THE KENT UNIVERSAL GLASS ELECTRODE pH METER

By G. TOOP

General Principles of the Apparatus

General

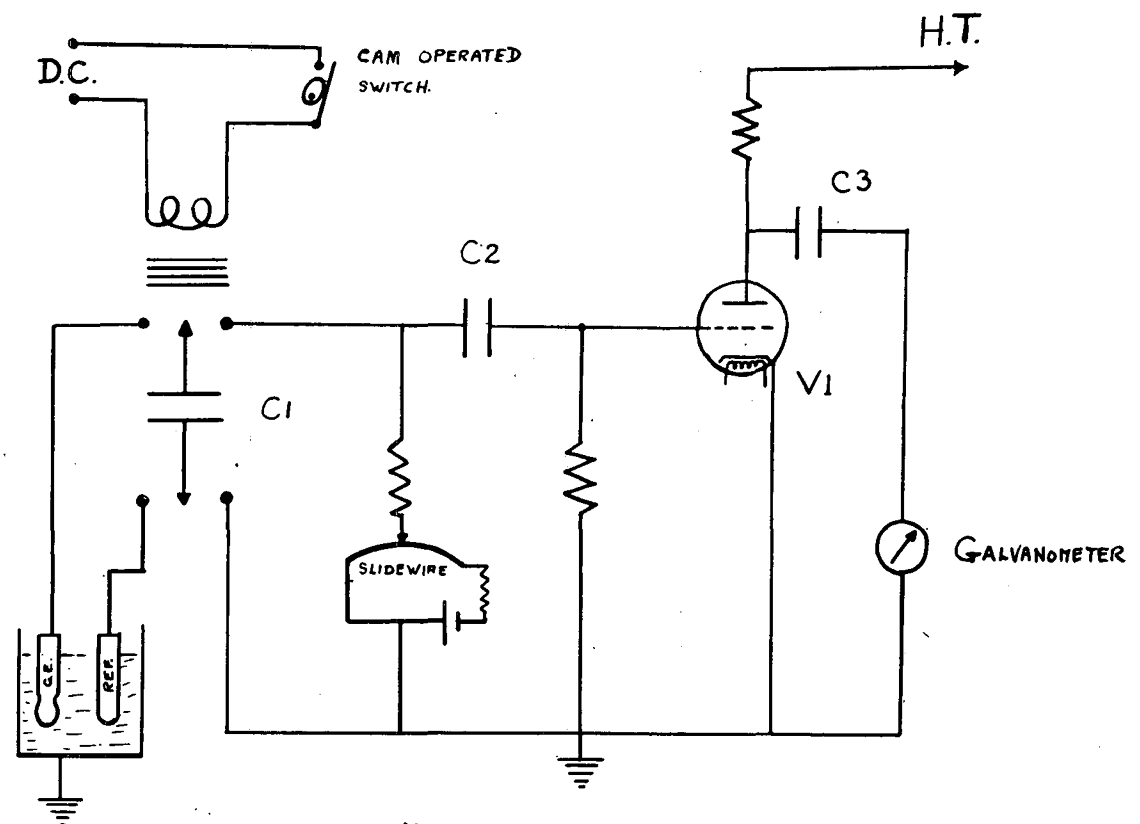
The pH of the solution under test is a function of the concentration of dissociated hydrogen ions. It is possible therefore to measure the pH by measuring the potential produced by the hydrogen ion activity and the most convenient means of doing this is by the glass electrode and a suitable reference cell.

Since the potential produced across a glass membrane having a solution of constant pH on one face, is a function of the pH of the solution on the other face, the determination of the unknown pH is reduced to the measurement of this potential. In order to complete the circuit via the measuring instrument and back to the solution, it is necessary to introduce a reference cell in the solution which will do so without itself introducing varying potentials at the various interfaces. The calomel electrode has this property of producing a constant E.M.F. independent of the pH of the solution.

In order to make it possible to prevent polarisation of the electrodes, and in order to prevent excessive voltage drop, due to the high resistance of the electrodes, it is essential to utilise circuits which virtually demand no current from the electrodes, and the Kent system is designed to do this without the use of specially-selected electrometer valves and similar devices.

Principle of Operation

Referring to the simplified circuit diagram (Fig. 1), a condenser, C.1, is arranged so that it is alternatively connected across the electrodes and then across the instrument potentiometer. The switching is done by a special relay operated every two seconds by a cam-operated switch in the instrument drive system. If the slidewire of the potentiometer is correctly positioned and the meter is therefore registering the true pH of the solution, the E.M.F. charge on the condenser will equal that developed by the potentiometer and no current will flow, but if the E.M.F.'s are unequal, the condenser will either charge from or discharge to the amplifier circuit via the condenser C2. The pulse is applied to the grid of the amplifier and the resultant pulse in the anode circuit is passed via C3 to the galvanometer, which deflects accordingly. The cam-



SIMPLIFIED CIRCUIT - KENT pH METER FIG 1 operated switch is synchronised with the clamping mechanism of the galvanometer, so that it is clamped while deflected. The deflection of the galvanometer is detected by the self-balancing potentiometer mechanism which automatically moves the slidewire in such a direction as to move the deflection at the next cycle, and thus at the same time moves the indicator towards the true pH reading.

Two users adjustments are provided—one for adjusting the sensitivity of the instrument—and one for assymetry adjustment, due to slight variations between glass electrodes and variations which may occur with ageing of electrodes.

Temperature Compensation

The E.M.F. of the electrodes varies not only with the pH of the solution, but also with their temperature, and therefore it is necessary to employ an automatic correction, so that the meter reads the true pH of the solution at that temperature. It will be appreciated that the pH of a solution can also vary with temperature and that this cannot be compensated, since no two solutions have the same characteristic. However the user only requires to know the pH at the working temperature, which is always correctly indicated and the solution characteristic need only be taken into account when checking a sample, since the sample temperature must be kept at the working temperature if serious errors are to be avoided.

The law connecting the E.M.F. developed by the electrodes with the temperature is of the form:

$$E = Eo + bT + cT \text{ ph},$$

where T is absolute temperature.

The Kent system employs a resistance thermometer in the solution, which forms one arm of a Wheatstone bridge, which is balanced at 25°C. If the temperature varies from 25°C., the resistance alters, the bridge is unbalanced and a correcting potential is applied to the potentiometer circuit via a second slidewire which is positioned by the meter according to the pH. The correcting potential is thus made a function of temperature and also of pH and perfect compensation for temperature changes at the electrodes is achieved.

The Salient Points Ensuring Accuracy and Reliability

These can perhaps best be covered by mention of a description of the equipment itself.

The installation consists of three units (see Fig. 2).

(i) The primary unit which incorporates the electrodes.

(ii) The electrometer unit which holds the amplifier, relay and switching condenser, as well as the power pack.

(iii) The pH meter which incorporates the potentiometer slidewire galvanometer and self-balancing mechanism.

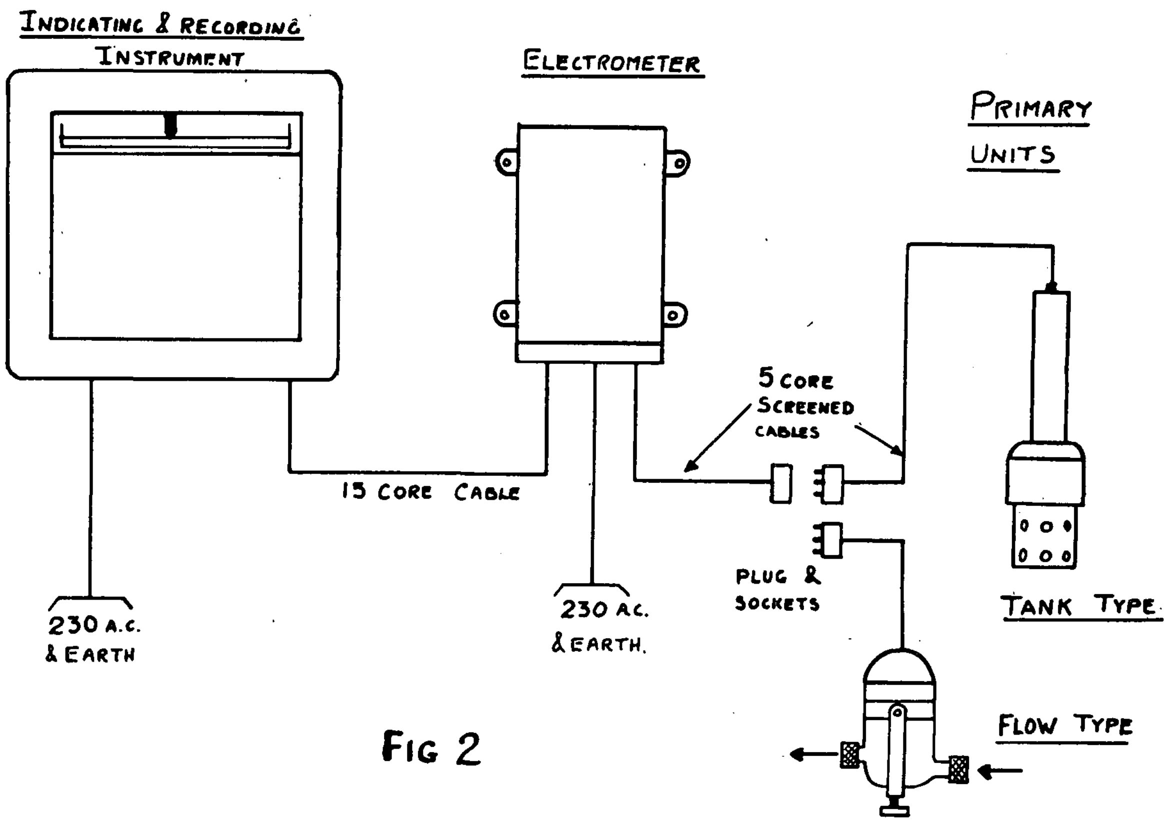


FIG 2

(1) *Primary Unit*

There are two types of primary unit—the tank type for direct insertion into tanks and troughs, and the flow channel type, in which a sample is piped to a chamber surrounding the electrodes. The two types are basically similar, and in fact the main portion is interchangeable. Referring specifically to the flow channel type, Fig. 3 (*a*), the head is designed to prevent ingress of moisture, and is constructed so that only non-corrodable materials are in contact with the solution.

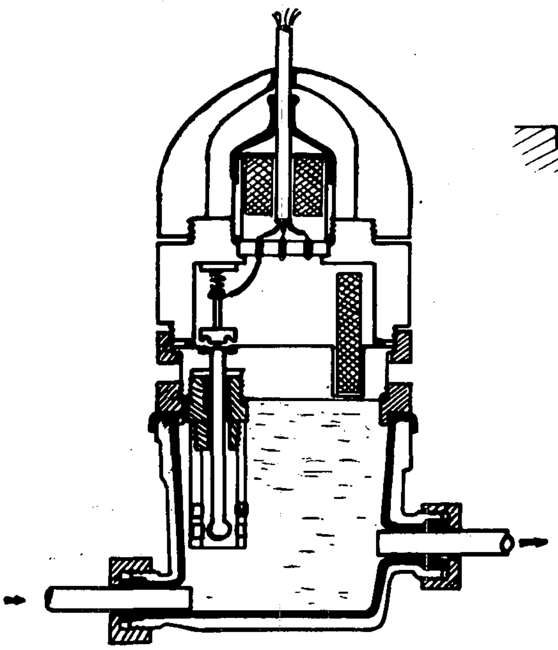
The sample pipes are directly inserted into the rubber lining of the chamber, which acts as a gland at the connections, so that glass, metal or plastic pipes of the correct O.D. can be used. The rubber lining also acts as the sealing gasket between the pressure chamber and the head, which is machined from silvanite. The connecting cable enters the head via a rubber seal and the entry chamber contains a silica-gel drier. The electrodes enter the head via rubber-sealed joints and again a drier unit is incorporated in the space. In order to seal the chamber when an electrode is withdrawn, spring-loaded plungers press down upon a rubber sealring when either of the electrodes is removed from the head. A copper screen surrounds the inside of the chamber and is connected to the earth lead of the cable, so that static charges on the insulating material of the head are earthed.

Reference Cell (*Fig.* 3 (b))

The reference electrode is of patented design, consisting of a rubber sheath into which a porous ceramic ball is fitted to act as the salt bridge. The calomel electrode is a ready-made-up unit in a plastic housing which fits into the top of the rubber sheath, the latter being half filled with KCl crystals and topped with KCl solution. It will be appreciated that with this design the risk of contamination of the electrode is very small and in most cases the electrode has a life of many months without requiring renewal of the KCl. By using a rubber sheath which can deform to equalise pressure inside and out the passage of solution in or out of KCl, is practically prevented altogether. The sheath also acts as its own seal when the locking nut is tightened into the head.

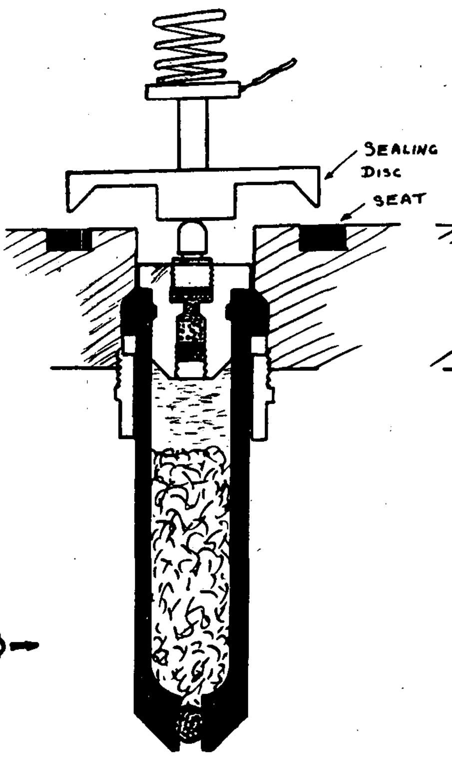
Glass Electrode (*Fig.* 3 (c))

This is a relatively robust item and can stand any reasonable handling. The ballistic circuit makes it possible to use electrodes of high resistance (80 megohms) and advantage is taken of this to use a relatively thick membrane. It is a self-contained



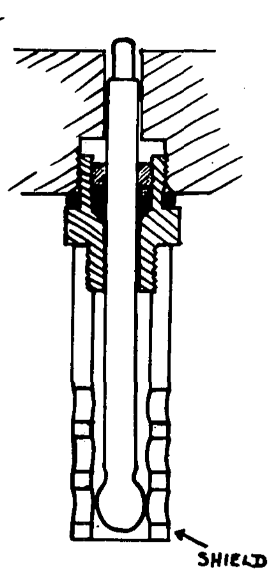
FLOW CHANNEL TYPE PRIMARY UNIT

FIG 3A



REFERENCE ELECTRODE

FIG 3B



GLASS ELECTRODE

FIG 3C

electrode and can be removed from the head by loosening its lock-nut, all glass electrodes being quite interchangeable. It is protected from erosion and physical damage by a perforated silvanite guard, and the whole electrode system and resistance thermometer are further protected by another guard in the case of tank type units.

Resistance Thermometer

This is completely enclosed in a rubber sheath which is sealed into the head by a locking nut and skid ring.

Generally then it can be said that the whole primary unit is designed for industrial conditions and is adequately protected against both damp and physical damage when in use.

5-Core Cable

The cable connecting the primary unit to the electrometer is a special 5-core cable with the two electrode leads insulated by a plastic and shielded by a braided copper screen, which acts as an earth lead.

Electrometer Unit

The electrometer is completely sealed and once installed should rarely, if ever, need attention. All the cables enter via "O" ring rubber glands, the joint in the case is sealed by a rubber gasket and two silica gel driers are fitted inside to remove all moisture from the air in the case. The terminal block for the electrodes is of polystyrene for high insulation. The relay unit which operates the switching of the condenser from the electrodes to the potentiometer is of special design using gold wire contacts and with all leads passing through a polystyrene block. The single valve is a double triode 12A×7 or similar type obtainable from most suppliers and not requiring any slection, since the ballistic circuit makes the amplification characteristic relatively unimportant. The supply for the circuit is passed via a constant voltage transformer, so that normal voltage and also frequency variations do not affect the instrument.

Multelec

The receiving instrument is a self-balancing potentiometer of proved design and is in most respects identical with the standard Kent temperature and millivolt recorders, except for the cam switch and additional temperature compensating slidewire. Since the ballistic circuit is used, there is no drift, due to change of valve characteristics, and the only adjustment required is to the asymmetry adjustment when checking on buffer after changing electrodes. In most cases electrodes agree within about 0·1 pH without any adjustment. Since the electrode system is quite separate from the amplifier and metering circuits it is possible to earth the whole installation and the reference electrode is not used for this purpose as in some systems.

Important Points to be Watched When Installing and Operating

Primary Unit

Before installing the equipment it is essential to choose the correct equipment for the particular installation.

The choice of primary unit lies between the tank type and the flow channel, and the limitations of the two types can be seen from the graph 4A. The flow channel can be used up to 100°C. and 80 p.s.i. pressure as the extremes, the black line indicating the limiting values between these extremes. The tank type can be used up to 80°C., providing only the electrodes are immersed, but below 60°C. the whole unit can be immersed if desired, the length of extension tube being up to a maximum of five feet.

Electrodes

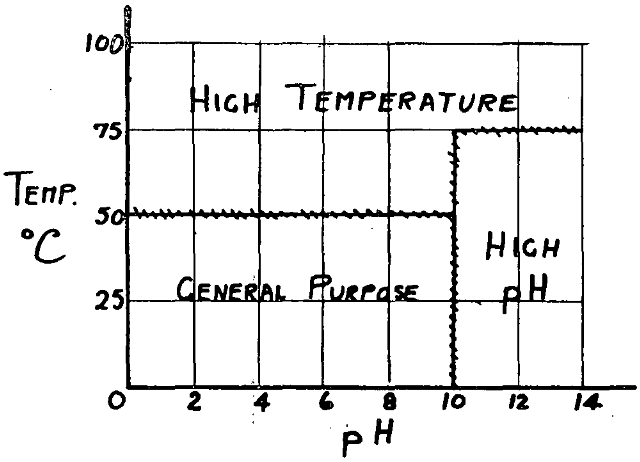
Three types of glass electrode cover the whole field of operation, the approximate limits of the types being shown by the latched line on the graph 4 B. All are identical in size and can be freely interchanged without any change in the rest of the installation. The general purpose electrode can be used above 50°C. and 10 pH, but in both cases its life will be shortened and it is prone to sodium errors above 10 pH. The high alkaline electrode is of lithium glass and reduces the error very considerably. The high temperature electrode cannot be used below 50°C., since its resistance becomes excessive, and in fact when buffer checking it, the buffer solution must always be heated up above 50°C.

Change-Over

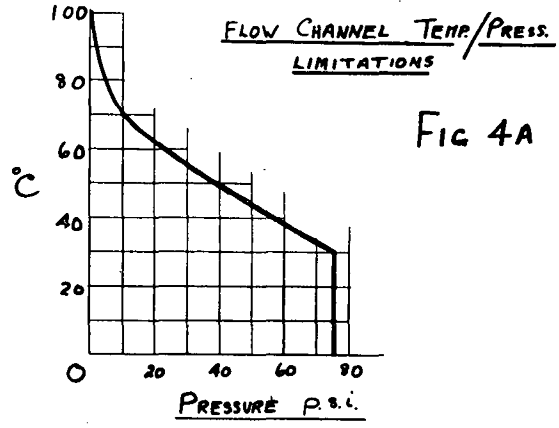
If the operating conditions are severe, due to high temperatures, or heavy build-up of deposits on the electrodes, it is advisable to have stand-by primary units which are plugged in while the normal unit is being cleaned or having its driers renewed. The spare units should always stand in water ready for use, so that the electrodes are soaked. When in store the reference electrode should be fitted with the sealing cap supplied, so that it does not deteriorate.

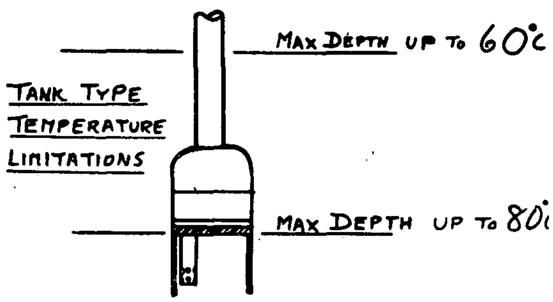
Positioning

The electrometer unit should be put in an accessible and relatively dry spot, so that if it is opened up at any time it does not become excessively damp



Class Electrode pH/Temp.
Limitations
Fig 4B





or dirty. It is possible to have the electrometer up to 300 feet from the primary unit, so that it should always be possible to find a suitable spot. The meter itself is a robust mechanism, but in view of the quantities of bagasse and similar dust flying in most mills, it is best to protect the whole instrument if possible by placing it in an outer case with a glass front. The instrument can be up to 600 feet from the electrometer if required.

Maintenance

This is undoubtedly a vexed question, because pH meters are no doubt relatively complex affairs and on the other hand sugar mills in this country do not employ instrument mechanics. This is, of course, not the case in the U.K. and U.S.A., where instruments and automation are making their mark in sugar as much as they are in other process industries. The fact that this Association is discussing pH and that manufacturers are here in on the discussion indicates that the industry is alive to the possibilities, but the opinion I formed when visiting many mills last year was that instruments are not really considered essential to the running of the plant and therefore do not get the same consideration as for example the pumps and motors. I feel therefore that if the industry is going to take instrumentation and later automation seriously and get the full benefits from it, there is a need to give the whole question much more consideration.

For example one steel-works in Pretoria where conditions are nowhere near as bad as the average mill not only builds its instrument panels behind glass faces as is done in the U.K. and U.S.A., but also air conditions the cubicle. While I do not for a moment say this is essential, I do say it indicates that that factory does appreciate that working instruments make money by more accurate control of processes and greater efficiency, and they are prepared to spend time and money in order to get the return. Instruments which are not maintained and which are not kept working, are a waste of money. I would suggest therefore that there should be some person in every factory who is made responsible for the instruments as a whole and who is given the opportunity to learn enough to maintain them properly in between normal service visits by the suppliers. If meters need complete overhaul, then as far as my own firm goes, we are prepared to carry it out and no doubt if men are available to be trained, this could also be arranged.

While it is probably not necessary to have an instrument engineer in each factory, in my opinion it is essential that each factory or group should aim at getting a reasonably intelligent mechanic to take on the maintenance.

The trend in all process industries is towards continuous processes in which the automatic control of all variables is normal and it seems inevitable that this must sooner or later come to the cane sugar industry. Thus in view of the world-wide shortage of trained instrument men, due to the unprecedented growth of instrumentation, it is suggested that now is the time to earmark suitable men for training on instruments, so that as the inevitable developments take place, these men grow in experience to meet the need of the times.

Returning now to the specific details of maintenance on Kent pH equipment, it can be said that the electrometer itself should not need any maintenance, except that the driers should be regenerated between campaigns. To regenerate the silica-gel driers they are heated for about eight hours at 50°C. In the case of the receiving instrument, the maintenance consists of straightforward oiling of bearings as indicated in the instructions, and of minor adjustments, which are quite within the scope of a normally intelligent fitter—providing that man is properly *detailed* to look after the meters, is given the *time* to carry out the work and is *disciplined* when they are neglected.

The primary units are however a different matter and they will definitely need periodical attention, the frequency depending upon the nature of the duty. For example, when dealing with liquids in the range above 60°C. it will probably be necessary to renew the drier in the head about every month, and in this case we would recommend that the complete primary unit be unplugged and taken to some dry spot in the laboratory or instrument shop where it can be opened up and a spare drier fitted. Since it is so easy to plug in a spare primary unit, this does not involve any particular trouble.

The reference cell can be recharged with KCl at the same time, although this is more a precaution than a necessity. In applications where build-up of sulphates and other salts is experienced, the best solution is to use a spare primary unit, which is plugged in as soon as incrustation begins to affect the operation, the built up unit then being cleaned.

In many cases it is possible by careful choice of sampling position to avoid or reduce the build-up of deposits. For example in one application in a uranium plant it was found that up to $\frac{1}{32}''$ of hard deposit formed in an hour or two, so that after six to eight hours the electrodes ceased to function. On investigation this was found to be due to the fact that the liming process, which was carried out in a large mixing tank, was not being carried to completion in the tank, due to by-passing of the lime to the exit pipe and consequently the major part of the deposition of solids occured in the exit pipe itself. By ensuring adequate mixing in the tank, not only was it found possible to run the electrodes for a month or so without cleaning, but the frequency at which the plant was forced to shut down to clean the pipes was reduced considerably.

In passing it is fair to mention that this particular application was given us as a particularly difficult one to run a test of our equipment, since the meters supplied with the plant had been given up as useless, the electrodes lasting only a day or less in the highly erosive slimes, and the glass R.T. and reference cells getting broken while being cleaned. The Kent electrode system was still functioning after one month when the trial ended, and in fact the tank type unit which was used and has been in use since on many other tests, is in use today.

While on the subject of electrode durability, perhaps you will forgive me if I quote an extract from a paper presented by Doctor D. Gross of Tate & Lyle, Research Laboratory, Keston, England, to the International Congress of Agricultural Industries, Madrid, 1954. Entitled "Recent Studies of pH Measurement and Control in the Sugar Industries." "The author has used various makes of commercially available glass electrodes in his pH measurements at high temperatures, such as made by Beckman Cambridge, Electrofact, Kent, as well as home-made electrodes of Corning 015 glass with great variations of membrane thickness, shape, inner reference electrode and electrolyte. Of these the glass electrodes by George Kent Ltd. proved to be superior with regard to pH response, durability and reproducibility."

We are of the opinion that success of pH measurement in the sugar industry will depend not only upon choosing the best equipment, but also upon applying that equipment to the best advantage in conditions peculiar to the cane sugar industry. In fact we feel that however good the equipment may be it will fail unless (*a*) it is installed after due experimentation on each type of application to ensure that it is applied to the best advantage; and (*b*) there is an adequate spares and service organisation to back up the factory staff as necessary.

At the present time Kents are conducting tests on the sulphitation process at a factory in India and we hope to carry out trials at a local factory in a few weeks. We understand that so far no pH instruments have been successful on the sulphitation process in India, although quite a number of various makes have been bought and installed. Preliminary reports from our engineers indicate that the problems are by no means easy to solve and that control will also present difficulties, unless advanced techniques are employed, involving control of other variables affecting pH, presumably therefore the same or similar problems will arise here which can only be overcome by close co-operation between the suppliers and users of the instruments concerned.

May I say again that I am grateful for the opportunity of addressing you today and grateful to those of you who gave up so much of your valuable time to discussing your problems, when we visited you last year.