Operations Manual

Setup, Installation & Maintenance

Electrode Preparation & Maintenance

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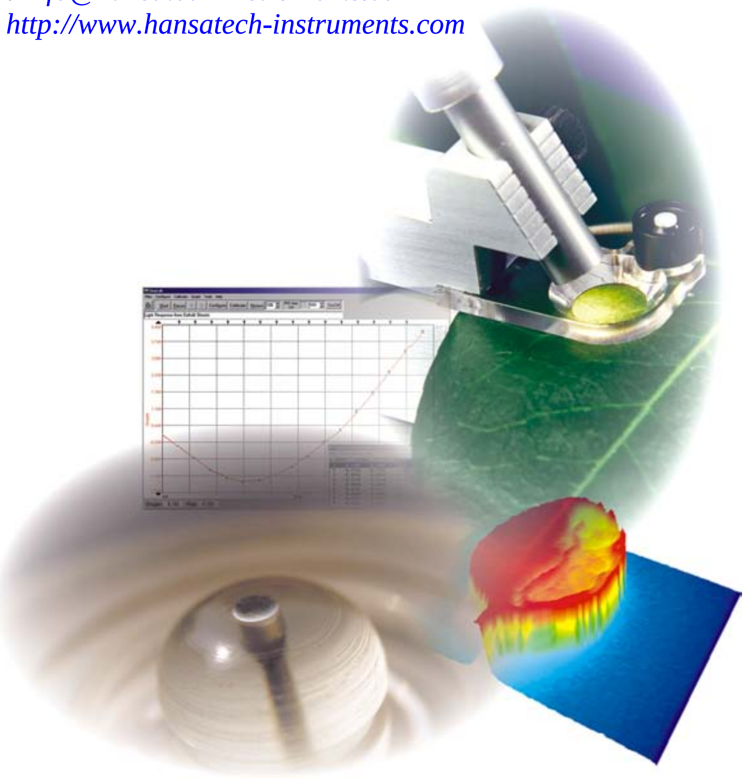

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Preface

This manual is designed to highlight the key features, setup procedures and general maintenance of the S1 Electrode Disc.

Document Conventions

If viewed electronically, blue highlighted text can be clicked in order to link to other parts of this document or to other documents and Internet locations. In order for the external links to be completed, an Internet connection must be established either via a standard or broadband dial-up modem or via a LAN (local area network) connection.

Notice

This instrument must not be used in situations where its failure could result in injury or death.

For applications where failure of this instrument to function correctly would lead to consequential damage, the analyser must be checked for correct operation and calibration at intervals appropriate to the criticality of the situation.

This manual is provided to help you install and operate the equipment. Every effort has been made to ensure that the information contained in this manual is accurate and complete. Hansatech Instruments Ltd does not accept any liability for losses or damages resulting from the use of this information.

Hansatech Instruments Ltd equipment warranty is limited to replacement of defective components, and does not cover injury to persons or property or other consequential damage.

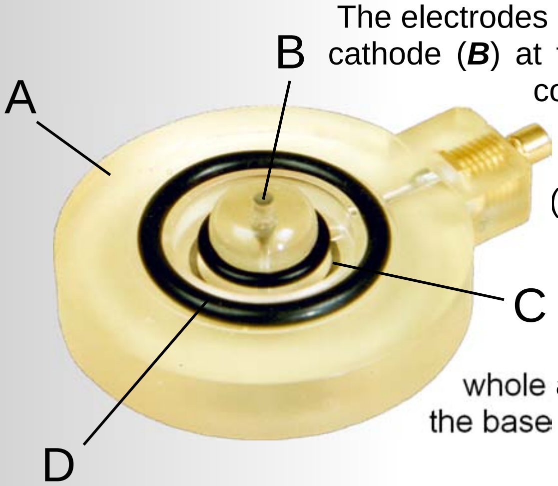
S1 is covered under warranty for one complete year, parts and labour included. This, of course, is provided that the equipment is properly installed, operated and maintained in accordance with written instructions contained within this manual.

The warranty excludes all defects in equipment caused by incorrect installation, operation or maintenance, misuse, alteration, and/or accident.

If for some reason, a fault is covered under warranty, it is the responsibility of the customer to return the goods to Hansatech Instruments Ltd or an authorised agent for repair or replacement of the defective part(s). For service, please contact us at the address at the back of this manual.

Introduction to the S1 Electrode Disc.

The Hansatech Instruments oxygen electrode disc is a specialised form of electrochemical cell known as a Clark type polarographic sensor. It comprises a resin bonded central platinum cathode and a concentric silver anode linked by an electrolytic bridge and continuously polarised by the oxygen electrode control unit.



The electrodes are set into an epoxy resin disc (***A***) with the platinum cathode (***B***) at the centre of a dome surrounded by a well that contains the silver anode (***C***). When set up a uniform electrolyte layer is held over the dome area of the electrode by a paper spacer and P.T.F.E. (polytetrafluoroethylene) membrane which is secured by an O-ring around the dome. The well that houses the anode also serves as a reservoir with electrolyte drawn up to the cathode by the paper spacer acting as a wick. An outer O-ring groove (***D***) surrounds the whole apparatus. The outer O-ring seals the electrodes into the base of an electrode chamber.

Electrode Disc Theory.

The oxygen electrode is a specialised form of electrochemical cell which consists of two electrodes immersed in an electrolyte solution. Typically, a 50% saturated solution of KCl is used in oxygen electrode systems. This is prepared by dissolving 17.5g of anhydrous salt in 100ml of de-ionised water at 25°C. Application of a polarising voltage of 700 mV ionises the electrolyte and initiates current flow via a series of electrochemical reactions. In the case of KCl electrolyte the following reactions occur:

Equation 1.

$$Ag \longrightarrow Ag^+ + e^-$$
$$Ag^+ + Cl^- \longrightarrow AgCl$$

Equation 2.

$$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + OH^-$$
$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

Oxygen is consumed during the electrochemistry, thus the magnitude of the current flow is related to the oxygen concentration of the surrounding media. This type of electrode sensor was first developed by Clark (1956) to measure oxygen in blood samples. As a result it is often referred to as The Clark Electrode.

Operational Principles.

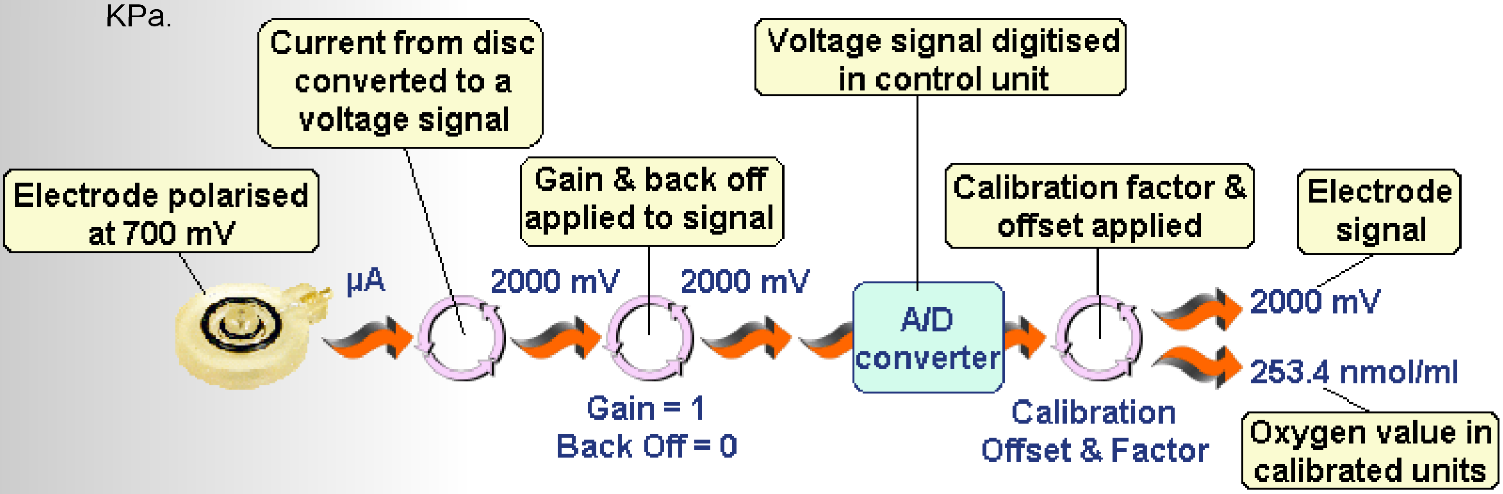
The following explanation are based around an electrode disc which is connected to one of the Hansatech Instruments Ltd PC operated electrode control units. For further details, please refer to the Oxygraph Electrode Control Unit manual (supplied with the Oxygraph Control Unit).

When the disc is correctly prepared and polarised at 700 mV, the nature of the electrochemical reactions at the disc cause a current to flow in the presence of oxygen.

This current is directly proportional to the amount of dissolved oxygen within the sample held in the reaction vessel.

The electronics within the control unit must take the current produced by the electrode disc and convert it into a reproducible unit. Several stages are taken applying various factors to the signal in order to present the signal from the disc as nmol/ml in liquid-phase measurements and µmol RTA (relative to air) in gas-phase measurements.

The diagram below shows the processes undertaken by the control unit in order to present the signal in calibrated units. In this example, the disc is placed in a stirred sample of air-saturated, de-ionised water held at 25°C at a standard atmospheric pressure of 101.72 KPa.



- The current produced by the electrochemical reactions in the presence of oxygen is first converted into a voltage signal. In air-saturated, de-ionised water, the control unit is designed to read approx. 2000 mV (approximately half the range of the instrument).
- Gain and Back Off are applied to the signal at this point. These values are automatically set during the calibration. However, these values always remain at Gain = approx. 1.0 and Back off = 0. In cases where measurements of small changes in oxygen are required, these values may be manually adjusted.
- The voltage signal is then passed through the 12 bit resolution A/D converter where the signal is digitised.
- Once digitised, the calibration offset and factor are applied to the signal allowing the signal to be displayed in the relevant calibrated units.

Electrode Preparation.

Due to the nature of the reactions taking place, the silver anode oxidises slowly with time. This is characterised by a black deposit on the electrode which may impair performance. If this occurs, the electrode should be cleaned. This is best achieved by gentle polishing of the unit using the materials supplied in the S16 ELECTRODE MAINTENANCE KIT or if this is unavailable, by using a suitable polishing paste or fine grade aluminium oxide powder suspended in a drop of de-ionised water placed on a cotton wool bud.

NEVER USE HARSH ABRASIVE AGENTS OR COMMERCIAL METAL POLISHES AS THESE MAY DAMAGE THE RESIN OR IRREVERSIBLY POISON THE CATHODE.

Further detail on cleaning and maintaining the electrode disc can be found in the Electrode Maintenance section.

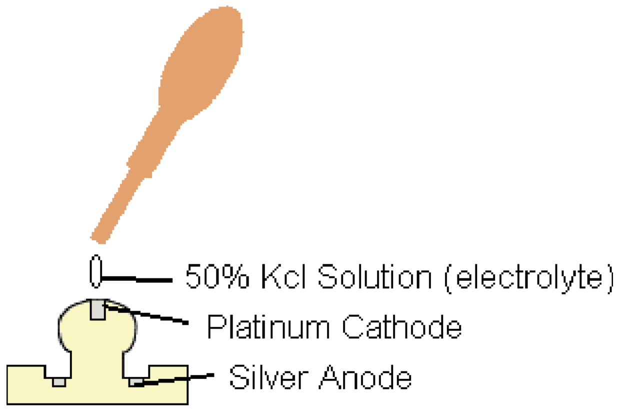
Before use, the electrode disc needs to be prepared in such away that an electrolyte bridge is formed between the anode and cathode in order for current to flow in the presence of oxygen. Various different compositions of electrolyte have been used however, a 50% saturated solution of potassium chloride works well in many different applications. The solubility of the anhydrous salt is 35g per 100g of water at 25°C. Hence the electrolyte solution is easily made by dissolving 17.5g of anhydrous salt in 100 ml of de-ionised water at 25°C.

The disc also requires a protective membrane which will prevent any deposits from the reaction mixture from settling on the cathode yet allow oxygen to diffuse freely so as not to jeopardise response time of the disc.

There are four preparation stages:

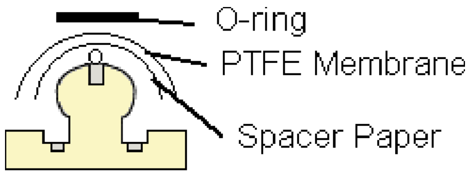
Stage 1.

Place a small drop of electrolyte on top of the dome of the electrode disc.



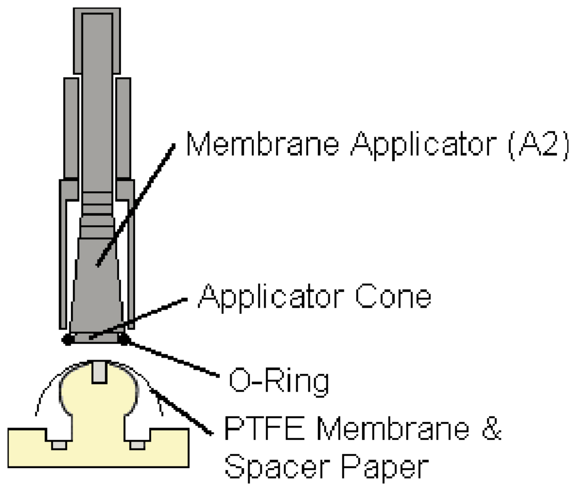
Stage 2.

Place a 1.5 sq. cm paper spacer (cigarette paper works particularly well as it is manufactured to a very tight thickness tolerance) over the electrolyte ensuring that at least one corner of the spacer is in the electrode well to act as a wick. Cover this with a similar sized piece of PTFE membrane.



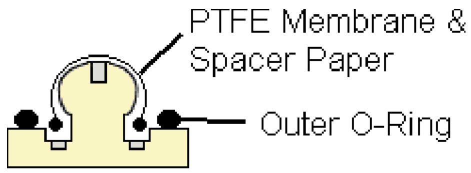
Stage 3.

Place the small electrode disc O-ring over the end of the applicator tool. Hold the applicator vertically over the dome and slide the applicator shaft down to push the O-ring over the dome.



Stage 4.

Check that the membrane preparation is smooth and that there are no trapped air bubbles. Top the reservoir well up with several drops of electrolyte.



It is vital to ensure that the larger O-ring is placed in position on the recess around the electrolyte well. If this second O-ring is not in place when the disc is installed into the electrode chamber, the silver anode will not be sealed from ambient air and measurements may be affected.

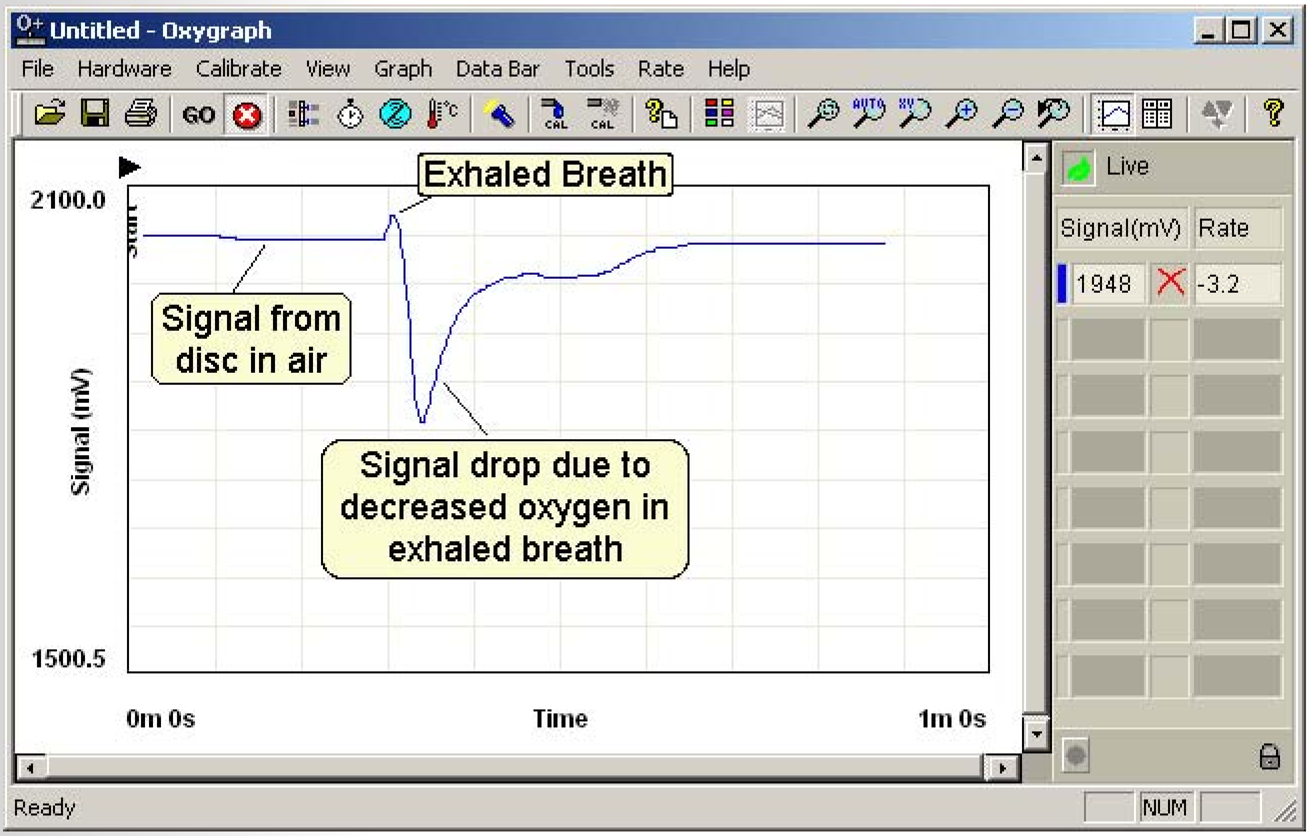
Testing the Response of the Prepared Electrode.

The following section uses Oxygraph Plus software in order to demonstrate the tests for electrode responsiveness. In other systems, the controls may be slightly different, however, the principles of the tests are identical.

Once the electrode disc has been successfully prepared, it is advisable to check the response of the disc prior to mounting the disc within the electrode chamber.

To check the response, connect the electrode disc to the rear of the control unit at the electrode input. Open the recording software and start a recording. The signal will take a few minutes to stabilise. A new or well maintained disc should read approx. 2000 mV in air.

Once stable, breathe exhaled air across the disc and observe the reaction on the graph screen. The signal should be plotted as in the diagram below.



The first deviation in signal after breathing across the disc is induced due to a large increase in temperature of our exhaled breath compared to ambient air temperature. Oxygen electrode discs are particularly sensitive to temperature and will show an increase in signal as a result. Since the temperature increase is only temporary, the oxygen signal will fall after a short time.

After the temperature related signal increase, a steep drop in signal is observed due to decreased oxygen levels in exhaled breath (approx 17%). The signal should the begin to return to the original level as the ambient oxygen begins to equilibrate around the electrode disc.

If the observed signal is not as shown above, it may be caused by an inadequate electrode preparation or worst case, a problem with the disc itself. Try cleaning the disc and re-preparing before repeating the test described above. If problems still occur, please contact Hansatech Instruments.

Once this test has been completed satisfactorily, mount the disc into the base of the electrode chamber. Depending on which measurement phase you are intending to use, different tests may be carried out in order to test the response of the disc *in situ*.

Electrode Disc Cleaning and Maintenance.

Electrode Maintenance.

Periodic maintenance is required if you are to maintain your electrode in good condition. It should be cleaned after use and before prolonged storage. It is particularly important that the electrode is never left to dry out with electrolyte in place, as crystallisation of electrolyte may cause the platinum/epoxy resin seal to be breached and crystalline electrolyte to be deposited around the cathode. If this occurs, the electrode will become rapidly unserviceable and will require replacement.

Cleaning is best achieved by following the procedure outlined below. (An electrode maintenance kit -ordering code S16- containing the items described is available. Please contact Hansatech Instruments for further details).

Cleaning Procedure.

It is important to use the correct polishing agent as harsh abrasive substances will damage the resin in which the electrodes are set. It should also be noted that many commercial metal polishes contain ammonia or solvents which may cause irreversible poisoning of the platinum cathode.

Silver Anode.

The silver electrode (anode) is subject to electrochemical deposition of chloride and oxide salts during use. This typically manifests as a brown/black deposit which forms on the surface of the Silver. Whilst deposition of small amounts of brown Silver Chloride is normal and desirable, excessive deposits or deposits of black oxides will cause a rapid deterioration in electrode performance and may result in lower signal levels, signal drift and increased signal noise.

Select a small cotton bud from the maintenance kit. Cotton buds vary a little in size, so check to see that the diameter of the cotton bud will allow it to be fully inserted into the well of the electrode, thus allowing contact with the silver electrode in the base of the well. If the bud is a little large, carefully reduce the size of the cotton bud by removing a layer of cotton wool from the tip until the bud will fit the well. Moisten the bud with a little distilled water.

Apply a small amount of either the Rapid Hansatech Polishing paste (revised cleaning kits supplied from 01/10/01) or the No. 1 Coarse Hansatech Polishing paste (supplied in earlier cleaning kits with Coarse and Fine pastes) to the tip of the bud.

Insert the bud into the well of the electrode and gripping the bud just above the tip, apply moderate pressure and gently rotate the bud around the electrode well in a circular motion 6 - 10 times. Observe the Silver anode. Continue to gently polish the silver electrode until all brown or black deposits on the surface of the silver are removed and the surface of the silver is highly polished.

Platinum Cathode.

The platinum cathode is not subject to such deposition and all that is necessary is to maintain a scratch-free highly polished finish using the procedure outlined below.

Apply a small amount of the Rapid Hansatech Polishing paste (revised cleaning kits supplied from 01/10/01) or the No. 2 Fine Hansatech Polishing paste (earlier 2 part cleaning kits with Coarse and Fine pastes) to the unused end of the cotton bud moistened with a little distilled water , or if preferred to a small piece of moist cotton wool. Now, using a circular motion, gently polish the platinum cathode located in the centre of the electrode dome.

It is important to restrict the polishing motion to the platinum and avoid as much as possible contact with the epoxy resin surrounding the platinum.

Excessive polishing of the cathode area is to be avoided as this will eventually lead to a change of curvature of the electrode dome, which will result in deterioration of electrode performance. When finished, the platinum cathode should have a “mirror finish”.

If the surface of the platinum has become scratched, repeat the above procedure using the Rapid Hansatech Polishing paste (revised cleaning kits supplied from 01/10/01) or first using the No. 1 Coarse Hansatech Polishing paste, followed by the No. 2 Fine Polishing paste (earlier 2 part cleaning kits with Coarse and Fine pastes).

Rinsing and Drying.

Once the electrodes have been satisfactorily cleaned, it is important to remove all traces of the polishing paste from the electrode surfaces by rinsing the electrode with a small volume of distilled water whilst gently scrubbing these areas with a soft bristled brush. (A toothbrush is ideal). Avoid wetting the electrical connector of the disc during this procedure. Dry the electrode thoroughly using paper towel.

Storage.

Store the electrode, when not in use, in an air-tight vessel containing a desiccant such as Silica gel. Periodically replace or rejuvenate the desiccant.

The Importance of Good Electrode Maintenance.

Although the oxygen electrode disc is one of the smallest components of an oxygen measurement system, it is the most crucial component of the system. Therefore, maintaining the disc to a high standard is extremely important.

A significant proportion of technical support requests received by Hansatech Instruments Ltd relate to oxygen electrode disc performance. Of these requests, the vast majority are the result of failure to comply with recommended working practices and maintenance procedures. Some of the more common abuses of electrode discs include:

Failure to Maintain Electrode Disc.

If the electrode disc is not maintained, deposits of silver chloride (soft brown deposit) and/ or silver oxide (hard black deposit) will build up on the silver ring (anode) of the disc. The formation of silver chloride is normal and desirable in small quantities as it improves the stability of the sensor. It is easily removed by cleaning and will reform when the electrode is next polarised. By contrast, deposits of black silver oxide are to be avoided. Silver oxide is an electrical insulator and its formation will reduce the available surface area of the silver anode and result in a dramatic reduction or complete loss of electrode signal. The electrode disc should be maintained in accordance with our recommended procedure. Please refer to the Cleaning and Maintenance section.

This image shows a typical case of poor maintenance. The disc has not been cleaned after use and was not stored in a sealed container with desiccant away from strong sunlight. As a consequence, the epoxy resin has become prematurely discoloured due to a combination of strong sunlight and absorption of moisture from the environment. The silver anode is almost entirely covered with a deposit of black silver oxide. The platinum stud and dome are both dirty and badly scratched. This will cause an uneven layer of electrolyte beneath the membrane during measurement leading to un-stable and un-responsive signals. This disc is beyond economic repair.

In contrast, this disc has been maintained according to our recommendations and has been stored correctly in an air tight container with desiccant. The epoxy resin is clear, the silver anode is smooth and polished and the platinum cathode is scratch free. The area of the electrode dome surrounding the cathode is also free from abrasions and pits across the entire surface. An electrode disc, when kept in this kind of condition will provide years of high quality measurements.

Disc is Left to Dry Out After Use.

After use, the electrode disc should be stripped down, cleaned carefully and stored in a dry, air-tight container. If the disc is simply left, electrolyte will crystallise under the membrane and may cause irreversible damage to the electrode. The length of time that an electrode can be left prepared will depend upon local circumstances such as temperature and air flow through the laboratory. In general terms, we would recommend leaving a prepared electrode disc in a liquid-phase measurement system with stirred air-saturated water in the chamber overnight. The electrode disc can be kept polarised or switched off and re-polarised the next day dependant upon local working practices and user experience. In gas-phase measurements, the electrode is likely to dry out more rapidly and we would recommend stripping down and cleaning the electrode after each measurement day.

The KCl electrolyte dries out quickly in air and begins to crystallise. KCl is quite aggressive and will, by capillary attraction, deposit in any minor crevice. If the electrode is left to dry out several times, it is possible that the KCl will finally break down the seal between either of the metal electrodes and the epoxy resin surround and seep into the fissure formed where it will crystallise to further expand the fissure. This is most likely to occur between the platinum cathode and epoxy resin dome and regrettably will cause most damage at this point. Damage to the electrode can be observed under low power microscopy (x10 magnification) as a broad white collar around the neck of the platinum as shown in the image left. The effect of this will be to cause instability and drift of the electrode signal and a large increase in the level of electrical signal observed in zero oxygen (residual current). This will have the effect of reducing the ability of the electrode to measure small changes in oxygen flux and will eventually render the electrode unserviceable and beyond economic repair. The disc will require replacement.

Cleaning with Unsuitable Materials.

Hansatech Instruments Ltd offer the S16 cleaning kit for maintenance of the oxygen electrode disc. The kit contains special cleaning pastes which are recommended for optimal electrode performance. In the absence of this kit, users have resorted to cleaning the electrode with various abrasive compounds including commercial metal polishes or smoker's toothpastes etc. We would caution against the use of inappropriate materials as they may cause irreversible damage to the electrode. Some metal polishes are harmful to the disc as they can contain an ammonia base or solvent additive. These substances can cause irreversible poisoning to the platinum cathode and could also cause significant damage to the epoxy resin. Excessive cleaning with abrasive substances can badly scratch and alter the profile of the electrode dome which may cause an uneven layer of electrolyte across the cathode leading to instability, drift and lack of responsiveness of the oxygen signal.

The S16 electrode cleaning kit is supplied with all Oxygraph and Oxytherm Systems and can also be obtained by contacting us directly. Details of the cleaning procedure can be found in the Cleaning and Maintenance section.

Support Information.

Purchasers of Hansatech Instruments Ltd products can be assured of ongoing support and prompt and efficient attention to enquiries at all times.

All products supplied by Hansatech Instruments are guaranteed for 12 months from the time of despatch against manufacturing faults or defective materials. The guarantee does not cover damage caused by misuse or unauthorised attempts to repair.

If difficulties are experienced with the equipment, please contact Hansatech Instruments for advice. If necessary, equipment may be returned for repair/replacement during the warranty period. No charge will be made for parts/labour under warranty but we reserve the right to charge for customs clearance and return carriage if appropriate.

For repairs outside of the warranty period, please contact us at the address below for an estimate of cost and instructions regarding the return of equipment.

If the product was purchased via a distributor, please contact them for advice in the first instance.

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