(12) UK Patent Application (19) GB (11) 2 146 436 A

(43) Application published 17 Apr 1985

(21) Application No 8421458

(22) Date of filing 23 Aug 1984

(30) Priority data

(31) 3330358 (32) 23 Aug 1983 (33) DE

(71) Applicant
Walter Nicolai,
Maria Louisen Strasse 144, D-2000 Hamburg 60, Federal Republic of Germany

(72) Inventor
Walter Nicolai

(74) Agent and/or Address for Service
Fitzpatricks,
Kern House, 61/62 Lincoln's Inn Fields, London WC2B 6EX

(51) INT CL⁴
G01N 27/52

(52) Domestic classification
G1N 19B4 19D10 19D11 19X1 19X5 25B 25C4B2 25C4B 25DX 25E1 25E2 BMX
U1S 1054 1287 1303 G1N

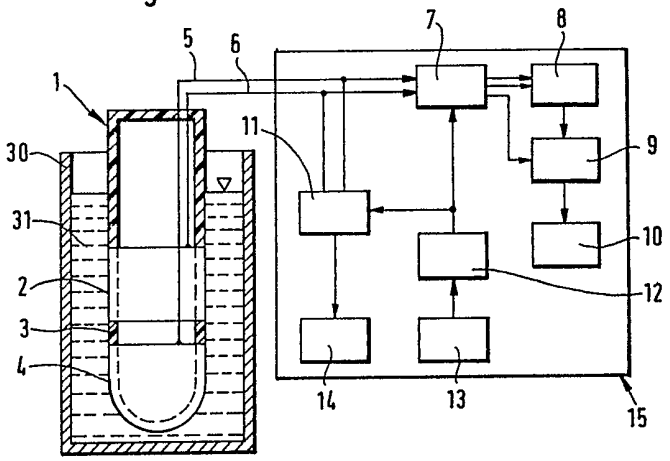
(56) Documents cited
None

(58) Field of search
G1N

(54) Redox potential meter

(57) A redox potential meter, more particularly for measuring the redox potentials of physiological media *in vivo*, by means of two electrodes (2,4) of different metals or one metal of different valences, the electrodes being carried by a measuring probe (1), includes a circuit to indicate the time of effective introduction of the probe (1) into the measuring medium. The output of differential amplifier (7) is coupled via function unit (9) to indicator (10). Function unit (9), which may be a switch, relay, peak voltage detector or instantaneous value store, is controlled by a logic signal from threshold circuit (8) which is produced when a predetermined voltage amplitude detected by electrodes (2), (4) rapidly changes, circuit (8) comprising an RC signal processing stage including a diode, and transistor followed by a monostable multivibrator. Function unit (9) may be controlled to provide for the direct or delayed indication of the redox potential values. The possibility is described of integrating the meter function units into the probe to reduce liability of the system to malfunction. The measuring (4) and reference (2) electrodes of the probe are replaceable if necessary.

Fig. 1



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Fig. 1

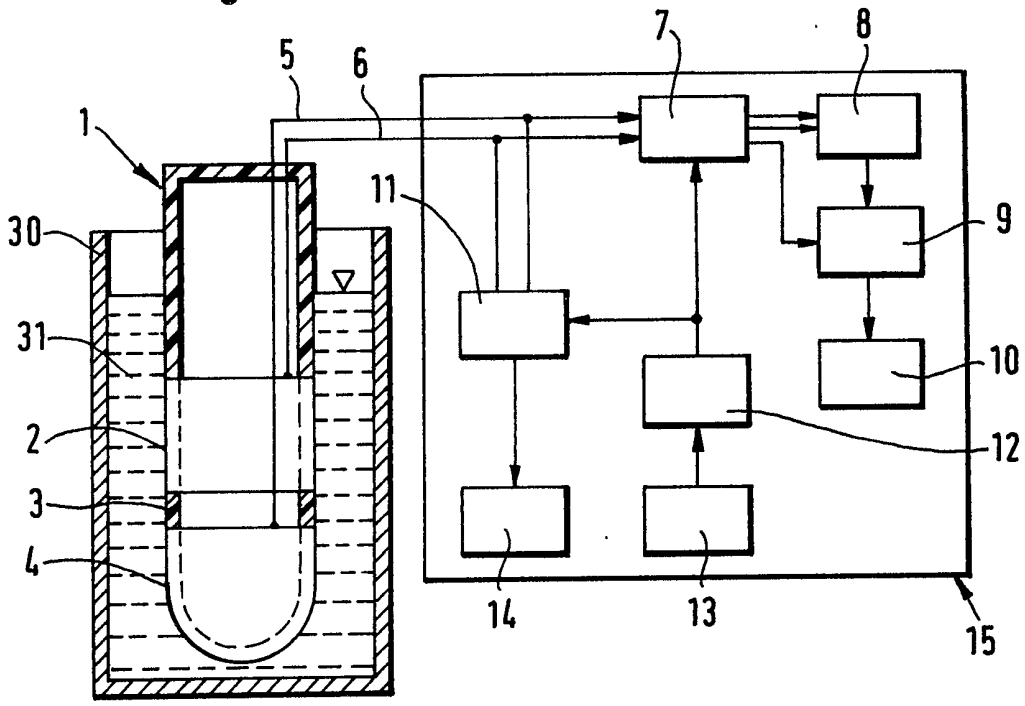
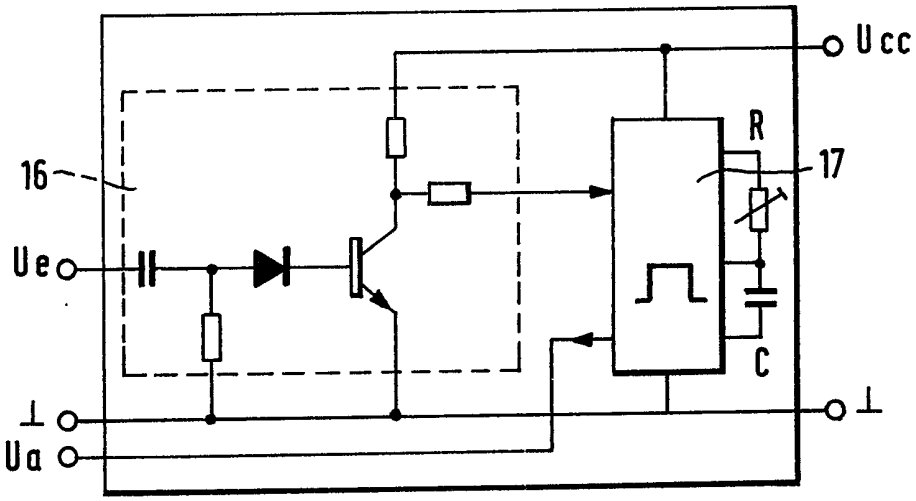


Fig. 2



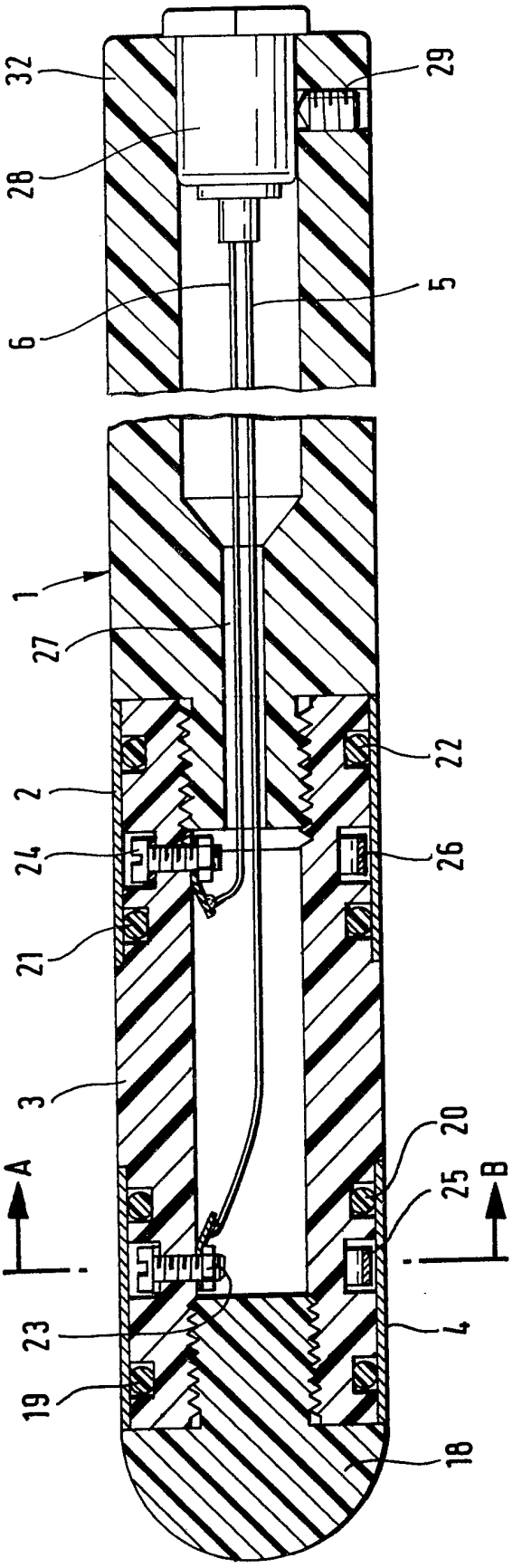


Fig. 3

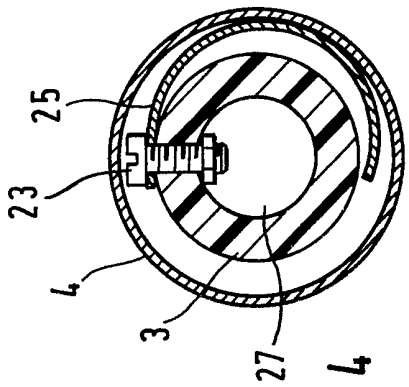


Fig. 4

SPECIFICATION

Redox potential meter

This invention relates to a redox potential meter, more particularly such a meter for measuring the oxidation or reducing characteristics of physiological media.

Meters for determining the redox potentials of aqueous solutions having different reducing and oxidation power, using two electrodes of different metals or of one metal of different valences are known. Their operation is based on the fact that when the electrode combination is immersed into aqueous solutions in which redox reactions take place, potentials occur at the electrode surfaces, their differences being measured and indicated by means of voltmeters. Redox potential measurement has become increasingly significant particularly in physiological applications, e.g. in monitoring redox reactions in the vaginal tract of humans and mammals *in vivo*.

In some electrometric redox potential tests there is a certain importance in detecting and displaying the oxidation and reduction characteristics of the media under examination as a function of time. This requirement applies particularly in the case of media of small solution volume in relation to the redox-active area of the probe electrodes, as for example on insertion *in vivo* (in the vagina).

In many of these applications the actual measuring operation frequently takes place in just a few seconds and for the purpose of better evaluation it was hitherto necessary continuously either to print out or record the measurements, although this necessitates considerable expenditure.

In other cases, redox meters are required in which the measurements are available and can be called on at the transducer output at a specific time after introduction or application of the probe electrodes, or else the measurements are required to be peak values of each individual measuring sequence in order to give reproducible results, while the meters are required to be operated and evaluated by unskilled users. In such cases too, the measuring operation previously had to be either continuously printed out or recorded.

The prior-art redox potential meters are so designed that the redox probe (redox sensor) is connected to the redox meter via a flexible cable plug connection or a permanent cable connection. Meters of this kind are liable to malfunction when used frequently, since the cables readily become faulty due to cable movements at the connections, and tend to break. The same applies to fatigue of plug connections unless very expensive precision plugs are used.

An object of the invention is to show a way of avoiding the above disadvantages of known systems in a meter of the kind referred to hereinbefore, and how the oxidation and reducing characteristics of media under examination can be measured with minimum technical outlay automatically – depending upon the time of introduction of the probe into, or its application to, the medium under examination – from a freely selectable predeterminable time and with a freely selectable measuring duration after introduction or application of the probe, and how the maximum redox potential at any time can be detected during each measuring operation.

Another object of the invention is to provide a redox potential meter of the kind referred to hereinbefore, with which the progress of the measuring operation per unit of time is automatically recognisably established in order that it can be evaluated.

In a redox potential meter of the kind referred to hereinbefore, these objects are achieved according to the invention by the providing that, the transducer is coupled to a parallel circuit consisting of a function unit controlling the indicator unit and a threshold circuit; the threshold circuit triggers a logic signal automatically on detecting a rapid change in a predetermined voltage amplitude detected by the probe electrodes; and the function unit is so controlled by such a logic signal that the redox potential measurements fed through the function unit are transmitted immediately or with a delay to the indicator unit directly or indirectly.

The threshold circuit may, for example, be in the form of a voltage and polarity detector, a window detector (window discriminator), a comparator or a similarly operative device, preceded by a signal processing stage to give an adequate flank slope. The threshold circuit output stage may advantageously be a monostable multivibrator with or without pulse width control or a similarly operative device.

A particularly simple advantageous construction of the threshold circuit is obtained by using an R-C signal processing stage comprising a diode and transistor followed by a monostable multivibrator as the output stage.

The function unit may be constructed as an electronic or opto-electronic series switch, mechanical relay, peak voltage detector (peak voltage store) or instantaneous value store (sample and hold) or a similarly operative device.

If the positive or negative maximum with respect to a predetermined equilibrium rest potential of zero is to be stored and indicated for a specific time during the development of the redox potentials during measurement, the function unit according to the invention may be a peak voltage detector circuit (peak voltage store). Circuits of this kind are known and can be constructed both as inverting and non-inverting circuits. A specific peak voltage detector designed for the specific polarity must be used for each voltage polarity. The storage capacitors of the peak voltage detectors are discharged before each measuring operation by the logic pulse signals of the threshold circuit, before the positive or negative maximum is stored and displayed on the indicator during the progress of the redox potential measurement.

Known selection circuits (blocking circuits), e.g. voltage and polarity detectors, can be used to ensure that positive measurement voltages at the output of the transducer block the peak voltage detector for negative maximum values while negative measurement voltages at the output of the transducer block

the peak voltage detector for positive maximum values.

If required, circuits of this or a similar kind prevent two maximum values of different polarity from being displayed (during the dame measuring operation), since this would result in an unclear redox characteristic without a knowledge of the sequence of the maximum value displays. If, however, the sequence of maximum displays is additionally indicated, as can be achieved by known circuits, there is no need to block the second maximum display at any time.

Adjustment of the pulse width of the logic output signals from the threshold circuit can be used, for example, to control the time at which the peak voltage measurement starts, since the measurement, storage and indication of the redox potentials is not effected until completion of the threshold signal generation and hence after completion of the discharge of the storage capacitors in the peak voltage detector circuits. Interfering potentials which arise as a result of the introduction of the probe into, or its application to, the medium under measurement and which might falsify the result of the measurement are thus able to be eliminated (masked). If a known tendency indicator circuit is connected to the outputs of the peak voltage detectors, optical and/or acoustic signal generators can indicate when the probe and hence the indicator unit have reached their final redox potential value.

If it is required to store and indicate the progress of the redox potential voltage per unit of time during a measurement of the positive or negative potentials with respect to a predetermined (optionally predeterminable) equilibrium rest potential of zero, at a given time after the probe has been introduced into or applied to the medium under measurement, the function unit used according to the invention may be an instantaneous value store. If a logic signal is triggered from the threshold circuit at the time when the probe is introduced into or applied to the medium under measurement and the signal is fed to the control input of the instantaneous value store, its storage capacitor is switched via an electronic switch to the transducer output directly or indirectly for a given calling time (indirect), the duration of which is determined by the logic control signal pulse width, and hence the instantaneous voltage values occurring during this calling period are detected in respect of size and polarity and the last value at any time is stored. The stored measurement is fed to the indicator unit or to further evaluation via a high-impedance amplifier. The voltage values occurring at the transducer output during the calling period are displayed continuously.

If storage of the redox potential values is not required, and yet any falsification of the measurement due to probe intoduction or application effects is to be eliminated, the function unit according to the invention may also be in the form of an electronic or opto-electronic series switch or mechanical relay, the series switch or relay being controlled by the threshold circuit logic output signals.

As already indicated above, the immediate or delayed indication of the measured redox potential values is obtained basically by the preset or freely selectively adjustable duration of the threshold circuit logic output signal.

In another advantageous embodiment of the invention, all the function groups of the meter, such as, for example, the transducer, the potential difference compensator, the threshold circuit, function unit, display unit, any optical and/or acoustic signal generator, controls (switches or buttons), power supply (batteries, transformers, voltage regulators), and the measuring electrode and reference electrode (including any compensating electrodes), are a component part of the probe. The transducer, potential difference compensator, threshold circuit, function unit and, if required, transformer and voltage regulator, may be in the form of a common integrated circuit and be disposed inside the hollow probe; the power supply, signal generators, controls and indicator can be accommodated in the handle part.

The probe may be so constructed that the measuring electrode and the reference electrode, together with any additional compensating electrode, may be replaceable both when the probe and the meter are separate units and when they are integrated, i.e. with the meter in the probe, in other words they can be changed for other electrodes by simple operations.

Embodiments of the invention will now be described with reference to the accompanying drawings, which diagrammatically and in a highly simplified form show at:-

Figure 1 a block schematic view of a redox meter embodying to the invention;

Figure 2 an embodiment of a threshold circuit for controlling the function unit on introduction of the probe into the medium under measurement; and at

Figure 3 one example of a probe for redox measurements in the vaginal tract of humans or mammals.

In Figure 1 of the drawing, the fluid-tight rod-shaped measuring probe 1 is immersed in a vessel 30 containing the aqueous medium 31 under examination. The measuring electrode 4 (metal Me 1) may, for example, be formed from chromium, and the reference electrode 2 (metal Me 2) from platinum or gold; the measuring electrode and the reference electrode may also be formed from metals of different valency. The two electrodes are separated from one another by a highly insulating zone 3, the material of which has minimal liquid absorption characteristics. The arrangement of the electrodes on the measuring probe may be reversed. The measuring probe 4 is connected by a lead 5, and the reference electrode 2 by a lead 6, to a transducer 7, e.g. a differential amplifier, disposed in meter 15, and a potential difference compensator 11, (e.g. a device according to German Patent Application P 33 23.040.4-52). Transducer 7 is coupled to a threshold circuit 8 and a function unit 9 as shown. The control input of the function unit 9 is also connected to the signal output of the threshold circuit 8 and the output of the function unit 9 is connected to the input of an indicator 10. A signal generator 14 connected to the potential difference compensator 11 is in the form of an optical and/or acoustic signal generator and indicates the state of operation or rest of the

potential difference compensator 11.

A power supply 13, which may be a battery, delivers a positive and, if necessary, a negative voltage directly or indirectly via one or more transformers to the active elements described above. An actuating element 12, which may be a switch or button, for switching the instrument on and off is provided.

Figure 2 of the drawing illustrates one embodiment of the threshold circuit 8 in the form of a particularly simple and advantageous construction. The signal treatment stage 16 formed by an R-C network, a diode, and a transistor delivers an adequately steep negative flank at its output (in this embodiment illustrated in highly simplified form) as soon as there is a voltage rise at the output of the transducer 7 on introduction of the probe 1 into the medium 31 under examination (see Figure 1 of the drawing). This negative pulse flank triggers the monostable multivibrator 17 to its operating state, from which it is reset to its inoperative state only after expiry of the time governed by its external R-C circuit.

The duration of the output pulse from the monostable multivibrator 17 may be adjusted over wide limits by means of the variable resistor R or by variation of the capacitance C.

Figure 3 of the drawing illustrates one exemplified embodiment of the redox measuring probe 1 in the vaginal tract of humans or mammals, in which embodiment the measuring electrode 4 and the reference electrode 2 can be replaced very easily. The measuring probe 1 is a three-part moulding made of highly-insulating material and consists of the electrode carrier 3, the probe head 18 – which is preferably rounded at its front end and which has an external screw thread at its rear end – and a handle part 32. A socket 28 for connection of a measuring cable plug is recessed into the rear part of the handle 32. Socket 28 is located, for example, by a grubscrew 29. The handle part 32 tapers at the front end and is externally screwthreaded. The entire measuring probe is internally hollow (interior 27) except for the head 18 (although this can also be made hollow). The front and rear parts of the interior 27 of the electrode carrier 3 are each internally tapped to receive the screwed-in head 18 and handle 32. Six grooves are also recessed into the outer wall of the electrode carrier 3 to receive O-ring seals 19, 20 21 and 22, and screwed solder connections 23 and 24 with leaf springs 25 and 26. The measuring electrode 4 consisting of the metal Me 1 and the reference electrode consisting of the metal Me 2 can be pushed up and down on the electrode carrier 3 after the head and the handle part 32 have been unscrewed subsequent to removal of the socket 28 and separation of the excessive length of the leads 5 and 6 from the socket 28) and are in permanent pressure contact with the associated prestressed leaf springs 25 and 26. The later are in turn connected to the socket 28 via the screwed solder connections 23 and 24 and the over-length leads 5 and 6 in the interior 27 of the probe 1. (For reasons of clarity the over-length of the leads 5 and 6 is not shown in the drawing). The O-rings 19, 20, 21 and 22 prevent the medium under measurement and other liquids from entering the grooves for the leaf springs 25 and 26 and hence also the probe.

In order to give the user of the redox meter an idea of the duration of the measuring operation, the threshold circuit control signal – preferably its end flank – can start a preset or adjustable clock which delivers an optical and/or acoustic signal after expiry of its preset delay.

The end flank (trailing edge) of the threshold circuit control signal can also directly trigger a signal to indicate the final redox value, if the function unit is constructed as an instantaneous value store, with said signal being used, for example, to drive a monostable or bistable multivibrator, to the output of which an optical and/or acoustic signal generator is connected.

In order to indicate the final redox potential value to users of the redox potential meter incorporated in the probe, when the redox potential measurements are carried out in the vagina, the final value signal generator in the tendency indicator circuit in the case of function units having peak voltage detectors, and also the final value signal genertor in the case of function units having instantaneous value stores, may be constructed as a vibrator which briefly sets the probe or parts thereof into gentle but perceptible vibration.

The operation of the device according to the invention is not restricted to redox measurement applications for measuring and indicating positive or negative deviations of redox potentials from a predetermined zero value. The meter may also be so adjusted, by known steps, as to indicate only positive or only negative voltage values which can in turn be converted to comparable redox scale values.

CLAIMS

1. A redox potential meter, more particularly for measuring the oxidation and reducing characteristics of physiological media (e.g. secretions in the vaginal tract of humans or mammals), comprising a measuring electrode and a reference electrode, which are carried by a measuring probe, a transducer connected to the probe electrodes, means for indicating the measured redox potentials, and a potential difference compensator for compensating for any equilibrium rest potential deviations; wherein the transducer is coupled to a parallel circuit consisting of a function unit controlling the indicator unit and a threshold circuit; the threshold circuit triggers a logic signal automaticaly on detecting a rapid change in a predetermined voltage amplitude detected by the probe electrodes; and the function unit is so controlled by such a logic signal that the redox potential measurements fed through the function unit are transmitted immediately or with a delay to the indicator unit directly or indirectly.

2. A meter according to claim 1, wherein the function unit is formed as an electronic series switch, an opto-electronic series switch or as a relay.

3. A meter according to claim 1, wherein the function unit is formed as a peak voltage detector (peak voltage store) for positive and negative vol-

tages.

4. A meter according to claim 1, wherein the function unit is formed as an instantaneous value store.

5. A meter according to any one of claims 1 to 4, wherein all the functional elements of the meter (such as, for example, the transducer, the potential difference compensator, the threshold circuit, function unit, display unit, optical and/or acoustic signal generator, controls, power supply and the measuring electrode and the reference electrode) are part of the probe.

6. A meter according to any one of claims 1 to 5, wherein the measuring electrode and the reference electrode of the probe are replaceable.

7. A meter according to claims 1 and 3, further including a tendency indicator circuit connected to the peak voltage detector output and arranged to trigger an optical and/or acoustic signal when the probe and hence the indicator unit have reached their final redox potential value.

8. A meter according to any one of claims 1 to 5, wherein a preset or adjustable clock is started by the control signal from the threshold circuit, preferably by the end flank of said signal, and after expiry of an adjusted delay the clock generates an optical and/or acoustic signal.

9. A redox potential meter according to claim 1 and as herein described with reference to the accompanying drawings.

Printed in the UK for HMSO, D8818935, 2/85, 7102.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.