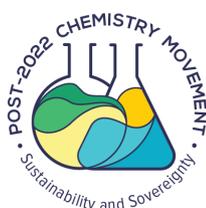


Thermal Infrared Enthalpimetry Method for the Determination of Hypochlorite in Bleaching Solutions

Flavia M. Dalla Nora,^a Alessandra S. Oliveira,^a Fabio A. Duarte,^{ib}
Alexandre J. Cichoski^a and Juliano S. Barin^{ib}*,^a

^aGrupo 3i, Departamento de Tecnologia e Ciência dos Alimentos, Universidade Federal de Santa Maria, 97105-900 Santa Maria-RS, Brazil

^bDepartamento de Química, Setor de Química Ambiental e Industrial, Universidade Federal de Santa Maria, 97105-900 Santa Maria-RS, Brazil



Thermal infrared enthalpimetry (TIE) was used for hypochlorite determination in commercial hypochlorite-based bleaching solutions. Experimental parameters were evaluated for the reaction with a hydrogen peroxide solution. The most relevant conditions were 5% H₂O₂ (m/m) solution, stirring speed of 250 rpm, dispensing rate of 0.57 mL s⁻¹, and 10 s after reaction for the simultaneous temperature readings of four replicates. Agreement to reference method NBR 9425 ranging from 98.2 to 103.2% was achieved, with a low variation among measurements (relative standard deviation < 3.5%). The number of analytical operations was reduced, and only H₂O₂ solution was required as a greener reagent. A low amount of residues was generated (2.4 and 152.8 mL for each replicate in TIE and official method, respectively), and the application of the green analytical procedure index (GAPI) showed the greenness of the proposed method.

Keywords: active chlorine, thermal infrared enthalpimetry, quality control, green chemistry, thermography

Introduction

Chemical disinfectants based on chlorine have been widely used mainly due to their convenience and low cost.^{1,2} Bleaching products based on hypochlorite are unstable and can form chlorine gas, chlorite and chlorate during storage.³ The quality control of products with hypochlorite is required in some countries, and in Brazil, its concentration of active chlorine in commercial formulations ranges in general from 2.0 to 2.5% (m/m; 3.9 to 5.6% for concentrated ones).⁴

Commercial bleaching solutions are analyzed in the official method by iodometric titration method.^{5,6} They are laborious and spend high amounts of reagents and time that impair their use for continuous monitoring during industrial processes. Alternative methods, such as colorimetric,⁷⁻⁹ fluorimetric,¹⁰ voltammetric¹¹ could be used for hypochlorite determination in several samples, but generally for low concentrations of hypochlorite, as presented in drinking water.

Thermal infrared enthalpimetry (TIE) was used to develop an alternative method. TIE is a fast and ease-of-use method, with noninvasive temperature monitoring of multiple reactions provided by the combination of disposable microplates, a multichannel pipette, and an infrared camera.¹² The principle is to measure the temperature variation between a solution of analyte and a reagent in stoichiometric excess, which is added using a multichannel pipette. The temperature of multiple reactions is monitored through an infrared camera. TIE methods were developed to control food and medicines based on neutralization, precipitation, redox, and complexation reactions.¹³⁻¹⁷

An alternative method to determine simultaneously total acidity and salt content in pickled vegetables using TIE was proposed.¹⁸ In this approach, microplates were charged with a stoichiometric excess of NaOH and AgNO₃ with subsequent sample addition. The total acidity and salt content were simultaneously determined based on the temperature rise derived from the heat released from reactions. Agreements to the conventional method ranged from 94 to 103%. However, TIE enabled 240 acidity and salt content measurements *per* hour, which in conventional titration requires 2 days. Another

*e-mail: juliano@ufsm.br

Editor handled this article: Rodrigo A. A. Muñoz (Associate)

application using TIE as an alternative method was proposed to determine the saponification value in edible oils.¹⁹ In this method, a step of sample preparation was performed in the same reactor used in the determination step, allowing the integration of the analytical process. An agreement ranging from 97.4 to 102.1% was obtained using 41 times lesser reagents and consuming 625 less energy than the conventional method. Similar behavior can be found in other TIE methods, which allowed higher sample throughput and a reduction of energy and reagent consumption concerning conventional methods.²⁰⁻²²

This work proposes an ease-of-use, rapid and green method for the determination of hypochlorite in hypochlorite-based bleaching solutions by TIE. Simple dilution and determination steps were carried out in a single reactor avoiding excessive handling and improving the throughput. Temperature variation after adding reagent in stoichiometric excess (H_2O_2) was monitored through an infrared camera, and the analyte was determined using a calibration curve. The influence of H_2O_2 concentration, stirring speed, dispensing rate, the acquisition time of temperature data, and sensitivity were evaluated. Results obtained by TIE were compared with those obtained by the official method NBR 9425.⁵ A green analytical chemistry metric was applied to compare the proposed method with the official one.

Experimental

Instrumentation

The temperature was determined using a long-wave infrared camera (7.5-13.0 μm , FLIR E60 model, FLIR, Wilsonville, USA), which provides 320×240 pixels images at a frame rate of 30 Hz. Data processing was performed using the software ResearchIR (FLIR, version 3.5). The reactions in the TIE method were carried out in disposable polystyrene 24-well microplates (Evergreen Scientific, Buffalo, USA) with an internal volume of 3.0 mL in each well. The addition of solutions in the wells was performed with an electronic multichannel pipette (eight channels) with volume ranging from 0.050 to 1.200 mL (Research Pro 1200, Eppendorf, Hamburg, Germany). For homogenization, a magnetic stirrer (Centauro, Brazil) was used. The energy consumption of equipment was measured using a power meter (Fluxe 43B model, Fluke Corporation, Everett, USA).

Samples, reagents, and standards

Ten samples of sodium hypochlorite solutions from different manufacturers with an informed concentration

range from 2.0 to 2.5% (m/m) were purchased in a local market (Santa Maria, RS, Brazil). Sodium hypochlorite (10-15%, Merck, Darmstadt, Germany) was used to prepare reference solutions by simple dilution in water. Potassium iodide (Vetec, Duque de Caxias, Brazil), glacial acetic acid (Vetec, Duque de Caxias, Brazil), and a starch (Vetec, Duque de Caxias, Brazil) solution (0.5%, m/v) were used for titration. Sodium thiosulfate was standardized with potassium dichromate, according to ABNT NBR 11589.⁶ This solution was used to determine the active chlorine in conventional titration and verify the concentration of sodium hypochlorite stock solution. In TIE determination, 50% H_2O_2 (m/m; Vetec, Duque de Caxias, Brazil) was used to prepare solutions in several concentrations. Ultrapure water obtained from Milli-Q system (Direct-Q 3 UV, 18.2 M Ω cm, Millipore Corp., Burlington, USA) was used in both methods.

TIE analysis

Samples and water were added (600 μL of each one) directly in the microplate wells using a multichannel pipette. A polytetrafluoroethylene-covered magnetic stir bar (3.0 \times 6.5 mm) was added for homogenization, followed by stoichiometric excess of H_2O_2 (1.2 mL, using the multichannel pipette) to determine hypochlorite in four wells simultaneously. The procedure for TIE measurements is shown in Figure 1.

The infrared camera monitored the temperature before, during, and after H_2O_2 solution addition. The camera was positioned in a tripod at 40 cm from microplates. The software used a circle with 180 pixels to extract temperature data from each well. The temperature difference was calculated using the mean of 2 s before and 10 s after the reaction and was obtained using the equation $\Delta T = T_f - T_i$, where T_f is the final temperature, and T_i is the initial temperature. The temperature and relative humidity were corrected in the software for all measurements. Reference solutions were used to construct a calibration curve ranging from 0.3 to 1.5% (m/v) of sodium hypochlorite.

Evaluation of the temperature measurement in TIE

During H_2O_2 decomposition, the release of oxygen causes the formation of bubbles on the surface of the solution. Thus, interferences in the temperature measurement were observed because the temperature of the bubble is different from the solution. However, as is well known, the reaction between KI and sodium hypochlorite does not present this drawback. In this sense, a comparison with both reactions was performed to evaluate

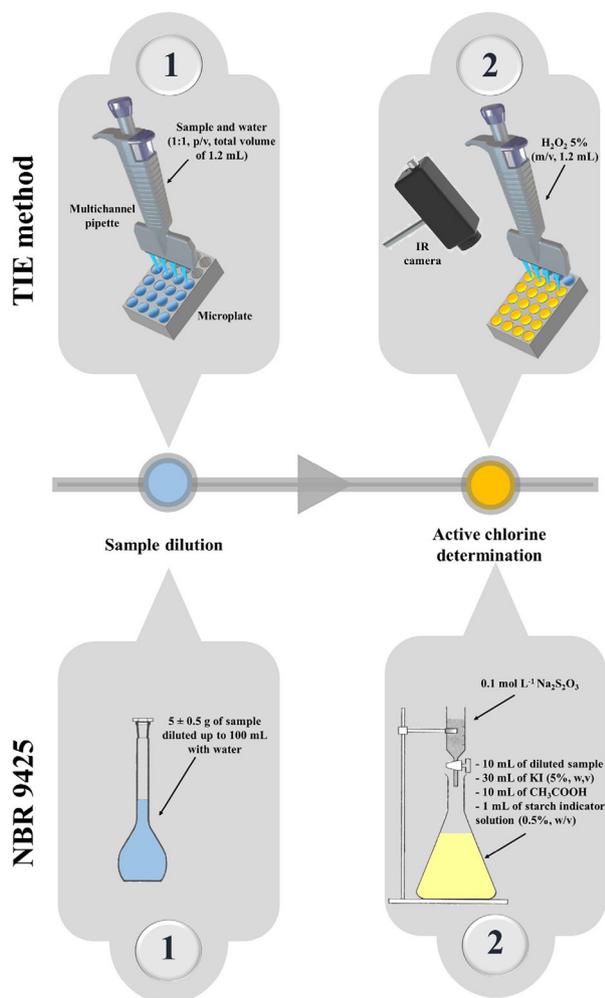


Figure 1. Procedures used for hypochlorite determination in bleaching commercial solutions.

temperature measurement. This evaluation was performed from 6 to 12 s after the addition of 5% H_2O_2 (m/m) and 30% KI (m/v). All results were evaluated considering the measurements' relative standard deviation (RSD). The accuracy of the proposed method was performed based on the comparison of results obtained with the NBR 9425 method.⁵ A comparison of features and drawbacks of TIE and NBR 9425 was made based on the Green Analytical Procedure Index (GAPI) in terms of green analytical chemistry attributes.²³ The GraphPad Prism version 8.0.0 for Windows²⁴ was used for statistical analysis.

Analysis by official method

Active chlorine was determined by the official method NBR 9425.⁵ For this, 5.0 ± 0.5 g of sample was weighed in a volumetric flask and diluted up to 100 mL with water. After, 10 mL of this solution was transferred to an Erlenmeyer flask and was added 30 mL of 5% KI (m/v) solution, 10 mL of glacial acid acetic, and 1 mL of starch solution. The

flask containing all reagents was titrated using 0.1 mol L^{-1} $\text{Na}_2\text{S}_2\text{O}_3$, and the active chlorine content was calculated based on reaction stoichiometry.

Results and Discussion

Evaluation of the temperature measurement in TIE

The temperature monitored using the infrared camera is superficial, then any interference in the surface could provide inaccurate results. In this sense, interferences in the measurements can be observed since the presence of bubbles could impair the results. The reaction temperature in preliminary experiments was considered after 10 s of excess reagent addition, which was enough for full gas release from wells. No bubbles were observed on the surface in such time, which allowed reproducible temperature measurements (Figure 2).

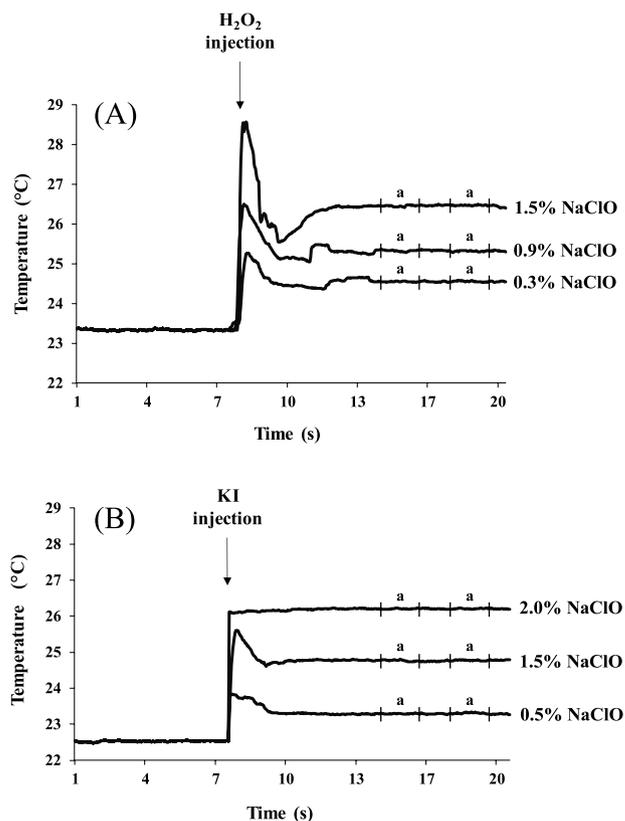


Figure 2. Evaluation of the signal for TIE using different solutions in stoichiometric excess: (A) 5% (m/m) H_2O_2 and (B) 30% (m/v) KI.

A study using KI as a reagent in stoichiometric excess was performed to confirm if 10 s was a suitable time for temperature measurement of reaction. Potassium iodide (30%, m/v) was used because no gases are released from its reaction with sodium hypochlorite. Thus, sodium hypochlorite solutions of 0.3, 0.9 and 1.5% were used

for H_2O_2 , and 0.5, 1.5 and 2.0% for KI as a reagent in stoichiometric excess. These parameters were chosen considering the enthalpy values of the reaction.

Temperature variation from the reaction among sodium hypochlorite with an excess of H_2O_2 and KI solutions is shown in Figures 2A and 2B, respectively. As can be observed, after the addition of H_2O_2 (Figure 2A) the temperature variation was not stable due to the formation of bubbles, which were removed by stirring. This behavior was observed up to 6 s after adding reagent in stoichiometric excess, remaining without significant difference (Tukey's test, $p > 0.05$) by the following 6 s. The same study was made for KI as an excess reagent, presenting stable temperature variation during all monitored times. Therefore, this proves no heat loss from wells in the evaluated times, which allows the measurement of reaction temperature in the proposed method 10 s after reagent addition.

Evaluation of the reaction of bleaching solutions with hydrogen peroxide

A reference solution of sodium hypochlorite (1.5%, m/v) was mixed with H_2O_2 solutions in a concentration ranging from 1 to 10% (m/m). According to the results shown in Figure 3, no significant differences (Tukey's test, $p > 0.05$) were observed for the temperature values. Blanks were also evaluated for these solutions by mixing them with water in the same experimental conditions used for reference solutions. No temperature rise was observed from 1 to 10% H_2O_2 solutions, and only for 20% H_2O_2 (m/m) the effect of heat dilution was detected. In this sense, the 5% H_2O_2 was chosen due to the low variation within the measurements.

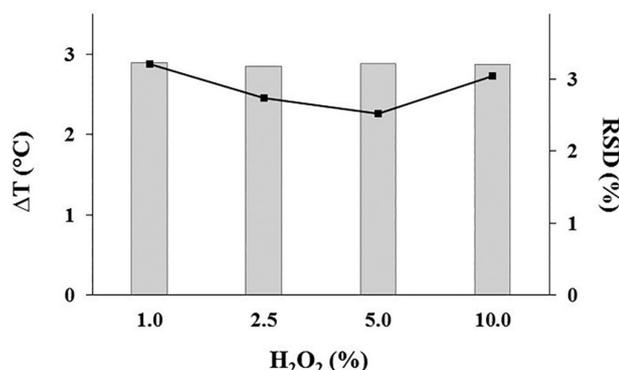


Figure 3. Influence of concentration of H_2O_2 (% m/m) on the temperature variation ($n = 8$; gray columns). Relative standard deviation of measurements showed as lines.

Evaluation of parameters for the TIE method

Previously to the determination by TIE, an evaluation of experimental parameters was performed to ensure low

deviation among measurements. As already demonstrated, TIE showed that stirring speed and dispensing rate impact the results.^{18,20} In this way, 1.2 mL of sodium hypochlorite solution (1.5%, m/v) was mixed with 1.2 mL of 5% H_2O_2 (m/m) as a reagent in stoichiometric excess.

As shown in Figure 4A, higher stirring speeds provided a lower standard deviation. This behavior is observed because the oxygen formed during the reaction was removed faster with intense stirring, providing more homogeneous results. On the other hand, higher deviations were observed for experiments without stirring, which was related to the formation of stable bubbles in the solutions, impairing the precision and accuracy of the temperature measurement. In the highest stirring speed (350 rpm), the lowest temperature variation was caused by the spill out of solutions from the wells. Then, a compromise condition (250 rpm) between the highest temperature variation with the lowest deviation was chosen as the condition for subsequent evaluations.

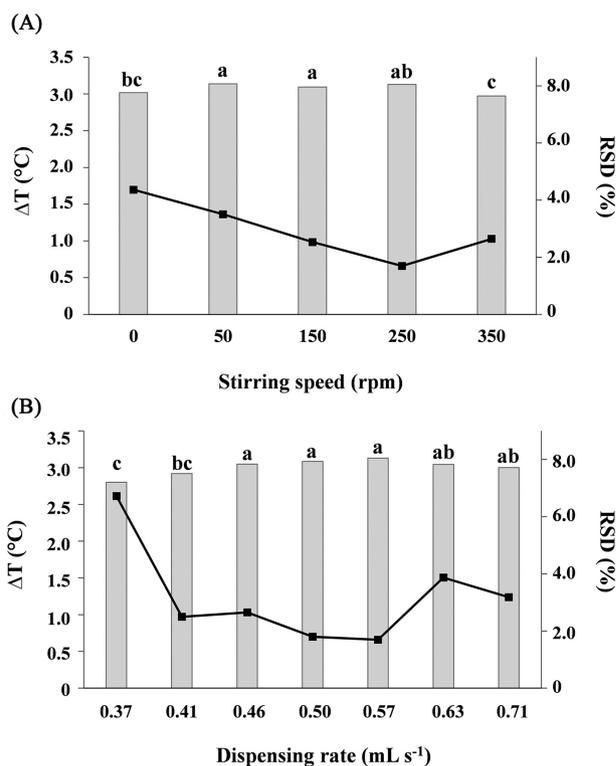


Figure 4. Influence of some parameters on TIE measurements: (A) stirring speed, (B) dispensing rate; reaction for 1.5% (m/v) sodium hypochlorite and 5% (m/m) H_2O_2 solutions. Bars followed by the same letters do not differ (Tukey's test, $p > 0.05$).

The dispensing rate was also evaluated, and the highest temperature variation and the lowest deviation was achieved for 0.57 mL s^{-1} (Figure 4B). This value follows the results found in similar works using TIE.^{18,20} In these works, lower dispensing rates increased the standard deviation due to the time that tips remained in front of a camera, impairing data

acquisition. Therefore, the dispensing rate of 0.57 mL s⁻¹ was selected for further measurements.

Determination of hypochlorite in commercial products

After the parameters optimization, the proposed method was applied to determine hypochlorite in commercial samples, and the results were compared to those obtained by conventional titration according to NBR 9425. For TIE, the calibration curve ($y = 2.015x + 0.061$) showed suitable determination coefficient (R^2) = 0.996 ranged from 0.3 to 1.5% (m/v) sodium hypochlorite. The 95% confidence intervals for slope, y-intercept and x-intercept were 1.882 to 2.147, -0.061 to 0.184 and -0.097 to 0.029, respectively. Analysis of variance (ANOVA) was applied to the calibration curve data and no deviation from linearity was observed (P -value = 0.886).

As shown in Table 1, all values obtained for the four commercial samples were in agreement (from 98.2 to 103.2%) with conventional titration, and no significant difference was observed (Student's t -test, $p > 0.05$). The variation of the conventional method measurements was lower than TIE, with RSD ranging from 0.8 to 1.8% and 1.8 to 3.3%, respectively. The miniaturization of the proposed method could explain these results, in which the sample volume was reduced 16 times for TIE compared to NBR 9425. An important aspect of the proposed method is the possibility of reusing the microplates after washing for several samples, assuring minimal disposal of materials.

Table 1. Results for hypochlorite in bleaching commercial solutions obtained by TIE ($n = 20$) and NBR 9425⁵ ($n = 3$). No significant difference was observed between methods for all samples (Student's t -test, $p > 0.05$)

Manufacturer	Hypochlorite / (% , m/v)	
	TIE	NBR 9425
1	2.64 ± 0.05	2.62 ± 0.02
2	2.50 ± 0.07	2.52 ± 0.02
3	2.79 ± 0.06	2.78 ± 0.02
4	2.47 ± 0.05	2.46 ± 0.04
5	2.27 ± 0.04	2.25 ± 0.04
6	2.33 ± 0.08	2.36 ± 0.02
7	1.59 ± 0.04	1.54 ± 0.02
8	2.63 ± 0.07	2.64 ± 0.02
9	2.59 ± 0.04	2.55 ± 0.04
10	2.24 ± 0.04	2.28 ± 0.02

TIE: thermal infrared enthalpimetry.

The limit of detection (LOD) and limit of quantification (LOQ) values obtained in the present work were 0.03 and 0.1% (m/v), respectively, which were considered suitable

for determining the hypochlorite concentration in the samples. It is important to mention that such values are lower than those found in other methods, ranging from 0.4 to 1.2% (m/v).^{25,26}

According to the standard requirements, active chlorine concentration in bleaching must be between 2.0 and 2.5%. In this sense, one sample presented values lower than this parameter. The other nine samples evaluated presented concentrations higher than the maximum limit allowed.

Greenness evaluation

GAPI is often performed considering the entire analytical method, from sample collection to final determination, presenting itself as a complete tool for evaluating and comparing methods. All the data considered for this evaluation were presented in Table 2, and the results of GAPI for the proposed and official method are shown in Figure 5.

In the pictogram, it was possible to see that the proposed method allows the hypochlorite determination to be greener. It is essential to highlight that the TIE method avoids using many reagents typically used in the conventional method. In the conventional analysis, KI, acetic acid, starch and 0.1 mol L⁻¹ Na₂S₂O₃ (1.5 g, 10.0 mL, 1.0 mL, 7.0 mL, respectively, which are required for one replicate) were used as reagents. They were not required in the TIE method, which used only hydrogen peroxide. The only reagents used in the proposed method are water (50 times lower than the conventional method) and 5% (m/m) hydrogen peroxide, which are not required in the conventional analysis. Using H₂O₂ as the reagent, instead of the high amount of several reagents used in the conventional method, is beneficial since it is used at a low volume (1.2 mL). The decomposition products of H₂O₂ are just water and oxygen, which is an improvement to the method proposed by Jonnalagadda and Gengan,²⁷ who determined hypochlorite in bleaching solutions using reactions with H₂O₂ followed by permanganate and photometric determination.

The analysis by TIE requires using a multichannel pipette, magnetic stirrer, and an infrared camera, which spent only 0.001 kWh *per* measurement. In contrast, the conventional analysis does not employ any electrical equipment. The proposed method provided results of one replicate in 0.2 min, while it was required 5 min using conventional titration. Therefore, a higher throughput was observed for TIE reaching up to 300 replicates *per* hour. Only about 12 replicates *per* hour could be performed in the conventional method.

Table 2. Green Analytical Procedure Index parameters for analytical procedures to determine hypochlorite in bleaching solutions by NBR 9425 and TIE method

Category	TIE	NBR 9425
Sample preparation		
Collection	–	–
Preservation	–	–
Transport	–	–
Storage	store the sample at room temperature and without light	store the sample at room temperature and without light
Type of method: direct or indirect	dissolution and determination in the same reactor	require a previous dilution with water
Scale of sample preparation	–	–
Solvents/reagents used	green solvents/reagents used	non-green solvents/reagents used
Additional treatments	none	none
Reagent and solvents		
Amount	0.6 mL of water	100 mL of water
	0.6 mL of sample 1.2 mL H ₂ O ₂ 5%	5 g (4.8 mL) of sample 30 mL of KI 5% (1.5 g) 10 mL of acetic acid 1 mL of starch indicator 7 mL of Na ₂ S ₂ O ₃ 0.1 mol L ⁻¹ (0.01 g) total: 152.8 mL + 1.51 g
Health hazard	green solvents	green solvents
Safety hazard	low flammability or instability	low flammability or instability
Instrumentation		
Energy	0.001 kWh	0 kWh
Occupational hazard	emission of vapors to the atmosphere (only O ₂)	emission of vapors to the atmosphere
Waste	2.4 mL	152.8 mL + 1.51 g
Waste treatment	recycling	require passivation
Quantification	yes	yes

TIE: thermal infrared enthalpimetry.

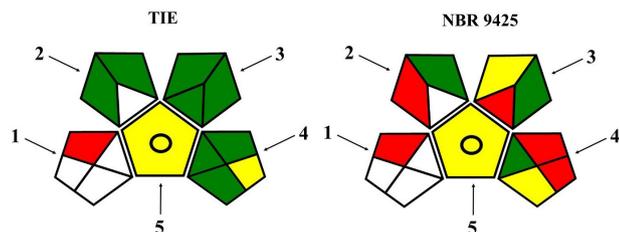


Figure 5. GAPI assessment of the green profile of the NBR 9425 and TIE method for determining hypochlorite in bleaching samples. The colors of green, yellow and red represent the characteristics of good, regular, and bad in relation to green analytical chemistry, respectively, and white are related to not applicable. (1) Sample collection, preservation, transport, and storage; (2) sample preparation; (3) reagents and compounds used; (4) instrumentation; (5) general method type.

Conclusions

Thermal infrared enthalpimetry was suitable for hypochlorite determination using only hydrogen peroxide solution as reagent. The proposed integration process enables the hypochlorite determination in bleaching with suitable precision (ranged from 1.8 to 3.3%) and accuracy (ranged from 98.2 to 103.2%) in comparison to the official

method. The proposed TIE method allows the analysis of 300 replicates in one hour, while the conventional method enables about only 12. The miniaturization of the method and the integration of processes provide environmental advantages, such as removing some reagents and maintaining the analytical performance. Considering the release of only water and oxygen by the reagents in the proposed method, it is possible to confirm that the proposed method is greener than the conventional one, and it is a promising alternative for routine analysis.

Acknowledgments

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, grant numbers 309513/2019-7 and 438718/2018-6) and Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS, grant number 17/2551-0000979-7) for supporting this study.

References

1. Park, K. Y.; Choi, S. Y.; Lee, S. H.; Kweon, J. H.; Song, J. H.; *Environ. Pollut.* **2016**, *215*, 314.
2. Liu, W.; Wei, D.; Liu, Q.; Du, Y.; *Chemosphere* **2016**, *154*, 491.
3. McFadden, M.; Loconsole, J.; Schockling, A. J.; Nerenberg, R.; Pavissich, J. P.; *Sci. Total Environ.* **2017**, *599-600*, 533.
4. Agência Nacional de Vigilância Sanitária (ANVISA); Resolução da Diretoria Colegiada (RDC) No. 109, de 6 de setembro de 2016, Dispõe sobre *Regulamento Técnico para Produtos Saneantes Categorizados como Alvejantes à Base de Hipoclorito de Sódio ou Hipoclorito de Cálcio e dá Outras Providências*; Diário Oficial da União (DOU), Brasília, No. 173, de 08/09/2016, p. 38, available at https://www.in.gov.br/materia/-/asset_publisher/Kujrw0TZC2Mb/content/id/23530129/do1-2016-09-08-resolucao-rdc-n-109-de-6-de-setembro-de-2016-23529977, accessed in March 2022.
5. ABNT NBR 9425: *Hipoclorito de Sódio - Determinação do Cloro Ativo por Método Volumétrico*, ABNT: Rio de Janeiro, 2005.
6. ABNT NBR 11589: *Preparação, Padronização e Estocagem de Soluções para Análises Químicas*, ABNT: Rio de Janeiro, 2017.
7. Lima, M. J. A.; Nascimento, C. F.; Rocha, F. R. P.; *Anal. Methods* **2017**, *9*, 2220.
8. Dou, J.; Shang, J.; Kang, Q.; Shen, D.; *Microchem. J.* **2019**, *150*, 104200.
9. Zhou, M.; Li, T.; Zu, M.; Zhang, S.; Liu, Y.; Zhao, H.; *Sens. Actuators, B* **2021**, *327*, 128905.
10. Uriarte, D.; Vidal, E.; Canals, A.; Domini, C. E.; Garrido, M.; *Talanta* **2021**, *229*, 122298.
11. Malmir, M.; Afkhami, A.; Madrakian, T.; Soltani-Felehgari, F.; Madrakian, E.; *Anal. Bioanal. Chem. Res.* **2020**, *7*, 99.
12. Barin, J. S.; Tischer, B.; Oliveira, A. S.; Wagner, R.; Costa, A. B.; Flores, E. M. M.; *Anal. Chem.* **2015**, *87*, 12065.
13. Oliveira, A. S.; Schlessner, S. K.; Voss, M.; da Costa, A.; Moraes Flores, E. M.; Barin, J. S.; *Anal. Chem.* **2020**, *92*, 14959.
14. Voss, M.; Schlessner, S. K.; Ferreira, D.; Oliveira, A. S.; Deprá, M. C.; Jacob-Lopes, E.; Barin, J. S.; *Anal. Methods* **2019**, *11*, 4983.
15. Ferreira, D. F.; Tischer, B.; Cichoski, A. J.; Menezes, C. R.; Wagner, R.; Costa, A. B.; Barin, J. S.; *J. Braz. Chem. Soc.* **2020**, *31*, 421.
16. Teixeira, I. D.; Tischer, B.; Santos, R. O.; Alessio, K. O.; Helfer, G. A.; Kipper, L. M.; Barin, J. S.; da Costa, A. B.; *Food Anal. Methods* **2020**, *13*, 260.
17. Santos, R. B. D.; Filoda, P. F.; Teixeira, I. D.; Helfer, G. A.; Santos, R. O.; Oliveira, A. S.; Barin, J. S.; Tischer, B.; Costa, A. B. D.; *Talanta* **2019**, *200*, 67.
18. Tischer, B.; Oliveira, A. S.; Costa, A. B.; Cichoski, A. J.; Barcia, M. T.; Wagner, R.; Barin, J. S.; *J. Food Compos. Anal.* **2017**, *63*, 34.
19. Dalla Nora, F. M.; Oliveira, A. S.; Lucas, B. N.; Ferreira, D. F.; Duarte, F. A.; Mello, R. O.; Cichoski, A. J.; Barin, J. S.; *Anal. Methods* **2018**, *10*, 3770.
20. Tischer, B.; Oliveira, A. S.; Ferreira, D. D. F.; Menezes, C. R.; Duarte, F. A.; Wagner, R.; Barin, J. S.; *Food Chem.* **2017**, *215*, 17.
21. Oliveira, A. S.; Nora, F. M. D.; Mello, R. O.; Mello, P. A.; Tischer, B.; Costa, A. B.; Barin, J. S.; *Talanta* **2017**, *171*, 335.
22. Oliveira, A. S.; Ballus, C. A.; Menezes, C. R.; Wagner, R.; Paniz, J. N. G.; Tischer, B.; Costa, A. B.; Barin, J. S.; *Food Chem.* **2018**, *258*, 59.
23. Plotka-Wasyłka, J.; *Talanta* **2018**, *181*, 204.
24. *GraphPad Prism*, version 8.0.0; GraphPad Software, San Diego, California, USA, 2018.
25. Ramos, L. A.; Prieto, K. R.; Cavalheiro, E. T. G.; Cavalheiro, C. C. S.; *J. Chem. Educ.* **2005**, *82*, 1815.
26. Zaporozhets, O. A.; Pogrebnyak, O. S.; Vizir, N. N.; *J. Water Chem. Technol.* **2011**, *33*, 31.
27. Jonnalagadda, S. B.; Gengan, P.; *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2010**, *45*, 917.

Submitted: October 31, 2021

Published online: March 24, 2022

