Characterizing Chloride Interference in the Wet Chemical Oxidation of Organics: Application to TOC Measurements

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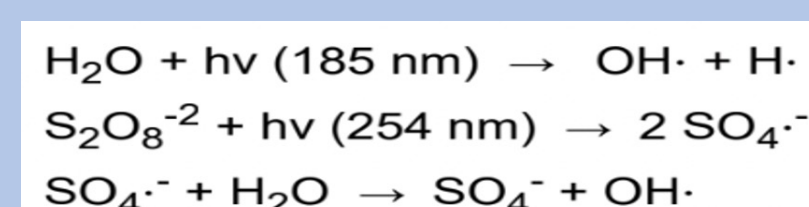Chemical Biochemical and Environmental Engineering

Motivation and Aims

Total organic carbon (TOC) measurements allow for the quantification of the quality of water through the amount of organic carbon present. The relationship between carbon quantity and water quality are inversely proportionate, meaning that more carbon is an indicator of water with many impurities. There are multiple ways to measure the TOC of a sample, however the focus will be on wet chemical oxidation (WCO). WCO allows for lower concentrations of carbon to be detected. This is useful because environmental samples such as seawater, groundwater, and stormwater, contain low concentrations of organic carbon. Chloride is ubiquitous in the environment and often appears in aqueous solutions. For this reason, it is important to study its interference within the TOC analyzer and more importantly, how it skews the results after analysis. This method of analyzing water quality is of interest being that it indicates the trajectory of human health based on the quality of water that is consumed. The primary aim of this study is to investigate the interference of chloride in wet chemical oxidation through experimentation with various carbon background concentrations.

Background

Carbon undergoes various chemical reactions in the analysis process. The reactor in the analyzer is a spiral quartz tube which is wrapped around a UV lamp. As the UV lamp emits light, strong chemical oxidizing agents are formed, appearing in the form of hydroxyl radicals. However, when chloride is present, persulfate ions ($S_2O_8^{2-}$) favor the oxidation of chloride, resulting in a decrease of persulfate concentration, ultimately interfering with the TOC measurements. [1]

$$H_2O + h\nu\ (185\ nm) \rightarrow OH\cdot + H\cdot$$
$$S_2O_8^{-2} + h\nu\ (254\ nm) \rightarrow 2\ SO_4\cdot^-$$
$$SO_4\cdot^- + H_2O \rightarrow SO_4^- + OH\cdot$$

With minimal chloride present, the hydroxyl radicals convert organic carbon into CO_2. CO_2 reacts with water in the DI water stream to form carbonic acid which dissociates into hydrogen ions and bicarbonate ions.

$$Organic\ Compounds + OH\cdot \rightarrow CO_2 + H_2O$$
$$CO_2 + H_2O \rightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
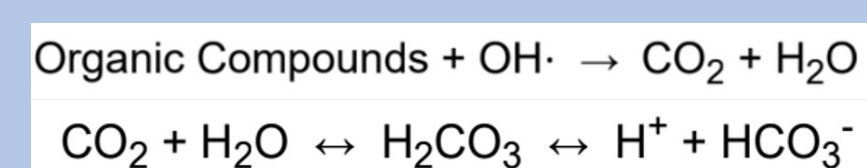
DI water is pumped through the analyzer, collecting H^+ and HCO_3^- ions as well as H_2CO_3 and CO_2 molecules . These ions and molecules are pumped to the conductivity cells. CO_2 is used in the conductivity cells of the analyzer to measure the total carbon(TC) and inorganic carbon(IC). The formula, TC-IC=TOC, is then used to acquire the TOC of the sample.

Components of TOC Analyzer:
1. 8 valve pump which collects sample
2. Reagent Cartridges
   a. 6M Phosphoric Acid (Acid reagent)
   b. 15% Ammonium Persulfate (Oxidizing reagent)
3. Mixing Coil
4. Half of sample is sent to UV reactor, other half sent to delay coil
5. CO2 Transfer Module
6. Gas permeable membrane
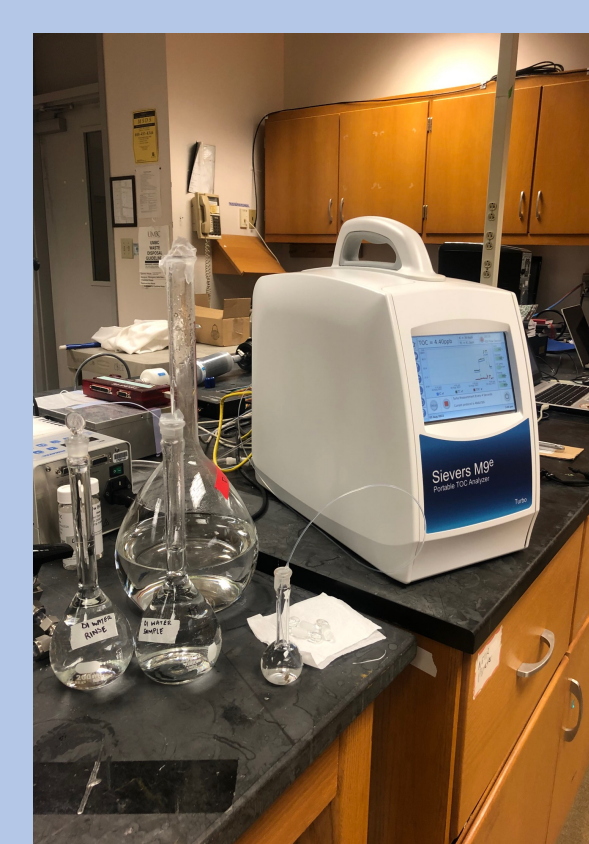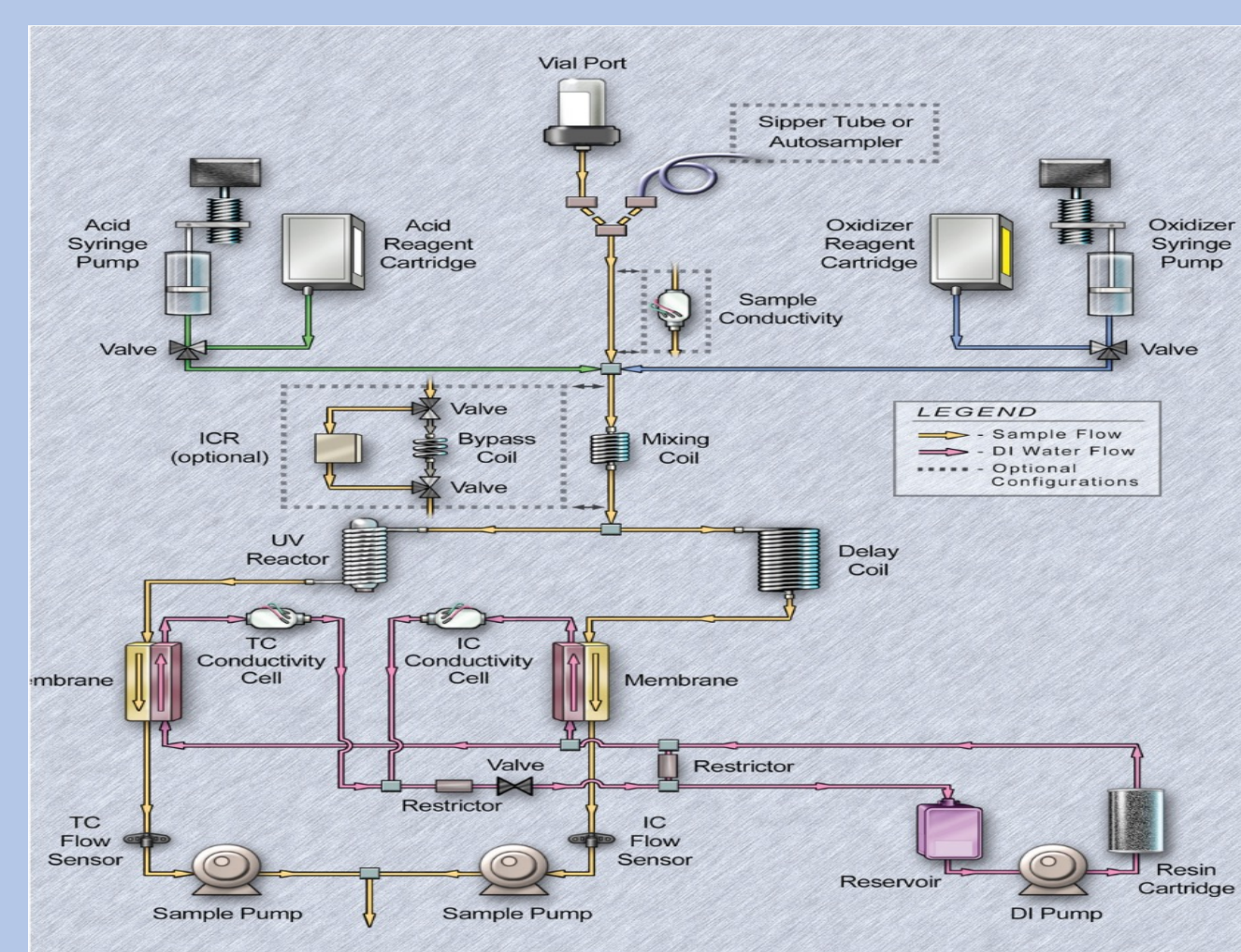7. Ion exchange resin bed
8. Conductivity cell
9. Waste stream

Image 1: Sampling set up

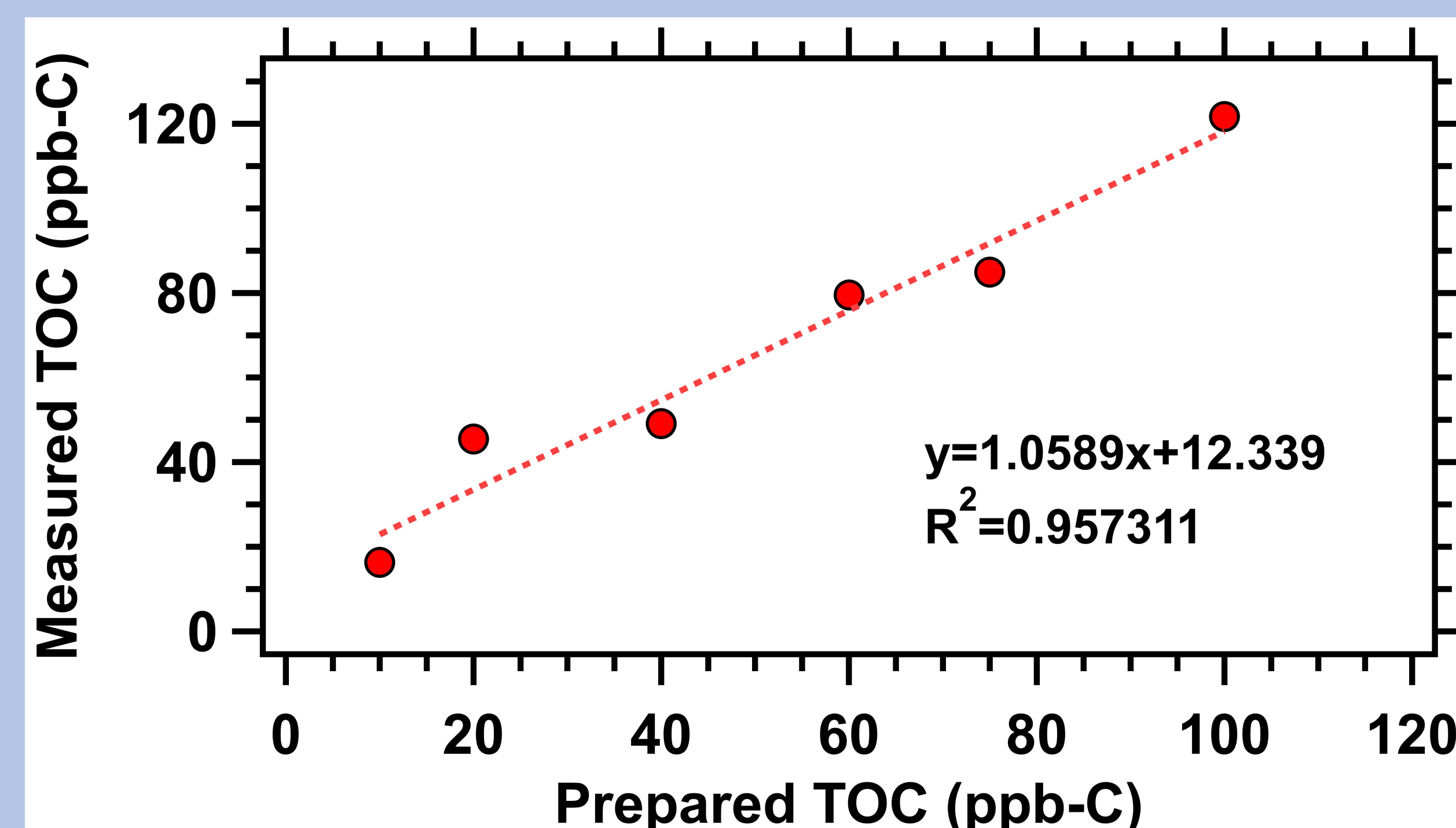## References

[1] Aiken, G. R. (1992). Chloride interference in the analysis of dissolved organic carbon by the wet oxidation method. *Environmental Science & Technology*, *26*(12), 2435–2439. https://doi.org/10.1021/es00036a015
[2] Sakamoto, T., & Miyasaka, T. (1987). Study confirming the accuracy of a method for measuring TOC by wet oxidation. *Ultrapure Water*, *4*(9), 24–31.
[3] Suez. (2018). *Sievers M9/M9e TOC Analyzers*.
[4] van Zomeren, A., Koper, R., Dijkstra, J. J., & Comans, R. N. J. (2021). Chloride Interference during Analysis of Dissolved Organic Carbon Using Wet Chemical Oxidation Methods. *ACS ES&T Water*, *1*(5), 1295–1301.

Acknowledgements

Results

Figure 1: Verification curve for acetate solution.

y=1.0589x+12.339
R^2=0.957311

Figure 1 shows a verification curve for an acetate solution. An R^2 value of 0.957 gives confidence that significant discrepancies in carbon recovery during chloride interference experiments do not point to equipment error; this allows us to instead draw conclusions about the extent of chloride interference in the TOC measurement process.
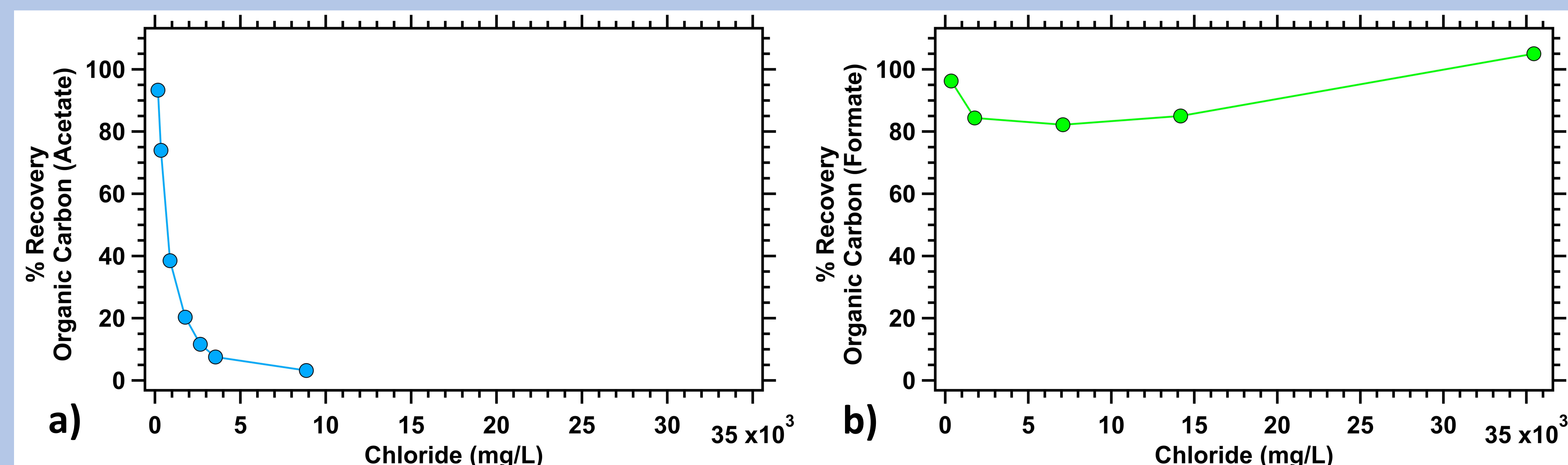

Figure 2: Recovery of 250 ppb-C acetate (a) and formate (b) as a function of sample chloride concentration by Sievers M9e TOC analyzer.

y = - 0.11043 x + 0.01488
r^2 = 0.97

Formic NaCl
Corrected Formic NaCl
pH = 2.5

Figure 2 shows the percent recovery of 250 ppb-C acetate (a) and formate (b) by the Sievers M9e TOC analyzer. Acetate recovery decreases from 93.3% at 177 mg/L to 74.0% at 354 mg/L, suggesting the limit for accurate measurements of acetic acid exists between zero and 177 mg/L chloride. This is lower than the threshold reported by van Zomeren et al., which found that WCO methods for TOC analysis are effective at chloride concentrations lower than 500 mg/L. Formate recovery sees a decrease from 96.2% at 355 mg/L to 84.4% at 1770 mg/L, but it increases again after 7100 mg/L, suggesting that formic acid recovery is less impacted by chloride interference than acetic acid.

Figure 3 shows data from an experiment on the partitioning of formic acid with an aqueous phase containing NaCl alongside the corrected data. The linear relationship suggests a Setschenow constant of -0.11 kg mol-1, meaning formic acid tends to partition into aqueous NaCl over the vapor phase.
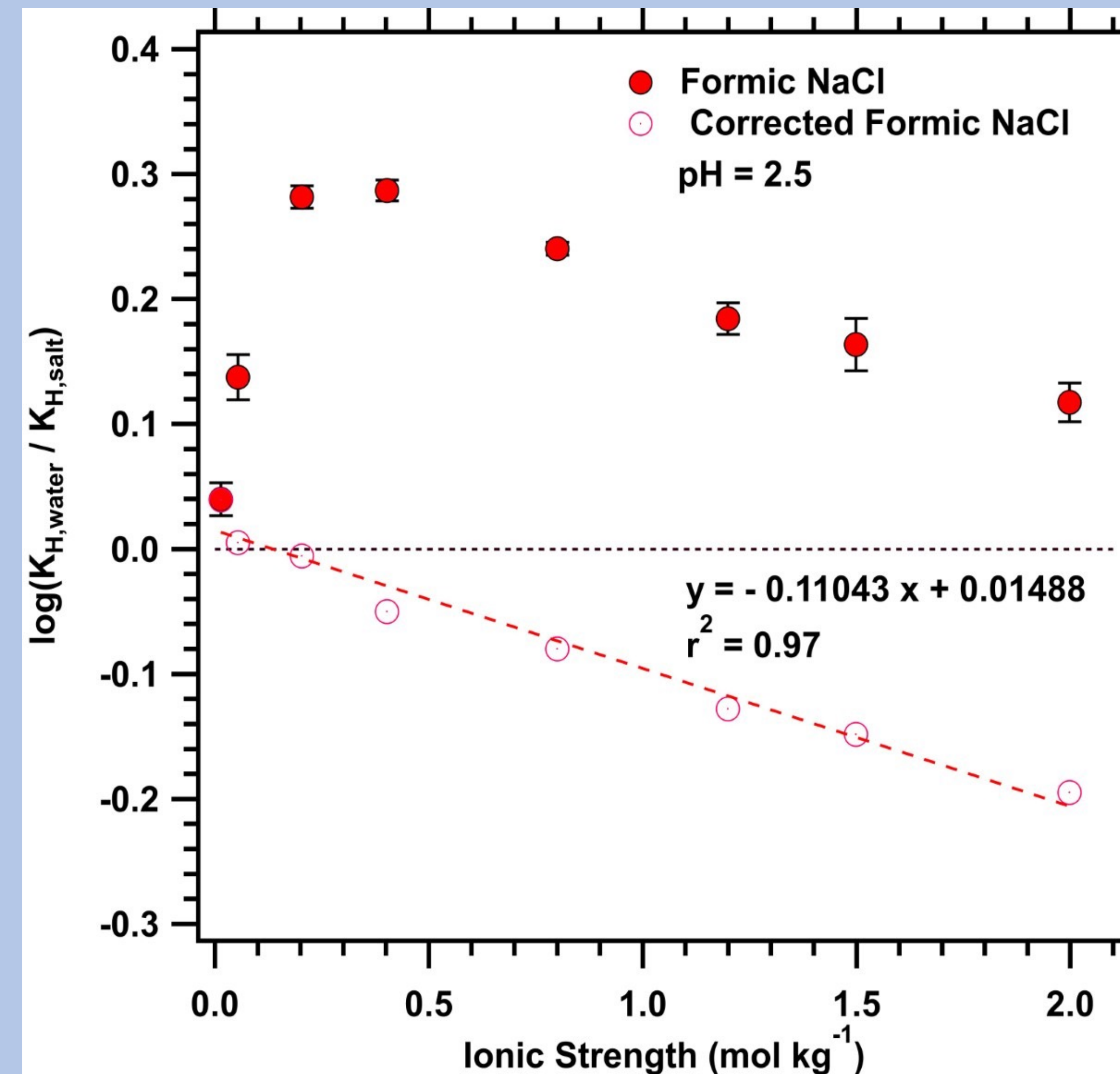
Figure 3: Corrections to past mist chamber experiments studying the partitioning of formic acid in aqueous aerosols containing NaCl. Corrections were made using TOC recovery values reported by van Zomeren et al. [4]