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COMPARISON OF MANUAL AND ONLINE INSTRUMENTAL METHODS FOR ANALYSIS OF TOTAL ORGANIC CARBON IN PULP AND PAPER INDUSTRY EFFLUENTS

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ABSTRACT

The determination of total organic carbon (TOC) is an important analytical tool for monitoring organic matter in industrial effluents. However, the cost of instrumental analyzers may limit their use in resource-constrained laboratories. This study evaluated a manual wet-oxidation titrimetric method for TOC determination in pulp and paper industry effluents and compared its results with those of an online instrumental analyzer. The manual procedure involved oxidation with potassium dichromate in an acidic medium, followed by back-titration of the residual oxidant with ferrous ammonium sulfate. Potassium hydrogen phthalate standards spanning 100–1,000 mg C L^{-1} were used to evaluate the analytical response, yielding a linear relationship (R^2 = 0.9988). Both methods were subsequently applied to pulp mill effluent samples treated with electric plasma for up to 420 min. The measurements exhibited a strong linear relationship (R^2 = 0.986) and showed similar trends in TOC reduction during treatment. These findings suggest that the manual procedure may offer a lower-cost option for monitoring TOC in the investigated effluent matrix. Further studies assessing bias, precision, recovery, and matrix effects are needed before the two methods can be considered interchangeable.

Keywords: Total organic carbon; Pulp and paper effluent; Wet oxidation; dichromate titration; Online analyzer; Electric plasma.

1 INTRODUCTION

Total organic carbon (TOC) is widely used to assess the organic carbon content of industrial effluents and to monitor the performance of wastewater treatment processes. It also provides a useful analytical parameter for research on the removal and transformation of organic contaminants.

TOC measurements may be correlated with biochemical oxygen demand (BOD) and chemical oxygen demand (COD), provided that matrix-specific relationships have been established. Unlike BOD and COD, TOC quantifies carbon rather than oxygen demand and is not directly determined by the oxidation state of organic compounds. Consequently, these parameters provide complementary information about effluent composition [1].

Instrumental TOC analysis can determine total carbon (TC) and inorganic carbon (IC), allowing TOC to be calculated by difference. An alternative approach is wet oxidation with potassium dichromate, followed by titration of the remaining oxidant. This approach is related to the Walkley–Black method, originally developed for organic carbon determination in soils. Because oxidation efficiency and potential interferences vary among matrices, its performance must be assessed specifically for industrial effluents [2, 5].

In the titrimetric approach, organic matter is oxidized by dichromate in a strongly acidic medium. The oxidant consumed is estimated from the difference between the amount initially added and the amount remaining after digestion [4].

This study compared a manual dichromate-based titrimetric procedure with an online instrumental TOC method using pulp and paper industry effluent collected before biological treatment (EBBT). The effluent was subjected to electric plasma treatment, as described by MATIAS et al. (2018) [3], to provide samples covering a range of organic carbon concentrations.

2 MATERIALS AND METHODS

2.1 Standard solution of potassium biphthalate 1,000 mg L^{-1}

Potassium hydrogen phthalate ($KHC_8H_4O_4$), previously dried at 105 °C for 2 h, was used to prepare a stock solution in deionized water. A mass of 2.1250 g was dissolved and quantitatively transferred to a 1,000 mL volumetric flask, which was filled to the mark. The stock solution was reported as 1,000 mg L^{-1}, and working standards of 100–900 mg L^{-1} were prepared by dilution.

2.2 Standard solution of potassium dichromate 0.167 mol L^{-1}

Potassium dichromate ($K_2Cr_2O_7$; 49.025 g), previously dried at 140 °C for 1 h, was dissolved in deionized water and quantitatively transferred to a 1,000 mL volumetric flask. The solution was diluted to volume to obtain a nominal concentration of 0.167 mol L^{-1}.

2.3 Solution of ammonium ferrous sulfate 0.20 mol L^{-1}

Ammonium ferrous sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$; 78.400 g; Isofar) was dissolved in 50 mL of concentrated sulfuric acid. The solution was diluted with deionized water, quantitatively transferred to a 1,000 mL volumetric flask, and made up to volume. Because ferrous ions can oxidize during storage, the solution should be freshly prepared or standardized before use.

2.4 Ferroin indicator solution

A mass of 1.485 g of o-phenanthroline (Carlo Erba) and 0.695 g of $FeSO_4$ was dissolved in deionized water. The solution was transferred quantitatively to a 100 mL volumetric flask and diluted to the mark.

2.5 Total Organic Carbon (TOC) Analysis by Titration

The manual procedure used potassium dichromate ($K_2Cr_2O_7$) as the oxidizing agent in a strongly acidic medium. The oxidation reaction is represented schematically in Equation 1:

$$2Cr_2O_{7(aq)}^{2-} + 3C_{(aq)} + 16H_{(aq)}^{+} \rightarrow 4Cr_{(aq)}^{3+} + 3CO_{2(g)} + 8H_2O_{(l)} \quad (1)$$

Digestion was performed with external heating to promote oxidation of organic carbon. Residual dichromate was subsequently determined by titration with ammonium ferrous sulfate, using ferroin as the endpoint indicator (Equation 2).

$$Cr_2O_{7(aq)}^{2-} + 6Fe_{(aq)}^{2+} + 14H_{(aq)}^{+} \rightarrow 2Cr_{(aq)}^{3+} + 6Fe_{(aq)}^{3+} + 7H_2O_{(l)} \quad (2)$$

An aliquot of 5.00 mL of EBBT pulp mill effluent was transferred to a digestion tube. Potassium dichromate solution (2.00 mL, 0.167 mol L^{-1}) and concentrated sulfuric acid (7.50 mL) were added. The tubes were placed in a digestion block preheated to 170 °C and maintained at this temperature for 30 min. After cooling, the contents were quantitatively transferred to 250 mL Erlenmeyer flasks and diluted with deionized water to approximately 80 mL.

After cooling, three drops of ferroin indicator were added, and the solutions were titrated with 0.20 mol L^{-1} ammonium ferrous sulfate until the color changed from green to dark violet. Six reagent blanks were prepared using 0.167 mol L^{-1} potassium dichromate (reported volume: 5.00 mL) and 7.50 mL of concentrated sulfuric acid. Three blanks underwent digestion, whereas three remained unheated at room temperature. The unheated blanks were intended to account for dichromate loss during heating

Instrumental measurements were performed using a QuickTOC online analyzer (LAR Process Analysers AG) operated at CENIBRA, with a reported measurement range of 5–4,000 mg C L^{-1}.

3 RESULTS AND DISCUSSION

3.1 Standard curve of TOC by titration

A calibration experiment using potassium hydrogen phthalate standards was conducted to evaluate the response of the manual titrimetric procedure. Figure 1 compares the nominal TOC concentrations with the values obtained by titration.

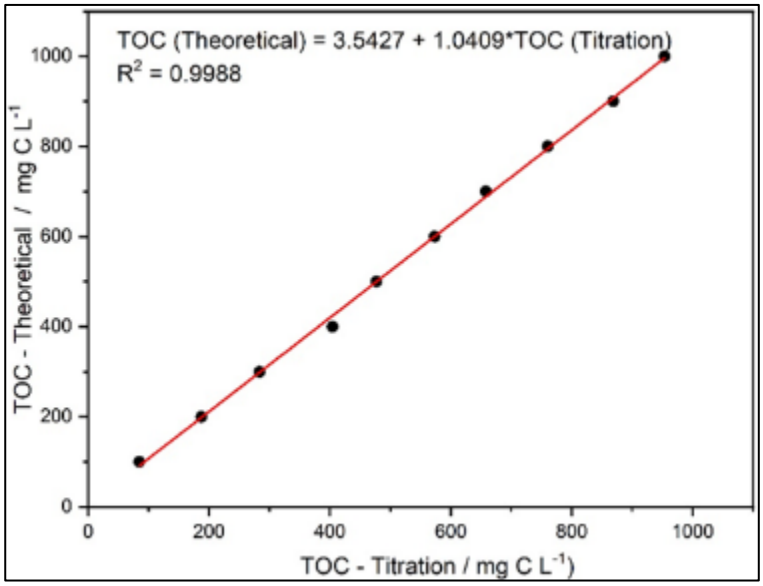


Figure 1: Correlation between theoretical TOC values and values found by titration.

The calibration data exhibited a strong linear relationship (R^2 = 0.9988; Figure 1), indicating a consistent analytical response across the tested standards. However, linearity alone does not establish accuracy, recovery, or agreement with instrumental measurements. The manual procedure uses relatively inexpensive reagents, which may make it attractive for laboratories without access to an online TOC analyzer.

3.2 Comparison of manual and instrumental titration methods in pulp and paper effluent before biological treatment (EBBT)

The two methods were applied to EBBT pulp mill effluent samples subjected to electric plasma treatment for 0–420 min. Figure 2 presents the TOC concentrations obtained by each method as a function of treatment time.

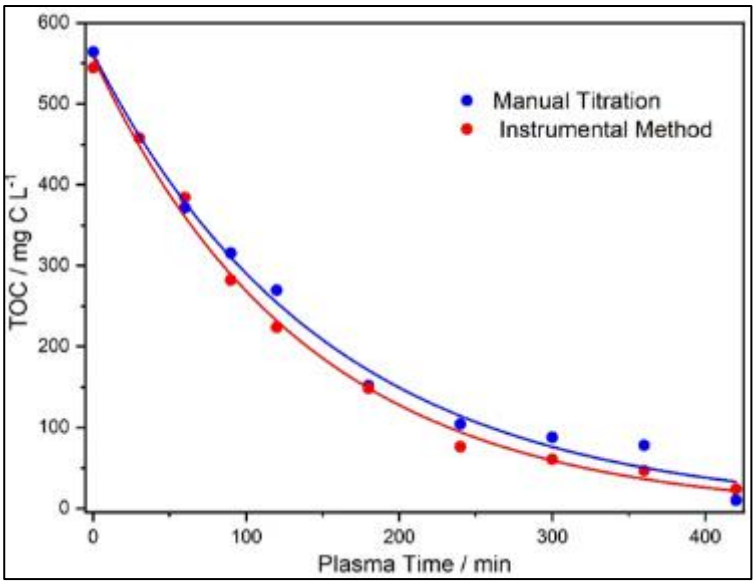


Figure 2: TOC values for a pulp and paper mill effluent sample, before biological treatment (EBBT), obtained by manual titration and by instrumentation, after application of electric plasma between 0 and 420 minutes [3].

To examine the relationship between the measurements, instrumental TOC values were plotted against those obtained by manual titration (Figure 3).

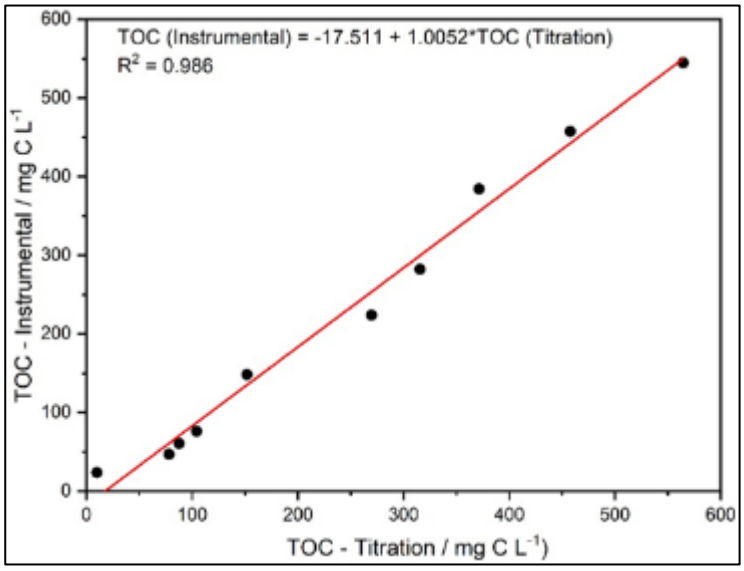


Figure 3: Correlation of TOC measurements for pulp and paper mill effluent sample before biological treatment (EBBT) obtained by manual titration and by instrumentation after plasma application between 0 and 420 minutes.

Both methods indicated a progressive decrease in TOC concentration with increasing plasma treatment time (Figure 2). The measurements were strongly linearly associated (R^2 = 0.986; Figure 3). The fitted relationship nevertheless suggests that systematic differences may occur between methods, particularly across the concentration range. Manual titration may also be affected by endpoint identification, volumetric handling, incomplete oxidation, and matrix-specific interferences. Therefore, the observed correlation supports the potential usefulness of the manual method for tracking treatment trends but does not, by itself, demonstrate analytical equivalence. Replicate measurements, recovery experiments, and an agreement analysis would strengthen the validation.

4 CONCLUSION

The manual dichromate-based titrimetric method showed a strong linear response to potassium hydrogen phthalate standards (R^2 = 0.9988) and a strong association with online instrumental TOC measurements in plasma-treated pulp and paper industry effluent (R^2 = 0.986). Both methods captured a similar decline in TOC during treatment.

These results suggest that manual titration may provide an accessible, lower-cost approach for monitoring organic carbon trends in the studied effluent matrix, particularly within the investigated concentration range. However, the present evidence does not establish that the manual and instrumental methods are interchangeable.

Before routine application or extension to other industrial effluents, the procedure should be evaluated for analytical recovery, repeatability, bias, quantification limits, and matrix interferences. Clarification of the standard preparation and blank correction procedures is also necessary for reproducibility.

STATEMENTS ON COMPLIANCE WITH ETHICAL STANDARDS

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Disclosure of conflict of interest

The authors declare no conflicts of interest.

Data Availability Statement

The data supporting the conclusions of this study are available upon reasonable request to the corresponding author.

REFERENCES

[1] APHA - AMERICAN PUBLIC HEALTH ASSOCIATION; AWWA - AMERICAN WATER WORKS ASSOCIATION; WEF - WATER ENVIRONMENT FEDERATION. (1998). Standard methods for the examination of water and wastewater. 20. ed. Washington: APHA, 1998.Standard Methods for the Examination of Water and Wastewater, 20th Ed.

[2] MENDONÇA, E. de S.; MATOS, E. da S. (2005). Matéria orgânica do solo: métodos de análises. Viçosa – MG, 107p.

[3] MATIAS, A. A.; REIS, C.; REIS, E. L.; SILVA, C. M.; DAMASCENO, O. I. C.; NEVES, A. A. (2018). Pulp Mill Effluent Treatment Using Plasma Obtained by High Voltage Electrolysis. J. Braz. Chem. Soc., 29(12), 2535-2541.

[4] CARMO, D. L.; SILVA, C.A. (2012). Métodos de quantificação de carbono e matéria orgânica em resíduos orgânicos. Rev. Bras. Ciênc. Solo, 36(4), 1211-1220.

[5] RHEINHEIMER, D. S.; CAMPOS, B. C.; GIACOMINI, S. J.; CONCEIÇÃO, P. C.; BORTOLUZZI, E. C. (2008). Comparação de métodos de determinação de carbono orgânico total no solo. R. Bras. Ci. Solo, 32(1), 435-440.