Practical applications of sensor-based methodologies for monitoring peracetic acid (PAA) as a disinfectant of fresh produce wash water

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(M.I. Gil)
ABSTRACT

An accurate sensor for peracetic acid (PAA) is needed to monitor and control the disinfection of fresh produce wash water. Inaccurate measurements can result in underdosing and unsafe produce or overdosing with huge cost implications. In this study, five methods were compared for measuring PAA in process water from washing apples, tomatoes, red sweet peppers, and lemons. A reversed phase HPLC-DAD method for the determination of PAA in water was adapted for process wash water and used as a reference method. The results showed that HPLC offered high selectivity for PAA and precise and reproducible measurement for its quantification. However, as HPLC is not suitable for in-line applications in processing plants and requires highly skilled technicians, installation and maintenance costs, other analytical methods were examined including a redox titration, a reflectometric method and two electrochemical methods (an amperometric in-line probe and a chronoamperometric method with disposable single-use electrode sensor). The drop titration kit overestimated PAA because of the interferences from other oxidizing agents such as hydrogen peroxide (HP) apart from it required substantial time to perform the measurements plus the extensive training of the technical personnel to ensure confidence in the results. The reflectometric method with disposable test strips, although fast and objective, overestimated PAA due to the wash water with a high content of suspended organic matter that needed the addition of high concentrations of PAA, coexisting with HP. From the two electrochemical methods studied, the in-line amperometric sensor underestimated the PAA concentration in lemon wash water as the PAA could not freely diffuse through the membrane through the active electrode because of the organic matter present in the wash water released from the lemon peel. In contrast, the chronoamperometric sensor showed good selectivity for PAA
without interferences, with reliable results across all the wash water types and PAA concentrations.

Keywords: Peroxyacetic acid; test methods, disinfection; disposable sensors.

1. Introduction

Accurate monitoring and recording of water disinfection in commercial packing and processing facility lines is an essential component of a sound postharvest quality and safety program (Suslow, 2017). Process water must be treated with a disinfectant to minimize that water-borne microorganisms, whether postharvest plant pathogens or agents of human illness, be rapidly acquired and taken up from the water to produce (Gil et al., 2009). The disinfectant must be constantly replaced as the concentration declines rapidly as a result of the oxidation of soluble organic materials present in the wash water. The residual concentration of the disinfectant must be measured and controlled throughout operational limits to avoid microbial risks of the washed product (Tudela et al., 2019). If the concentration is not adequately replenished, it may compromise food safety. Therefore, the concentration of residual disinfectant in the wash water is considered the most critical control factor for preventing cross-contamination in produce washing systems (Gombas et al., 2017). Precise measurements of the antimicrobial agent through specific sensors and test methods are needed to enable control of the disinfection process.

Peracetic acid or peroxyacetic acid (PAA) is a water-soluble oxidant with great potential as an antimicrobial agent in produce wash water (Vandekinderen et al., 2009; Van Haute et al., 2015). Most commercial PAA formulations are an equilibrium mixture of PAA, hydrogen peroxide (HP), and acetic acid (AA). PAA is employed as a sanitizer
in the food processing and beverage industry. This includes meat and poultry processing plants, canneries, dairies, animal houses, green houses breweries, wineries and soft drink plants where it is used in clean-in-place (CIP) systems with solutions of less than 500 mg L\(^{-1}\) applied to equipment (ECETOC, 2001). For fresh produce, PAA is typically applied up to 100 mg L\(^{-1}\) in the wash water but higher concentrations are used for surface sanitation. The Spanish Food Safety Agency (AESAN) in the positive evaluation report for PAA on citrus and tomatoes approved 0.4 % for citrus and 0.2 % for tomatoes.

The analytical methods for assaying and monitoring PAA in water solutions include redox and acid/base titrations (Greenspan & McKellar, 1948; Sode, 2014), spectrophotometric/colorimetric and electrochemical methods (Awad et al., 2001; Higashi et al., 2005; Cavallini et al., 2013). Chromatographic methodologies such as gas-chromatographic (GC) and high-performance liquid chromatographic (HPLC) methods have also been described for the analysis of PAA in aqueous solutions (Furia et al., 1984; Kirk et al., 1992; Pinkernell et al., 1996; Pinkernell et al., 1997a; Effkemann & Karst, 1998). Most of these methodologies have tried to individually analyze PAA by achieving high selectivity and less cross-reaction with the coexistent HP (Luukkonen & Pehkonen, 2017). An additional disadvantage is the presence of impurities in the wash water that can affect the detection of PAA. The compounds removed from the surface of the product and those released from the damaged areas can accumulate in the wash water (Casani et al., 2005; Mundi & Zytner, 2015). This organic matter is highly dependent on the type of product and can diminish PAA effectiveness (Vandekinderen et al., 2009) and interfere in the measurement of the residual values.

Several commercial amperometric sensors are available for the continuous measurement of PAA levels for in-line determination. However, the accuracy is limited for the frequent calibration that requires (Pinkernell et al., 1997b). The continuous
measurement of PAA can be achieved by commercially available in situ probes. One of these probes is the ProMinent DulcoTest® CTE PAA probe, a membrane-capped, amperometric with two electrode sensor for continuous measurement of PAA in water. Additionally, the electrochemical behaviour of PAA in the presence of HP was studied by direct voltammetric determination using cyclic or square-wave voltammetry and amperometric detection (Awad et al., 2001). In collaboration with other authors, they studied the effect of different electrode materials, including various metal and carbon electrodes, on the electroreduction of PAA and HP (Denggerile et al., 2004). Both PAA and HP were highly sensitive to electrode material and electrochemically and separately reduced at gold, silver, copper, platinum, palladium, glassy carbon and basal-plane pyrolytic graphite electrodes. Additionally, the corresponding electrokinetic parameters at gold, silver and glassy carbon were determined. When a gold electrode was used, two well-separated peaks for the reduction of PAA and HP were used for the simultaneous analytical determination of both species (Awad, 2012). More recently, some of these authors have studied the influence of the crystallographic orientation of the gold electrode (Awad & Ohsaka, 2015). Similarly, a selective amperometric sensor based on a polybenzimidazole-modified gold electrode (PBI/Au) and pulsed amperometric detection was used for PAA quantification (Hua et al., 2011). However, all these methodologies are unsuitable for the in-situ monitoring of PAA in commercial operations.

To the best of our knowledge, there is not an easy and accurate sensor for measuring PAA in a wide range of concentrations and types of fresh produce wash water. The application of these analytical methods to real samples could help to measure the disinfection of process wash water and control the risk of microbial contamination. This study aimed at evaluating different commercial sensors and test methods for the quantitative analysis of PAA to reliably determine residual concentrations in the wash
water of different types of fresh produce. The impact of different matrix effects in the
wash water from washing apples, tomatoes, peppers, and lemons was evaluated.

2. Materials and methods

2.1 Chemicals

The chemicals used were: 2-[(3-[2-(4-Amino-2-(methylsulfanyl)phenyl]-1-
diazenyl)phenyl)sulfonyl]-1-ethanol (ADS) (>99%), 2-[(3-(2-(4-amino2(methylsulfoxy)phenyl)-1-diazenyl)phenyl)sulfonyl]-1-ethanol (ADSO) (>99%)
(GiottoBiotech, Florence, Italy), acetonitrile optima LC/MS grade (99.99%) (Fisher
Chemical, Pittsburgh, PA, USA), acetic acid glacial (≥99.7%) (Merck-Millipore, Merck
KGaA, Darmstadt, Germany), ultrapure water type 1 was purified in the laboratory using
a MilliQ water purification system (Merck KGaA, Darmstadt, Germany).

2.2 Fresh produce wash water

Four types of wash water with similar physicochemical and microbiological quality
characteristics to that found in commercial packaging lines were prepared. Unwaxed
‘Royal Gala’ apples, ‘Daniela’ tomatoes, ‘California’ red sweet peppers and ‘Verna’
lemons were purchased in a local market the day before starting the trials. Fruits were
transported to CEBAS-CSIC lab and stored in a cold room at 7 ºC partly closed with
plastic bags to reduce water losses until use. For each trial, around 22.5 kg of fresh
produce was used. Fruits were individually thrown from a height of 2 m to a plastic
container to simulate damages that occur during handling in packaging lines. Tap water
(15 L) was added to the container and then, the fruits were left for 72 h at room
temperature. On the day of the trials, the fruits were removed and the wash water filtered
using a polyamide mesh of 0.25 mm pore size. Total Organic Carbon (TOC) content and
the Chemical Oxygen Demand (COD) were measured following the standard photometric method (Spectroquant NOVA 60, Merck) (APHA, 2014).

2.3 Experimental set up

A dynamic system was used for evaluating the different sensors and test methods (Gómez-López et al., 2014). This system incorporates the wash water and the PAA into a washing tank (6 L), simulating the washing of fresh produce by immersion (Figure 1). Two peristaltic pumps, two flow valves and a control board are all part of the system. This dynamic system allows the constant entrance of wash water from the concentrated wash water solution described before into the washing tank that initially contained only tap water plus 200 mg L\(^{-1}\) PAA. The constant entrance of the organic matter at a flow of 6 L h\(^{-1}\) and the manually controlled PAA concentration simulated a commercial washing tank. Physico-chemical analyses were carried out as previously described in section 2.2. Water samples were taken at different time intervals and analyzed by the various test methods, as described below.

PAA used was prepared from a commercial solution (Citrocide Plus, Productos Citrosol SA, Spain), of 15% (w/v) PAA + 17% (w/v) AA + 23% (w/v) H\(_2\)O\(_2\). The desired concentration of PAA (≈ 200mg L\(^{-1}\)) as recommended in some raw products, including citrus and tomatoes was maintained along the time (AESAN, 2016).

2.4 Analysis of PAA by HPLC-DAD

For this study, a high-performance liquid chromatography with photodiode array detector (HPLC-DAD) method using a thiomethoxy azo compound as a selective reagent was carried out as a reference technique for the quantification of PAA in process water (Effkemann & Karst, 1998). This HPLC-DAD analysis was performed previously in
drinking water and slightly modified for process wash water. This protocol is based on
the indirect quantification of PAA through the oxidation of a colorimetric substance, the
sulfide ADS to the corresponding sulfoxide (ADSO) by the action of PAA and the
subsequent detection by HPLC-DAD with little influence of H\textsubscript{2}O\textsubscript{2}.

An HPLC with a photodiode array detector (Agilent 1290 Infinity) couple with a single
quadrupole mass spectrometer detector in series (6120 Quadrupole, Agilent
Technologies, Santa Clara, CA, USA) was used for the chromatographic separations.
Samples (10 μL) were injected in a reverse phase Agilent Zorbax Eclipse XD8-C8 (5 μm
particle size, 4.6x150 mm) (Agilent Technologies, Waldbronn, Germany). The column
temperature was set at 25 ºC, and the flow rate at 1 mL/min. The mobile phases were
ACN/W, starting from 20% ACN in a gradient to reach 85% at 8 min. The gradient was
maintained for 1 min to return to the initial conditions at 10 min in a total time of analysis
of 12 min. The wavelength was set at 410 nm (ref. 600 nm). The retention time was 4.3
min for ADSO and 5.9 min for ADS. A calibration curve was prepared using a stock
solution of ADSO (0.544 mM) by dissolving 2 mg ADSO in 10 mL of ACN/W (50/50).
Then, different concentrations of ADSO were obtained by the dilution of different
volumes of the stock solution in ACN/H\textsubscript{2}O.

2.5 Commercial sensors and test methods for measuring PAA

Four analytical methods were compared for the quantification of PAA.

\textit{Titration method:} The classical redox titration with cerium sulfate in the first titration
for HP followed by iodometric titration for PAA (Greenspan & Mackellar, 1948) has been
the most popular method for monitoring PAA applications. However, the time-consuming
of the titration has hindered its application in photometric assays and online monitoring
systems. \textit{Currently, the most common test method for dilute PAA solutions is drop
titration kits (Donabed, 2018). The drop count kit is a simplified iodometric version of the redox titration method based on the number of drops used until a colour change occurs. In the present study, PAA concentrations were measured using a PAA drop count test kit (AquaPhoenix Scientific, Hanover, PA, USA). For PAA measurements, 10 mL of wash water sample was used. The endpoint of the test was signaled by a distinct change in the sample from deep blue to no color at all. Concentrations were calculated by multiplying the number of drops of 0.1 N sodium thiosulfate consumed in the titration by 15 mg/L per drop, to obtain the level of PAA in mg/L.

Reflectometric method: The application of test strips with reflectometric readings is another methodology with practical application particularly using iodide ion as catalyst in the oxidation of chromogenic substrates to achieve selectivity for PAA in the presence of HP (Fischer et al., 1990). A commercially available Reflectoquant® system was used with the RQflex® 10 reflectometer (Merck, Darmstadt, Germany) and the corresponding PAA disposable strips (75-400 mg/L). Before measurement, the reflectometer was calibrated using the bar-code strip. The reaction was initiated by immersing the test strip for 3 s in the water sample. The excess water was shaken off of the test strip before inserted it into the adapter of the reflectometer. The PAA concentration was read from the display after 15 s.

Amperometric sensor: A semipermeable membrane amperometric probe (Citrocide® System, Productos Citrosol S.A.) placed in a flow cell was used as precise, in-line monitoring of PAA in samples of process water. The semipermeable diffusion membrane isolates the sensing electrodes from the measured sample, providing long-term stability without electrode fouling problems.

Chronoamperometric method: PAA concentrations were measured using the PAASense (Palintest, Gateshead, UK), based on the electrochemical reduction of PAA
and the amperometric detection. This technique involves applying a fixed voltage to a
disposable single-use electrode and recording the resulting current over time. The
magnitude of the current is proportional to the concentration of PAA in the sample. There
was no need to dilute the sample for the range of PAA concentrations analyzed in this
study.

2.6 Statistical analysis

Data were represented using Sigma Plot 14.0 Systat Software, Inc. (Addilink Software
Scientific S.L., Barcelona, Spain). For the statistical analysis, IBM SPSS statistics 25 was
used. Levene’s test was used for assessing the homogeneity of variance. For each trial, a
t-test at $P < 0.05$ was carried out to compare the HPLC method with each commercial
sensor and test method for the same TOC or COD levels. Two trials were carried out per
type of wash water, and three water samples were taken each 15 min as replicates. The
results from one trial are represented in Figures and the results from the other trial are
represented in the Supplementary material.

3. Results

3.1 Analysis of PAA in process water by HPLC

A representative chromatogram for apple wash water is shown in Figure 2 in which
the UV-Vis spectra for the sulfide and sulfoxide are presented. ADS and ADSO were
accurately separated by HPLC and detected by UV at 410 nm, without any matrix effects
from the release of compounds from the apple into the wash water. As with apple wash
water, the wash water from other product types did not present matrix effects or
interferences in the wash water that affected the detection of PAA by HPLC. The
maximum PAA concentration that could be directly calculated according to a linear
calibration curve was 0.185 mM, which corresponds to 14 mg L\(^{-1}\) of PAA. Thus, for the determination of PAA in the process water, a dilution factor was used to bring the sample concentrations into a linear range for HPLC-DAD measurement.

3.2 Monitoring PAA in apple wash water

The comparison of the four analytical methods with the HPLC analysis for the quantification of PAA in apple wash water showed that when the organic matter measured as TOC increased, the concentration of PAA was overestimated using the redox titration and the reflectometric method (Figure 3). The amperometric sensor measurements at low TOC differed significantly from those obtained by HPLC. In contrast, the chronoamperometry measurements did not differ from the results obtained by HPLC at all TOC concentrations. These achievements make that the chronoamperometric sensor was the most suitable method for PAA quantification in the apple wash water. Results obtained in a second trial in which the four commercial sensors and test methods were assessed (included as Supplementary material) confirmed these results. The redox titration also overestimated the PAA concentration, as demonstrated in the first trial.

3.3 Monitoring PAA in tomato wash water

When the commercial methods were examined for measuring PAA in tomato wash water, it was observed that the PAA concentration decreased initially because PAA was oxidizing the organic matter present in the wash water, except for the redox titration that significantly overestimated the PAA compared to HPLC (Figure 4). A t-test revealed that there were significant differences (\(P < 0.05\)) between the results obtained by HPLC and those from the redox titration and the reflectometric methods. For almost all TOC values, there was an overestimation of around 12\% in the PAA concentration with the redox
titration and 13% with the reflectometric method (Figure 4). For all TOC values, there
was no significant difference between the results by HPLC and those obtained by the
amperometric or the chronoamperometric sensors (Figure 4). These findings indicate that
the amperometric and the chronoamperometric sensors showed superior accuracy and
precision for PAA measurement in tomato wash water than the drop titration kit and the
reflectometric method. When the commercial sensors were compared in a second trial,
slight differences were observed concerning the reflectometric method overestimating
PAA when TOC increased (Supplementary material).

3.4 Monitoring PAA in pepper wash water

When the organic matter was measured in red pepper wash water as TOC, the results
were not consistent due to the interferences of the compounds that exude from the fruits,
probably carotenoid pigments that interfered with the photometric measurements. As the
spectrophotometer reading for TOC is at 410 nm, the measurement was affected by the
pigment absorbance. For that reason, COD was measured instead to characterize the wash
water. Our experimental data confirmed that HP at the concentration present in our trials,
as a potential interfering substance of the COD test, affected the COD measured in less
than 1% respect the theoretical value (Talinli & Anderson, 1992; Kang et al., 1999). We
could confirm that the interferences in COD value of the samples containing HP were
insignificant even at high COD. When PAA was analyzed in pepper wash water, the same
trend observed in tomato wash water was shown, but it was even more pronounced
(Figure 5). The t-test revealed that there were significant differences between the results
obtained by HPLC and those from the redox titration and the reflectometric methods. For
all COD values, there was an overestimation of about 48% in the PAA concentration
when using the reflectometric method and 17% with the redox titration kit. In general, the
amperometric measurements were similar to HPLC, with only one measure that differed significantly from the HPLC method. It was remarkable that for all COD values, there were no differences between the measurements by the chronoamperometric sensor and the HPLC analysis. The same trend was confirmed when comparing the commercial sensors and test methods in the second trial (Supplementary material).

3.5 Monitoring PAA in lemon wash water

In the experimental trials with the lemon wash water, it was shown that among the four analytical methods, the redox titration overestimated the PAA concentration for the HPLC analysis, particularly at low and medium TOC (200-400 mg/L) (Figure 6). The reflectometric method gave similar results to HPLC, although in some samples, there was a slight under-estimation. For the amperometric sensor, there was a clear matrix effect observed when the TOC increased (Figure 6). On the other hand, the chronoamperometric sensor was precise and accurate for PAA measurements, similarly to HPLC, with the highest sensitivity and selectivity without interferences from the lemon organic matter. In a second trial with the double TOC content (1000 vs. 500 mg/L), the same results were observed, confirming that the amperometric sensor was affected by the matrix effect of the lemon wash water while the chronoamperometric sensor was the most accurate method.

4. Discussion

In the process water where fresh fruit and vegetables are washed, PAA must be added continuously to maintain the microbiological quality, avoiding cross-contamination. Generally, process water is replaced with clean water at least once a day, while the PAA is monitored and adjusted between the operational limits throughout the day. Several
analytical methods have been proposed for measuring PAA in air samples and aqueous solutions (ECETOC, 2001; Sode, 2019). Some of these methods have critical operating disadvantages, including low sensitivity, complex procedures, expensive instruments and reagents (Domínguez-Henao et al., 2018). Furthermore, in the case of water disinfection, the time required to perform these measurements, and the training of the technical personnel to ensure confidence in the results are also important aspects.

Regarding the HPLC analysis, previously, the UV detection at 206 nm was found appropriate for PAA quantification (Kirk et al., 1992). However, at this UV length, many compounds that are released from the plant tissue, such as polyphenols could interfere. In the present study, we found that the HPLC-DAD analysis for PAA determination based on the oxidation of ADS to ADSO offered high selectivity in all the wash water examined without interferences at 410 nm. Thus ADS is a suitable reagent for the indirect quantification of PAA in process wash water (Effkemann & Karst, 1998; Pinkernell et al., 1997; Baj, 1994). However, as HPLC needs a careful experimental setting with expensive instrumentation and reagents, other test methods must be used for measuring PAA in commercial applications.

The titration and spectrophotometric methods using DPD chromophore with catalase have been described satisfactorily in the range between 0.5 - 10 mg/L PAA. However, for higher concentrations as the ones evaluated in this study, the procedure required dilution with consequences of inaccuracy and time-consuming tests (Cavallini et al., 2013). Our results showed that the commercial titration method was not accurate as there was always an overestimation of PAA, which could probably be due to HP presence. In the recent review by Sode (2019) dedicated to redox titrations the interferences by HP and the methods developed to eliminate are well revised. Sully & Williams (1962) determined PAA and HP in the presence of each other by taking advantage of the significant
differences in their rates of reaction with iodine at 5°C. However, the measurement of PAA was not selective by the titration kit used as it was probably affected by HP which is always present in PAA solutions. In the kit’s protocol, the interferences of HP, as well as other oxidants, are mentioned. Another additional problem observed with the titration kit used was the lack of precision in the number of drops, which is reflected in the standard deviation of the samples as compared with other methodologies tested. The titration kit may allow measuring low PAA concentrations with excellent selectivity over other oxidants (Donabed, 2018), but it cannot be recommended for high PAA concentrations.

An interesting approach is the application of disposable test strips with photometric reading for peroxycarboxylic acids in the presence of HP (Fischer et al., 1990; Pinkernell et al., 1997b). The photometric detection of PAA has been performed in four characteristic regions of the visible and near-infrared spectrum in the range 405–815 nm in tap water using an optimized methodology in which before spectrophotometer measurement the sample is mixed with a chromogen, an iodide, and a buffer containing the reagent (Fischer et al., 1990). This photometric determination of PAA in which in combination with starch as an indicator, iodide as a catalyst in the oxidation of chromogenic substrates is used for test strips to achieve selectivity for PAA in the presence of HP. In our study, the Reflectoquant® test was examined as a reflectometric method commonly used for the selective determination of PAA concentration when HP is present (Hoštálková et al., 2013). Our results showed that this reflectometric method could cause the incorrect readjustment of the PAA dosing. In the preparation of PAA from HP and AA, both PAA and HP coexist in large excess particularly when high content of organic matter (14000 mg L⁻¹ TOC in pepper and 2000, 1200 and 500 mg L⁻¹ COD in, apple, tomato and lemon wash water, respectively) plus the interfering compounds
released from the fresh produce to the wash water that can also affect the reflectometric readings.

Recently, Sode (2019) stated that there is still demand for the correct selection of analytical methods and equipment for PAA, preferably by in-line monitoring or at least by in-situ measurement. Our results showed that the in-line monitoring of PAA measurements with the amperometric sensor was accurate in the process water from apples, tomatoes, and sweet peppers, but not for lemons. The probe is typically used in a flowcell with a submersible sensor and a permeable membrane that isolates the sensing electrode from the measured sample. This type of design provides long-term stability without electrode fouling problems. However, PAA was not able to freely diffuse through the membrane, and come in contact with the active electrode and be detected. Further studies conducted in our group indicated that the organic matter present in the process water from washing lemons, probably the lipophilic compounds of terpenoid nature from the damaged lemon peel, could be responsible for blocking the diffusion membrane temporally as it was regenerated it after a persistent washing. The amperometric sensor, even with frequent checks, showed significant limitations and cannot be recommended for controlling the target PAA dose.

The best method for in-situ monitoring of PAA was the chronoamperometric method with a disposable single-use electrode sensor as a precise, real-time tool for efficient process control without the interfere of HP and the organic matter (Hua et al., 2011). In the present study, we observed the high selectivity of this sensor for low and high PAA concentrations, giving the additional advantage that no dilutions were required. When compared with other analytical methods, chronoamperometry was the most appropriate and the recommended sensor for measuring and controlling PAA in fresh produce wash water as a simple, rapid, and accurate method. The chronoamperometric sensor is based
on suitable electrodes materials and on the application of electrochemical parameters, which are Palintest proprietary information. It provided reliable results for a wide range of produce wash water and PAA concentrations.

5. Conclusions

To measure the residual PAA concentration is crucial for monitoring the disinfection of process water when handling fruit and vegetables to avoid the unnecessary application of excessive disinfectant, which can have cost implications or low concentrations with the unnecessary risk of foodborne pathogens. HPLC-DAD analysis provides a highly sensitive and selective method for quantification of PAA in the process water. In this study, the drop titration kit cannot be recommended due to the overestimation because of the interferences with oxidants such as HP. The reflectometric method overestimates the results due to the high content of organic matter and the needs of high PAA with HP as a potential interferent, making this method unsuitable for the commercial application in process wash water. The amperometric sensor, although it is an in-line method of high sensitivity, it is not suitable for the detection of PAA in lemon wash water because of the strong matrix effect. PAA was not diffused throughout the membrane that isolated the sensing electrode from the measured lemon wash water sample. For the same PAA concentrations, the chronoamperometric method was the most satisfactory method for monitoring PAA in different process water matrices, including those from washing apples, tomatoes, sweet peppers and lemons. No significant differences between HPLC and the chronoamperometric sensor were observed, indicating that there were no interfering oxidants in the wash water such as HP or other the interfering species that affected the measurements with this sensor because of the specificity of the electrode materials. The new portable PAASense monitoring device has economic feasibility as a
testing unit that employs chronoamperometric technology which is unaffected by color, 
turbidity, and organic matter present in the wash water besides its subjectivity, and wide 
range of measurements without dilution.

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Table 1. Physicochemical characteristics including pH, oxidation-reduction potential (ORP) and electrical conductivity (EC) of wash water from apples, tomatoes, sweet peppers, and lemons.

<table>
<thead>
<tr>
<th>Wash water</th>
<th>pH</th>
<th>ORP</th>
<th>EC</th>
<th>TOC/COD (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mV)</td>
<td>(µS/cm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apples</td>
<td>4.33 ± 0.35c</td>
<td>437.7 ± 11.2b</td>
<td>523.9 ± 18.2b</td>
<td>600-2000</td>
</tr>
<tr>
<td>Tomatoes</td>
<td>4.58 ± 0.20b</td>
<td>426.2 ± 8.2c</td>
<td>752.7 ± 138.3a</td>
<td>400-1100</td>
</tr>
<tr>
<td>Peppers</td>
<td>3.87 ± 0.35d</td>
<td>460.7 ± 12.9a</td>
<td>801.6 ± 224.4a</td>
<td>7500-13500</td>
</tr>
<tr>
<td>Lemons</td>
<td>4.91 ± 0.10a</td>
<td>408.9 ± 6.8d</td>
<td>463.2 ± 26.9b</td>
<td>400-550</td>
</tr>
</tbody>
</table>

Values for pH, ORP and EC are the mean of 27 replicates ± standard deviation of the samples analyzed in both trials. Values are intervals between the lowest to the highest TOC in apples, tomatoes and lemons and COD in peppers. For each parameter, values with different letters in the same column are significantly different (P < 0.05) according to Tukey test.
Figure 1. Dynamic system simulating a commercial washing tank of fresh produce. Peracetic acid (PAA) was added continuously to the wash water to maintain a residual concentration of 200 mg L\(^{-1}\). PAA concentrations were analyzed through the use of different methodologies in water samples taken at different time intervals.
**Figure 2.** Chromatogram showing the separation of ADS and ADSO at 410 nm and the UV spectra of ADS and ADSO of an apple wash water sample with 50 mg/L peracetic acid (PAA) and 500 mg/L total organic carbon (TOC).
Figure 3. Quantification of peracetic acid (PAA) in apple wash water by different methodologies when increasing the total organic carbon (TOC) content. A star near symbols indicates significant differences at P < 0.05 compared with the results by HPLC.
Figure 4. Quantification of peracetic acid (PAA) in tomato wash water by different methodologies when increasing the total organic carbon (TOC) content. A star near symbols indicates significant differences at P < 0.05 compared with the results by HPLC.
Figure 5. Quantification of peracetic acid (PAA) in sweet pepper wash water by different methodologies when increasing the chemical oxygen demand (COD) content. A star near symbols indicates significant differences at P < 0.05 compared with the results by HPLC.
Figure 6. Quantification of peracetic acid (PAA) in lemon wash water by different methodologies when increasing the total organic carbon (TOC) content. A star near symbols indicates significant differences at $P < 0.05$ compared with the results by HPLC.
Supplementary information

Performance of methodologies for measuring peracetic acid (PAA) in a second trial in wash water from apples (A), tomatoes (B), sweet peppers (C) and lemons (D) when increasing the total organic carbon (TOC) content. A star near symbols indicates significant differences at P <0.05 compared with the results by chronoamperometry sensor.

![Graphs showing PAA concentration vs. TOC and COD for different samples.](image)