#104

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## Total Residual Chlorine (2nd of 2 articles)

Tim Loftus

Whether you use chlorine gas or sodium hypochlorite to disinfect the wastewater, both have one thing in common – in solution they are reactive and very unstable. The chlorine wants to change from a high oxidizing level to a more stable reduced one. Because of this it is impossible to preserve a sample for residual chlorine. Any sample taken for residual chlorine analysis must be tested immediately. According to EPA, this means the sample must be tested within fifteen minutes of collection.

There are also other concerns when sampling for residual chlorine. Exposure to sunlight and sample agitation reduces the chlorine to ineffective forms. Additionally, a dirty sample collection bottle, whether glass or plastic, can create a chlorine demand. All these interferences will give you lower residual chlorine values than what may actually be present in the field. All of these interferences can also be avoided with proper sample collection and handling.

Oftentimes there may be other interferences that cannot be avoided. Oxidizing agents such as bromine in estuary and marine samples, oxidized forms of manganese as well as some other metals, peroxides, turbidity, and color are often found in wastewaters at levels that will interfere with residual chlorine analyses. There are different methods used to analyze residual chlorine. Each method is subject to different interferences and detection limits. Choose a method that will most accurately measure residual chlorine at your plant based on your expected interferences and detection limits. Three of the most common methods used for residual chlorine analysis are listed below. These descriptions are very basic. Refer to the actual test methods listed in Chapter 40 Code of Federal Regulations, part 136 for a complete description of each procedure, reagents needed, and potential interferences.

Maine DEP Monthly O & M Newsletter

Maine and WEF's Operation Forum

Penobscot Watershed and Development of a TMDL

EPA Binational Toxics Strategy

Maine Rural Water Association

Maine Wastewater Operator Certification Guide

Maine Is Technology Newsletter

Maine Wastewater Control Association

Maine Wastewater Engineering Firms

Amperometric titration. A sample is titrated with phenylarsine oxide (PAO). After the PAO reacts with chlorine and an excess of PAO becomes present, the electrical polarity of the solution changes. The point in the titration when this change in the electrical current happens, as measured by an ammeter, correlates to the chlorine concentration. This method requires a good deal of operator skill to produce reliable results. However, this method is not affected as much as the other methods by turbidity, color, manganese, and iron – all interferences in many types of wastewater.

Titrations that produce a color change. There are two basic titration procedures that are accepted for NPDES reporting. The first one involves titrating a sample with sodium thiosulfate and using starch as the indicator. The other one involves titrating with ferrous ammonium sulfate and using N,N-diethyl-p-phenylenediamine (DPD) as the indicator. In both methods a sample is titrated until a specific color change emerges. The amount of titrant used to the color change correlates to the amount of residual chlorine is in the sample. Color and turbidity interfere with the titration end-point color. Different forms of metals and other oxidizing agents can produce a positive interference in these methods.

DPD Colorimetric. DPD is added to a sample and, through a series of reactions, a chemical is produced that is red in color. The color intensity correlates to the residual chlorine concentration. A spectrophotometer is used to measure this intensity of the red color. Sometimes, for a quick non-NPDES check, the sample's color is compared to DPD- specific color wheel to determine chlorine concentration. This is the easiest method to use for analyzing residual chlorine. But it too is affected by a number of interferences, most notably color, turbidity, and oxidizing agents.

It's important to use the proper residual chlorine test method to avoid most, if not all, of the interferences that are found in wastewater. Accurate results aid in better control of your facility's disinfection system, which will help in saving money (by not wasting disinfection chemicals), and in meeting your NPDES permit.

Even if your NPDES permit states which method to use for effluent residual chlorine analyses, you need to be familiar with the other methods, especially if you have an industrial pretreatment program. For example, when sampling an industry for cyanide you must test for residual chlorine before preservation. If any is found you must neutralize the chlorine with ascorbic acid. However, the residual chlorine method you use for your plant effluent may not give accurate results if applied to an industrial waste. A false residual chlorine reading in an industrial waste sample may lead to

improper cyanide sample preservation. As a result of this, an industrial user may be discharging cyanide to your facility above permit limits.

The information in this article is very general. As usual, check your federal, state, and local regulations. You may have additional regulations or requirements that you must meet.

If you have any questions, suggestions, or comments, please contact NEWEA Lab Practices Committee Chair Tim Loftus at (508) 949-3865 timloftus@msn.com.


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| ●Acidity and Alkalinity | ●Normality |
| ●Ammonia Nitrogen | ●Making Normal Solutions |
| ●BOD Test Requirements | ●Phosphorus 1 |
| ●BOD Test Requirements 2 | ●Phosphorus 2 |
| ●BOD Test Requirements 3 | ●QC Samples |
| ●Chain of Custody Procedure | ●Record Keeping |
| ●Chemical Storage | ●Rounding Digits |
| ●Coliform and E. Coli Testing 1 | ●Sample Contamination |
| ●Coliform and E. Coli Testing 2 | ●Significant Digits |
| ●Coliform and E. Coli Testing 3 | ●Sample Handling for NPDES |
| ●Control Charts | ●Signs of Toxicity |
| ●Dilution Solutions | ●SOPs |
| ●Matters of Perspective pH Part 1 | ●Total Chlorine Residual |
| ●Matters of Perspective pH Part 2 | ●Total Chlorine Residual-2 |
| ●Method Detection Limits | ●Total Suspended Solids |
| ●Molarity | |

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|---|---|
| ●pH Measurements | |
| ●Nitrogen | |