| CALIBRATION OF TESTING APPARATUS | EXP 61 |
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The reliability and accuracy of apparatus readings depend on a number of factors, including their calibration and maintenance.

Read the technical documentation provided with the apparatus in order to familiarise yourself with the features of each piece of equipment.

## 1) pH-meter

### a) Calibration

- Zero calibration (sometimes called ∆pH) : buffer solution at pH 7.
- Slope calibration : buffer solution at pH 4 or pH 10.
- Rinse and mop up the excess water on the electrode between the two buffers.

We recommend the occasional use of a reference buffer for calibrating the slope in the range of the pH being tested (acid : pH 4, base : pH 10), but is should be noted that base buffers are not very stable.

The frequency of calibration depends on the expected accuracy : in normal operating conditions, weekly calibration is sufficient.

Since the electrode slope varies according to temperature, steps must be taken to have the same temperature between the calibration buffers and the solution being tested, failing temperature adjustment or automatic compensation.

### b) Maintenance

*Cleaning probes* :

Aside from tap water cleaning during normal operation, it may be necessary to take more efficient defouling measures :

- Scale formation : hydrochloric acid at 10%;
- fatty substances : detergent or soda diluted to approx. 5%;
- Hydroxides, suspended solids : water

Proteins in effluents from the farm-produce industries can clog the diaphragm. In this event, the electrode must be immersed in a mixture of HCI and pepsin.

These proteins may be destroyed by producing sulphides though biodegradation.

A black diaphragm indicates the onset of reference electrode poisoning by the sulphides. If the diaphragm is the only element affected, the reference electrode can be treated with thiocarbamide in order to obtain a stable reference voltage.

A sensing electrode with an excessive loss of sensitivity can be reactivated in hydrofluoric acid at 1% for 1 minute. This is exceptional shock treatment, as hydrofluoric acid, even at 1%, is a dangerous substance and a glass electrode would not withstand it for long. Re-moisten the electrode by soaking it in water for 24 hours.

*Question :*

*Probe or measuring apparatus ?*

This can be answered by disconnecting the probe from the housing and using a bit of wire (paper clip) to short-circuit both terminals of the apparatus' coaxial connector. Zero adjustment should then be possible.

*Trouble shooting :*

- The glass electrode may be cracked.

- The filling liquid may be soiled; there may be an air bubble.

- A scale overshoot (pH - 1 or + 14, for instance) often means a severed cable, or faulty plugs or sockets. In this case the apparatus measures all ambient electric energy around the severed area.

  Unstable display may be caused by a missing or contaminated electrolyte : change the filling liquid, contact the manufacturer to obtain its exact make-up (generally KCI 1, 2 moles/saturated litre for temperatures varying between O and 60°C).

  Slow electrode reactions or a low accuracy rate in the readings may be due to dry storage of the electrode. Re-moisten the glass membrane by soaking it in plain water for 24 hours.

## 2) CONDUCTIVITY METER

### a) Calibration

***Zero calibration*** (if necessary : recently developed apparatus no longer require this adjustment) ; keep the probe out of water or place a switch on a few instruments in a certain position.

***Slope calibration*** :

Standard solutions of KCl 1 ; 0,1 ; 0,01 ; 0,001 moles/litre have a conductivity which varies according to temperature. The NF T90-111 standard provides a corrective coefficient chart.

These standard solutions can be prepared or bought ready-to-use from the manufacturer. It is recommended to use only part of the contents for calibration and through the solution away after use.

Once the range switch has been turned to the « measuring » position, place the cell in a solution with known conductivity and temperature values. Using the calibration potentiometer, bring the needle to the indicated value.

It is best to calibrate to 20 or 25°C in order to use theoretical standard values, since it is tricky pinpointing conductivity at other temperatures by simple extrapolation.

### b) Concentration in dissolved electrolytes

A solution’s conductivity depends on its concentration of dissolved electrolytes.

Measuring concentration by means of conductivity must be done after calibration using a corrective coefficient chart because the function is not linear. Furthermore, each electrolyte has a different mobility, which makes it difficult to obtain quantitative results for mixtures. In this event, conductivity essentially indicates the nature of the pollution and facilitates comparison (monitoring accidental pollution at the outlet of a treatment plant).

### c) Maintenance

Check the state of the electrodes (furring and other scale formations tend to diminish the cell’s sensitivity).

The electrodes must be cleaned with tap water, by soaking in hydrochloric acid at 10%, or with detergent.

They must be stored in distilled water to prevent algae from developing.

*Trouble-shooting :*

When exposed to the open air or disconnected, the probe must indicate nil (infinite resistance).

Some manufacturers make it possible for the user to restore the platinum deposit on the electrode when its surface has been damaged.

## 3) CHLORINE TESTER

### a) Calibration

***Electrical zero*** : by flushing water through a dechlorinating filter (active charcoal), the chlorine count at the outlet will be nil. It is thus possible to calibrate in the original environment, whereas the use of distilled water would cause discrepancies due to the differences in conductivity and temperature.

***Slope*** : on the basis of successive colorimetric tests to determine the chlorine content of the water entering the apparatus, calibrate the apparatus using the average of the obtained results.

**N.B.** this type of sensor picks up all types of oxidiser, so be careful to measure the appropriate elements.

A high chloramine count can also affect the measurement : monitor the pH4 buffer supply.

### b) Maintenance

***Sensor*** :

The electrochemical device (ammeter) requires clean electrode surfaces. Make sure that the reaction tank is constantly stocked with self-cleaning devices (sand, beads, plastics, etc.).

Monitor the level and if necessary top up the pH 4 buffer reagent and iodine tanks if these have been supplied by the manufacturer.

In the event of a shut-down, albeit short, it is recommended that the sensor’s water supply be maintained so that the electrodes are constantly immersed and cleaned.

***Trouble-shooting***

The oxidation of copper electrodes can lead to their replacement in the relatively long term.

It should be noted that these apparatus are usually set up permanently for testing or adjustment purposes.

*Probe or housing ?*

When the electrodes are out of water and dried, the reading must be nil.

## 4) r<u>H-meter</u>

### a) Calibration

As the sensing electrode’s features remain consistent with time and temperature, slope adjustment or compensation should not be necessary.

***<u>Note</u>***

The cleaning system (mechanical, abrasive or chemical) must be chosen in accordance with the type of scaling. After chemical cleaning, leave the probe immersed for an hour.

In the laboratory, check for complete cleanliness of the metal electrode by scratching it with a fingernail or a very fine abrasive (sometimes supplied with the probe).

The Redox potential varies according to the pH (ions $H^+$) ; for this reason, the pH must be the same in the case of comparative readings.

It is not necessary to store sensing electrodes in water.

### b) <u>Maintenance</u>

The bonding of oxygen or hydrogen to the electrodes during measurement sometimes results in very long response times.

Manufacturers provide means to combat these problems by mechanical cleaning or by passing alternate current between two tips of a noble metal.

Cleaning of the reference electrode is subject to the same rules governing the pH-meter.

*Trouble-shooting*

*Probe or housing ?*

The same procedure can be used as with the pH-meter but in addition, a pH probe is able to react to $H^+$ ions. For testing purposes the probe can be placed in buffers with pH 4 and 10. The reading, without necessarily being valid, will tend towards the pH of the solution.

## 5) OXIMETER

### a) Calibration

***Zero calibration*** (if necessary).

This is done by immersing the electrode in a saturated sulphite solution (zero $mgO_2$). Put sufficient quantities of sulphite in the phial to obtain a solid deposit which will a long period of preservation by keeping the phial sealed.

***Slope calibration*** :

For ground measurements, open-air calibration is sufficient (100% dissolved oxygen).

The temperature at which the quantity of dissolved oxygen at saturation point must be read is given by the probe.

Once the probe has been placed in the test tank a few minutes previously, take the water temperature by turning the measuring switch to the appropriate position.

An approximate value is given by the temperature/oxygen saturation matching charts included in the user manuals or by the following equation :

$$\mathrm{mgO_2} = \frac{528}{35 + \mathrm{T°C}}$$

Some manufacturers have built a function into their apparatus making it possible to directly read the value of the saturation in question, depending on the temperature of the sensor.

To avoid a temperature variation during open-air calibration, it is sometimes advisable to place everything in water. In this way, the air in the casing and membrane will be kept at water temperature.

Be careful however, as the oxygen concentration in the casing will drop rapidly as it is consumed by the sensor (see NFT 90.032 standard for oxygen solubility charts).

**Note** :

*Measurement* : the probe must be at the same temperature as the water being measured; wait for equilibrium.

The probe must be constantly shaken during the measurement in order to circulate the fluid on the probe membrane.

Clean the probe with water and never allow finger contact with the membrane.

Chlorinated water interferes with the measurement.

Oxygen solubility decreases in saline water (0,048 mg/l for salinity of 1 g/l at 20°C) : the saturation percentage will therefore be lower in salt water.

### b) Maintenance

The most delicate element is the membrane separating the electrolyte from the external environment.

- Clean with large volumes of water and if necessary with detergent to eliminate traces of oil or grease.

- Rinse abundantly and store the probe in a container with a few millilitres of water.

With continuous measuring systems, manufacturers offer automatic cleaning systems using water and specific chemical substances to dissolve fur and biological deposits.

***Trouble-shooting :***

*Probe or housing ?*

Disconnect the probe or remove the membrane, clean the electrodes in alcohol : zero calibration should now be possible.

If calibration is no longer possible, or the strongly fluctuating display is unstable or takes long to reach equilibrium, change the membrane and the electrolyte. Clean with alcohol, rinse out well with remaining electrolyte.

Before taking new readings, leave the apparatus in the « measuring » position for at least an hour, with the probe in water to moisten the membrane.

## 6) TEMPERATURE

### a) Calibration

***Zero °C*** : use a pile of melting ice.

***Slope °C*** : Using a precision thermometer (mercury) as a comparison, adjust the slope to room temperature if the latter is not too low (20°C), or else in luke-warm water.

***Note*** : these extremely reliable sensors only have one defect which is caused by their temperature lag. It is therefore necessary to wait a few minutes for the reading to stabilise.

### b) Maintenance

Kept in glass, metal or resin-coated tubes, these sensors require practically no maintenance aside from calibration (wipe them down from time to time).

***Trouble-shooting :***

The sensors can be checked with an ohmmeter as long as they are disconnected from the apparatus. Infinite resistance indicates that the sensor must be changed. (Reverse the ohmmeter polarities in the case of thermal resistors).

***Note*** : calibration and maintenance periodicity indicated in the previous paragraphs may have to be modified according to the nature of the water being tested and the importance of the parameter being tested in the process.