Research Article

Shailesh K. Dhoke*

Determination of total hardness of water sample by titration using double burette method: an economical approach

https://doi.org/10.1515/cti-2024-0095
Received September 16, 2024; accepted September 16, 2024; published online October 2, 2024

Abstract: Titration is one of the most prevalent methods practice in almost all laboratories. Worldwide every curriculum for science and engineering undergraduate students has titrations included in their laboratory sessions. However, there are few drawbacks associated with it when it comes to chemical discharge and cost due to excess consumption of titrants, titrand and related chemicals during titration. Further, the method is an exhaustive time consuming process. In present study, conventional titration method using single burette used for determination of total hardness of water has been explored in different perspective by adopting a double burette method approach. Based on a comparative laboratory study it was found that a double burette method is not only safer and faster but also relatively more economical.

Keywords: titration; hardness; two burette method; safer; economical

1 Introduction

Analysis of water quality for its properties, pollution monitoring and developing standard guidelines for its specific use is an important aspect of water technology (Maiti, 2004 pp. 1–99). Various analytical techniques are used for studying water quality. Among the different techniques available, the most classical method for analysis of water properties like acidity, hardness, alkalinity, other constituents and contaminants by using titration is a usual practice in almost all laboratories (Belle-Oudry, 2008 pp. 1269–1270; Hunt & Wilson, 1995 pp. 378–380; Kimaru et al., 2018 pp. 2238–2242; McCormick, 1973 pp. 136–137; Simões et al., 2020 pp. 89–98). Titration method involves determination of the volume of a titrant of known concentration that is used to react quantitatively with the measured volume of titrand till the end point of the reaction. The volume of titrant determined is used to calculate the concentration of titrand.

As a part of curriculum water technology is also included in chemistry syllabus for high school and undergraduate students in most of the academic institutes worldwide. The course content includes theory detailing the properties of water, types of hardness, alkalinity, ill effect of untreated water, softening methods and its standard requirement for consumption and use in various industries. The curriculum also included laboratory session for experiential learning on determination of various properties of water. One such laboratory experiment includes determination of hardness of water using Ethylenediaminetetraacetic acid (EDTA) by complexometric titration method (Frank, 2004 pp. 257–263; Hammer & Hammer, 2013 pp. 26–37; Johnston et al. 1958 pp. 601–606). EDTA and its use in analytical chemistry as metal complex forming ligand is well studied in literature.

Traditionally, determination of hardness of water is carried out using single burette method (Hammer & Hammer, 2013 pp. 26–37; Manahan, 2011 pp. 269–270, Maiti, 2004 pp. 1–99). The single burette method is

***Corresponding author: Shailesh K. Dhoke**, Modern Education Society's Wadia College of Engineering, Pune 411001, India, E-mail: bond.shai@gmail.com. https://orcid.org/0000-0002-3411-8221

well-established and documented in literature which involves pipetting out a known volume of an analyte solution or titrand in a conical flask, adjusting the pH of 10 using a standard buffer solution and addition of few drops of Eriochrome Black T indicator (EBT). Addition of EBT turns the color of water solution (containing e.g. Ca^{+2} and Mg^{+2}) to wine red. The content is then titrated with the titrant i.e. EDTA solution till the end point of the complexometric reaction i.e. wine red to blue (Maiti, 2004 pp. 1–99). The procedure is repeated at least three times to get readings that are in close agreement.

Although, determination of hardness using single burette method is very popular there are some drawbacks associated with this method. One of the primary drawbacks with single burette titration method was that the analyte solution (acid, base or other reagent) were pipetted out by mouth. Therefore, there was a high chance of accidental swallowing of the chemicals by untrained high school and graduate students that can pose serious threat to the life of students. Fortunately, practice of pipetting of analyte solution is prohibited long back. Nowadays, wheel style pipette fillers and Peleus balls are used with volumetric pipettes.

However, another drawback that is to be taken into consideration is related to time and energy consumption i.e. laborious as a result of an exhaustive step involved while repeating the titration for obtaining at least three consecutive readings. The additional step includes transferring the titrant in a beaker and refilling the burette, pipetting out the fresh test analyte solution into the flask and addition of buffer followed by indicator. This is further associated with drawbacks like utilization of excess of chemicals and discharge of effluent after titration. Use of excess of chemicals pose burden on the budget grant of chemistry laboratories. Moreover, excessive use and discharge of chemical cause pollution to water bodies and add extra cost on water treatment.

To overcome the drawbacks associated with the traditional titration method, various methods are being explored to determine the hardness of water and are reported in literature. In one of the study, spectrophotometric titration of water sample was performed with the aim to avoid the problems like excess addition of titrant and surpassing the end point that introduce error in measurement associated with traditional method (Gordon et al., 2001 pp. 1089–1090). Another study reported hardness determination using acoustic wave sensors that comprise of coated piezoelectric quartz crystals with the aim to overcome the laborious and time consuming methodology associated with traditional titration method (Marta et al., 2007 pp. 102–106). Similar approach in determination of hardness of natural water using potentiometric sensor array which make use of ion-selective electrodes has also been reported (Saurina et al., 2002 pp. 89–98). Further, an ion-chromatography in conjunction with spectrophotometer has also been used and reported as rapid and advantageous method to estimate the hardness of water compared to EDTA titration method (Smith & Fritz, 1988 pp. 87–93).

Although the methods reported are efficient and innovative, the instruments used are not only expensive but there is a recurring cost associated with their maintenance and calibration. Further, their use is primarily restricted for research purpose and not for laboratory sessions involving large number of students. Therefore, to address the drawbacks associated with single burette method a new approach with different prospective in determination of hardness of water was explored by adopting double burette method from the laboratory manual of University of Wisconsin-La Crosse (Kelkar et al., 2001 pp. 14–22). Unfortunately, information about the use of double burette method in water hardness determination is not available in literature. Thus, exploration of double burette method to reduce the step involved in the procedure, time of performance and the cost associated with consumption/discharge of chemicals is the rationale behind the present study. This is a laboratory procedure developed to determine the total hardness of water sample without deviating from the basic principle of titration involved in determination of water hardness together with acquisition of data to estimate the probable reduction in the cost of chemicals used.

1.1 Principle involved in hardness determination

EDTA method involves titration of water sample against disodium salt solution of EDTA. This titration is carried out using Eriochrome black-T (EBT) indicator and at pH = 10. To maintain pH = 10 alkaline buffer solution (mixture of NH_4Cl + NH_4OH) is added. When Eriochrome black-T indicator is added to water sample containing Ca^{2+}, Mg^{2+} ions at pH = 10, it gives wine red colour to the water sample due to formation of a weak, soluble complex of metal cations with indicator as represented in equation 1.

$$Ca^{2+} \text{ or } Mg^{2+} + EBT \xrightarrow{\text{Buffer pH = 10}} [Ca\text{-}EBT] \text{ or } [Mg\text{-}EBT]$$

Typical Hardness Causing Ions Present in Hard Water Sample; Blue Color; Wine Red Complex (Weakly Stable)

When wine-red coloured solution is titrated with EDTA solution, unstable complexes of Eriochrome black-T are quickly converted into more stable complexes of EDTA. At this stage Eriochrome black-T is released from the metal - complexes, which gives or discharges blue color to the solution as represented in equation 2.

$$[Ca\text{-}EBT] \text{ or } [Mg\text{-}EBT] + EDTA \xrightarrow{\text{Buffer pH = 10}} [Ca\text{-}EDTA] \text{ or } [Mg\text{-}EDTA] + EBT$$

Stable Colorless Complex; Blue Color

Thus, in EDTA titration using Eriochrome black T indicator, the end point is indicated by change in color from wine red to blue.

1.2 Experimental overview

The experiment is performed using two titration methods. Method 1 makes use of classical single burette method (SBM) in which titrant is taken in burette and titrand is taken in a conical flask. Method 2 adopts double burette method (DBM) in performing the same titration. Double burette method as the name suggests comprise of two burettes in which both titrand and titrant are taken separately. The noticeable key feature of DBM is that after completion of titration, the solution is not discarded instead to the same solution, titrand is added using burette and titration is carried out as a consecutive step.

Both the titration methods comprises of two steps (1 and 2). Step 1 consists of titration between standard $ZnSO_4$ solution with EDTA solution i.e. standardization of EDTA solution. Step 2 consists of titration between standardized EDTA with sample hard water i.e. hardness determination. Each step (1 and 2) also includes addition of buffer solution and few drops of EBT indicator just before the titration. Both method 1 and method 2 is conducted during two 2-h laboratory practical session respectively.

In single burette method, three trials are performed such that each trial consists of step 1 followed by step 2 to obtain three consistence reading. While in double burette method, only one trial is performed such that step 1 and Step 2 are performed consecutively to obtain three readings in each step respectively. Burette readings are noted at the end point which is observed when the water sample turns from wine red to blue in color. A schematic of experimental overview showing steps involved in SBM and DBM is given in Figure 1 and the procedure followed in DBM is shown in Figure 2.

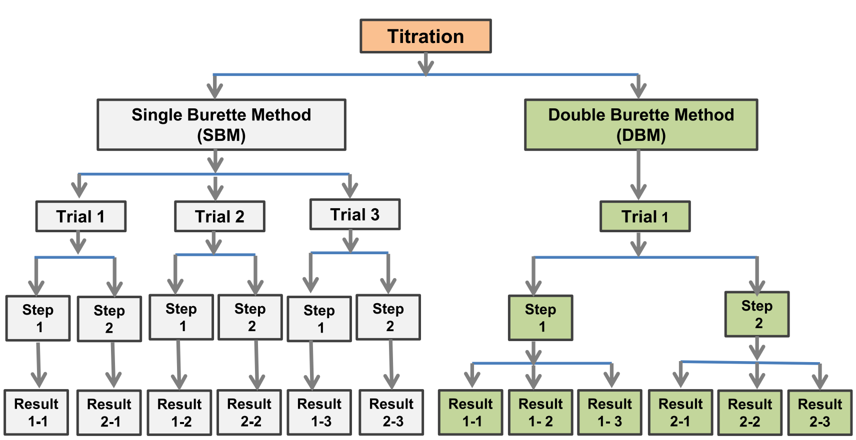

Figure 1: Experimental overview showing steps involved in single burette method and double burette method.

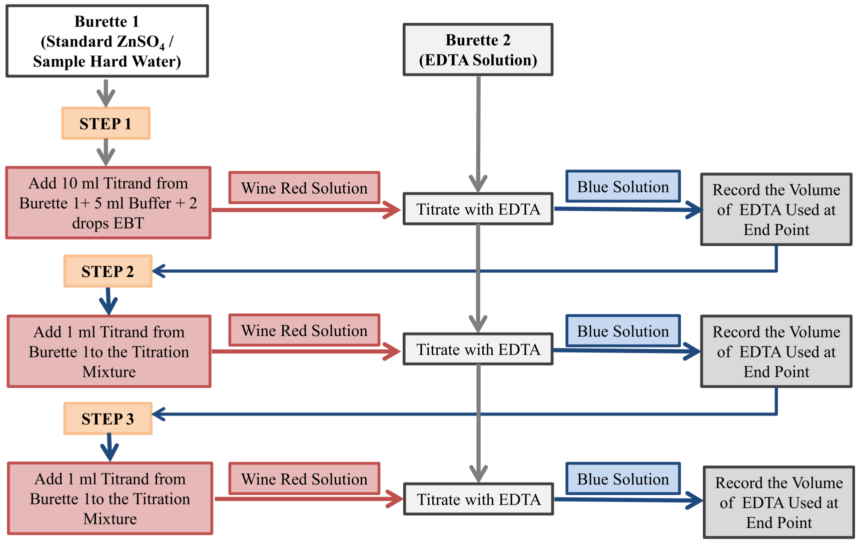

Figure 2: Schematic showing procedure followed in double burette method.

For this study a class of 60 undergraduate engineering students was divided in two batches of 30 students. Each batch of 30 students was assigned to perform the titration in pairs by using single burette method and double burette method, respectively. Students were made familiar with the concept of hardness, types of hardness, degree of hardness, various units of hardness and their inter-relationship, EDTA titration method for hardness determination, ill effect of hard water with reference to boiler corrosion and preventive measures, various methods of water softening, their advantages and disadvantages in the regular chemistry class. For performing the experiment all required solution was prepared by laboratory assistant before the laboratory session and student handout was provided at the time of performance.

2 Students learning goals

Students learning goals focuses on understanding the principle of complexometric titration, estimating quantitatively the hardness of given sample of water and to compare the benefits of double burette method with classical single burette method in terms of ease of performing experiment, chemicals cost reduction, time of performance and reduction in effluent discharge i.e. environmental hazards. The benefit of using such experiential learning methods for students helps them apply their theoretical knowledge effectively in practice. Some of the pedagogical benefits that the learner can achieve with this laboratory activity include:

- Understanding the importance of estimating hardness of water by titration method.
- Distinguishing the benefits of innovative methods over classical method.
- Developing thought process on innovating alternative methods in reducing cost and environment damage associated with the existing process.
- Appreciating co-operative learning by working in groups and sharing experience.
- Developing motor skills in handling and operating apparatus while performing titration.

3 Learning assessments

In order to measure the understanding of the students through experiential learning, learning assessments in terms of quiz test that comprise of total 20 multiple choice questions (MCQs) each carrying 1 mark. Out of total 20 questions, 15 questions were based on theory and experimental observation to demonstrate competency in understanding the basic principle of hardness determination using titration method. For example, questions were designed to recognize cause, types and units of hardness, reaction involved in EDTA complexometic titration, importance of pH control and end point observation. The remaining 5 questions designed were numerical on calculating total hardness of water sample to demonstrate competency in quantitative aptitude through problem solving. The questions designed were based on given quantity of hardness causing salt dissolved in water sample and volume of given concentration of EDTA consumed by water sample during titration, respectively. The questions were designed to account for Blooms taxonomy levels of 1–3 only (i.e. remember, understanding and analyse). For MCQ test a pass threshold of 95 percentage mark was set. Therefore, out of total 60 students number of students scoring 19 marks was set as criteria for evaluation. Finally, the percentage of attainment level in terms of learning outcome was determined using following relation.

$$\text{Percentage Learning Outcome} = N/T \times 100$$

where, N = Number of students scoring ≥ threshold of 95 % marks in quiz out of 20 marks. T = Total number of students.

4 Learning outcomes

Learning outcomes of the present study were categories into student's prospective i.e. student cognitive learning and economic prospective i.e. cost reduction analysis. The impact of experiential learning on the conceptual understanding and learning ability of the students was monitored by assessment tools like quiz (MCQs) related to hardness determination. Whereas, cost reduction analysis were carried out to identify and highlight economic benefits of the adopted double burette method.

4.1 Student cognitive learning

Determination of hardness of water sample was carried out independently by SBM and DBM, without deviating from the principle of EDTA-complexometic titration, therefore both the methods have same impact on understanding the concept of hardness and corresponding learning outcome. It can be noted that the student learning ability is not compromised when a new procedure i.e. DBM is followed. The percentage learning outcome obtained was 95 % indicating that the experiential learning has better impact on the understanding the concept of hardness. Students were able to correlate the theoretical aspect of water technology with practical approach. This was noted from their response to the MCQs design to understand their cognitive level.

Students were also able to develop confidence in quantitative estimation of amount of hardness present in water sample. This was reflected by the ease with which students were able to solve numerical on determination of hardness. They were also able to visualize the concept of complex formation between EDTA and metal ion causing hardness as a result of observed color change at the end point of the titration. They understood the importance of buffer solution in maintaining pH = 10 of the water sample during titration. Further, they were able to appreciate EDTA as an important complexing agent in estimation of hardness. It is to be noted that during experiential learning the greatest challenge experience by students who followed single burette method keeping time management to performing experiment in given time slot. Whereas, students who followed double burette method were able to perform the experiment with ease and in sufficiently less time. The time taken by students using single burette method was around 50–60 min, that was reduced to 15–20 min using double burette method. The time saved during titration can have benefit of utilizing it in doing calculations, writing assignments related to the experiments and analyzing different water samples.

4.2 Cost and waste reduction analysis

In order to estimate the probable cost reduction, a comparative study was carried out by primarily considering the consumption of chemicals like zinc sulphate, EDTA, buffer (NH_4Cl + liquid NH_3), EBT indicator during titration. Additionally, total utilization of deionized water for making solutions, ethanol for indicator preparation, total volume of effluent discharge and time consumed in performing the titration was also estimated. The total volume of chemicals consumed during titration by each batch in either of the methods is given in Table 1. Based on the data obtained, a comparative consumption of chemical during titration by both the methods was estimated and is shown in Figure 3.

From the data approximated in Figure 3, it can be clearly seen that in case of double burette method there is a significant reduction in the use of chemicals. The estimated reduction in consumption of each constituent chemical by two burette method was 0.01 M $ZnSO_4$ (40–45 %), 0.01 M EDTA (47–50 %), buffer solution (30–33 %) and EBT Indicator (50 %). The total volume of chemicals utilized in double burette method was 40 % less compared to single burette method. Based on the consumption of chemicals it can be estimated that the cost of chemicals can be reduced to 40–50 % by employing double burette method, considering the concentrations of solution used in present study and the current cost of chemicals. Moreover, the amount of chemical consumed in single burette method can be utilized for 2–3 more batches of student by adopting double burette method. If this data is extrapolated for large number of students or batches per accademic year one can conclude that the double burette method consumes relatively less chemicals suggesting reduction in corresponding cost of the chemicals.

Table 1: Total volume of chemicals consumed in performing the titration per batch.

Chemicals Consumed per Batch	Single Burette Method	Double Burette Method
Volume of 0.01 M zinc sulphate	900 mL	360 mL
Volume of 0.01 M Na_2EDTA (both for standardization and hardness determination)	1,050 mL	495 mL
Volume of buffer solution (NH_4Cl + liquid NH_3)	900 mL	300 mL
Volume of EBT indicator (approximate)	60 mL	30 mL
Total volume consumed and effluent discharge	2,910 mL	1,185 mL
Total utilization of distilled water for making solutions	3,000 mL	1,300 mL
Time consumed in performing the experiment	50–60 min	15–20 min
Deviation in results i.e. total hardness of water sample in present study	622.95 ± 19.77 ppm	644.65 ± 22.83 ppm

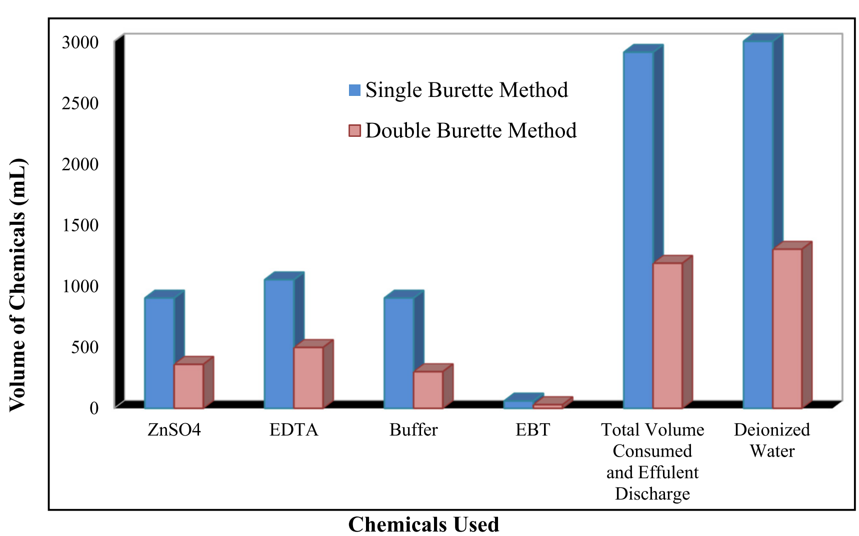

Figure 3: Relative consumption of chemicals per batch during titration.

Further, since all solutions are made in deionized water it can also be inferred that the reduction in chemical consumption in double burette method adds on to the total cost reduction as a result of reduction in the use of electricity for production of deionized water in laboratory. This is clear from the 40 % reduction of total volume of deionized water utilized in making solution on adopting double burette method. A 50 % reduction in the use of EBT indicator also indicates a reduction in 50 % use of ethanol for the preparation of EBT indicator, which also contributes towards the total cost reduction. It is to be noted that reduction in utilization of 0.01 M $ZnSO_4$ and 0.01 M EDTA using DBM is due to the reduction in number of trials involved compared to SBM, where for each trial a fresh solution is used for titration. Similarly, reduction in the consumption of buffer solution and EBT indicator using DBM can be attributed to the fact that the reagents are added only once during the start of titration, whereas in SBM these reagents are added during each and every trials.

The double burette method also showed a reduction in effluent discharge per batch by 40 % compared to single burette method, estimated on the basis of total volume of titrant and titrand used in both the methods. Also, no accountable difference in result outcome was observed by both the titration methods for a given water sample, indicating the effective use of double burette method for determination of hardness of water.

5 Conclusions

In determination of total hardness of water by EDTA titration, a classical single burette method and a new double burette method was compared without deviating from the principle of titration. The double burette method was found comparatively easy, rapid and economical. The method has as found to be advantageous in reducing discharge of chemicals making it safer for the environment. The method can prove useful for educational institutes of underdeveloped countries in reduction of chemical cost. Further, the method can be applicable to other titration methods involving bulk consumption of chemicals.

Acknowledgments: The author acknowledges Modern Education Society's Wadia College of Engineering Pune for providing library facility and encouragement to write this manuscript.
Research ethics: Not applicable.
Informed consent: Not applicable.
Author contributions: Acquisition and analysis of data, literature survey and writing of manuscript.
Use of Large Language Models, AI and Machine Learning Tools: Not applicable.
Competing interests: The author declares no conflicts of interest regarding this article.
Research funding: This research received no specific grant from any funding agency.
Data availability: The data that support this study are available in the article and also given in supplementary information.

References

Belle-Oudry, D. (2008). Quantitative analysis of sulfate in water by indirect EDTA titration. *Journal of chemical Education*, *85*(9), 1269–1270.

Frank, M. D. (2004). *Determination of Hardness in a Water Sample, Environmental laboratory exercises for instrumental analysis and environmental chemistry* (pp. 257–263). New Jersey: John Wiley & Sons.

Gordon, J. S., Harman, S., Weiss, K., & Pettegrew, B. (2001). A microscale spectrophotometric determination of water hardness. *Journal of chemical Education*, *78*(8), 1089–1090.

Hammer, M., Sr., & Hammer, M., Jr. (2013). *Chemistry, Water and wastewater technology* (pp. 26–37). London: Pearson New International Edition.

Hunt, D. T. E., & Wilson, A. L. (1995). *Analytical techniques, The chemical analysis of water, general principles and techniques* (pp. 378–380). Cambridge: The Royal Society of Chemistry.

Johnston, M. B., Bernard, A. J., Jr., & Flaschka, H. A. (1958). EDTA and complex formation. *Journal of chemical Education*, *35*(12), 601–606.

Kelkar, S. L., Dhavale, D. D., & Pol, P. G. (2001). Microscale experiments in chemistry-the need of the new millennium 3. Micro-Scale inorganic quantitative analysis and new methods of titrations for introduction at all levels in chemistry laboratories. *Resonance*, *6*(2), 14–22.

Kimaru, I. W., Corigliano, A. T., & Zhao, F. (2018). Using classical EDTA titrations to measure calcium and magnesium in intravenous fluid bags. *Journal of chemical Education*, *95*(12), 2238–2242.

Maiti, S. K. (2004). Physical and chemical analysis of water and effluents. In *Handbook of Methods in Environmental Studies Vol. 1: Water and Wastewater Analysis* (pp. 1–99). Jaipur (India): ABD Publisher.

Manahan, S. E. (2011). *Fundamentals of Aquatic Chemistry, Water Chemistry: Green Science and Technology of Nature's Most Renewable Resource* (pp. 269–270). New York, NY: CRC Press.

Marta, I. S. V., Oliveria, A. B. P., & Gomes, M. T. S. R. (2007). Determination of the total hardness in tap water using acoustic wave sensors. *Sensors and Actuators*, *127*(1), 102–106.

McCormick, P. G. (1973). Titration of calcium and magnesium in milk with EDTA. *Journal of chemical Education*, *50*(2), 136–137.

Saurina, J., Lopez-Aviles, E., Le Moal, A., & Hernandez-Cassou, S. (2002). Determination of calcium and total hardness in natural waters using a potentiometric sensor array. *Analytica Chimica Acta*, *464*(1), 89–98.

Simões, G. B., Badolato, P. V. E. S., Ignácio, M. D., & Cerqueira, E. C. (2020). Determination of zinc oxide in pharmaceutical preparations by EDTA titration: A practical class for a quantitative analysis course. *Journal of chemical Education*, *97*(2), 522–527.

Smith, D. L., & Fritz, J. S. (1988). Rapid determination of magnesium and calcium hardness in water by ion chromatography. *Analytica Chimica Acta*, *204*, 87–93.

Supplementary Material: This article contains supplementary material (https://doi.org/10.1515/cti-2024-0095).