conductance (in micro-Siemens) and the sum of the cations and anions (in milligrams per litre) for every sample, and this appears as a factor in the computer print-out. The electrical conductance value is also used to establish whether or not and to what extent the sample should be diluted to match the concentration ranges of the automated continuous flow analytical systems used for the chemical analyses.

For the two manual measurements a relatively large volume of sample (approximately 100 mℓ) was required. A special sample handling technique which differed widely from the technique for the chemical analyses had to be adopted. Two well-trained technicians had to operate the equipment and had to be permanently in attendance at their work benches while the tests were performed. Reading the values shown by the instrument meters and jotting them down are slow and tedious tasks, giving rise to errors. In contrast, a single technician with less experience can man a dual channel continuous flow analytical system and with little effort can rapidly produce accurate results which can be readily checked and fed into the data acquisition system.

It became evident that the automation of the pH and conductance measurements was not only highly desirable but urgently necessary so as to remove a major bottle-neck in the flow of samples through the laboratory.

Available Methods

Numerous applications of ion-selective electrodes as detectors in automated systems for routine water quality analysis have been reported in the literature. Many of these systems are better suited to *in situ* monitoring of flow streams than to the laboratory analysis of discrete samples which might vary greatly in respect of pH and concentration of dissolved salts. In some cases electrode response was slow and the rate of analysis was as low as 10 determinations per hour. In other cases relatively large sample volumes are required. Amongst the descriptions of automated methods for the direct determination of ions using ion-selective electrodes are those for sodium by Jacobson (1968), water hardness by Sekerka (1974), fluoride by Oliver (1969), Brand (1974) and Erdmann, and ammonia by Potts (1975). Information on automated systems for pH measurements is rather meagre (Oliver, 1969; Tis News, 1975). This dearth of detailed information is even more noticeable in the case of automated systems for the measurement of electrical conductance (Sekerka, 1974).

It is planned to continue this programme of interlaboratory calibration studies by means of regular distribution of samples for analysis, which will enable the participating laboratories to continuously assess the effectiveness of their analytical procedures.

Acknowledgements

References

AMERICAN SOCIETY FOR TESTING AND MATERIALS (1975). *Annual Book of ASTM Standards: Part 31: Water*. Philadelphia, Pennsylvania.
DIXON, W.J. and MASSEY, F.J. (1969). *Introduction to Statistical Analysis*, 3rd Edition. McGraw-Hill, New York.
EKEDAHL, G., JUNKER, P., and RONDELL, B. (1975). Interlaboratory study of methods for chemical analysis of water. *Jour. Water Poll. Contr. Fed.* **47** (4) 858-866.
EKEDAHL, G. and RONDELL, B. (1973). Interlaboratory study of methods for chemical analysis of water: I. Major elements. *Vatten.* **29** 341.
GREENBERG, A.E., MOSKOWITZ, N., TAMPLIN, B.R. and THOMAS, J. (1969). Chemical reference samples in water laboratories. *J. Am. Wat. Wks Ass.* **61** 599-602.
KINGFORD, M., STEVENSON, C.D., and EDGERLEY, W.H.L. (1973). Collaborative tests of water analysis (The Chemaqua programme). I. Sodium, potassium, calcium, magnesium, chloride, sulphate, bicarbonate, carbonate and conductivity. *New Zealand Jour. of Science,* **16** 895-902.
McFARREN, E.F., LISHKA, R.J. and PARKER, J.H. (1970). Criterion for judging acceptability of analytical methods. *Analyt. Chem.* **42** (3) 358-365.
McGIRR, D.J. and WALES, R.W. (1973). *Interlaboratory quality control study No. 4: Arsenic, cadmium, cobalt, mercury and nickel.* Inland Waters Directorate, Canada Centre for Inland Waters, Burlington, Ontario.
RONDELL, B. (1973). Interlaboratory study of methods for chemical analysis of water: II. Metals. *Vatten,* **29** 357.
TRAVERSEY, W.J. and WALES, R.W. (1970). *Interlaboratory quality control study No. 1: calcium, total hardness, sodium, and potassium.* Department of Energy, Mines and Resources, Ottawa, Ontario.
WALES, R.W. and McGIRR, D.J. (1973). *Interlaboratory quality control study No. 3: Copper, chromium, lead, manganese and zinc.* Inland Water Directorate, Canada Centre for Inland Waters, Burlington, Ontario.
WALES, R.W. and TRAVERSEY, W.J. (1972). *Interlaboratory quality control study No. 2: total phosphate, organic nitrogen, nitrate nitrogen and organic carbon.* Department of the Environment, Ottawa, Ontario.
UNITED STATES (1956 *et seq.*). *Reports of studies conducted by the Analytical Reference Service: Study Nos. 1 et seq.* Department of Health, Education and Welfare, Public Health Service, Cincinnati, Ohio.

An interface module capable of taking any commercially available electrode and designed specifically as a module for an existing continuous flow analytical system, has been developed in the USA. The availability of such automated systems for the determination of pH, fluoride and ammonia was announced towards the end of 1975 (Tis News, 1975) but it appears unlikely that these systems will be for sale very soon.

Object

This study was undertaken to investigate the possibility of developing a reliable, automated dual channel system for the simultaneous measurement of pH and electrical conductance from a single sample aliquot. The primary goal of the development project was to design a relatively cheap system around the two existing instruments which previously had been used for manual measurements, and in such a way as to obviate any sacrifice as regards accuracy and precision and any extensive modifications to the equipment so that the instruments would still be suitable for manual use at any time. Other objectives of the study were:

1. To design a flow system with an efficient wash cycle between samples so that the rate of measurement would not be less than 30 determinations per hour (in order to keep pace with the automated chemical analyses).

2. To find the most suitable flow system, cells and electrodes which would ensure that the carry-over from a high value sample to a low value sample following immediately after it, or vice versa, would be negligible.

3. To restrict the sample volume required for the two measurements to 20 mℓ or less – the maximum that can be placed in a 13 cm x 1,6 cm diameter test tube which fits the sample plate of the existing samplers used with the other automated systems.

4. To bring the sample handling technique into line with that adopted for the other automated analyses.

5. To record results in the same format as that produced by the other automated systems, viz. on a 25 cm wide recorder strip chart suitable for processing by the existing data acquisition system as well as the system based on a laboratory-based minicomputer planned for the near future.

The Automated Dual Channel System

Modules and accessories

The automated system for the simultaneous determination of pH and electrical conductance consists of the modules and accessories listed below:

1. Sampler fitted with two sample pick-up probes 1,2 mm internal diameter, two glass wash receptacles and a sample plate to take 40 glass test tubes 13 cm long x 1,6 cm diameter.*

2. Peristaltic proportioning pump with air-bar device for precision air segmentation and capable of taking 26 manifold pump tubes.*

3. Manifold tray with fittings.

4. A temperature controlled water circulation bath with internal cooling coil.†

5. pH meter with combined immersion type electrode.††

6. Conductivity meter with micro flow type measuring cell.††

7. Range controller.

8. Two single pen potentiometric recorders.**

Modifications to modules

A minor modification to the standard sampler is required to provide a momentary, voltage-free contact signal to the microcomputer which will reset the operation cycle of the computer program. This signal was obtained by fitting an additional microswitch with shielded cable lead to the mounting plate of the sampler drive motor cam in such a position that the switch is only briefly closed every time the sample probe is transferred into the sampling position.

An external servo-mechanism attachment is fitted to the conductivity meter. The other modules are not modified in any way.

Automatic Range Selection

The automatic selection of the appropriate setting of the measuring range and frequency on the conductivity meter is a vital prerequisite to the effective automation of the conductance measurement. Internal structural changes that could diminish the suitability of the instrument for manual measurements had to be avoided. Automatic range and frequency selection were achieved by fitting an external servo-mechanism attachment to the conductivity meter and by adding a range controller designed and constructed by the Electronic Instrumentation Division of the National Electrical Engineering Research Institute, Council for Scientific and Industrial Research, Pretoria.

The servo-mechanism and range controller are shown in Figure 1 and are described in the appendix.

The System for the Measurement of Electrical Conductance

The operating cycle

The sequence of events in the sample/wash cycle of the sampler and the corresponding delay cycle generated by the computer, are shown schematically in Figure 2.

From the time the sample probe is transferred to the first sample receptacle on the sampler tray until the leading seg-
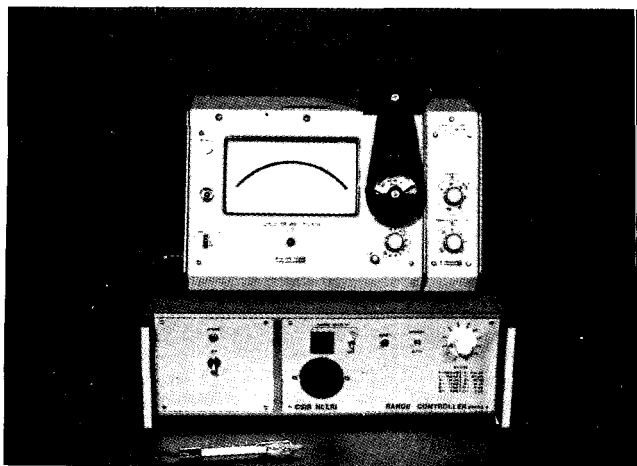
Figure 1
Servo-mechanism and range controller

ment of the sample enters the measuring cell, approximately 60 seconds elapse (depending on the length and diameter of the transmission flow lines).

When the microcomputer receives the voltage-free contact signal from the sampler it generates a 64-second delay to alert the system to the arrival of the sample. During the first 32 seconds of the delay cycle the microcomputer leaves the output signal of the conductivity meter switched through to the recorder which therefore records the conductance value of the liquid in the measuring cell during that period (water wash in the case of the first sample and the wash-out of the previous sample in the case of continuous running). During the next 32 seconds the microcomputer forces the recorder to display a pen trace at analog zero while the microcomputer itself observes, at one second intervals, the output of the greater-than-full-scale-deflection comparator circuit and the permanent range register and energizes the stepping motor via its associated interface to

make any clockwise or anti-clockwise adjustments of the rotary range selector switch of the conductivity meter so that the electrical conductance value of the sample in the measuring cell produces a meter scale reading between 30 per cent and 90 per cent of the full scale deflection.

If the meter needle deflection falls outside these limits with the range selector switch at the settings for lowest sensitivity (zero range display) or for highest sensitivity (range 11 display), as in the case of a sample having an electrical conductance value outside the range of the conductivity meter or in the case of a disconnected, short-circuited or empty measuring cell, the computer switches off the power to the meter, makes no range adjustments and generates an alarm.

At the end of the 64-second delay period the microcomputer causes the value of the selected range to be displayed on the front panel, at the same time converting this value into an equivalent analog signal which it passes to the recorder for three seconds followed by a signal equal to analog zero for two seconds. Then the microcomputer switches the output of the conductivity meter through to the recorder, maintaining this connection right up to the end of the first half of the 64-second delay cycle for the following sample.

The system described here was operated at a rate of analysis of 30 samples per hour, with a sample to wash ratio of 1:1. During continuous running the sampler will therefore transmit a "sample ready" signal to the computer at intervals of 120 seconds. The computer will generate a fresh delay cycle of 64 seconds on receipt of each such signal. The length of the flow lines has been so adjusted that the leading segment of every sample arrives at the measuring cell 48 seconds after the corresponding "sample ready" signal is received by the computer.

Although each sample flows through the measuring cell for 60 seconds, the events during the first 21 seconds of this period are not reflected on the recorder chart trace. The conductance
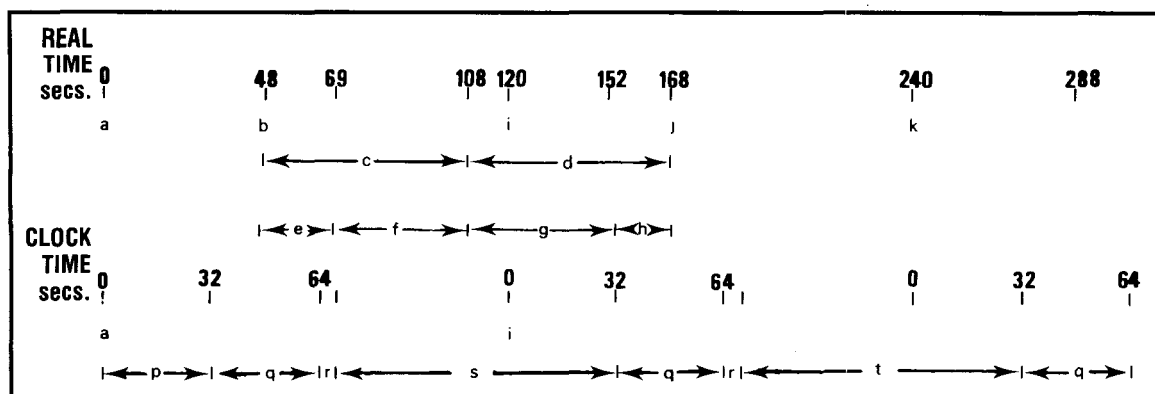
Figure 2
The operating cycle of the system for the measurement of electrical conductance

Legend
a. Sample probe transferred to sample cup No. 1. "Sample Ready" signal transmitted to computer
b. Sample No. 1. starts arriving at measuring cell after 48 seconds
c. Sample No. 1. flows through cell for 60 seconds
d. Wash liquid flows through cell for 60 seconds
e. First portion (21 seconds) of sample cycle not recorded
f. Second portion (39 seconds) of sample cycle recorded as peak plateau
g. First portion of wash cycle (44 seconds) not recorded
h. Last portion of wash cycle (26 seconds) not recorded

i. Sample probe transferred to sample cup No. 2. Sample ready signal transmitted to computer
j. Sample No. 2. starts arriving at measuring cell
k. Sample probe transferred to sample cup No. 3.
p. Recorder displays EC value of wash liquid
q. Recorder displays analog zero, the computer observes output signal of 90% F.S.D. comparator circuit
r. Range display for 3 secs and analog zero for 2 secs on recorder
s. Recorder displays peak plateau and wash cycle of sample No. 1.
t. Recorder displays peak plateau and wash cycle of sample No. 2.

Figure 3
Recorder chart trace for electrical conductance measurements. (Chart speed
1 cm per minute)

Figure 4
Flow diagram: electrical conductance .

Legend
JCC – jacketed capillary coil

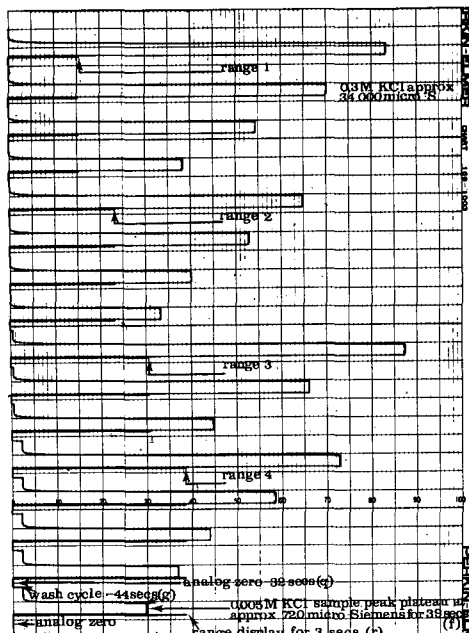value of every sample is recorded as a flat peak plateau for the last portion of 39 seconds duration only, being followed immediately by the fall curve representing the wash out of the cell during the first 44 seconds of the wash cycle. The last 16 seconds of the wash cycle are not recorded as the recorder pen is forced to trace a value of analog zero in readiness for the next sample.

A typical recorder chart trace yielded by a series of potassium chloride solutions ranging from 0,3 molar to 0,005 molar strength and having conductance values of approximately 34 000 to 700 microSiemens per cm (μS/cm) is shown in Figure 3. Recorder chart speed was set at one centimetre per minute. Selector switch settings were from 1 to 4.

The pen response to the computer switching, to the sample conductance value and to the wash of the measuring cell for each operating cycle can be readily identified. The corresponding portions of the operating cycle for the 0,005 molar potassium chloride sample are shown in brackets after the annotations on the chart trace.

The flow system

Two large, air-segmented sample streams were used with confluence prior to entering the jacketed coil. The length of the flow lines was adjusted in such a way that the two leading segments of every sample arrived simultaneously at the point of confluence but phased to avoid collision and merging of the air bubbles.

A thermostatic bath with cooling coil device was used to circulate water through the jacketed capillary coil and measuring cell jacket. The bath temperature was adjusted so that the temperature of the analytical stream leaving the measuring cell was exactly 25°C. The flow of tap water through the cooling coil of the bath was adjusted so that the heating element was switched on and off at intervals of approximately 30 seconds.
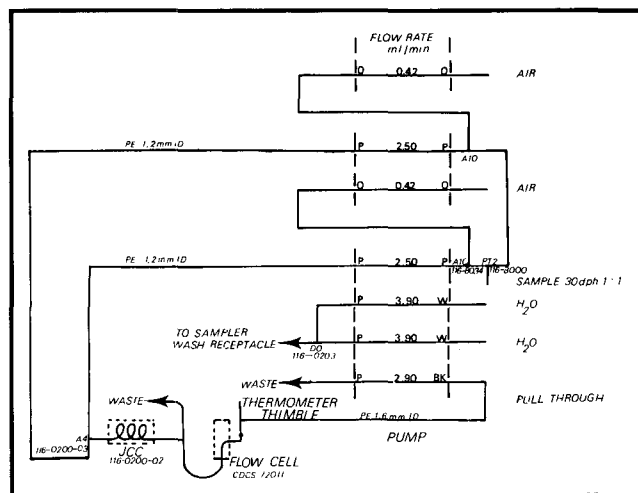
The flow diagram for electrical conductance measurements is shown in Figure 4. The arrangement of the components and fittings in the flow system is shown schematically in Figure 5. Details of the micro flow type measuring cell are shown in Figure 6.

Calibration

The micro flow type measuring cell was selected for incorporation in the automated system as it was the only available cell with the desired "wash" characteristics. Unfortunately it has a cell constant of 2,6 cm, whereas the conductivity meter provides for cell constant selector switch settings of 1,00 cm and 0,316 cm only. The micro cell was therefore used with a cell constant setting of 1,00 cm and for instrument calibration the cell constant correction dial was used to obtain the desired meter reading. When used in this mode with the 2,6 cm micro flow type cell, the instrument measuring ranges did not correspond to those for the 1 cm immersion type cell; e.g. a 0,01 molar potassium chloride solution with a conductance value of 1 413 μS/cm at 25°C is measured on a range setting of 6 with the 1 cm cell but on a range setting of 4 with the 2,6 cm cell.

A calibration procedure, based on simple factors to convert meter scale readings, and the corresponding recorder pen deflections, to the conductance value (μS/cm) of the sample, was devised. Obviously only one of the two meter scales could be used, and the choice fell on the upper scale of 0 to 5. After

Figure 5
Arrangement of components and fittings

Figure 6
Micro flow type measuring cell

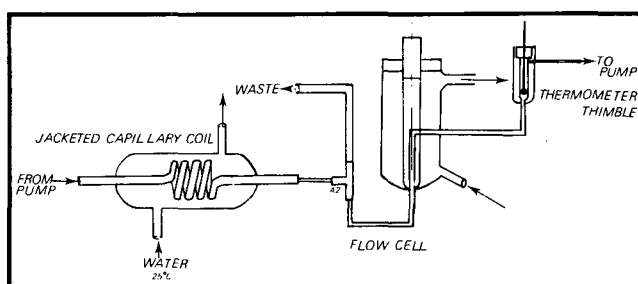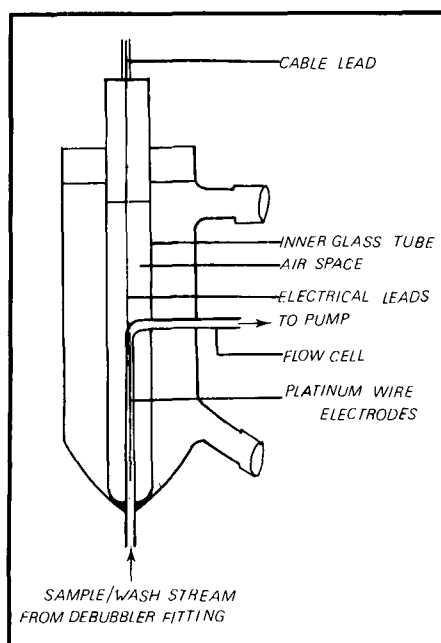recorder zero adjustment a potassium chloride solution of suitable strength to provide a meter needle deflection of between 3 and 5 on the upper scale was aspirated into the flow system at steady state. The recorder pen deflection was then adjusted by means of the recorder span adjustment control (screwdriver adjustment) to bring it into correspondence with the upper meter scale reading i.e. so that the recorder pen deflection as a percentage of full scale deflection equalled exactly the meter scale reading multiplied by 20.

A 0,01 molar potassium chloride solution was then aspirated into the system continuously and the cell constant correction dial of the conductivity meter was used to adjust the meter needle deflection to a reading of exactly 3,5325 on the upper meter scale. The recorder pen deflection was 20 times higher, vis., 70,65 per cent full scale deflection. The conductance value at 25°C of the 0,01 molar potassium chloride solution is 1 413 μS/cm which is the meter scale reading of 3,5325 multiplied by 400 or the recorder pen deflection of 70,65 per cent of full scale deflection multiplied by 20.

Potassium chloride solutions varying from 0,0005 molar to 0,5 molar concentration were used to establish the conversion factors for the other working ranges, to construct a calibration curve for the 2,6 cm micro flow type cell, and to draw a comparison between results obtained with the automated system,

TABLE 1

CALIBRATION: COMPARISON OF CONDUCTANCE VALUES (μS/cm) OBTAINED WITH KCl SOLUTIONS MEASURED WITH A 2,6 CM MICRO FLOW TYPE CELL EMBODIED IN AN AUTOMATED SYSTEM WITH THERMOSTATIC CONTROL, MEASURED MANUALLY WITH A COMMERCIAL 1 CM IMMERSION TYPE CELL WITH BOTH MANUAL TEMPERATURE COMPENSATION AND AFTER THERMOSTATING THE SOLUTIONS AT 25°C AND MEASURED WITH A STANDARD 1 CM CELL AT 25°C (AMERICAN PUBLIC HEALTH ASSOCIATION, 1971)

KCl Solution (Molar)	Range	Per cent Recorder FSD	Factor	Conductance Value			
				2,6 cm Cell (Automated)	1 cm Cell (Compensated)	1 cm Cell (At 25°C)	Standard Cell (At 25°C)
0,0005	6	37,8	2	75,6	78,2	78,1	73,9
0,0006	6	47,2	2	94,4	97,6	97,4	—
0,0008	6	61,8	2	123,6	125,8	124,7	—
0,001	6	82,4	2	164,8	165,5	167,0	147,0
0,002	5	46,7	6,4	298,8	317	319	—
0,003	5	70,0	6,4	448	449	448	—
0,004	5	91,4	6,4	585	582	582	—
0,005	4	37,6	20	752	755	755	717,8
0,006	4	43,2	20	864	880	875	—
0,008	4	57,7	20	1 154	1 159	1 160	—
0,01	4	71,0	20	1 420	1 413	1 413	1 413
0,02	3	43,8	64	2 803	2 780	2 770	2 767
0,03	3	64,2	64	4 108	4 060	4 050	—
0,04	3	85,2	64	5 452	5 220	5 290	—
0,05	2	32,8	200	6 560	6 700	6 700	6 668
0,06	2	39,0	200	7 800	8 010	7 820	—
0,08	2	51,2	200	10 240	10 600	10 200	—
0,1	2	63,8	200	12 760	13 100	12 900	12 900
0,2	1	37,7	640	24 128	25 300	24 500	24 820
0,3	1	53,7	640	34 368	36 500	35 590	—
0,4	1	68,8	640	44 032	47 800	46 580	—
0,5	1	82,3	640	52 672	58 200	57 000	58 640

TABLE 2

**ACCURACY: COMPARISON OF CONDUCTANCE VALUES (μS/CM) OBTAINED WITH SAMPLES
MEASURED IN AN AUTOMATED SYSTEM WITH THERMOSTATIC CONTROL AND EMBODYING
A 2,6 CM MICRO FLOW TYPE CELL AND MANUALLY WITH A 1 CM IMMERSION TYPE
CELL WITH BOTH MANUAL TEMPERATURE COMPENSATION AND AFTER
THERMOSTATING THE SAMPLES AT 25°C**

Sample No.	Range	Per cent Recorder F.S.D.	Factor	Conductance Value		
				2,6 cm Cell (Automated)	1 cm Cell (Compensated)	1 cm Cell (at 25°C)
1	3	41,8	64	2 675	2 635	2 660
2	3	32,1	64	2 045	2 010	2 050
3	3	43,8	64	2 803	2 725	2 829
4	6	81,5	2	163	157	162
5	6	80,5	2	161	157	160
6	3	41,0	64	2 624	2 590	2 610
7	3	52,0	64	3 328	3 260	3 310
8	3	42,3	64	2 707	2 660	2 700
9	2	48,8	200	9 760	9 750	9 820
10	3	45,3	64	2 899	2 890	2 890
11	1	64,2	640	41 088	43 800	43 550
12	3	32,2	64	2 060	2 050	2 050
13	3	55,6	64	3 558	3 470	3 495
14	3	58,8	64	3 763	3 660	3 700
15	3	42,5	64	2 720	2 670	2 690
16	6	57,8	2	116	114	116
17	5	58,7	6,4	375	364	369
18	2	58,6	200	11 720	11 650	11 780
19	6	54,4	2	108	105	107
20	5	44,7	64	286	278	280
21	1	34,3	640	21 952	22 400	22 200
22	2	36,6	200	7 320	7 300	7 350
23	3	41,4	64	2 649	2 580	2 645
24	5	43,5	6,4	278	271	277
25	5	85,0	6,4	544	530	540
26	6	69,0	2	138	137	138
27	4	32,2	20	644	641	650
28	2	29,0	200	5 800	5 805	5 850
29	5	80,4	6,4	514	515	510
30	5	87,6	6,4	560	550	555

the manual method using a 1 cm immersion type cell and the manual method using a standard 1 cm immersion type cell (American Public Health Association, 1971). Table 1 shows the factors used to convert the per cent recorder full scale deflection to sample conductance value and a comparison of conductance values obtained with the potassium chloride solutions using the automated system with the 2,6 cm cell, the 1 cm immersion type cell with a manual temperature compensator attachment, the 1 cm cell with samples that had been placed in a thermostatic bath at 25°C, and the standard 1 cm cell at 25°C. The results are in very good agreement (within approximately 2 per cent) for all solutions having conductance values below 12 900 μS/cm. For samples with higher conductance values the readings obtained with the automated system will be progressively lower than those obtained with a 1 cm cell. For such samples the total dissolved salts content can still be calculated from the conductance values obtained with the automated system but a higher factor must be used.

Conductance values obtained with the 2,6 cm micro flow type cell and with the 1 cm immersion type cell as shown in fifth and sixth columns of Table 1, clearly demonstrate the gradual drop in conductance values with increasing concentration.

Precision

Results obtained by replicated measurements of a surface water sample with a 2,6 cm micro flow type cell embodied in an automated system with thermostatic control, show that the automated system is capable of measuring the conductance value of an actual sample with a very high order of precision. Of the seventeen replicated measurements, sixteen values were all within 0,2 μS/cm of the average value of 147,4 μS/cm, but one gave a reading of 148,0 μS/cm which may be considered as an outlier. Even with the inclusion of this outlier the range for the seventeen measurements is only 147,2 to 148,0 μS/cm, the

standard deviation is 0,21 μS/cm and the relative standard deviation (coefficient of variation) is 0,14 per cent.

Other tests performed on potassium chloride solutions and on samples with higher conductance values showed that precision is adversely affected by even slight temperature fluctuations in the flow stream, and that the standard deviation naturally increases as the conductance value of the sample increases although the relative standard deviation remains fairly constant. If the temperature of the flow stream can be maintained within very close limits, say, 25°C plus or minus 0,1°C, the relative standard deviation should remain well below 0,5 per cent irrespective of the conductance value of the sample.

Accuracy

Table 2 shows the results obtained by measuring the conductance values of a batch of 30 samples taken at random, using the automated system and manually using a 1 cm immersion type cell with manual temperature compensation and manually with the 1 cm cell after the samples had been equilibrated at 25°C. For 24 out of the 30 samples the values agree to within less than 1 per cent; for five others the differences in the corresponding values are less than 2 per cent; and in the case of one sample only are these percentages exceeded and is the difference approximately 6 per cent. This particular sample is, however, rather exceptional in that it is highly saline with a conductance value of over 40 000 μS/cm.

Carry-over

To establish the effectiveness of the wash of the flow lines between samples and to determine the extent to which a high salinity sample can affect the value of a low conductance sample analysed immediately after it, a series of tests was conducted with solutions of potassium chloride (0,5 and 0,0005M) and actual high and low salinity samples. The high value samples had conductance values greater than 50 000 μS/cm whereas the low value samples had conductance values less than 100 μS/cm. The automated system with the 2,6 cm micro flow type cell was operated at a rate of 30 determinations per hour with a sample to wash ratio of 1:1. Every high value sample was followed by two replicates of the corresponding low value sample.

Even under such adverse conditions it was found that the values of the low conductance samples, due to carry-over, are always positive and the carry-over effect contributes to a mean error of 2,87 μS/cm (with standard deviation equal to 1,38) for the twelve replicates.

There is no carry-over effect from a low value sample to a high value sample.

Dilutions

In order to establish the effect of possible variations in the extent to which salts in highly saline water samples are dissociated into ions as compared to the dissociation of the potassium chloride in the corresponding solutions used as calibration standards, a series of dilutions of a high salinity sample was prepared and the conductance of each dilution measured on the automated system. Conductance values of dilutions corresponding to concentrations of the original sample ranging from 100 per cent to 40 per cent are roughly equal to those of potassium chloride solutions ranging from 0,5 molar to 0,2

molar strength as shown in Table 1. These values were then plotted on a single sheet of graph paper as calibration curves of conductance against potassium chloride molar strength and as conductance against percentage original sample. The two curves are shown in Figure 7.
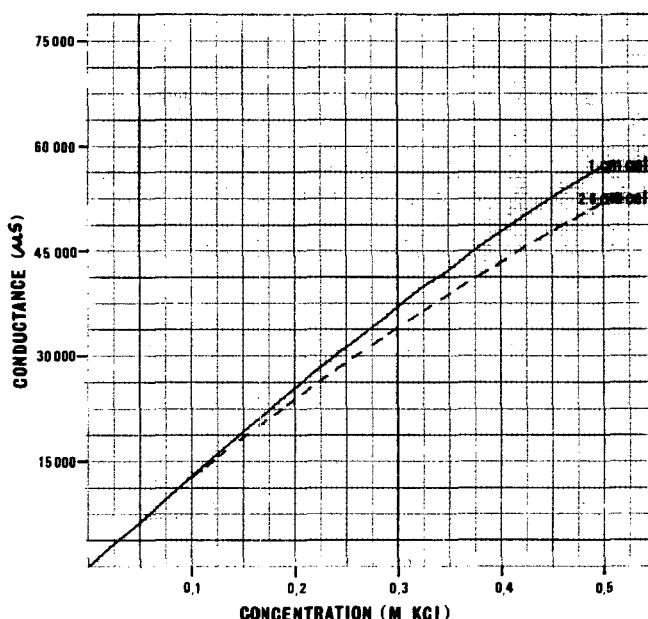

Figure 7
Dilutions of a high salinity sample and of a KCL solution

The curves are very similar as regards shape, slope and curvature and lie parallel to each other. Point X on the sample curve corresponds to Point Y on the potassium chloride calibration curve. A diluted smple with 91 per cent of its original concentration will therefore have a conductance value equal to that of the 0,5 molar potassium chloride solution, vis. 52 672 μS/cm. When a trace on transparent paper of the sample curve was prepared and placed over the potassium chloride curve in such a position that Points X and Y coincided, there were hardly any noticeable deviations over their entire length.

It was concluded that even in highly saline samples the salts in solution are dissociated to the same extent as in a corresponding potassium chloride standard solution. This might be due to compensation factors associated with the greater variety of ions present in the sample. There are also indications that it might be possible to calculate the conductance of a sample from the value obtained with an accurate dilution of that sample. Such a technique might prove useful in cases where insufficient sample is available for the normal conductance measurement.

Additions

In an attempt to confirm the validity of the conclusions drawn from the results obtained in the sample dilution tests, a low salinity sample was spiked with varying measured volumes of a 0,05 molar potassium chloride solution. Each mixture was prepared in a 100 mℓ volumetric flask. The same five pipettes were used to place the required volume of potassium chloride

solution and a corresponding volume of distilled and deionised water to a total volume of 30 mℓ in each flask which was then filled to the graduation mark with the low salinity sample. The conductance value of the original sample was 91 μS/cm. As each mixture contained 70 mℓ of the original sample its contribution to the conductance value of the mixture was taken as 63,7 μS/cm and was rounded off to 64 μS/cm. The contribution of the potassium chloride in each mixture was taken from previous measurements as tabulated in Table 1 or calculated from those results. For every mixture the sum of these two contributing conductance values is calculated. Within the range of ± 400 to ± 1800 μS/cm, the maximum difference between the calculated and the measured conductances is ± 20 μS/cm. The calculated and measured conductance values are thus in very good agreement.

The System for the Measurement of pH

Limiting factors

The volume of sample required for rapid electrode response and efficient wash of the electrode between samples at a fairly fast rate of analysis proved to be the major limiting factor as regards the choice of electrode assemblies. Commercially available micro flow type electrodes proved unsuitable. It was therefore decided to use the same semi-micro combined electrode which had been used for the manual pH measurements. The electrode was inserted into an over-flow type thimble of acrylic resin which had a glove-like fit on the lower portion of the electrode. The electrode was clamped in position so that the glass bulb was just clear of the bottom of the thimble where the debubbled flow stream enters.

The flow system

A relatively large sample stream was used and was segmented by large air bubbles at the probe via the air-bar device of the pump. A large diameter (1,2 mm) probe of Kel-F tubing was used. Transmission flow lines were of 1,6 mm internal diameter polyethylene. A pulse suppressor of polyethylene tubing 0,38 mm internal diameter and 5 cm long was inserted in the flow line between the pump and the debubbler fitting as suggested by Oliver et al (1969) to eliminate the blips and spikes which were defacing the recorder chart trace. The pulse suppressor did not prove entirely successful and a platinum wire, as used by Jacobson (1968) to eliminate electrical noise, was added. Best results were obtained when the platinum wire was inserted into the input arm of the debubbler fitting and attached to a thin stranded copper wire which was not earthed as suggested but merely acted as an aerial to disperse static charges.

The flow diagram for pH measurement is shown in Figure 8.

Calibration

The instrument output on the unexpanded scale setting was used in order that the system could cope with any sample with a pH value between 3 and 11. As the pH 0 to 14 scale is an arbitrary one adopted purely for the sake of convenience in showing values lying above or below the neutral point, conventional techniques for matching instrument meter needle deflection to pen position on the recorder chart could not be applied. True zero is in fact a deflection corresponding to a reading of

Figure 8
Flow diagram pH

pH 7 and if deionised water is used as a wash liquid between samples, chart trace peaks corresponding to pH values of samples would lie on either side of this central base line, pointing in opposite directions and those near pH 7 would tend to merge. Clearly defined peaks, all pointing in the same direction, were obtained by using a wash liquid of low pH value (2 to 2,5) but this value cannot be used to set the recorder chart trace base line using the zero control knob. The pH meter is calibrated manually using pH 7 and pH 10 buffer solutions. A pH 7 buffer solution is then aspirated into the flow system for several minutes. When the instrument meter needle is on a scale reading of 7, the zero set control knob of the recorder is used to bring the pen to exactly 50 per cent of full scale deflection on the recorder chart. A pH 10 buffer solution is then aspirated into the system. When the instrument meter needle is on a scale reading of 10 the recorder span variable resistor (screw-driver adjustment) is used to bring the pen to exactly 80 per cent of full scale deflection.

When the wash solution is aspirated into the system the recorder pen will trace a wash base line at approximately 5 per cent of full scale deflection. No attempt must be made to use the zero set control knob of the recorder to set this wash base line to any specific value. If the wash base line is too high or too low, the pH of the wash liquid must be adjusted to bring the base line to the desired level.

Figure 9 shows a recorder chart trace obtained by aspirating a range of commercially available buffer solutions* into the system.

Precision

The recorder chart trace obtained in a test performed on a surface water sample is shown in Figure 10. The pH and electrical conductance of the sample were measured manually beforehand and the values obtained were: pH 7,35 and conductance 220 μS/cm. The average for 26 replicates of this sample measured on the automated system was also pH 7,35 although the range of values for this test was pH 7,32 to pH 7,38. The standard deviation was 0,018 pH units and the relative standard deviation (coefficient of variation) was 0,245 per cent.

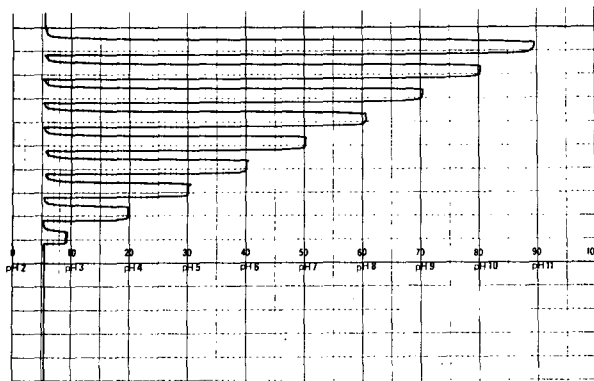*Puffer-Titrisol. Manufactured by E. Merck, 61 Darmstadt, Germany.

Figure 9
Calibration of pH system: recorder chart trace

The chart trace peaks showed a distinct tendency to level off at the top, but when the sample was aspirated constantly for several minutes the recorder pen traced a "steady state" plateau at 53,7 per cent full scale deflection, which corresponds to pH 7,37. This type of sample (with low conductance value) analysed at a rate of 30 determinations per hour with a sample to wash ratio of 1:1, does therefore not attain steady state conditions in the system, and variations in peak height must be expected. Subsequent tests proved that with most types of samples peak heights lie much closer to the steady state plateau. This is clearly demonstrated by the analysis peaks and "steady state" plateaus of three out of the four water samples shown in Figure 11.

Accuracy

Results in Table 3 show the excellent agreement between pH values of a batch of surface and ground-water samples obtained with the automated system and measured manually. Due to unforeseen circumstances the automated and the manual measurements could not be performed at the same time. The manual measurements were made several days later and changes in
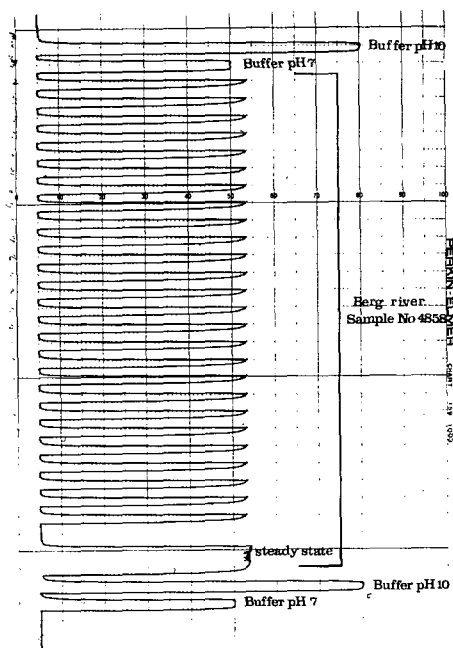
TABLE 3

ACCURACY: AUTOMATED pH MEASUREMENT

Sample No.	pH			Conductance (μS/cm)
	Manual	Automated	Difference	
1	8,7	8,75	0,05	2 660
2	8,3	8,42	0,12	2 050
3	8,65	8,72	0,07	2 829
4	7,8	7,7	0,10	162
5	8,7	8,27	0,43	160
6	10,1	10,1	0	2 610
7	9,5	9,38	0,12	3 310
8	8,6	8,54	0,06	2 700
9	7,6	7,77	0,17	9 820
10	8,1	8,12	0,02	2 890
11	8,0	8,12	0,12	43 550
12	8,1	8,0	0,10	2 050
13	7,95	7,95	0	3 495
14	8,55	8,60	0,05	3 700
15	7,0	8,92	0,08	2 690
16	9,1	9,02	0,08	116
17	8,6	8,60	0	369
18	9,3	9,02	0,28	11 780
19	9,85	9,58	0,27	107
20	8,8	8,97	0,17	280
21	7,9	8,03	0,13	22 200
22	8,25	8,30	0,05	7 350
23	8,4	8,63	0,23	2 645
24	9,2	9,13	0,07	277
25	8,8	8,68	0,12	540
26	7,65	7,73	0,08	138
27	8,8	8,72	0,08	650
28	7,85	8,3	0,45	5 850
29	9,45	9,3	0,15	510
30	8,8	8,78	0,02	555

Mean value of the difference = 0,12 μS/cm.
Standard deviation of the difference = 0,11 micro-Siemens.

Figure 10
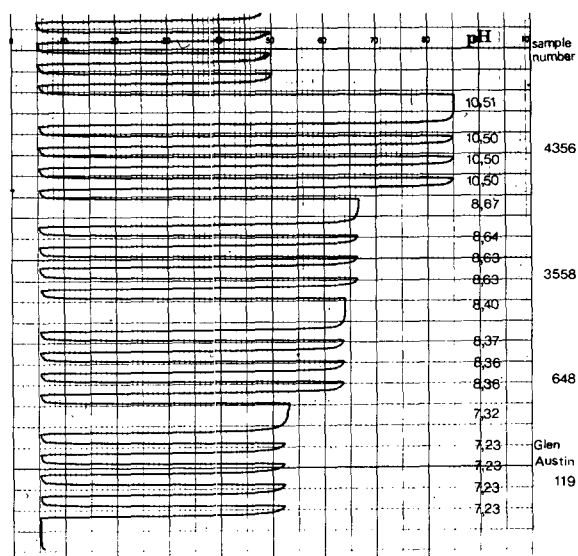*Precision of pH system: recorder chart trace*

Figure 11
Accuracy of pH system: recorder chart trace

pH could have occurred during that time. Nevertheless, 17 out of the 30 samples showed differences of less than 0,1 pH unit.

The electrical conductance of these samples was measured previously by manual methods and these values are also shown in the table.

Samples with high conductance values showed very good agreement while those with conductance values below 200 μS/cm tended to show greater variations.

Further tests carried out with other samples confirmed these findings. Figure 11 shows chart trace peaks and steady state values for four samples. Samples with high conductance values produced smooth chart traces and results of excellent precision and accuracy; those with low conductance values (less than 200 μS/cm) produced slightly jagged chart traces and less accurate results. If very accurate results for low conductance samples are desired, the automated system should be operated at a rate of analysis of 20 or even 10 samples per hour.

Carry-over

The wash solution has a very low pH but a very weak buffering capacity. There is, therefore, no danger of carry-over from a high pH sample even to a fairly low pH sample which follows immediately after it through the flow system. That the reverse, viz., that there is no carry-over from a low pH sample to a high pH sample, is also true can be inferred from the excellent degree of accuracy and precision as reflected by the chart traces in Figure 11.

Discussion

In view of the time factor and the limitations as regards the construction of special measuring cells and accessories, all the desirable refinements could not be incorporated into the two automated systems. Commercially produced automated systems will not become available for some time. The manual measurements performed up to now are tedious and prone to errors. The suggested systems have several other advantages over the manual measurements, e.g., the ease with which the correctness of results can be verified.

The feasibility of an efficient automated system for rapid and reliable measurement of the electrical conductance values of water samples has been demonstrated. The available measuring instrument previously used for the manual determinations has been successfully incorporated in the automated system without any major modifications, although a separate range controller module had to be added.

The rate of analysis is adequate and there is virtually no cross-contamination between samples.

The calibration of the system is rapid and uncomplicated. The conductance values of samples measured on the automated system are in good agreement with results obtained by manual measurement. The available micro flow type cell proved to be suitable and the precision of measurements obtained with it is excellent, but the cell could possibly even be improved by redesigning it to match the controls of the measuring instrument and to improve its temperature controlling capabilities.

The validity of conductance values obtained for high salinity samples when the system is calibrated with a 0,01 Molar potassium chloride solution may be questioned, but the errors can never be as serious as some encountered up to now with the manual measurements. The validity of the pH values obtained with the suggested automated system is beyond dispute. An added advantage of both systems is the chart traces which are permanent records of results. Values can be read off directly from the chart traces with far greater ease and accuracy than from the instrument meter scales. The chart traces are compatible in all respects with the present data acquisiton system.

Conclusions and Recommendations

The suggested automated dual channel system meets all the requirements stated at the outset. There is undoubtedly scope for improvement, particularly as regards the aspects listed below:

1. Improved thermostatic control of the flow stream by the use of a jacketed mixing coil with greater pre-heating capacity and a re-designed micro flow type measuring cell. The coil should be of thin-walled glass tubing not greater than 1,6 mm internal diameter and of adequate length to ensure that the flow stream is at the desired temperature (25°C) before it enters the measuring cell. In the case of the measuring cell (Figure 6) the inner glass tube which insulates the electrical leads should be raised to the bend in the flow cell so that the lower portion of the flow cell comes in direct contact with the circulation water. The lower ends of the platinum electrodes could be insulated by small blobs of glass placed externally on the flow cell or by embedding in the glass junction between the flow cell and water jacket.

2. Reduction of the cell constant of the conductance measuring cell from 2,6 cm to 1,0 cm to bring it into line with the adjustment controls of the conductivity meter. Alternatively, the instrument must be modified to provide for a cell constant setting of 2,6 cm. It may be possible to achieve this merely by reducing the diameter or length of the platinum electrodes. An increase in the diameter or volume of the flow cell should be avoided.

3. Reduction of the sample volume required for pH measurements by designing a micro flow type pH cell embodying the type of combination electrode used in the present system or other suitable micro-electrodes. A reference electrode with a micro-bore open liquid junction may help to improve electrode response.

   Orders have already been placed for some accessories designed to realise these objectives.

   The ultimate refinement of the system for conductance measurements may even include the incorporation of the servo-mechanism, or its electronic equivalent, and perhaps the entire range controller assembly in the instrument cabinet of a redesigned conductivity meter.

Acknowledgements

controller and those portions of the paper referring to its functions in the system is also gratefully acknowledged.

References

AMERICAN PUBLIC HEALTH ASSOCIATION, AWWA and WPCF (1971). *Standard Methods for the Examination of Water and Wastewater*, 13 Ed., 39, 323 to 325.
BRAND M.N., GRAFSTEIN P., PIRRITANO R.J., SALPETER J. and TOPF M.H. (1974). Electrode Applications in Water Monitoring by Autoanalysis: The Determination of Fluoride. Paper presented at the *Technicon Instruments Corporation Conference*, Pittsburgh, Cleveland, Ohio.
ERDMANN D.E. (1975). Automated Ion-selective Electrode Method for Determining Fluoride in Natural Waters. *Environmental Science & Technology* 9 (3) 252 and 253.
JACOBSON H. (1968). Analysis with Ion-Specific Electrodes. *Annals New York Academy of Sciences*, 486.
OLIVER R.T., LENZ G.F. and FREDERICK W.P. (1969). The Determination of Fluoride in Vegetation and Gases by Automated Direct Potentiometry. Paper presented at the *Technicon International Congress*, Chicago, Illinois, 4 to 6 June.
POTTS J.R., PIRRITANO R., TOPF M. and DELGROSSO R. (1975). Application of a Gas Sensing Ion-Selective Electrode to Determine Ammonia in Water and Wastewater by an Auto Analyzer System. Paper presented at the *26th Pittsburgh Conference on Applied Chemistry and Applied Spectroscopy*. Cleveland, Ohio, 3 to 7 March.
SEKERKA I., LECHNER J.F. (1974). Automated Simultaneous Determination of Water Hardness, Specific Conductance and pH. *Analytical Letters* 7 (6) 399-408.
TIS NEWS. Fall 1975. 1 (2) 3, 4-6. *Technicon Industrial Systems*, Tarrytown, New York 10591.

Appendix

The Range Controller

The Servo-mechanism

The multi-wafer rotary range selector switch of the conductivity meter is set to the required range by a stepping motor and associated belt gear drive. The drive ratio is 1:6 and an end position switch indicating the lowest sensitivity range is fitted to the mechanism. Two of the four windings of the stepping motor are simultaneously energized by 1A or 0,4 A step or hold currents respectively, supplied by the electronic control unit. The servo-mechanism is mounted on top of the conductivity meter and is provided with a protective cover plate.

The electronic control unit

The entire electronic control unit is housed in a standard ELMA cabinet which also serves as a base for the conductivity meter as shown in Figure 1. The unit is connected directly to the electrical mains supply, and the conductivity meter is in turn connected to a power outlet socket in the rear of the range controller. The cabinet houses the necessary power supplies, the NEERI 40 microcomputer, associated interfaces and operating controls.

The power supplies

Voltages for the microcomputer and associated interfaces are stabilized. Power for the stepping motor is supplied from an unregulated power supply through torque increasing circuitry.

The NEERI 40 microcomputer

The microcomputer controls the operation of the system by execution of the program stored in the memory. The computer card embodies a crystal controlled clock generator, central processing unit, memory and I/O interface, program memory and input and output ports. Operating controls and external devices like servo-mechanism, conductivity meter and recorder are connected to these ports via individual interfaces.

Operating controls

The operating controls and indicators are mounted on the front panel of the control unit. These include:

1. Mains switch with neon light indicator.

2. Two digit (7 segment LED) range display and associated on - off switch.

3. Reset push-button for resetting the alarm and restarting the computer program.

4. Mode selection switch for manual or automatic operation.

5. Manual range selector – twelve position rotary switch – for range selection in manual operation or calibration.

6. Audible alarm for indication of non-permissible conditions and defects of the conductivity meter or measuring cell.

Sockets mounted on the rear panel provide for interconnections of the electronic control unit, the servo-mechanism, the sampler, the recorder, and the conductivity meter. When required a remote alarm loudspeaker can also be connected to the controller.

Interfaces

The interfacing of the microcomputer with other devices and controls is provided by two printed circuit boards in the electronic unit. The interface circuitry includes:

1. Decoders and drivers for the digital range display.

2. Encoder for the manual range selector switch.

3. Analog buffers and reference voltage sources for the conductivity meter output.

4. Comparator circuits (which ensure switching to a less sensitive range if the meter needle overshoots 90% of full scale deflection, or switching to a more sensitive range if the meter needle deflection is less than 30% of full scale deflection).

5. The digital to analog converter circuit (which provides a 0 to 1 Volt signal corresponding to the selected range).

6. The recorder control circuit (which regulates the recorder analog trace to show either analog zero, measuring range or sample conductance value).

7. Current amplifiers for the stepping motor excitation (which under the control of the microcomputer ensure clockwise or anti-clockwise rotation).

8. Amplifiers for the alarm loudspeakers and mains trip switch (which disconnects the power from the conductivity meter in the case of emergency).