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Care, Maintenance and Fault Diagnosis for pH Electrodes

A REAGECON TECHNICAL PAPER

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Abstract

Analysts frequently encounter pH measurement problems caused by poor electrode performance. Diagnosis and rectification of these problems can be time consuming, leading to poor analytical results and inefficient use of analysts time. The diagnosis of many individual pH electrode faults has previously been published but a complete, straightforward regime that diagnoses all common electrode faults has never been reported in the scientific literature. This paper presents a unique, comprehensive, easy to follow regime, which can be used to identify and rectify electrode faults. As many common faults can be prevented through adequate care and maintenance the paper also describes the correct care and maintenance steps required to prevent the occurrence of these problems. Adopting the guidance given in this paper will allow analysts to achieve high quality pH measurements and reduced incidence of poor performance of their pH measurement system.

1 Introduction

pH measurement is an important analytical technique which is used on a daily basis in a wide range of applications. Decisions made based on these results can have wide ranging consequences in such areas as food safety, product integrity, health or environmental protection. It is important for analysts to have full confidence in the quality of their measurements to ensure that the decisions made based on these decisions are correct. Poor quality pH measurements will also generate additional demands on analysts' time and budgets through the need to question results.

There are many factors that can have adverse effects on the accuracy of pH measurement, one of these being the correct care and maintenance of pH electrodes. Improper care and maintenance of pH electrodes will result in reduced electrode life span, and increased testing costs. The effort involved in proper care and maintenance of pH electrodes will repay itself in prolonged lifetime and optimal response characteristics, thus giving the user full confidence in their pH measurement results.

Occasionally problems are encountered when performing pH measurements. In such an instance it is necessary to identify the cause of the fault and takes suitable action to eliminate it. This paper outlines a comprehensive and structured scheme for the systematic trouble shooting of pH measurement faults. If an unsatisfactory response is observed the user can follow these steps to identify the cause of the fault in their pH measuring system. Once the cause of the problem has been identified, the analyst

can then take the appropriate measures to rectify the problem and to prevent its recurrence.

2 Care & Maintenance of pH electrodes

To ensure accurate and reliable analytical measurements, a routine care and maintenance regime should be adopted. In addition to giving the correct measurement result, correct care and maintenance of pH electrodes will result in improved electrode performance and prolonged working life. It also reduces the necessity for corrective intervention, thus saving time and money.

2.1 Care prior to use

It is important to handle pH electrodes carefully to avoid damage to the glass membrane. Upon receipt, it should be carefully unpacked and connected to the pH meter. To comply with good laboratory practice, only electrodes supplied with a certificate of quality should be used. The certificate should be retained to provide traceability through the lot number of the electrode and filed for quality assurance purposes.

Prior to first measurement, the electrode should be gently shaken down in the manner of a fever thermometer to dislodge any air bubbles, which may have settled within the electrode⁽¹⁾. For liquid-filled electrodes the fill hole aperture should be open to the atmosphere during measurement⁽¹⁾ to allow pressure to equalise (this does not apply to gel-filled electrodes). The electrode should be well supported, ideally in an electrode support stand.

2.2 Care in Use

During use the following points should be borne in mind:

- Electrodes should be calibrated using two buffers that bracket the expected value of the sample. Calibration should be performed on a daily basis or more frequently if sample throughput is high.
- Stirring the sample during measurement is recommended but is not essential. The same procedure must be followed for both calibration and pH measurement⁽²⁾.
- The meter's drift control function should be enabled, alternatively, the time for the pH value to stabilise should be standardised.
- The electrode should be rinsed with a wash bottle of purified water between measurements. Do not rub the electrode with tissue paper as this induces static charges, which results in drift⁽³⁾.
- Keep the electrical parts of the electrode (the cable and connector) dry at all times.
- After the measurement has been completed, remove the electrode from the sample. For short-term storage, suspend the electrode in a pH 4 buffer or for longer term (e.g. overnight) in specially formulated electrode storage solution - this will ensure the electrode is kept in an optimum condition for rapid response times and to prolong its lifespan.

The essential point in taking measurements is that the sequence of activities should be consistent from sample to sample and for calibration.

2.3 Care in Storage

It is important that the sensing membrane is kept wet at all times and therefore electrodes are supplied with a storage device, which contains a small amount of electrode storage solution. This device together with the electrode box should be reserved for long-term storage.

2.4 Preventative Maintenance

The implementation of a preventative maintenance program for pH electrodes can result in substantial savings in terms of wasted reagents and time. During use, electrodes can suffer from contamination to the membrane and diaphragm, which will result in measurement errors or slow response. Adoption of a regular preventative maintenance regime will help reduce or eliminate such errors thus providing confidence in the accuracy of any pH measurements made with these electrodes.

The exact details of the appropriate maintenance steps to be taken will depend on the nature of the samples being measured. Table 1 outlines various chemical remediation steps that may be undertaken as either a preventative or corrective action to restore a poorly functioning electrode.

Problem	Solution	Treatment
Protein (e.g. dairy products, foodstuffs etc.)	1% Pepsin in 0.1 mol/l HCl	Soak for 8 hours. Rinse with purified distilled or deionised water and calibrate.
Sulphides (e.g. from albuminoids, wines etc.) (Evident by a blackened diaphragm)	7.5% Thiourea in 0.1 mol/l HCl	Soak until discolouration is removed. Rinse with distilled or deionised water and calibrate.
Oily liquids and fats (e.g. butter, greases, petroleum products, effluents etc.)	Ethanol (or acetone)	Soak a tissue with solvent and rub the electrode until clean. Immerse in 3 mol/l KCl for 1 hour. Rinse with distilled or deionised water and calibrate.
Limescale	0.1 mol/l HCl	Soak for 15 minutes. Rinse with distilled or deionised water and calibrate.
Electrode membrane allowed to dry out	3 mol/l KCl	Immerse for 8 hours. Rinse with distilled or deionised water and calibrate.
Test solution diffused into the electrode (this may be evident as discolouration or cloudiness in the electrolyte)	Use correct electrolyte filling solution appropriate to the electrode e.g. 3 mol/l KCl or non-aqueous filling solution	Empty the contaminated electrolyte and refill with fresh electrolyte. Rinse with distilled or deionised water and calibrate.

Table 1: Preventative maintenance actions

3 Fault Diagnosis:

There are three major components to a pH measuring system:

- the meter
- the solutions (calibration solutions and samples)
- the electrodes.

Any of these components can cause measurement errors, the identification of which can prove to be challenging to an analyst. By adopting a systematic approach to trouble shooting the cause of the error can be readily identified. Once the fault has been identified, appropriate remedial action can be taken to eliminate the error and to help prevent its recurrence.

3.1 Meter Faults

The pH meter is generally least likely to cause trouble, however it is always possible that an instrument fault can occur. Routine calibration with an electrode using certified pH buffers will not conclusively reveal that there is a fault with the meter, as any observed error could be contributed to by the other components in the measurement system. A thorough investigation of a pH meter involves the use of specialised equipment, an option which is not readily available to most users.

For this reason it is recommended that an annual calibration be performed on the instrument. This involves the checking of each of the instrument's function to ensure that they conform to the manufacturer's specifications. It includes the use of certified, traceable electrical simulators and standards

to verify that the instrument is processing all input signals correctly.

3.2 Electrode Faults

3.2.1 Fault Identification

Before beginning any investigation work, always check the following:

- The electrode is connected to the meter and the meter is switched on.
- The electrode connector is plugged into the correct channel on the meter (for multiple input meters)
- The electrode cable and connectors are clean, dry and corrosion free
- The temperature probe is properly connected or the correct temperature is entered manually

To determine if the electrode is the source of the fault, proceed as follows:

- Switch the meter to the millivolt mode (mV) and place the electrode in fresh pH 7 buffer. Allow the electrode to stabilise and note the potential in millivolts.
- Remove the electrode from pH 7 buffer, rinse with purified water and then with pH 4 buffer. Place in fresh pH 4 buffer, allow the electrode to stabilise and observe the potential after one minute and after two minutes.
- From the above readings calculate the Fault Diagnosis Parameters outlined in Table 2.
- Compare the values obtained against those in Table 3 to identify the cause of the fault

Parameter	Calculation	Optimum value
Asymmetry potential (E _o)	mV reading in pH 7.00 buffer	± 25 mV
Slope	mV reading in pH 7.00 buffer - mV reading in pH 4.00 buffer	160 – 180 mV
Drift	mV reading in pH 4.00 buffer (1 min) – mV reading in pH 4.00 buffer (2 min)	± 1.5 mV

Table 2: Fault Diagnosis Parameters

Fault Class	Cause	E _o (mV)	Slope (mV)	Drift (mV)
Electrode OK	Electrode and meter OK, problem with sample	± 25	160 - 180	± 1.5
Terminal Electrode Fault	Glass membrane cracked	55-65	<10	± 1.5
	Reference element poisoned	>±25	160 – 180	>±1.5
	Cable/electrical damage: short circuit	± 25	<10	± 1.5
	Aged membrane/old electrode	± 25	50-150	± 1.5
	Cable/electrical damage: open circuit	>±25	<10	>±1.5
Electrolyte Problem	Wrong or contaminated electrolyte	>±25	160 – 180	± 1.5
Soiled Electrode	Membrane/diaphragm coated with sample deposits	>±25	50-150	>±1.5
	Diaphragm blocked	± 25	160 - 180	>±1.5

Table 3: Identification of common pH electrode faults

3.2.2 Fault Remediation

For Terminal Electrode Faults, the only course of action is to replace the electrode, but there will have been a time saving in the rapid identification of such problems. A high incidence of Terminal Faults indicates that either inadequate electrode care is being carried out or that the electrodes used are not suitable for their application. For other Fault Classes, the following actions can be taken to rectify the problem:

- Electrode OK: If the results obtained for E_o, slope and drift are within the acceptable ranges the meter and electrode are functioning correctly – the problem lies with the sample. Refer to section 3.3 for more details.
- Electrolyte Problem: It is important to use the correct electrolyte solution for the type of electrode being used, as different electrodes require different electrolytes. If the incorrect electrolyte solution is used, measurement errors will result. In addition, during use the electrolyte can become contaminated due to ingress of sample through the diaphragm. To determine the correct electrolyte solution, refer to the manufacturers instructions for the specific electrode under investigation. Gel filled electrodes cannot be refilled and thus must be replaced.
- Soiled Electrode: These faults can result from poor care and maintenance of the electrode or from chemical attack by the sample. Perform the appropriate cleaning regime as outlined in section 2.4 to rectify the problem and instigate a regular preventative Care and Maintenance regime to prevent the recurrence of this fault.

It is good working practice to routinely measure and record the asymmetry potential (E_o) and slope in a control chart. This will give trend data on the

electrode's performance and may therefore provide early warning of a potential malfunction.

3.3 Sample Problems

Having completed the above checks, the electrode may still be showing drift or exhibiting erratic readings. The problem is almost certainly due to an inappropriate selection of electrode for the intended application.

The following are typical examples:

- Highly concentrated mineral type samples, which have a high concentration of dissociated ions can cause a phenomenon known as “liquid junction potential error” due to different ion mobilities. In this case, a specialised electrode with a double junction is recommended⁽⁴⁾.
- Low ionic strength samples such as pure water, rain water or soft water can lead to erratic readings and severe drift. In this case an electrode with a low resistance membrane and a diaphragm that facilitates a high outflow of electrolyte is required to minimise the liquid junction potential⁽⁵⁾.
- Samples that contain high concentrations of mercury, silver, lead, copper or other heavy metals such as those found in plating baths can cause irreversible diaphragm blockage, with conventional combined pH electrodes. In this instance an electrode with a free flowing diaphragm is recommended especially one where the diaphragm can be removed for easy cleaning⁽⁵⁾.

Reference should be made to electrode manufacturers documentation to try and select the best electrode for the application in question. In some instances the most suitable electrode may only be found empirically.

4 Conclusion

pH measurement is a common and important analytical tool in the modern laboratory. To ensure accurate results pH electrodes must be maintained in good working order. The implementation of a good care and maintenance regime will repay the time and effort involved in terms of improved working life for the electrode and more importantly, an improvement in the accuracy of pH measurement. It will also help to prevent the occurrence of possible problems in the future. Should a problem arise the application of a simple systematic approach to fault diagnosis has been devised by the authors to help determine the cause of the problem. Suitable steps can then be taken to eliminate the fault and prevent its possible recurrence

5 References

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Biographical Notes:

John J Barron is Managing and Technical Director of Reagecon Diagnostics Limited. The company, which was founded in 1986, is the largest producer worldwide of Conductivity Standards and is also a major producer of other chemical standards. Mr. Barron is an expert in several areas of analytical chemistry, including electrochemical analysis, good laboratory practice (GLP) and chemical metrology. He has written and lectured extensively and is credited with several scientific discoveries including stable low level conductivity standards.

Colin Ashton has worked in the Reagecon group since 1994 and is currently Head of the Chemical Metrology Department. A graduate of the University of Southampton, he has developed particular expertise in the development, stabilisation, manufacture and validation of cation, anion and electrochemical standards. He has particular scientific interest in all aspects of on line chemical analysis and has lectured and published on several areas of this field.

Leo Geary has worked for Reagecon Diagnostics Ltd. since 1998 and is currently the Senior Chemist in the Technical Services Department. In this role, he is involved in the provision of technical support for the complete Reagecon product range to customers to enable them to achieve high quality analytical results. This includes the provision of a traceable calibration and requalification service for all electrochemistry instruments.

This paper was presented as a poster at the 57th Annual Meeting of the International Society of Electrochemistry, which was held in Edinburgh in September, 2006. It forms part of a comprehensive series of papers that the authors have written covering all of the practical requirements for accurate electrochemistry measurement. These papers are available via Reagecon's website at www.reagecon.com.

Acknowledgements

The authors wish to extend their gratitude to Ms V. Byrne for her assistance in compiling this paper and Ms R. Cooney for proofing this paper. The authors wish to thank all of their colleagues who have provided technical assistance in compiling Reagecon's series of pH measurement papers.

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