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Comparative Evaluation of Methods to Quantify Dissolved Total Solids in Water Resources

AVALIAÇÃO COMPARATIVA DE MÉTODOS DE QUANTIFICAÇÃO DE SÓLIDOS TOTAIS DISSOLVIDOS EM RECURSOS HÍDRICOS

EVALUACIÓN COMPARATIVA DE MÉTODOS DE CUANTIFICACIÓN DE SÓLIDOS TOTALES DISUELTOS EN RECURSOS HÍDRICOS

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Abstract
The water resources evaluation through STD concentration (total solids dissolved) is one of the most specific ways to show natural interferences or even anthropic ones in the water resources of any ecosystem. Due to soils and urban areas occupation next to these water resources, it's necessary monitoring to determine if there is any anthropic action on them and verify the need of researching the most appropriate methods to its analysis. Therefore, this research aims to compare both Gravimetry and Conductometry analytical methods efficacy for STD determination. Gravimetry determines STD concentration from the drying sample and the obtained residue weight measurement afterwards. Conductometry obtains results by the presence of ions in solution using conductivimeter. The project analytical process was divided in two parts. First, tests were carried out with monovalent, bivalent and mixed ions synthetic samples. Second, samples were taken from 10 continental water points in Paranaguá and Pontal do Paraná. The samples were stored in polyethylene bottles and sent to LAVIMA (Evaluation Lab of Environment Impacts), where analytical tests were carried out with 5 replicas of each sample point. Thus, results were obtained with higher reliability. The gravimetry method results obtained in most of the synthetic samples were similar to the expected ones, but one of the monovalent reagents was ineffective by the conductometry technique. The measured continental samples from 3 points in Itiberê river, using gravimetry method, showed values equal to 16,336±3,962; 27,142±0,528 and 26,451±0,799 g. $L^{-1,}$ which confirm that these places are influenced by tides significantly. From the data, we conclude that the conductometry method is not advised to measure STD on samples with excessive presence of ions.

Keywords: *Gravimetry, Conductimetry, Anthropic Activity, Paranaguá.*

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RESUMO
*A avaliação dos recursos hídricos por meio da concentração de STD (sólidos totais dissolvidos) é uma das formas mais pontuais para indicar interferências naturais ou mesmo antrópicas nos recursos hídricos de qualquer ecossistema. Devido à ocupação de solos e áreas urbanas próximas desses recursos hídricos, se faz necessário o monitoramento para determinar se há alguma ação antrópica que esteja agindo sobre os mesmos, verificando-se a necessidade de pesquisar os métodos mais adequados para sua análise. Dessa forma**,** este trabalho teve como objetivo comparar a eficácia dos dois métodos analíticos na determinação dos STD, sendo a de gravimetria e de condutimetria. Na gravimetria determina-se a concentração de STD a partir da secagem da amostra, com posterior determinação da massa do resíduo obtido. Na condutimetria, os resultados são obtidos pela presença dos íons em solução com a utilização do condutivímetro. O processo analítico do projeto foi dividido em duas partes. Na primeira, realizaram-se ensaios com amostras sintéticas de íons monovalentes, bivalentes e mistos. Na segunda parte, coletaram-se amostras de 10 pontos amostrais, provindas de águas*

continentais, da região de Paranaguá e Pontal do Paraná. As amostras foram armazenadas em frascos de polietileno e encaminhadas para o LAVIMA (Laboratório de Avaliação de Impactos Ambientais), onde foram realizados os ensaios analíticos com 5 réplicas de cada ponto amostral. Assim, obteve-se maior confiabilidade nos resultados. Os resultados gravimétricos obtidos na maioria das amostras sintéticas se apresentaram similares ao esperado, no entanto um dos reagentes monovalentes se mostrou ineficaz pela técnica condutométrica. Nas amostras continentais avaliadas, observou-se que os 3 pontos diferentes do rio Itiberê apresentaram valores, no método de gravimetria, iguais a 16,336±3,962; 27,142±0,528 e 26,451±0,799 g. L^{-1}, sendo constatado que esses locais sofrem influência significativa das marés. A partir dos dados, conclui-se que o método condutimétrico não é recomendado para determinar STD em amostras com presença excessiva de íons.

***Palavras-chave**: Gravimetria, Condutimetria, Atividade Antrópica, Paranaguá.*

RESUMEN

La evaluación de los recursos hídricos a través de la concentración de STD (sólidos totales disueltos) es una de las formas más puntuales de indicar interferencias naturales o incluso antrópicas en los recursos hídricos de cualquier ecosistema. Debido a la ocupación de suelos y áreas urbanas cercanas a estos recursos hídricos, es necesario realizar un seguimiento para determinar si existe alguna acción antrópica que esté actuando sobre ellos, verificando la necesidad de investigar los métodos más adecuados para su análisis. Así, este trabajo tuvo como objetivo comparar la efectividad de los dos métodos analíticos en la determinación de la STD, siendo el de gravimetría y conductividad. En gravimetría, la concentración de STD se determina a partir del secado de la muestra, con posterior determinación de la masa del residuo obtenido. En conductividad, los resultados se obtienen por la presencia de iones en solución utilizando el conductímetro. El proceso analítico del proyecto se dividió en dos partes. En el primero, las pruebas se realizaron con muestras sintéticas de iones monovalentes, bivalentes y mixtos. En la segunda parte, se recolectaron muestras de 10 puntos de muestreo, de aguas continentales, de la región de Paranaguá y Pontal do Paraná. Las muestras se almacenaron en frascos de polietileno y se enviaron a LAVIMA (Laboratorio de Evaluación de Impacto Ambiental), donde se realizaron pruebas analíticas con 5 réplicas de cada punto de muestra. Así, se obtuvo una mayor confiabilidad en los resultados. Los resultados gravimétricos obtenidos en la mayoría de las muestras sintéticas fueron similares a los esperados, sin embargo, uno de los reactivos monovalentes demostró ser ineficaz mediante la técnica conductimétrica. En las muestras continentales evaluadas, se observó que los 3 puntos diferentes del río Itiberê presentaron valores, en el método de gravimetría, iguales a 16,336 ± 3,962; 27,142 ± 0,528 y 26,451 ± 0,799 g. L-1, comprobándose que estos lugares sufren influencia significativa de las mareas. De los datos se concluye que no se recomienda el método conductimétrico para determinar DTS en muestras con excesiva presencia de iones.

Palabras clave: Gravimetría, Conductimetría, Actividad Antrópica, Paranaguá.

I. INTRODUCTION

The water is one of most important and abundant compounds to all lives species from fauna and flora of the planet (VICTORINO, 2007). It's observed in its chemistry composition two hydrogen atoms linked by one of oxygen, which is an essential feature for presenting unique properties to the live beings (BACCI, PATACA, 2008). It's considered a public domain of high importance for being self-sustainable, which means that it has the capacity to restore its environmental characteristics naturally. However, with the increase of anthropic influences, there are people who care about quality and how it will be used to consume which is strongly connected to agriculture and industrial activities (GLORIA, *et. al.*, 2017).

The continental waters consumption covers 70% in agriculture, 20% in industry and the rest in human consumption. Due to the fact of these small quantity be used to human consumption, there is a worry about devaluation, enabling waste in urban solid waste generation that can be changed, occasionally, in pollutants of continental and oceanic waters. Besides that, with the population increase, there is the tendency to grow industrial waste, as well as domestic waste, that can cause contamination in ground and subsurface waters (ELIS, 2002).

The contaminations are determined by excessive concentration of factors that interfere in the water quality, dealing with physical, chemical and biological factors can be evaluated by the substances present in water, which are the water quality parameters, according to NSF (National Sanitation Foundation) (2016), non-governmental organization that establishes certifications of water quality to human consume. The most representative parameters are 9 in total, and one of them is the DTS (Dissolved Total Solids). Precisely, the interrelation between these nine parameters ensure water quality.

The DTS indicates concentration of solids in water body, which in excess can cause formation of pollutants in water resources. According to CONAMA (National Council of environment), concentrations of DTS can't surpass 500 $mg.L^{-1}$ in continental waters classification, divided in types 1, 2 and 3, proper to human

consume, highlighted from the resolution n° 357/05 (2005). If this stipulated measure is overtaken, the suspended residual solids in the water, by natural or anthropic way, indicate that it's being committed and affecting indirectly the aquatical lives, becoming a pollutant (LOUGON, 2013). These facts block the light penetration in deeper regions of hydric resource, what can decrease oxygen dissolved quantity in the environment, due to its low efficiency photosynthetic process, affecting the environment (REIS, CAVALLET, ROCHA, 2014).

There are several methods to determine dissolved solids concentration in liquid sample. However, normally the conductometric (BERGER et al., 2013) and gravimetric tests (DIAS, 2004) are used. According to Dias (2004), the gravimetric method consists in weighing a determined sample volume, with subsequents phases in heating temperature to evaporate the liquid phase and obtain the solid concentration, which results are obtained by simple mathematical calculation of proportion. This large quantity of phases shows that this methodology has a long period. While Berger (2013) indicates that DTS determination by conductometric test consists in simplified way, obtaining dissolved solids concentration from the present ions concentration analysis in samples, which analytic methodology is faster and practice. It is necessary the methodology evaluation be implemented in water quality determination for a better adaptation in the regional environmental reality (AGÊNCIA NACIONAL DAS ÁGUAS, 2019).

Thus, this study has the main objective to compare the efficiency between two analytical methods in DTS determination. Therefore, 10 geographical positions were chosen as samples from continental waters in Paraná coastal region. Also, analytical determinations from synthetic samples were analysed using chemical reagents with monovalent (NaCl), bivalent ($CuSO_4$ and $MnSO_4$) and mixed ions ($Ca(NO_3)_2$) to compare results with known concentrations.

II. EXPERIMENTAL PROCEDURE

The methodological procedure was done in the Laboratory of Environmental Impacts Evaluation (LAVIMA) of Biological Science Collegiate of Universidade Estadual do Paraná (UNESPAR), Paranaguá *Campus*.

In the following work, gravimetric and conductometric measures of DTS in synthetics and natural samples (from continental water) were accomplished. The measures and analysis were carried out during one year, the two first trimesters with synthetical samples and the next ones with natural samples. The synthetic samples included solutions prepared in laboratory with monovalents (NaCl), bivalents ($MnSO_4$ and $CuSO_4$) and mixed ions ($Ca(NO_3)_2$), and the natural ones contained waters from sampling points in coastal rivers in Paraná State.

2.1. Synthetic samples

The synthetic samples were measured in the first semester. So, each of the five replicas were done to minimize possible mistakes in analytical determination.

The solutions were prepared in different concentrations, beginning with the monovalent ion of salt sodium chloride (1,0; 20 e 160 $g.L^{-1}$), using a purity reagent analytical (P.A.). Afterwards, calcium nitrate ($Ca(NO_3)_2.4H_2O$) in the same concentrations previously described. Then, the bivalents ions of copper sulfate ($CuSO_4.5H_2O$) and magnesium sulfate ($MnSO_4.H_2O$), with distinct concentrations (1,0; 10 e 60 $g.L^{-1}$; 1,0; 20 e 120 $g.L^{-1}$, respectively.

2.2. Natural samples

Natural samples were collected during February/2018 and may/2018 from 10 sampling points (Figure 1) coming from coast rivers of Paraná state, located in the cities of Paranaguá/PR and Pontal do Paraná/PR, most of them from the river banks of Engenheiro Argus Tha Heyn highway (PR-407). The sampling was performed using a plastic small recipient tied by a string to collect sample. Using the same recipient, it was thrown in the sampling points, above and under the bridges, to water with drawal and insertion in polyethylene bottle (500 mL) and identified. After the sampling, the laboratory was guided to store them in the refrigerator. These points were numbered and identified using GPS, as demonstrated in Figure 1.

Ponto	Localização	Coordenadas
1	Rio Balneário - Praia de Leste	-25,697514; -48,475359
2	Rio Pery	-25,687604; -48,490303
3	Rio Guaraguaçú	-25,671996; -48,512652
4	Rio São Joãozinho	-25,664941; -48,518581
5	Rio da Vila	-25,585267; -48,567808
6	Riacho no Km 7 da Rodovia das Praias	-25,566760; -48,578610
7	Riacho no Km 1 da Rodovia das Praias	-25,615641; -48,548593
8	Rio Itiberê Valladarez	-25,524251; -48,505898
9	Rio Itiberê Marinha	-25,517519; -48,501867
10	Rio Itiberê próximo ao DETRAN	-25,542429; 48,524898

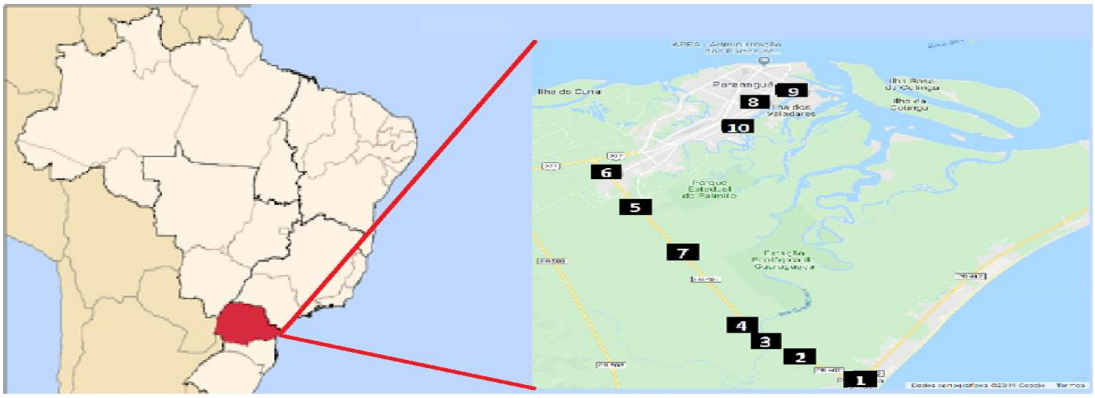

Figure 1: *Identification and Localization of natural sampling points with their respectively geographic coordinates. Source: Author*

All measures analysis of gravimetry and conductometry assays to determine DTS were realized in LAVIMA. The methods, respectively, were done as follows:

2.3. Gravimetry

This analytical method is based on the initial weigh of an empty beaker with subsequent sample aliquot and then its evaporation. The next step occurs drying the sample in a kiln at 105°C with constant weight, following cooling in the dissector. Each sequence of 10 assays, in this analytical process was carried out in a period of about 2 and 3 hours. Afterwards, the recipients were inserted, with dry residues, in the dissector for a cooling period (Figure 1), getting the final with initial mass, respectively and its solid mass was obtained.

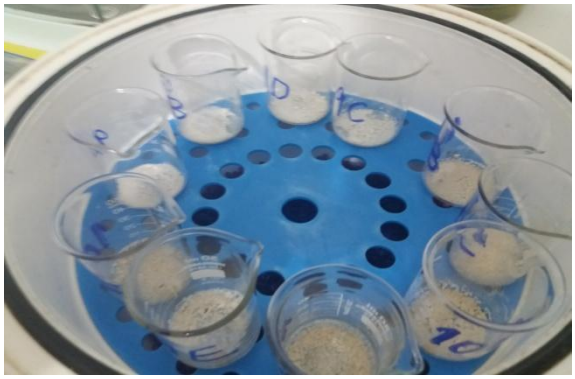

Figure 2: *Recipients with dry residues for the cooling period. Source: Author.*

After all this analytical procedure, the residues concentration present in samples were determined by mathematical calculations to express in mg L^{-1}, taken by solid mass in relation to aliquot volume added.

2.4. Conductivity

The presence of DTS was determined by the ionic conductivity of ions inside the samples using the conductivity meter mC150 from MS TECNOPON. The equipment was calibrated using a standard solution of KCl (Potassium chloride) where the conductivity is equals to 146,9 µS cm^{-1}.

2.5. Equipments

The equipments used in analytical procedures were: analytical balance (FA/JA electronic *balance operation*), magnetic stirrer (78HW-1), kiln, dissector, hot plate (*DB-IVAC*) and a conductivity meter (mCA-

150).

III. RESULTS AND DISCUSSION

3.1. Synthetic samples

The results obtained from these solutions prepared with reagents of $CuSO_4$ (Copper sulfate), $Ca(NO_3)_2$(Calcium Nitrate), $MnSO_4$ (manganese sulfate) e NaCl (Sodium Chloride) in the gravimetric method showed very close results to those expected of DTS, according to values in Figure 3.

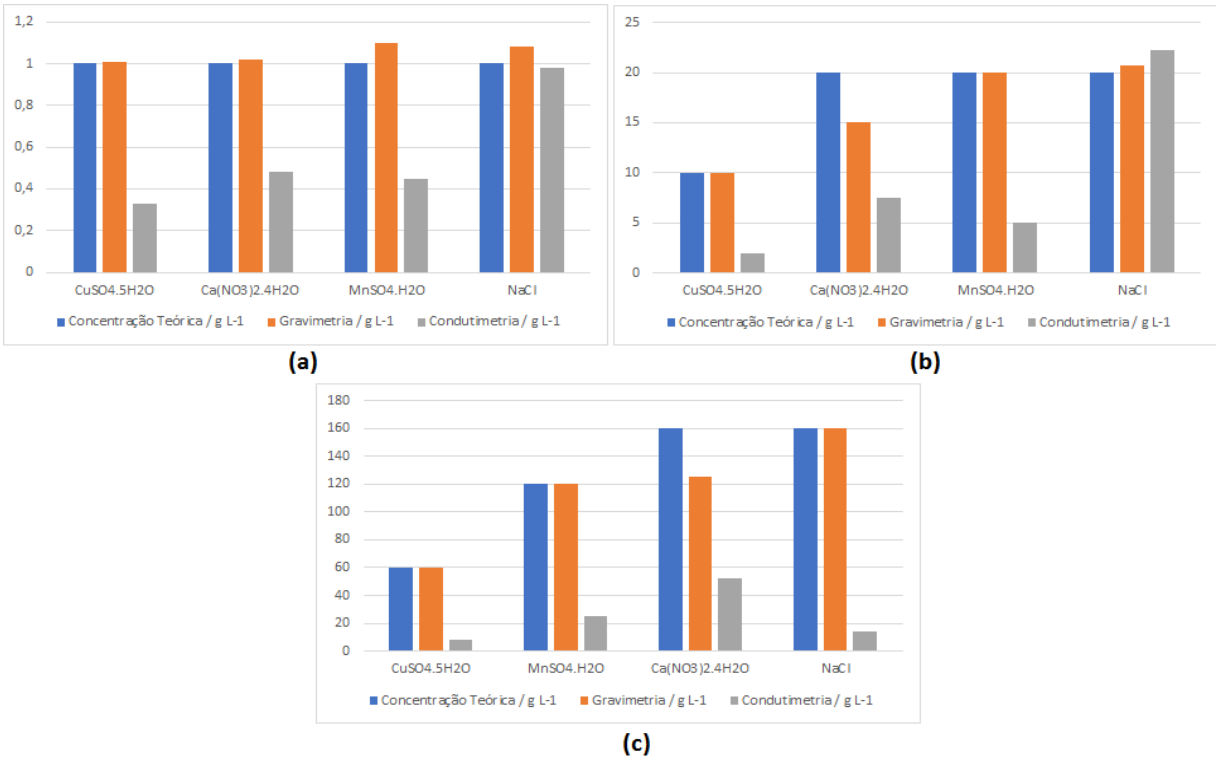

Figure 3: Obtained medium values of synthetic samples *($CuSO_4.5H_2O$, $Ca(NO_3)_2.4H_2O$, $MnSO_4.H_2O$ e NaCl) obtained from the concentration of DTS (Dissolved Total Solids) by gravimetric and conductometric methods based in theoretical sample concentrations (a)1* g L^{-1} *, (b) 10; 20 ;20 ;20* g L^{-1} *; (c) 60; 120; 160; 160* g L^{-1}. *Fonte: Author.*

It is observed that the results by the gravimetric way are according to theoretical value concentrations, and only two solutions with the highest concentration of $Ca(NO_3)_2.4H_2O$ showed different results from those expected. Remembering that just 38% of structure of that salt molecule is composed by hydration waters, therefore they can be eliminated by the temperature increase. Probably, in this case, the hydration water molecules of the chemical structure have been released and then the showed results are lower than the theoretical ones.

3.2. Natural samples

It was checked that the obtained results in natural samples by each analytical methodology were divergent (Figure 4). The conductometric way showed lower values results than the ones obtained by gravimetric, which also happened with synthetic samples (Figure 3).

It is understood that it is preferably not to use conductometric method to make DTS assay due to the fact that there are present substances in natural samples which don't have electric charge, making them not detectable by this methodology.

In most of the obtained results by conductometric way was observed values below those obtained with gravimetric. According to Martínez (2017), the chain of ions in solution depends on their characteristics in the electrolytic cell apparatus, the solution concentration, the solvent nature and ions. So, naturally, if there is an increase of ions in the solution, there will be an increase of their conductance proportionally, depending on basically of the physic-chemical properties of the element. It was verified that the relation between conductivity and ions concentration in the solution was caused by their increase, which resulted in the electrode repulsion due to the excess of them, decreasing the electric charge, so interfering with concentration analysis results of DTS in the cell.

If we evaluate from the environmental point of view, it is perceived that most of continental water samples are according to 357/2005 Resolution of CONAMA which maximum value is 500 mg L^{-1}.
However, the last three points sampling from Itiberê River had different values stipulated by CONAMA. This is due to the fact that the river suffers massive influence of tide process, where marine waters can be taken long after the sampling point of DETRAN (Sample 10). The sampling point 9 is the the nearest from Paranaguá bay, nearly 1 Km from the bay. The sampling point 8 is the second one in relation to Paranaguá bay, which is 2 Km of from the river mouth. Yet, the sampling point 10 is positioned 4,5 Km from the river mouth, showing that salt concentration decreases according to the distance as to Paranaguá bay proximity (STASZCZAC, ROCHA, 2018).
These last three points (Figure 3) are more distant from Itiberê river mouth, that's to say, the points that suffer by the tide process are the ones that represent greater equivalence by the analytical methodologies.
The sampling points 8, 9 and 10 (Figure 3) have very high DTS values because they are near Paranaguá central region, or also because they are next to the sea, where dissolved solids are accumulated, mainly sodium chloride due to the tide process (CUNHA, ROCHA, 2015).

IV. CONCLUSION:

It is concluded that the gravimetric method demonstrated more efficiency to determine DTS. The conductometric method is restricted to ionic solutions. When no ionic substances are dissolved in liquid sample, they are not detectable with conductivity, having lower results than the real one. So, gravimetric way demonstrates to be more efficient to be determined in aqueous solution. In this way, even if conductometry shows easier way to handle and a smaller analysis time, it is possible to say that gravimetric methodology is more reliable.

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