Technical Note 09

Seawater Chlorination

Introduction

The chemistry of the chlorination of seawater is more complex than many people realise and although the measurement of chlorine residuals is possible in seawater (and therefore automatic control of chlorine dosing), better results will be obtained if this is fully understood.

Chlorination Chemistry of Seawater

$NaBr+HOCl \rightarrow NaCl+HOBr$

Seawater contains about 65-80ppm dissolved bromides[1] most of which are sodium bromide. When you put chlorine in water it displaces (because it's more reactive) the bromine from the bromide and becomes a chloride. So for up to about 70ppm of total chlorine dosed what you actually have in the water is free bromine and combined bromine (NOT free and combined chlorine) so it is the total bromine that actually does the disinfection[2]. So why does everyone call it chlorination when technically it is bromination? Mainly because most people don't know this interesting bit of chemistry. So what? Normally it makes no difference at all in that bromine is an effective disinfectant, however there can be a lot of confusion when it comes to monitoring residuals and controlling dosing. Choosing the correct sensor to control the dosing is crucial.

CRIUS® HaloSense

	At salinity (PSS 1978): S = 35.000%			
	g/kg	ppm (mg/l)	mmol/kg	mM
Na^+	10.781	10781	468.96	480.57
K^+	0.399	399	10.21	10.46
Cl^-	19.353	19353	545.88	559.4
Br^-	0.0673	67	0.844	0.865
F^-	0.0013	1	0.068	0.07

Table shows concentrations of the major constituents in surface seawater. (Source: http://www.ocean.washington.edu/courses/oc400/Lecture_Notes/CHPT4.pdf***)***

Free Chlorine and Total Bromine

Due to the confusion on what is being measured it is easy for an engineer to specify the wrong equipment and calibrate it incorrectly. For example, it is common for a free chlorine sensor to be specified for seawater chlorination control. Most electrochemical free chlorine sensors will react to free bromine (not all so be careful!) but this isn't necessarily what you need for bromination control. Most authors agree that whilst the disinfection capability between free chlorine and combined chlorine differs, when it comes to free bromine and combined bromine, both forms of the chemical are equally good at disinfection so a better measurement would be total bromine, which requires a total bromine sensor.

Total Bromine Sensor in a Flow Cell

DPD and Seawater Chlorination

To add to this already confusing environment we need to look at calibrating online sensors or at using hand held photometers to track the residual. DPD is used extensively to measure chlorine residuals and it also reacts to bromine so can be used for both, however, DPD 1 measures FREE chlorine or TOTAL bromine. There is no easy way of measuring free bromine.

The situation can therefore arise where you have an online instrument specified as a free chlorine, actually measuring free bromine and calibrated as a total bromine (against DPD 1). An online DPD instrument must be specified for seawater (bromine) or the results it gives you will be poor.

Typically the best results are obtained by specifying a total bromine (total chlorine) sensor and calibrating it using DPD 1.

That, however, isn't the end of the story! When specifying an analyser it is crucial that we suppliers know that it is for use with seawater because the physical and chemical make up of seawater is very different to potable or process water and this can affect what we would supply to customers.

The effect of Salinity on Membrane Sensors

It is crucial for us to know if you are going to use a Pi sensor in seawater so we can provide you with a saltier electrolyte. Osmosis means that water moves from a low solute concentration to a higher solute concentration across a semi-permeable membrane. The electrolyte in our sensors is saltier than potable or process water so osmosis forces water into the end of the sensor, which the sensor is designed to cope with, however, with seawater the process is reversed and the water in the electrolyte can be forced out of the sensor into the sample. To solve the problem we supply electrolyte especially designed for sea water, with a higher salinity.

Estuarine Waters

Many seawater chlorination applications are estuarine in nature (partly seawater and partly fresh water) and it is the degree of dilution which determines which sensor and which electolyte you should use. Seawater has approximately 70ppm bromides and so up to 70ppm chlorine the replacement will be 100%. If the sea water is 50% fresh water then up to 35ppm chlorine will give 100% displacement. For example, if we looked at a 2ppm residual then the water could be only 3% seawater and 97% fresh water and you would still be measuring bromine, so a total bromine sensor calibrated with DPD 1 would be appropriate. For any water that is contaminated with sea water the seawater electrolyte is likely to be the most appropriate.

Total Bromine Sensor

Because bromine is heavier than chlorine, 1mg/L of chlorine is the same as ^1.6mg/L of bromine[3] so it is important to understand what you are measuring. DPD kits can be used in three ways for the chlorination of seawater.

1. **A chlorine DPD 1 kit will measure total bromine but will report the concentration as chlorine equivalent. If this is used to calibrate a Pi sensor, it should be a Pi total chlorine probe that will also then report in mg/L of chlorine equivalents.**
2. **A chlorine DPD 1 test kit can be used and the mg/L can be multiplied by 1.6 to give a total bromine reading, and if this is used to calibrate a Pi sensor it should be a Pi total bromine sensor.**
3. **A bromine DPD 1 test kit is the same as a chlorine test kit except that it does multiply internally and outputs as mg/L of total bromine. If the kit is used to calibrate a sensor, it should be a total bromine sensor.**

References

1. Goosen, M. F. A. & Shayya, W. H. *Water management, purification, and conservation in arid climates. Volume 2: Water purification.* (Univ. of Sultan Qaboos Univ.(OM), 1999).

2. Wiley, *White's Handbook of Chlorination and Alternative Disinfectants, 5th Edition*. (page 874, pages 122-129).

3. Wieser, M. E. *et al.* Atomic weights of the elements 2011 (IUPAC Technical Report). *Pure Appl. Chem.* 85, 1047–1078 (2013).