

PART TWO: CL17 FOR PERMANGANATE MEASUREMENT IN DRINKING WATER (TWO OXIDANTS)

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Introduction

The effects of elevated levels of iron and manganese have been discussed in drinking water treatment-related and regulatory literature and may be summarized as causing aesthetic problems in the distribution system such as staining and bad taste and odor. Although these metals have no adverse health effects, it is recommended to reduce levels of iron and manganese below the SMCL established by the U.S. EPA.

The main goal of water treatment with sodium or potassium permanganate is to provide adequate pre-oxidation to remove organics and/or dissolved metals, such as manganese and iron, from the water. Natural organic matter (NOM) removal is usually the primary goal for surface water treatment to minimize formation of disinfection byproducts (DBPs). Removal of metals by oxidation is usually the primary goal for ground water treatment; however, the general practice is to sequentially remove metals by precipitation and filtration.

Operational challenges usually come from determining and maintaining the correct feed of permanganate. The balancing act is between underfeeding permanganate and therefore not achieving the goal of NOM and/or metals removal and overfeeding that may lead to an unwanted pink color in finished water. In addition, over-oxidizing of Mn leads to its dissolution and therefore defeats the purpose of the treatment (inefficient filtration). To maintain such delicate balance, the analysis of treated water must be constantly conducted in process and therefore on-line instrumentation is preferred for such applications. Instrumentation should provide accurate results and be robust.

Measuring Permanganate with the CL17

To understand the Hach CL17 chlorine analyzer capabilities for permanganate analysis, several tests have been conducted both in the laboratory and in the field. Total chlorine chemistry was selected to use in testing as the formulation of these reagents provide better accuracy. The main goals of the laboratory test were to verify the linearity of response to permanganate, validate accuracy/precision specifications, and evaluate main interferences, including chlorine.

The laboratory testing established a linear response of the Hach CL17 analyzer to an array of potassium permanganate standard solutions within the range of 0 – 5 ppm. Based on this testing, it was concluded that the CL17 will respond to permanganate in water according to the existing calibration curve as currently established for residual chlorine.

Additional testing was conducted to evaluate the influence of several potential interferences usually present in source water. Major analytical performance specifications were derived from the laboratory test results and presented in Table 1.

A test was conducted to evaluate CL17 measurement of combined oxidants in the sample – permanganate and chlorine simultaneously present. The test revealed the CL17 reads a linear sum of the components' concentrations; no specific interaction between the components was detected.

Table 1: CL17 Performance for Permanganate Analysis in Water

Analytical Performance Specifications	
Measurement Range	0 – 5 ppm, as Potassium Permanganate
Precision	5% or 0.03 ppm, whichever is greater
Accuracy	±10% or 0.05 ppm, whichever is greater
Linearity	Existing CL17 calibration curve ¹
Interference	
Total Hardness (> 1000 ppm)	Negative, 10% at 1000 ppm
Total Alkalinity (> 300 ppm)	Negative, 7% at 300 ppm, 40% at 1000 ppm
Total Acidity (up to 150 ppm)	None
Chlorine	Positive, 100% at all levels ²

¹ No adjustment coefficient, displays mg/l (ppm) of Cl₂ = mg/l (ppm) of KMnO₄

² Chlorine and other oxidants are measured as TRO (total residual oxidant)

Therefore, it was concluded that the CL17 analyzer can be used for monitoring of either chlorine or permanganate with analytical accuracy. When both parameters are monitored together, a set of two instruments – one reading the first parameter, and another reading the sum – can be used to discern the residual concentration of the second chemical added to the sample sequentially. The positive results of the lab testing instilled confidence to proceed with a field study that was conducted at the Hummelstown drinking water treatment plant (DWTP), a facility managed by United Water in Pennsylvania.

Field Study

The Hummelstown DWTP has used permanganate for pre-oxidation and chlorine for post-chlorination for the past several years. The main idea of such treatment is to control NOM in the source water to minimize formation of DBP. The plant treats surface water coming from a creek with membrane filtration, including pre-oxidation with permanganate followed by primary disinfection with chlorine and post-chlorination after the filters.

The main challenge comes from the variability of source water quality. Source water has variable chlorine demand comprised of NOM/bacterial load and undergoes seasonal changes in iron and manganese. Pre-oxidation with KMnO_4 takes care of the metals and helps to reduce some of the NOM. However, the bulk of NOM and bacterial load is reduced by sequential chlorine addition (purchased 12.5% hypochlorite solution) prior to membrane filtration. Therefore, installation of two CL17 analyzers in sequence with enough contact time allowing formation of stable residuals should provide an opportunity to quantify concentrations of both oxidants. Also, cold weather presents challenges during winter months when permanganate loses its activity and may add to the manganese content of the water. Therefore, the facility reduces or stops the permanganate feed and offsets oxidation demands with chlorine, intermittently, when water is colder than 3°C during January and February.

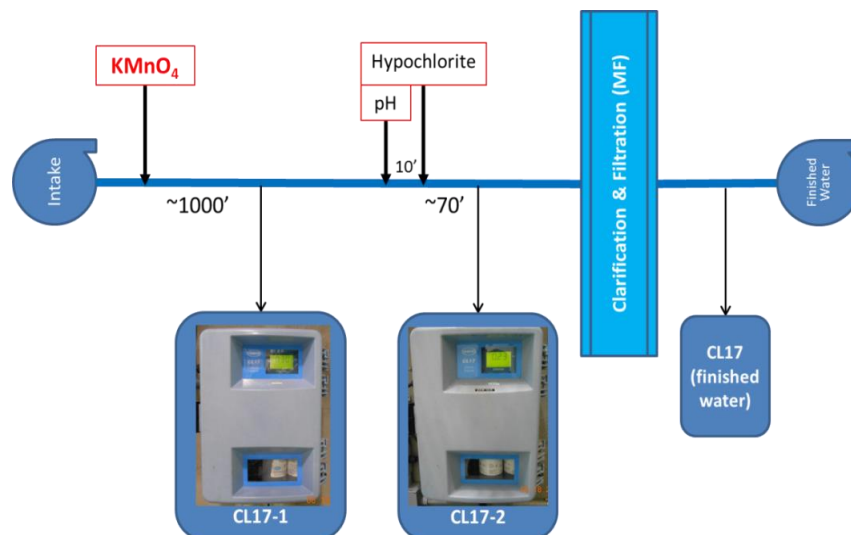


Figure 1: Schematic with distances between the chemical injection and sampling points

United Water looks for new methods and approaches to optimize facility performance and ensure water quality for the population served. The plant's management has used CL17 analyzers for trending of combined oxidant and was interested in applying the differential setup suggested by Hach to measure and discern both permanganate and chlorine residual concentrations. The general treatment process schematic is presented in Figure 1.

This permanganate residual measured by the first CL17 (CL17-1, Fig. 1) should define a stable offset for calculation of true free chlorine concentration from the readings collected by the second CL17 (CL17-2, Fig. 1). The true chlorine residual is derived from the measured combined oxidant concentration by subtracting the residual permanganate concentration (offset).

Based on this assumption, focus was placed on the concentration readings collected from these two analyzers by the plant's SCADA system. The plan was to quantify the offset by varying feed of the two oxidants and therefore cross-verifying the measured values and feed rates. General test procedure is outlined in Table 2.

Table 2: Test Algorithm to Establish True Residuals for Oxidants

TEST	KMnO_4	Chlorine
1	Regular feed	Regular feed
2	Decreased feed	Regular feed
3	Increased feed	Regular feed
4	Regular feed	Decreased feed
5	Regular feed	Increased feed

Data Analysis

Testing was conducted during in March 2015 to achieve the desired water temperature and demand. The collected results presented a challenge for analysis due to cyclical nature of the plant's operation caused by varying flow demand and corresponding control. Chemical feed is paced with flow fluctuations and produces a cyclical pattern registered by both CL17 analyzers and confirmed by independent pH readings collected at the facility.

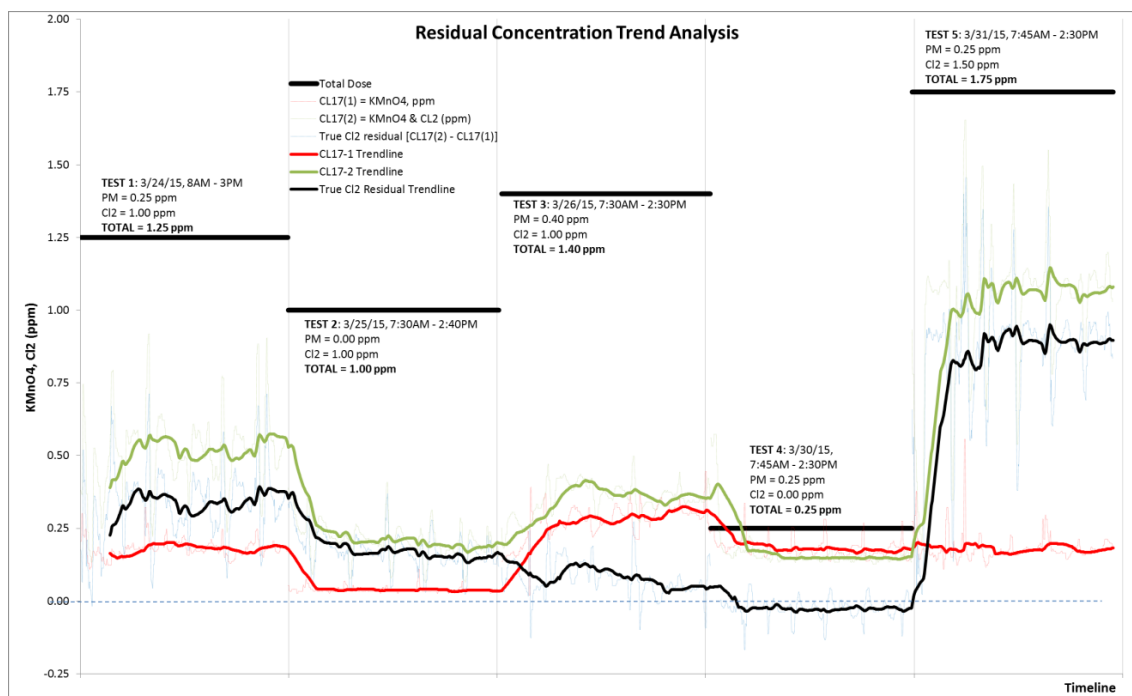


Figure 2: Correlations between total pre-oxidant feed and measured values for Permanganate (CL17-1, red line) and Chlorine (CL17-2, green line), and calculated "true chlorine residual" value (black line)

Therefore, due to the flow dependencies and some natural gaps in the test procedure, a trend analysis of measured and calculated residuals was conducted (Fig. 2). The analytical test results are presented in Table 3.

As seen from Figure 2 and Table 3, the calculated true chlorine residual trend correlated with general pattern and expectations (a higher total feed resulted in higher TRO readings and vice versa). Only the Test 3 results did not follow this pattern. In order to explain such experimental fact and rule out potential failure of the CL17 analyzers an additional data analysis was conducted. The data available for major water quality parameters (pH, Temperature, Turbidity, Alkalinity, and TOC) were analyzed and no specific parameter seemed to be responsible for the Test 3 unexpected result. Since all other potential factors were ruled out, the only viable explanation of the observed phenomenon was a sudden increase in chlorine demand prior to and during this particular test.

Table 3: Average Readings and Calculated Values for Expected and True Chlorine Residual for Each Test

	Date / Time	KMnO ₄ Dose, ppm	Cl ₂ Dose, ppm	Actual KMnO ₄ (CL17-1), ppm	Theoretical ³ CL17-2, ppm	Actual KMnO ₄ +Cl ₂ (CL17-2), ppm	True ⁴ Chlorine Residual, ppm
TEST 1	3/24/15 / 8:00AM – 3:00PM	0.25	1.00	0.18	1.18	0.51	0.33
TEST 2	3/25/15 / 7:30AM – 2:40PM	0	1.00	0.041	1.04	0.21	0.17
TEST 3	3/26/15 / 7:30AM – 2:30PM	0.40	1.00	0.27	1.27	0.35	0.08
TEST 4	3/30/15 / 7:45AM – 2:30PM	0.25	0	0.18	0.18	0.17	0.00
TEST 5	3/31/15 / 7:45AM – 2:30PM	0.25	1.50	0.18	1.75	1.03	0.84

³If all chlorine (oxidant) demand is satisfied by permanganate

⁴Calculated [CL17-2, ppm] – [CL17-1, ppm] = true chlorine residual

Chlorine Demand Analysis

Based on conducted analysis of chlorine demand showing a steady increase (Table 4), it was concluded that some bacterial contamination during the test was possible. Such contamination may be resistant to permanganate treatment creating a specific need for another oxidizer, e.g. chlorine. This would explain the observed experimental fact and may serve as confirmation of efficiency of the treatment process implemented at this facility, as well as usefulness of the online analysis that helped to detect such event.

Table 4: Chlorine demand analysis results - observations and calculations confirming the assumption

	KMnO ₄ Dose, ppm	Cl ₂ Dose, Ppm	Actual CL17-1 (KMnO ₄) average, ppm	KMnO ₄ demand ⁵ , ppm	Actual CL17-2 (KMnO ₄ +Cl ₂) average, ppm	Chlorine demand ⁶ , ppm
TEST 1	0.25	1.00	0.18	0.07	0.51	0.67
TEST 2	0	1.00	0.04 ⁷	NA	0.21	0.79
TEST 3	0.40	1.00	0.27	0.13	0.35	0.92
TEST 4	0.25	0	0.18	0.07	0.17	NA
TEST 5	0.25	1.50	0.18	0.07	1.03	0.66

⁵ The difference between permanganate feed and CL17-1 readings (averaged per test)

⁶ Calculated value: [Total Feed, ppm] – [Actual CL17-2, ppm] – [Permanganate Demand, ppm] = Chlorine Demand

⁷ Some interference, possibly, from dissolved iron and manganese

Permanganate demand (~0.07ppm) and chlorine demand (0.71 ± 0.07 ppm) was observed to be quite stable in all tests except Test 3 where demand increased. In this test the permanganate feed increased by 60% and its residual increased by approximately 50%, so the difference was about 10%. This difference in absolute values of calculated demand (0.06 ppm) cannot be considered significant given the established accuracy for permanganate measurements. However, the increase in chlorine demand during Test 3 was over 15% and the calculated absolute value (~0.2 ppm) was above the specified measurement uncertainty. Therefore, we may consider the observed phenomenon to be due to an increase in specific chlorine demand in the source water.

Conclusions & Recommendations

- The suggested method for determination of true chlorine residual by subtracting the measured permanganate concentration from the combined concentration of both oxidizers in the same water sample was established in the laboratory and verified in the field study.
- Practical application of the two CL17 analyzers sequentially measuring both residuals (permanganate and TRO) in water sample was confirmed as a good trending tool for control of challenging water treatment processes. The analyzers helped detect an unexpected increase in chlorine demand during the field test.
- The obtained results clearly indicate that the suggested setup can be used for analytical determination of true chlorine residual in the measured TRO and further testing at another facility with more stable water conditions (e.g. water temperature and chlorine demand) should be conducted to further prove such application.

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