Chlorine analyzer

Total Chlorine is define as

The sum of free chlorine and bonded chlorine results total chlorine

Total Chlorine = Free Chlorine + Bonded Chlorine

Bonded Chlorine

It is Chlorine compounds, which form during the presence of ammonium or organically bound nitrogen in the water as mono chloramine (NH_2CL) & di chloramine($NHCL_2$)

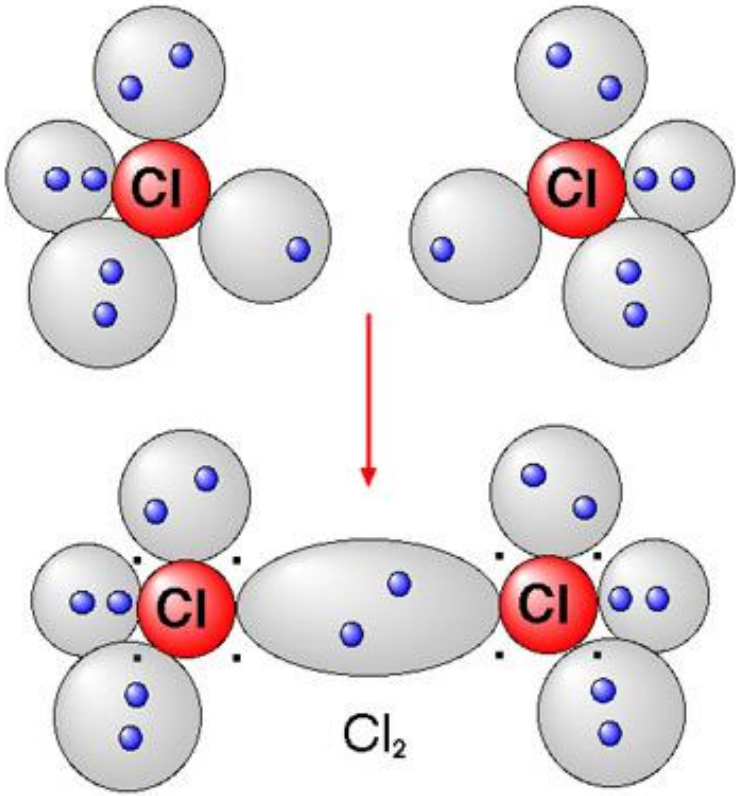
Free Chlorine

It is defined as the sum of molecular chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ions (OCl^-).

Active Chlorine (HOCl) or hypochlorous acid is a powerful disinfectant up to 100 times more efficient than hypochlorite disinfecting This means it takes 10 ppm of OCI- to do the same job of disinfecting as 0.1 ppm of HOCI

Chlorine Concentration

- Chlorine is an important chemical for water purification and in disinfectants
- Gas usually has a gaseous state of aggregation
- In nature it does not exist in an elemental form but mostly as the anion Cl^-
- Physically dissolved chlorine (Cl_2), hypochlorous acid and hypochlorite ions are in summary called free chlorine
- $Cl_2 + H_2O \rightarrow HOCl + HCl$

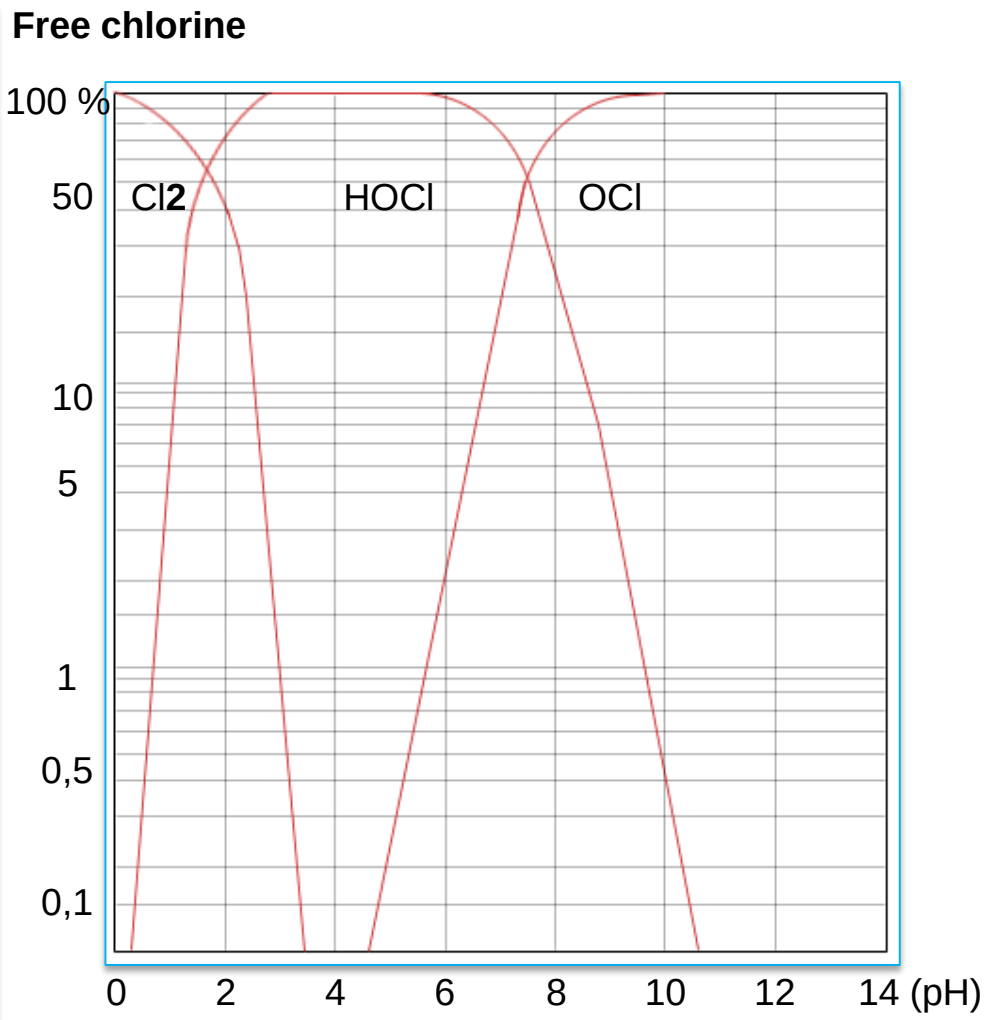


Dissociation Diagram

- If chlorine reacts with water, hypochlorous acid (HOCl) and hydrochloric acid (HCl) are produced

  $Cl_2 + H_2O \rightarrow HOCl + HCl$
- It is mostly responsible for the disinfection
- In hypochlorous acid further dissociates into hydrogen (H+)

  and hypochlorite ions (OCl^-), the hypochlorous acid concentration depends on the pH of the water
- The disinfecting power of chlorine is neglect able at values higher than pH ≥ 8



Water is chlorinated by treating it with chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) solution (bleach). When chlorine gas dissolves in water it produces hypochlorous acid (HOCl).

$$Cl_2 + H_2O = HOCl + H^+ + Cl^- \quad (1)$$

Sodium hypochlorite solution is a source of hypochlorite ions (OCl^-). Hypochlorous acid and hypochlorite ion are both forms of active chlorine and are related to one another by the following equation.

$$HOCl = H^+ + OCl^- \quad (2)$$

The important thing about equation 2 is that any solution of chlorine gas or bleach in water is a mixture of hypochlorous acid and hypochlorite ions. The relative amount of hypochlorous acid or hypochlorite present depends on pH and to a slight extent on temperature.

At 25°C (77°F) and a pH of 7.5, half of the chlorine is present as OCl^- and half as HOCl. At higher pH values, the quantity of OCl^- increases at the expense of HOCl and at lower pH values, the shift is toward conversion of OCl^- to HOCl. At a pH of about 5, nearly all the chlorine is present as HOCl, and at pH 9 nearly all the chlorine is present as OCl^- and at PH<2 Cl_2 present only.

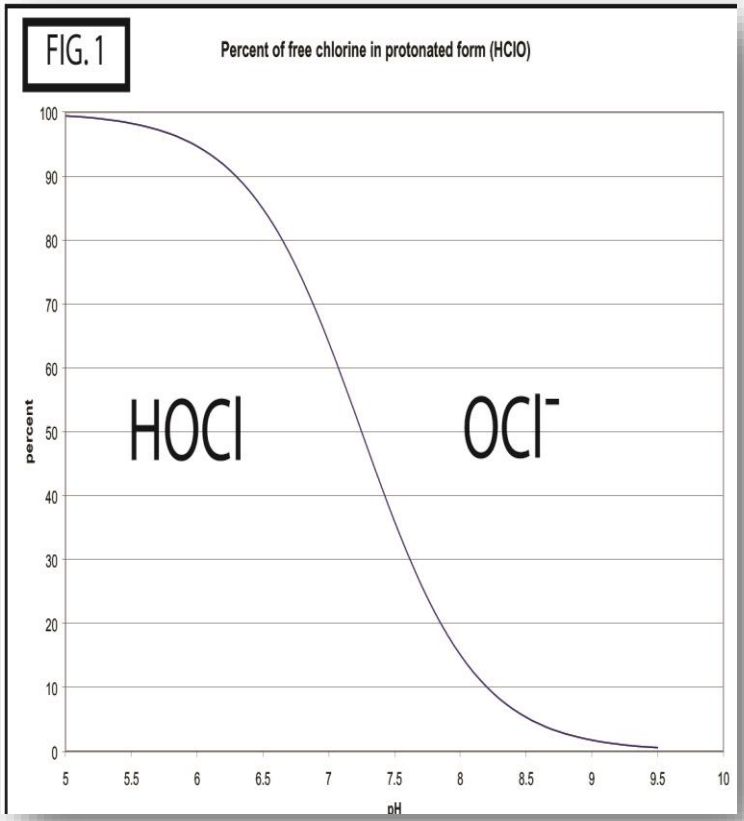
Since many chemical and electrochemical methods used to determine chlorine concentration cannot distinguish between them, it is common to express the two together as free residual chlorine (FRC): $OCl^- + HOCl = FRC$

THEORY OF OPERATION

FREE CHLORINE DEFINED.

Free Chlorine or "freely active chlorine" is defined as the sum of molecular chlorine (Cl2), hypochlorous acid (HOCl) and hypochlorite ions (OCl^-).

Molecular chlorine occurs at pH values <pH4. Hypochlorus acid and hypochlorite ions are in PH dependent equilibrium with one another as shown in FIG 1.



Measuring principle

The concentration of free chlorine is determined according to the amperometric measuring principle. The hypochlorous acid (HOCl) contained in the medium diffuses through the sensor membrane and is reduced to chloride ions (Cl^-) on the gold cathode.

$$HOCl + H+ + 2e– \rightarrow Cl^- + H2O$$

On the silver anode, silver is oxidized to silver chloride.

$$2Cl^- + 2Ag \rightarrow 2AgCl + 2e–$$

The electron release from the silver anode and electron acceptance on the gold cathode result in a current flow which is proportional to the free chlorine concentration in the medium under constant conditions.

The concentration of hypochlorous acid in the medium depends on the pH value. This dependence can be compensated by measuring the pH value in the flow assembly. The transmitter transforms the current signal into the measuring unit concentration in ppm (mg/l).

Function

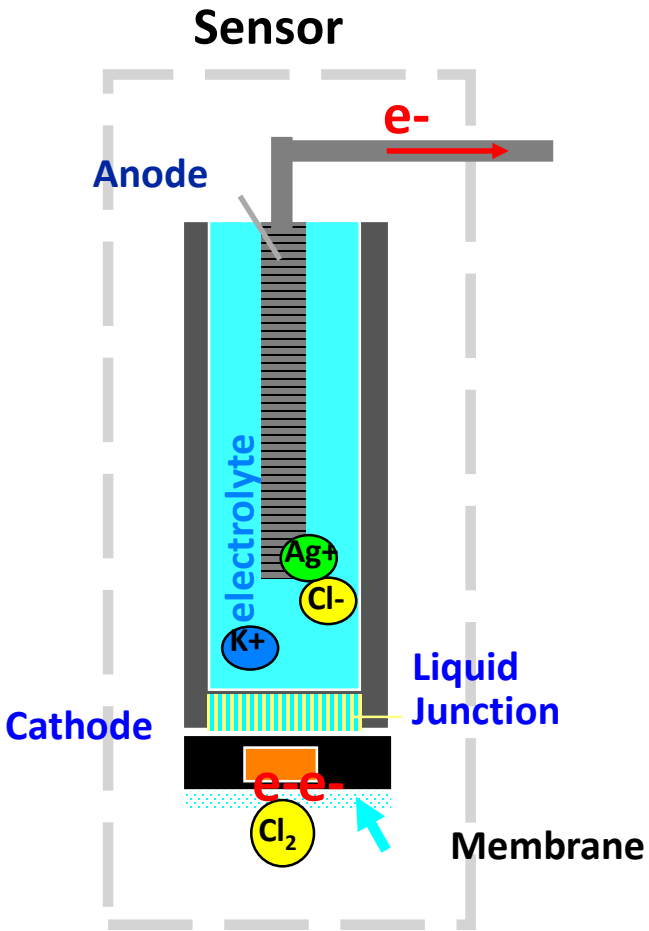
The membrane-capped CCS140 / CCS141 sensors consist of a cathode serving as the working electrode and an anode acting as the counter electrode. These electrodes are immersed in an electrolyte. Electrodes and electrolyte are separated from the medium by a membrane. The membrane prevents the loss of electrolyte and the penetration of contaminants. The CCS140 and CCS141 sensors are used for measurement of free chlorine.

CCS140 (for industrial water, pool water): 0.05 ... 20 mg Cl2/l (25 °C / 77 °F, pH 7.2)

CCS141 (for drinking water applications): 0.01 ... 5 mg Cl2/l (25 °C / 77 °F, pH 7.2)

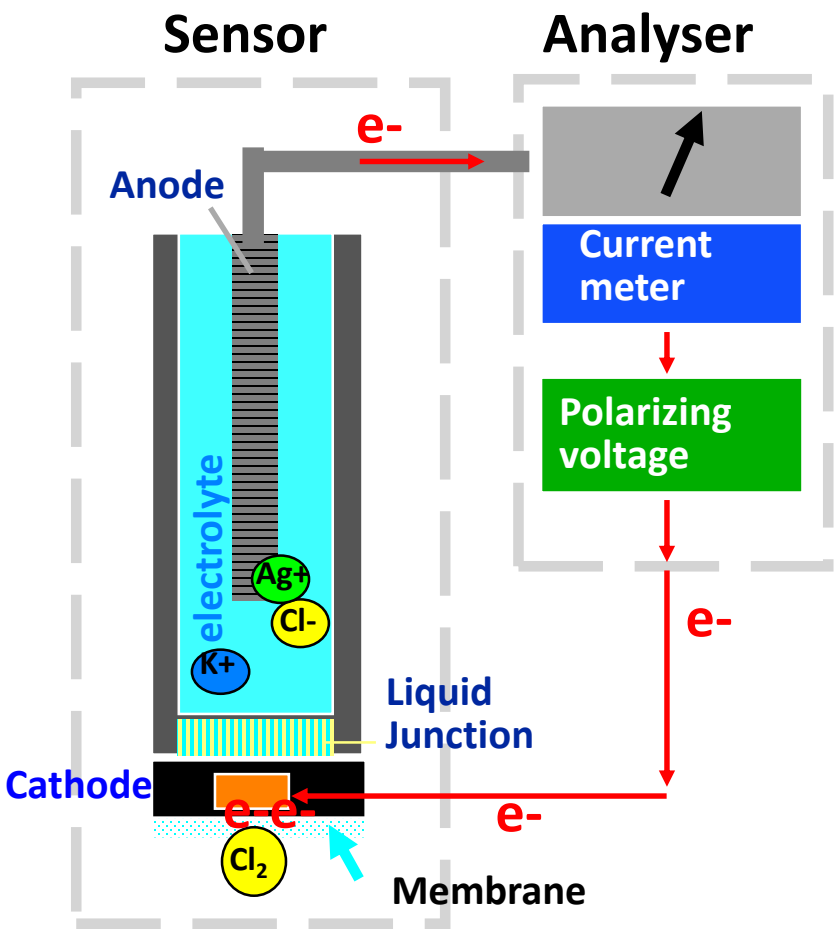
A needle valve regulates the flow within the range of 30 ... 120 l/h

Sensor Components



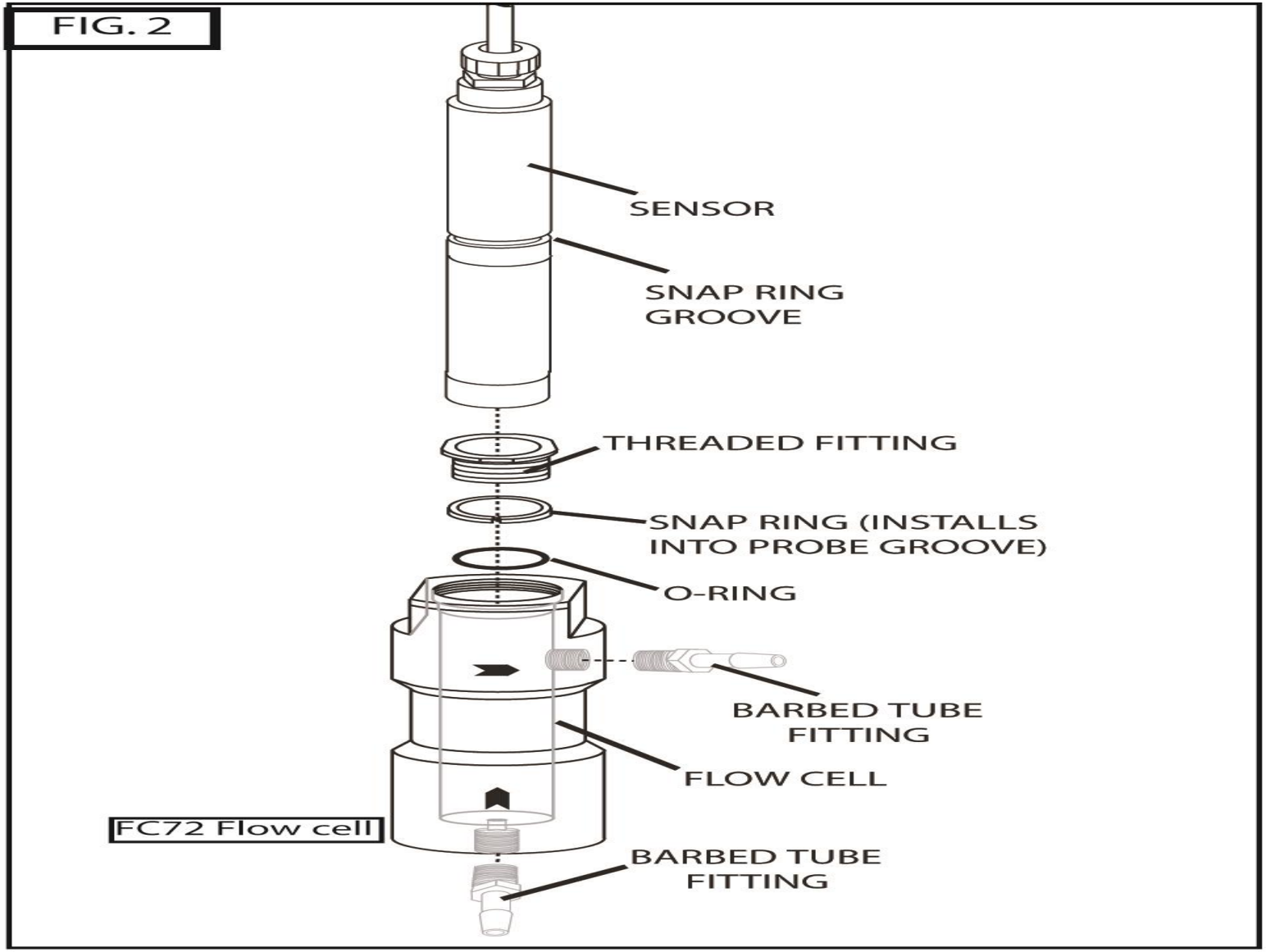
- Cathode
  - Specie of interest picks up electrons; specie is reduced
- Anode
  - Give up electrons to the cathode creating silver ions Ag+ on the anode
  - Negative chloride ions in the KCl electrolyte are attracted to the Ag+ combining to form AgCl coating
- Membrane
  - Limits rate of diffusion
  - Prevents diffusion of other species

How Does The Amperometric Sensor Work?

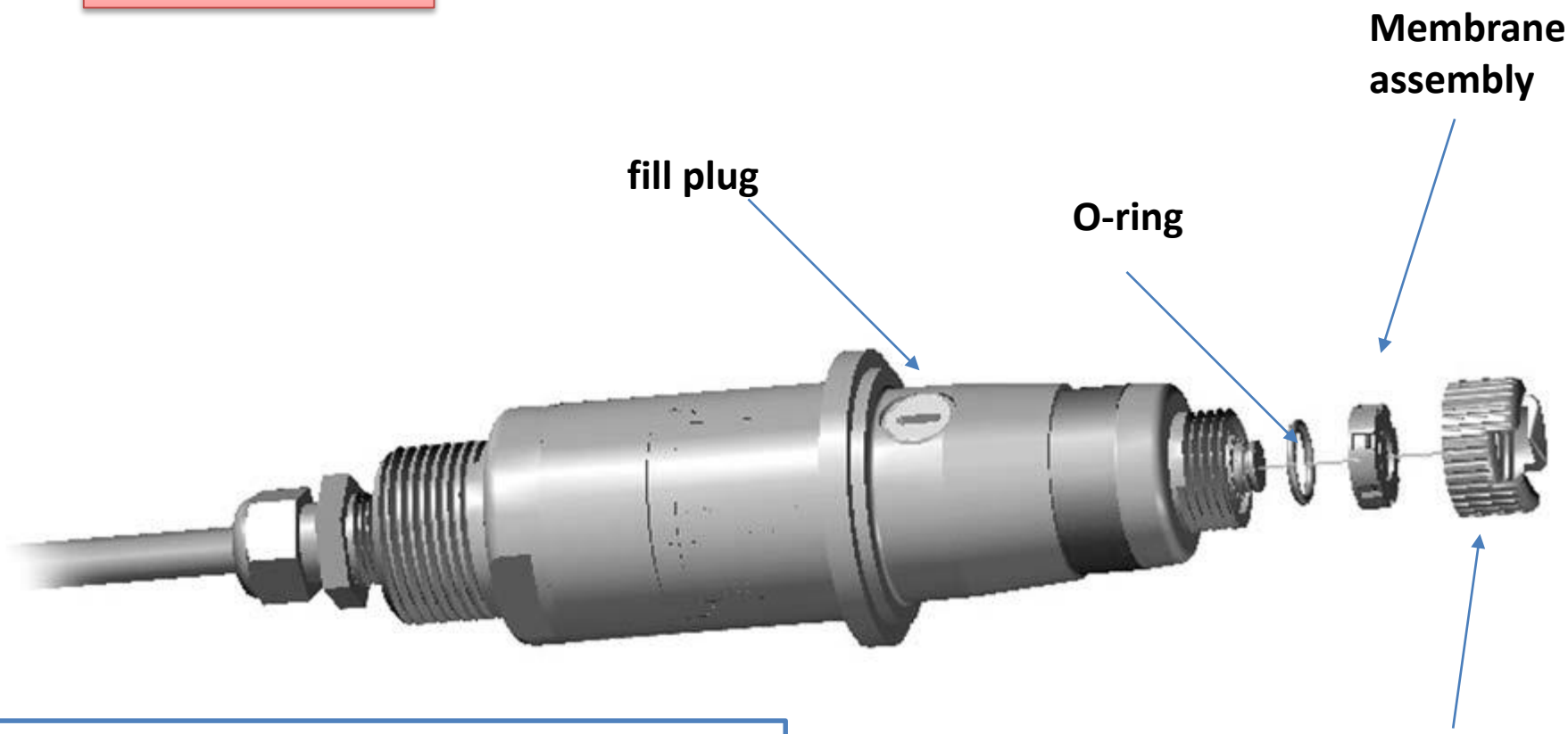


- **Current measurement**
  - Measure the current which is proportional to the concentration of the species in the process
  - Can be a few nA/ppm to mA/ppm
- **Polarisation voltage**
  - Enhances selectivity
  - Different for each specie
    - DO +675 mV
    - Chlorine -200 mV
    - Ozone -250 mV
    -

Free Chlorine sensor (CCS140/141)



MODEL 498 CL-01



STORAGE

The sensor must be stored in a flowing sample. Minimum sample flow is 0.5 gph (30 mL/min).

Do not let the membrane dry out.

If the sensor cannot be stored in a flowing sample...

CCS140 / CCS141

flow assembly CCA250

Liquisys M CCM 253

ENDRESS+HAUSER

Factor Affecting on Reading

*PH- value:-

-As the chlorine analyzer only detects(HOCL),but not hypochlorite ions($^{-}$OCL),so the reading is changing with changing PH-value.

-An increased PH-value will causes decreasing in the measuring value.

An acidification unit can be used to force the pH of the sample to between 5.5 and 6.5. HOCl is reduced at the gold working electrode (cathode).

-solving by using PH-compensation.

*Flow effect :-

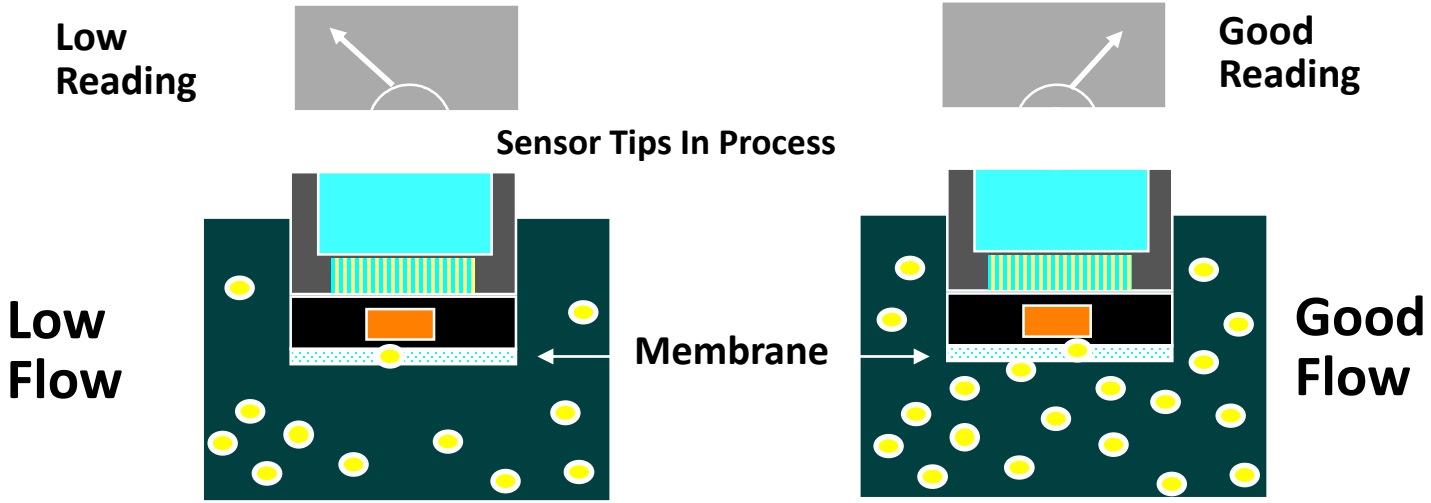
-The membrane requires a minimum flow velocity 15 cm/s corresponds to 30 l/h .

-At higher flow rate not effect on reading , but low flow affect on reading to decrease.

-solving by using flow assembly.

Mounting and Process Effects

- **Agitation and flow effects**
  - **Amperometric sensors consume the sample in the vicinity of the membrane. If there is not adequate turnover of fresh sample near the membrane, the sample will be depleted and low reading will result.**
  - **Sample agitation or a minimum flow rate must be maintained**



Temperature effect

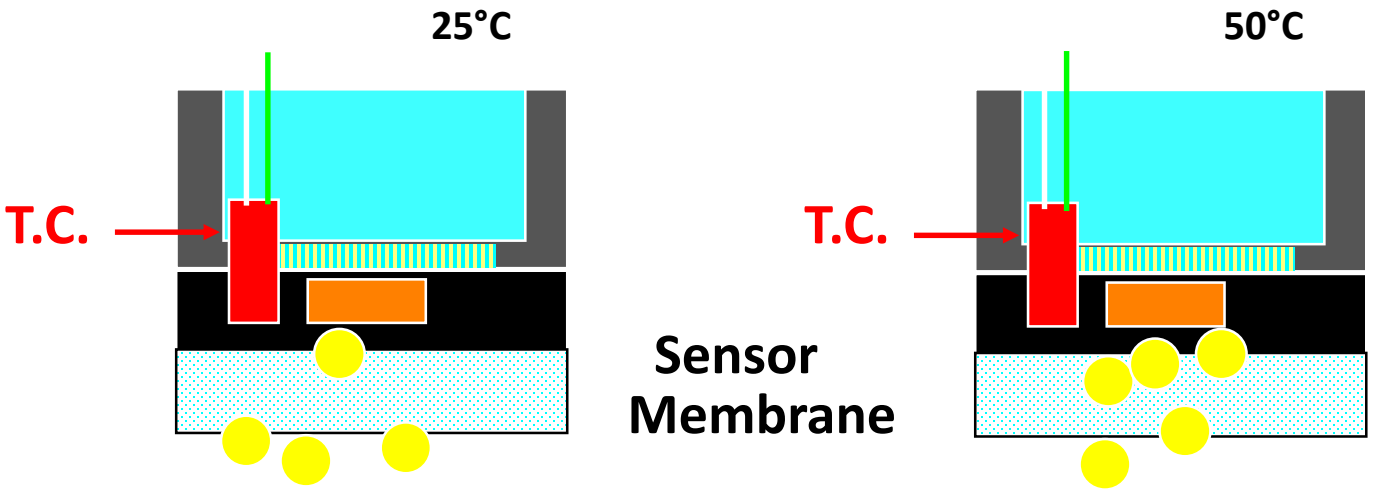
-Changing in the temperature of the measured water also influence the measurement signal.

-A temperature rise causes the measured value to increase as permeability of membrane increase by temperature.

-solving by using of temperature compensation.

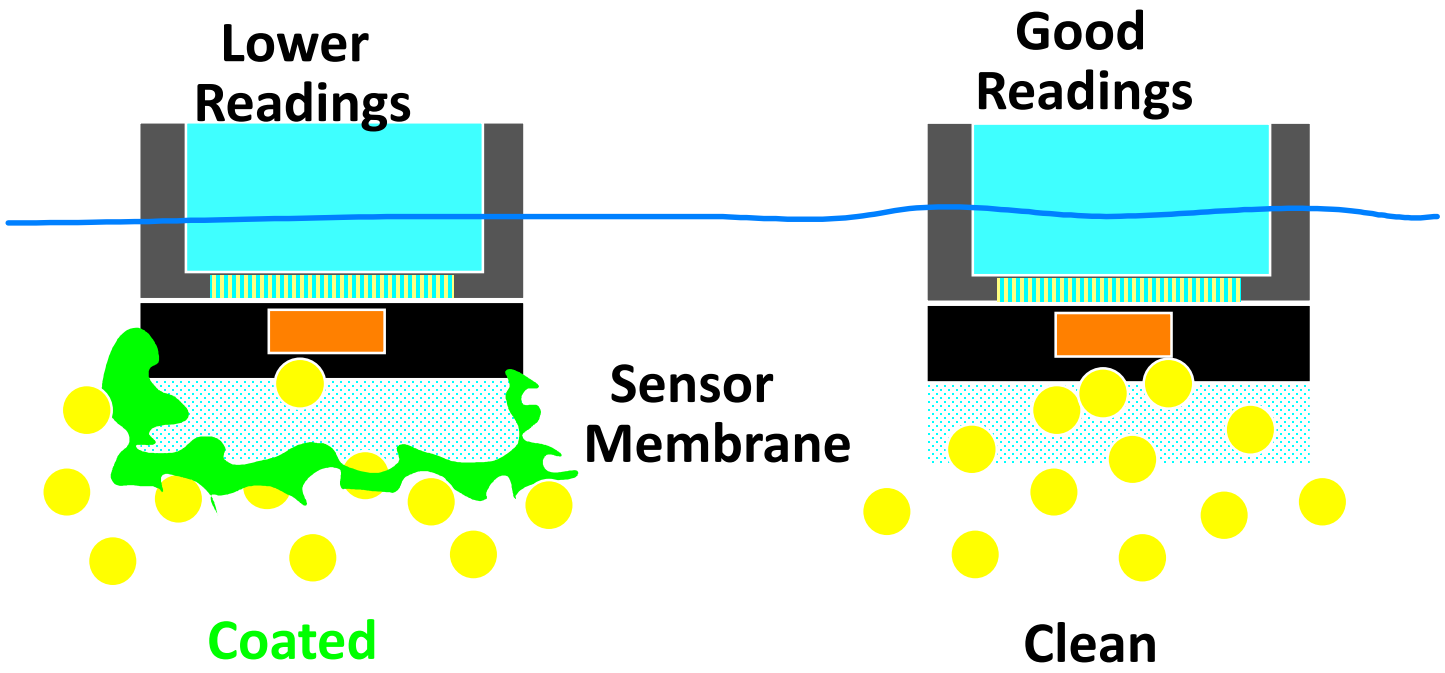
Mounting And Process Effects

- **Temperature effects**
  - Permeability of the membrane increasing diffusion rate
  - Concentration of the species being measured
- **Temperature compensation**
  - Temperature element installed and TC circuit in the analyser



Mounting and Process Effects

- **Membrane coating**
  - **Coating of the sensor membrane lowers the diffusion rate of the specie and causes low readings.**



CALIBRATION

IMPORTANT NOTE

SENSORS ARE SUPPLIED FACTORY CALIBRATED WITH A 4-20mA SIGNAL OUTPUT CORRESPONDING TO THEIR SPECIFIC RANGE (0-2, 0-5 OR 0-10ppm)

SPAN CALIBRATION IS NECESSARY WHEN RECEIVING A NEW SENSOR SINCE YOUR CONDITIONS MAY VARY FROM THOSE USED AT THE FACTORY FOR SPAN CALIBRATION

THE ZERO POINT CALIBRATION IS NOT NECESSARY SINCE THE ZERO SETTING IS VERY STABLE

Type of calibration

1-Zero calibration :-

-It done after slop calibration by passing zero free chlorine water through assembly for 10 minuet then press enter to change reading to zero .

2-Slope Calibration

***Ensure constant operating data (Flow-PH-Temperature).**

***Take sample from sampling point then adding DPD kit of free chlorine .**

***set the measuring transmitter read to the DPD(*N*,*N*-diethyl-*p*-phenylenediamine) value.**

TROUBLESHOOTING

ITME	PROBALME	SERCHING
CALIBRATION PROBLEMS	a) Sensor output HIGHER than DPD test	1) Run in time too short 2) Membrane cap damaged 3) Interference from water 4) Cable short circuit or damage 5) pH value less than pH 5.5
	b) Sensor output LOWER than DPD test	1) Run in time too short 2) Deposits on Membrane cap 3) Flow rate too low 4) Air bubbles on membrane 5) Surfactants in water 6) pH value more than pH 8.0 7) No electrolyte in membrane cap
	d) Sensor output UNSTABLE	1) Air bubbles on membrane 2) Membrane damage 3) Non-sensor problem

Questions ???

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