

Determination of chlorine in Passaic river water in New Jersey Newark area by titration method

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World Journal of Chemical and Pharmaceutical Sciences, 2024, 04(01), 001–006

Publication history: Received on 08 December 2023; revised on 28 January 2024; accepted on 31 January 2024

Article DOI: <https://doi.org/10.53346/wjcps.2024.4.1.0022>

Abstract

Much of the lower river suffered severe pollution during the 19th and 20th centuries because of industrial waste discharges and improper waste disposal practices on adjacent land. All drinking water, both tap and bottled, includes surface sources such as rivers, stream lakes, and reservoirs, and ground water source (wells) may be containing small amounts of some contaminants.

New Jersey's Passaic River has been a heavily polluted industrial waterway, for more than a century.

In this study, chlorine analysis has been done by EPA Titration method.

In Passaic River above Newark, New Jersey, the chlorine result has been found to be 7.00 mg/mL (ppm). In wastewater the chlorine discharge limit range is between 3 mg/L and 200 mg/L, depending on the season, and the industrial area.

Keywords: Chlorine Determination; Passaic River; Titration Method; New Jersey Newark Area

1 Introduction

Thousands of organic chlorine chemicals-chlorinated organics- are produced naturally by an array of biological and chemical processes in our environment. Many of these natural chemicals are identical to familiar manmade organochlorines: chlorophenols, chloroalkanes, polychlorobiphenyls (PCBs), and dioxins. Others are entirely new molecular entities and possess extraordinary biological properties similar to those of the natural products penicillin, morphine, and taxol^[1].

For almost 100 years, chlorine has been used by public water systems as a disinfectant because of its effectiveness against many microbial organisms that cause disease, including bacteria, virus and protozoans. Undeniably, chlorine disinfection of drinking water has saved millions of lives since its first use in U.S. drinking water supplies in Jersey City, N.J., in 1908 to control bacteria^[2].

All drinking water, both tap and bottled, include surface sources such as rivers, stream lakes, and reservoirs, and ground water source (wells) may contain small amounts of some contaminants^[3]. EPA has taken a large role in performing ongoing water analysis.

The **Passaic River** is a river, approximately 80 miles (130 km) long,^[4] in Northern New Jersey. The river in its upper course flows in a highly circuitous route, meandering through the swamp lowlands between the ridge hills of rural and

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suburban northern New Jersey, called the Great Swamp, draining much of the northern portion of the state through its tributaries.

In its lower (southern) portion, it flows through the most urbanized and industrialized areas of the state, including along Downtown Newark. The lower river suffered from severe pollution and industrial abandonment in the 20th century. In April 2014, the U.S. Environmental Protection Agency (EPA) announced a \$1.7 billion plan to remove 4.3 million cubic yards ($3.3 \times 10^6 \text{ m}^3$) of toxic mud from the bottom of lower eight miles (13 km) of the river. It is considered one of the most polluted stretches of water in the nation, and the project is one of the largest toxic cleanups ever undertaken in the nation.^[5]

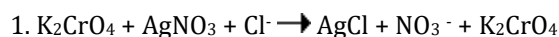
The Passaic River can be accessed via several county parks. One notable park is Stanley Park between Summit and Chatham. Other parks along the river are located in Passaic County. As part of the ongoing Newark revitalization effort by the city government, parkland is proposed along the banks of the river.

1.1 Scope and application

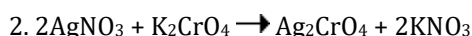
- This method is applicable to drinking, surface and saline water, and colorless, relatively clear, domestic and industrial wastes, stream river surface water, and swimming pool water.
- This SOP describes the method for use using Standard operating Procedure for the analysis of Chlorine Residual and Total Chlorine is based on Method 4500-Cl G from "Standard Methods for the Examination of Water and Wastewater" 22nd Edition (2012) ^[6].
- The practical range of determination is when 0.15 mg Cl⁻ to 10.0 mg Cl⁻ are present in the portion titrated. (i.e. if 50 mL sample is taken for titration – the concentration should be between 3 mg/L and 200 mg/L).
- In seawater (saline waters) all bromide and iodide ions will register as equivalent chloride concentrations.

2 Summary of method

A neutral or slightly alkaline solution is titrated with silver nitrate standard solution in the presence of a potassium chromate indicator. The end point is indicated when the initial yellow color becomes reddish due to formation of red silver chromate.



White precipitate

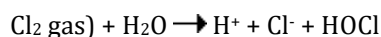


(orange)

In the chloride test using silver nitrate as the titrant and potassium chromate as the indicator, silver nitrate first reacts selectively with the chloride present in the sample to produce insoluble white silver chloride. After all the chloride has been precipitated, the silver nitrate reacts with the potassium chromate to form an orange-colored silver chromate precipitate, marking the end point of the titration. Potassium chromate indicator is combined with a buffer in Chloride 2 Indicator Powder (if HACH reagents are used).

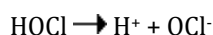
2.1 Chemistry of Chlorine

When chlorine gas is dissolved in water, it rapidly hydrolyzes (react with the H₂O molecules) to form hypochlorous acid:



Hypochlorous acid

The further dissociation of hypochlorous acid follows to produce hypochlorite ion:



3 Interferences

Substances in amounts normally found in potable waters will not interfere. Bromide, iodide and cyanide register as equivalent chloride concentrations as is the case when seawater is analyzed, or wastewater that is known to contain these ions. If the net chloride concentration is desired, specific analyses for these ions must be carried out or ion-chromatography is the preferred method in this case in which case the analysis must be subcontracted.

Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with dilute hydrogen peroxide. Add 1 ml H₂O₂ to 100 mL of sample and stir for one minute.

Orthophosphate in excess of 25 mg/L will interfere by precipitation as silver phosphate.

Iron more than 10 mg/L interferes by masking the end point.

3.1 Sample handling and preservation

Field sampling and analysis is performed mostly on-stream river surface water where applicable. In that case the sample is analyzed immediately using the field kit method.

Samples that are brought to the laboratory, such as river wastewater is analyzed within 15 minutes to meet the holding time requirement. Samples not analyzed within 15 minutes of sample collection must have the results qualified in the final report and cannot be used for compliance.

Sample Collection: The sampling has been followed NJDEP guidelines for collection, preservation and transport of water samples. The water samples have been collected from two-foot-deep flowing water level, and sediment as well in the Passaic River. The 10 laboratory cleaned sample amber glass or plastic bottle have been used for sampling between 1 mile, from 10 spots of both sides of the river, and then mixed them up to make it 1 L^[7]. Keep the sample cool to 2-6 °C by storing in a cooler with "blue ice" or regular ice^[8,9]. Holding time is twenty-eight (28) days^[10].

3.2 Apparatus

- Erlenmeyer flask, 250-mL.
- Burette, 50-mL.
- Stirrer with magnetic bar.

3.3 Reagents

3.3.1 Potassium chromate indicator solution.

- Dissolve 50 g K₂CrO₄ (ACS reagent grade 99%, CAS # 7789-00-6, Aldrich Cat # 21,661-5 or equivalent) in a little distilled water. Add AgNO₃ solution until a definite red precipitate is formed. Let stand for 12 hrs. Filter and dilute to 1 Liter with distilled water. Keep in a brown bottle.
- Alternatively, use HACH pillows identified as: "Chloride 2 Indicator Powder Pillows - For 100 mL Sample (Cat. # 1057-66).
- Note: MSDS from HACH confirms that the pillow contains K₂CrO₄.

3.3.2 Silver Nitrate, standard titrant - 0.0141 M (0.0141N)

- Prepare by dissolving 2.395 gm AgNO₃ in distilled water and dilute to 1000 mL. This solution must be standardized against a known NaCl standard solution every three months and each time a new standard is prepared.
- Store this reagent in a brown bottle.
- Note: 1) 1.0 mL of this solution is equivalent to 500 µg Cl⁻. 2) This standard may be purchased from HACH with Certificate of Analysis to confirm concentration. The standard purchased from HACH is 0.141M(0.141N) and is diluted 1 in 10 to obtain the 0.0141M standard. After dilution it must be standardized against a known NaCl standard solution. It must also be standardized every three months and each time a new standard is prepared.

3.3.3 Sodium chloride solution

- Prepare by dissolving 824.0 mg of pre-dried sodium chloride (pre-dried at 1400°C, for 1 hr) in distilled water and diluting to 1000 mL.

- Note: 1) 1.0 mL of this solution is equivalent to 500 μ g Cl⁻. 2) This standard may be purchased from HACH with Certificate of Analysis to confirm concentration.

3.4 pH adjustment solution

EPA Titration Method was used to determine chlorine in Passaic River wastewater pH 7.00 \pm 0.2 and using of the dichromate (K₂CrO₄) indicator color.

- For raising pH use sodium hydroxide, 1N solution.
1N NaOH: Dissolve 40 g of NaOH pellets in 1000 ml distilled water.

- For lowering pH use H₂SO₄, 1N solution.
1N H₂SO₄: Dilute 28 ml of conc. H₂SO₄ in 1000 ml distilled water.

Standardize the silver nitrate against the sodium chloride once every 3 months as described in the procedure below.

3.5 Potassium Permanganate solutions

- 1000 mg/L chlorine equivalent: Dissolve 891 mg of potassium permanganate in 1000 mL of chlorine free water.
- 100 mg/L chlorine equivalent: Dilute 10 ml of 1000 mg/L standard in 100 mL chlorine free water.
- 1 mg/L chlorine equivalent: Dilute 1 mL of 100 mg/L standard in 100 mL chlorine free water.

HACH Color standards: DPD-Chlorine-Low range secondary standards kit

D. I. Water: Recently boiled and distilled or deionized water

3.6 Procedure

- Use 100 ml of sample or a volume diluted to 100 ml and choose a standard titrant solution that corresponds to the expected chloride (Cl⁻) concentration. For samples expected to be from 0 to 500 ppm use 0.0141N AgNO₃ as the titrant. For samples with expected concentrations above 500 ppm use 0.141N AgNO₃ as the titrant.
- Use volumetric pipet or graduated cylinder to measure sample volume. If using less than 100 ml of sample for analysis dilute to 100 ml with distilled water.
- Transfer the sample into a 250 mL Erlenmeyer flask with a magnetic stir bar.
- Adjust the pH (using pH paper) to between 7.0 and 10.0 using either acid or base
- Add the contents of one (1) Chloride 2 indicator powder pillow (see Section 6.1.2) or add 1 ml of K₂CrO₄ indicator solution.
- Fill burette with titrant.
- Titrate the prepared sample while stirring on the stirring plate until the color changes from yellow to pinkish-yellow end point. Be consistent in end point recognition. If titrant volume exceeds 50 mL use smaller sample diluted to 100 ml.
- Reagent Blank check.
 - Repeat the titration with 100 mL distilled water sample. Note the volume of titrant required to reach the end point.
 - Note: A blank of 0.2 to 0.3 mL is typical.
 - When calculating actual volume required for sample titration subtract the blank volume.

3.7 Quality control

Run a duplicate every 20 samples, or once a month whichever occurs first. The RSD should be less than 10%.

Prepare a spike and spike duplicate for analysis in order to determine spike recovery and obtain information for accuracy determination.

The spike and spike duplicates should be run every 20 samples or once a month, whichever comes first. The spike recoveries should be between 80-120%.

The amount for spiking should be determined in such a way that the sample concentration should be roughly doubled.

$$\% \text{Recovery} = \frac{(\text{Conc spiked solution}) - (\text{Conc unspiked}) \times 35.45}{\text{Conc spike}} \times 100\%$$

Prepare the chlorine standard in the above range (see table) by adding 2mL acetic acid and 10 to 25 mL chlorine demand free water in a flask. Add about 1.0 gm KI. Pipette into the flask a suitable volume of the chlorine standard solution. Note that 1 mL of 0.025N Na₂S₂O₃ titrant is equivalent to about 0.9 mg chlorine. Titrate with standardized 0.025 N Na₂S₂O₃ titrant until the yellow iodine color almost disappears. Add 1 to 2 drops of starch indicator solution and continue titrating until the blue color disappears.

Determine a blank by adding identical quantities of acid, KI and starch indicator to the same volume of chlorine demand free water as for the sample. Perform the blank titration.

The actual concentration of the standard is then calculated as follows:

$$\text{mg Cl as Cl}_2 / \text{mL} = \frac{(A-B) \times N \times 35450}{\text{mL sample}}$$

Where:

N- Normality of titrant solution AgNO₃

A - mL titrant for sample

B - mL titrant for blank

4 Result and discussion

From the scores of hazardous substances in the Passaic River, EPA (Environmental Protection Agency) has identified hundreds of chemical companies that have polluted the Passaic River with countless hazardous substances. According to EPA, copper, lead, mercury, DDT, dieldrin, dioxins and furans, poly-chlorinated biphenyls (PCBs), and poly-aromatic hydrocarbons (PAHs) are the main pollutant in the Passaic River. This method has been fully evaluated with results from performance tests. In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Table 1 Results for chlorine as Cl₂

Sample ID Number	pH	matrix	Sample Volume(mL)	Titration (mL) Start	Titration (mL) Finish	Titrant Volume (mL)	Chlorine mg/L
Blank	6.28	DIW	50	0.00	0.20	0.20	
sample	7.17	ww	50	0.00	0.90	0,90	7.00
Sample dup	7.16	ww	50	0.00	0.90	0.90	7,00
Matrix spiked MS	7.22	ww	50	0.00	1.00	1.00	8.00
Matrix dup spiked MSD	7.22	ww	50	0.00	1.00	1.00	8.00
Check std -5.0 mg/L	7.20	w	50	0.00	0.70	0.70	4.99

4.1 Calculation / Precision

$$\text{Ave. Cl}^- = 7.00 \text{ mg/L}$$

$$\% \text{RPD} = 0.00\%$$

Titrant normality = 0.0141N

$$\text{sample} = \frac{(0.90 - 0.20) \times 0.0141 \times 35450}{50} = 7.00 \text{ mg/L}$$

$$\text{sample dup} = \frac{(0.90-0.20) \times 0.0141 \times 35450}{50} = 7.00 \text{ mg/L}$$

Check Std- 5.0 mg/L

Spike & Spike Duplicate:

$$\% \text{Recovery} = \frac{(\text{Conc spiked solution}) - (\text{Conc unspiked})}{\text{Conc spike}} \times 100\%$$

$$\% \text{ Recovery}_{\text{MS/MSD}} = \frac{(8.00) - (7.00)}{1.0} \times 100\% = 100\%$$

5 Conclusion

This study on chlorine as Cl₂ values of Passaic River wastewater, New Jersey determined by titration method. The average chlorine concentration of 7.0 mg/L has been found in contaminated river water [Table 1]. Percent recovery was 100%, and % RPD was 0.00 %. Moderate to severe seasonal variations in Chlorine (Cl₂) loads were also observed in the Passaic River Water.

Compliance with ethical standards

Acknowledgments

The authors are thankful to *Dr. Dunning Carol*, head of the Best Care College of Nursing, for giving us the opportunity to complete this work.

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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