

Comparing Catalysts of the Direct Synthesis of Hydrogen Peroxide in Organic Solvent: is the Measure of the Product an Issue?

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The direct synthesis of hydrogen peroxide has been for about 20 years a hot topic in “green” catalysis. Several methods, which are well established to measure the concentration of hydrogen peroxide in water are also applied to the analysis of reaction mixtures from the direct synthesis of H₂O₂. However, this step could not be always straightforward, because these mixtures contain almost invariably organic solvents and, sometimes, selectivity enhancers which can interfere in some, at the least, of the most popular titrimetric methods. This work presents a

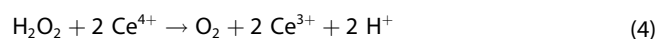
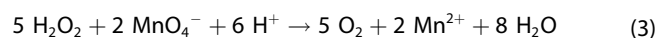
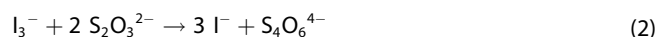
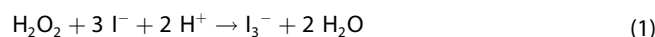
comparative investigation of iodometry, cerimetry, permanganometry (titrimetric methods) and spectrophotometric analysis of Ti^{IV}/H₂O₂ adduct, as applied to analysis of hydrogen peroxide produced by its direct synthesis. They account for more than 90% of the competent literature since 2000. Their pros and cons are highlighted to provide a guideline for the choice of the best possible method of analysis and for the comparison of catalytic results assessed in different ways in the context of the direct synthesis of hydrogen peroxide.

Introduction

The reaction of formation of hydrogen peroxide (HP) from its elements over heterogeneous palladium-based catalysts, commonly referred to as the “direct synthesis” (DS), has been intensively investigated for at least 20 years, with contributions from several research groups.^[1–7]

It outstands among many other catalytic reactions in that no organic substances are practically involved with the exception of methanol, which is most often used as the co-solvent in order to increase the solubility of dihydrogen and dioxygen in the aqueous liquid phase. Were gases more soluble in water this could be unnecessary. On the other hand, HP has a very simple molecular structure and is an unstable species. That’s why it is not amenable of quantitative analysis by direct spectroscopic methods in solution or by chromatographic methods. Therefore, analysis of the reaction mixtures of the DS mainly relies on classical volumetric analysis (redox titration) or colorimetric analysis (spectrophotometric determination of the adduct between Ti^{IV} and H₂O₂). These methods fit batch-wise testing, the most common one, which requires a single final measure, but they can be also exploited for experiments under semi-batch and continuous conditions. In addition, they are cheap, require a very simple work-up, if any, and are relatively easy to use for the skilled chemist.

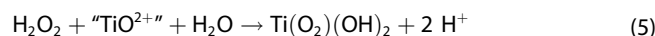
Reported methods for the volumetric analysis of H₂O₂ in DS reaction mixtures are iodometry [Eq. (1) and (2)], permanganometry [Eq. (3)] and cerimetry [Eq. (4)].



In iodometry, H₂O₂ oxidizes iodide ions to form triiodide (I₃⁻, much more soluble in water than I₂), which is titrated with a standard solution of thiosulfate. The latter would be of course able to directly reduce H₂O₂, but they are both colorless and there is not any indicator or any other way to detect the endpoint in the case of direct reaction.

By contrast, in permanganometry and cerimetry H₂O₂ is oxidized respectively by MnO₄⁻ and Ce⁴⁺ in acidic environment, where the latter are stronger oxidants than hydrogen peroxide itself. When permanganate is used to titrate H₂O₂ it also serves as auto-indicator, because its intense color is immediately apparent when all H₂O₂ has been consumed (i.e. from the endpoint on). In the titration with Ce⁴⁺ ferroin, a salt of tris-*o*-phenantrolineiron(II), is used as the indicator.

The colorimetric method entails the treatment of the reaction mixture with a strongly acidic solution of titanyl(IV) sulfate, which yields “pertitanic acid”, which is actually a yellow dihydroxoperoxo-species of titanium(IV) [Eq. (5)] with a strong absorption at 409 nm.



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For this paper we have reviewed 79 papers dealing with the DS and published since 2000 to date^[8–80] (Figure 1). Out of them three regrettably did not report how the amount of H₂O₂ was measured.^[81–83] In other 73 ones, iodometry was used in 32 cases; cerimetry in 20; permanganometry in 7 and colorimetric analysis with TiOSO₄ in 14. Colorimetry with either iron(II) salts and ammonium thiocyanate^[84] or copper(II) sulfate and neocuproine^[85] was respectively reported in further two papers and potentiometry^[86] in the last one of our set.

Our research group has been active on DS for 14 years^[71–78,87,88] and in this period we had occasion to test different methods for the analysis of H₂O₂ in the reaction mixtures. After having routinely used the iodometric titration for long, recently we have opted for the colorimetric measure with TiOSO₄ and started to wonder whether this change could be a reason of concern in comparing our data. It also occurred to us that this could be a more general problem, in that at least four different methods were used in almost 90% of the competent literature. In addition, it should be borne in mind that the reaction mixtures of DS could not meet the optimal conditions for the application of any of these methods of analysis. For instance, the concentration of H₂O₂ could be low, a common occurrence in DS, where diluted to very diluted solutions are usually obtained. Further, some components of the reaction mixture could interfere with the measure, such as fines from solid catalysts which produce scattering in colorimetric analysis or organic compounds which could be oxidized by the titrating reagent. In this context the interference of methanol in permanganometry is well known.^[89]

For the reasons above, we carried out a systematic assessment of the differences in the amount of H₂O₂ measured in the same DS reaction mixture with different methods and we report herein our results. To avoid misunderstandings, the reader should be aware that we did not adopt a strict analytical approach in this study. In fact, we aim at providing some practically useful piece of information to understand how reliable the comparison in the performance of different catalysts can be when different methods of H₂O₂ analysis are used and

which method could be the best suited according to the reaction conditions.

Results and Discussion

As mentioned in the introduction the methods which are most commonly employed to measure the concentration of HP in the reaction mixtures of the DS are adapted from literature methods which were not originally developed for this purpose. In particular all the titrimetric methods are based on redox reaction with possible interference from oxidizable or reducible species. Organic substances, such as methanol or alkyl bromides, or even inorganic additives such as hydrogen bromide are redox active and their effect on the result of the analysis should be carefully verified. Another reason of concern is the concentration of H₂O₂ in the reaction mixtures, which could not match the optimal conditions for the analytical method of interest. For these reasons five hydro-alcoholic solutions spanning more than one order of magnitude of H₂O₂ concentration (namely Titr1–Titr5, from ca 0.1 mM to ca 2 mM, Table 1) were prepared upon dilution of an aqueous Stock Solution and repeatedly analyzed with iodometry, permanganometry and cerimetry. The reliability of the analysis has been evaluated by comparing the H₂O₂ concentrations obtained from the titrations with their “known” values obtained from the dilution ratios of the Stock Solution.

Iodometric titration

The iodometric method undergoes well known interferences, the most important being the volatility of I₂ and the slow oxidation of iodide by O₂ dissolved in the liquid phase. They lead respectively to the under- and the overestimation of H₂O₂. Loss of I₂ by sublimation can be limited upon titrating cold solutions and using Erlenmeyer flasks instead of beakers.^[89] Moreover, although the reduction potential of the iodine/iodide system does not depend on pH for pH < 8 it is generally convenient to perform the titration in acidic environment to prevent the dismutation of I₂ to I[−] and IO₃[−], which occurs in basic media and to increase the potential of other oxidizing agents, which is generally higher under these conditions.

The iodometric titration of HP, is particularly advantageous, especially for commercial samples, because it is relatively little affected by the presence of stabilizers (such as boric acid,

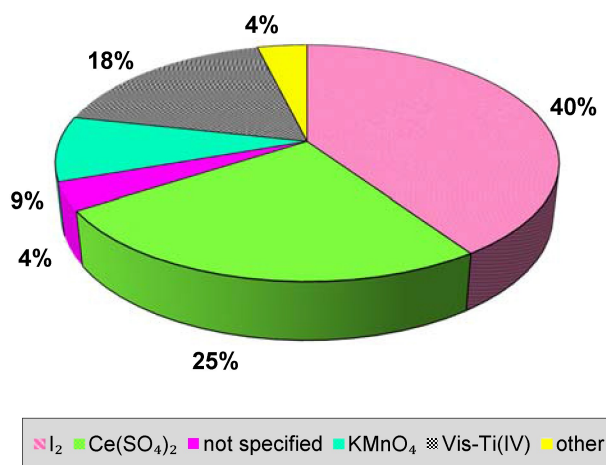


Figure 1. Methodologies for the assessment of the H₂O₂ concentration in catalytic studies of direct synthesis.

Solution	Concentration [mM]
Titr1	0.0933 ± 0.0029
Titr2	0.187 ± 0.005
Titr3	0.467 ± 0.010
Titr4	0.933 ± 0.021
Titr5	1.87 ± 0.04
Stock Solution	9.33 ± 0.14

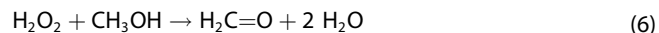
salicylic acid and glycerol) and thus provides more accurate results.^[89]

In spite of its strong oxidizing power, H₂O₂ reacts slowly with iodide and a catalyst, generally a high oxidation state transition metal compound such as sodium or ammonium molybdate(VI), is needed to speed it up. However, the catalyst can also increase the rate of the aerobic oxidation of iodide to I₂ hence it is sometimes recommended to carry on the titration under inert atmosphere. The slightly acidic conditions are even more important for the titration of H₂O₂ in that for pH ≥ 7 iodide ions catalyze the dismutation of HP to water and oxygen.^[90–93]

According to different literature procedures, iodometric titration of HP solutions obtained from DS is performed under different pH conditions. In this investigation, to ensure the reliability of iodometric titration, the oxidation of iodide with HP was alternatively promoted by adding a *slightly acidic* (10^{−3} M sulphuric acid) and a *strongly acidic* (5 M sulphuric acid) solution of sodium molybdate(VI). With the addition of 5 M sulfuric acid the final acid concentration in the titrated samples is ca 1 M, close to value prescribed by the literature procedure.^[89] On the basis of the stoichiometric ratios in the reactions between iodide ions and HP (2:1) and between iodine and thiosulfate ions (1:2), the concentration of HP can be determined from the volume of standard thiosulfate solution provided an excess amount iodide is supplied.

Figure 2 shows the results of the titrations of the Stock Solution as such and after 1:1 dilution with methanol. Both at low and high H⁺ concentration the iodometric titration underestimated the HP concentration, with a very large gap (ca 80%)

between the expected value at low H⁺ concentration and a much smaller one (ca 10%) at high H⁺ concentration. The results obtained for the aqueous stock solution and for the 1:1 hydro-alcoholic solution are strictly comparable, which suggests that the oxidation of methanol [Eq. (6)] does not interfere with the oxidation of iodide.



In addition, no consumption of thiosulfate was observed in the titration of pure methanol, which rules out possible interferences from the alcohol or from its impurities upon reaction with the titrating agent.

These results would suggest that a highly acidic environment is recommended to improve the accuracy, but the analysis of the even more diluted solutions Titr1–Titr5 shows that the situation is not that simple. The competent experimental values of their iodometric titrations are illustrated in Figure 3.

From them it appears that for concentrations up to 2 mM a low concentration of H⁺ is much more appropriate. In fact, only for Titr5 (1.86 mM) the results of the titrations in either mildly or strongly acidic environment are not too far. For Titr1–Titr4 the concentration of HP is largely underestimated in strongly acidic solutions, with a systematic decrease of the accuracy with increasing dilution of the analyte. No I₂ in Titr1 and only 41% of the expected amount in Titr2 was found.

This supports the hypothesis that a too high H⁺ concentration promotes reactions of HP which compete with I[−] oxidation so effectively to suppress it completely in very diluted solutions. The I[−]/H₂O₂ system is a rather complex one^[90–93] and

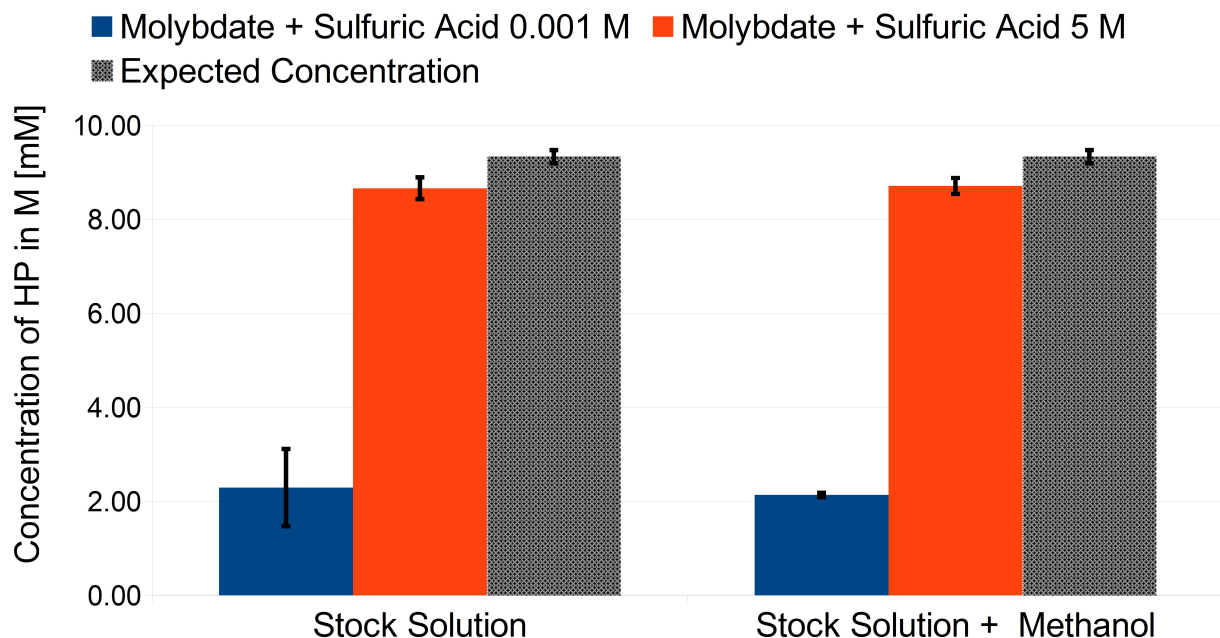


Figure 2. Iodometric titration under mildly and strongly acidic conditions (1 mM and 5 M H₂SO₄ solutions of Na₂MoO₄, respectively) of 1 mL of the aqueous Stock Solution as such (left) and after the addition of 1 mL methanol (right). All the concentrations are referred only to the volume of stock solution used for the analysis and compared to its known reference concentration (black bar).

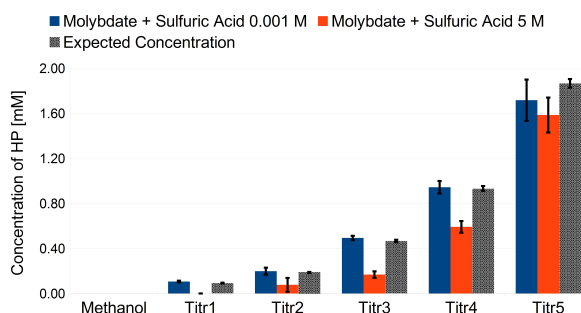


Figure 3. Concentrations of HP in the standard HP solutions Titr1-Titr5 from iodometric titration using mildly (blue bars) and strongly (red bars) acidic solutions of Na_2MoO_4 (1 mM and 5 M in H_2SO_4 , respectively). All the concentrations are referred only to the volume of Titr1-Titr5 solutions used for the analyses and are compared to the values expected from the respective dilution ratios of the Stock Solution (black bars).

this investigation was not aimed at disclosing the nature of these possible side-reactions. We cannot even rule out that a too high acidity made the oxidation of I^- by diluted HP exceedingly slow by turning the Mo(VI) catalyst, Na_2MoO_4 , into a little active form.

However, even in only slightly acidic environment the accuracy of the titration is dependent on the HP concentration, but in this case, it changes the other way around. Whereas a slight overestimate of HP concentration was achieved for Titr1-Titr4, in Titr5 (1.86 mM) it was underestimated by 8% (which became ca 80% in the 4.6 mM solution shown in Figure 2).

The molar ratio between HP and H^+ for the titrations under strongly acidic conditions is very low (from 10^{-6} to 10^{-4} for solution Titr1 and the Stock Solution, respectively), while in the titration under mild acidic conditions the HP/ H^+ ratio is much higher. In the case of the titration of solutions Titr1-Titr5 it ranges from $4.6 \cdot 10^{-2}$ to 0.93 and in the Stock Solution turns out to be 4.65. As two moles of H^+ are consumed per mol of HP in the reaction with iodide, a sufficient amount of acid must be provided. The amount of I_3^- produced in the reaction would be otherwise lower than the actual amount of HP in the solution. In addition, in a H^+ depleted solution the excess of HP could react with iodide to form dioxygen. In both cases the amount of HP detected by the titration would be underestimated. This could explain why the underestimation of the concentration of HP is so severe for the Stock Solution whereas HP is only barely detected in Titr5.

To summarize, our data indicate i) that the presence of methanol does not imply any sensible interference and ii) that, as a rule of thumb, for HP concentrations up to 2 mM, iodometric titrations should be better carried out with a low content of acid in the hydroalcoholic solution. A large to very large underestimation is to be expected otherwise for HP concentration up to at least 5 mM.

A further critical issue of the iodometric analysis of H_2O_2 methanol solutions obtained from DS is the color returning of the I_2 -starch complex at the end of the titration, severely affecting the determination of the endpoint. In fact, this is signaled by the disappearance of the blue color (violet when

methanol is the solvent) of the complex formed between starch and iodine. It is well known that after the end point, some iodine can be further produced by oxidation of iodide with atmospheric oxygen, with the solution color turning back to blue. For this reason, it is recommended to stop the titration when the solution remains colorless for at least 30 s after the last addition of thiosulfate. This issue could be even more relevant when the solvent are hydro-alcoholic mixtures, in which O_2 is more soluble than in pure water,^[94] which is the reason why they are commonly used in the DS. We observed that in the most diluted solution the production of I_2 went on only for a few seconds after the first color change, but could go on for several minutes in the most concentrated ones. In the analysis of 1 mL of the Stock Solution after the addition of 1 mL of methanol it lasted for ten minutes or even more. This can make the detection of the endpoint somewhat arbitrary and the measured HP concentration higher than its actual value. As a matter of fact, the titrations of the most concentrated solutions, Stock Solution and Titr5, where this issue is qualitatively more sensible, seem to be also affected by a higher uncertainty, both at high and low HP/ H^+ ratio.

In this context we also assessed the effect of bromide ions, which are commonly supplied in DS reaction as HBr as promoters.^[1] For this purpose the Stock Solution was titrated after the addition of an equal volume of a solution of HBr in methanol (200 ppm). In view of the relatively high HP concentration in this case we applied a high concentration of H^+ too. The production of I_2 past the endpoint was remarkable and this phenomenon, which was relatively faster at the beginning, went on for more than one hour. This suggests that in the presence of HBr and, possibly, of oxidized bromine species (aged HBr can contain some Br_2 , easily recognized from its yellow-red color) enhances the rate of oxidation of I^- by O_2 . Upon addition of the same solutions used for the iodometric titration of HP (Na_2MoO_4 , H_2SO_4 , KI) to a few mL of the 200 ppm HBr solution in methanol the formation of I_2 was clearly observed. This qualitative observation supports the conclusion that HBr remarkably enhances the oxidation of iodide by atmospheric oxygen. Accordingly, in addition to methanol HBr can also cause over-production of I_2 by air oxidation, which could lead to the overestimation of the concentration of H_2O_2 .

In conclusion, to reliably assess the concentration of H_2O_2 in real samples of DS reaction mixtures upon iodometric titration the conditions for the analysis should be carefully adjusted.

Permanganometric titration

With this method HP is oxidized to dioxygen with a standard solution of potassium permanganate under strongly acidic conditions. pH must be low to prevent the formation of brown solid MnO_2 , which is the favored reduction product under neutral or moderately basic environment and is a catalyst for HP disproportionation. At low pH the reduction of MnO_4^- yields the Mn^{2+} aquo-ion, almost colorless, hence permanganate acts an auto-indicator due to its own intense violet color. In aqueous solution of HP this titration is known to be very accurate.^[95]

Permanganometric titrations are usually autocatalytic reactions, in that the action of MnO_4^- is accelerated by Mn^{2+} ions. Accordingly, the first amount of added MnO_4^- could react so slowly that its violet color can be initially persistent. If the analyte is thermally stable, the solution is usually heated to speed up the build-up of Mn^{2+} in solution.^[96,97]

Organic substances are known to interfere with permanganometric titrations and their presence (and those of further reducing species) is spotted by the fading of the end point. For this reason, the iodometric titration is considered more reliable when oxidizable organic substances are present.^[89] Nevertheless, the permanganometric titration is often employed for the analysis of reaction mixtures obtained from the DS even when the solvent (or co-solvent) is an alcohol. Therefore, we tried to evaluate the accuracy of this analytical method for the DS mixture by titrating the Titr1-Titr5 solutions (Table 1) and the Stock Solution with a standard aqueous solution of potassium permanganate 0.2 mM. The Stock Solution was again analyzed as prepared and after 1:1 dilution with methanol. Low pH was ensured by the addition of 5 M sulfuric acid. The results are illustrated in Figure 4.

Unlike the iodometric titration, the amount of titrant consumed by the solvent itself is not negligible, even when HP is not present in solution. Accordingly, to take the MnO_4^- consumption by the solvent into account, a blank experiment was performed by measuring the volume of titrant consumed by 1 mL of methanol. The results of the permanganometric titrations, both the raw ones and those including the blank corrections, are summarized in Figure 4, along with the values known from the dilution ratios of the Stock solution.

The raw results of the titrations gave an apparent HP concentration much higher than the actual one. The over-estimation is much higher for the most diluted solutions: for instance, the apparent H_2O_2 concentration of Titr1 (0.300 mM) is more than 300% than the expected value of 0.093 mM. For the more concentrated solutions the gap is smaller, but still comparable with the known concentrations determined from the respective dilution ratios of the Stock Solution. The actual concentration of Titr5 is 1.86 mM, but it is over-estimated by

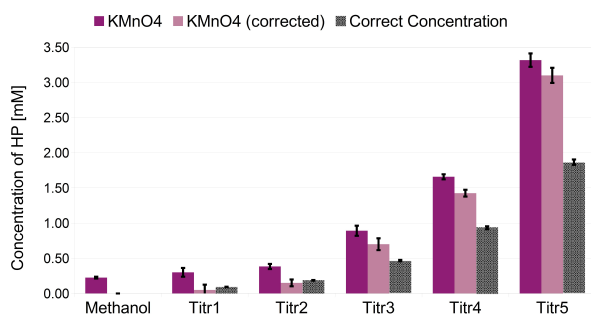


Figure 4. Titration of Titr1-Titr5 with standard aqueous KMnO_4 , 0.2 mM (purple bars). All the concentrations are referred only to the volume of Titr1-Titr5 solutions used for the analyses and are compared to the values expected from the respective dilution ratios of the stock solution (black bars). Pink bars represent concentrations corrected taking into account over-consumption of KMnO_4 because of methanol oxidation.

1.45 mM, with an apparent H_2O_2 of ca 3.3 mM. Interestingly, although the relative value of the KMnO_4 over-consumption decreases with increasing HP concentration, its absolute value increases by almost one order of magnitude. This implies that the reactions of H_2O_2 and of CH_3OH with KMnO_4 are not independent of each other and that a higher concentration of HP in some way promotes the oxidation of the alcohol. This unfortunately makes impossible to correct the results of the titrations by subtracting the amount of methanol oxidized by KMnO_4 in blank solutions, where no H_2O_2 was added.

When the straight Stock Solution (no methanol added) was titrated the HP concentration was in excellent agreement with the known value (Figure 5). On its own, however, this result is useless, because the latter value was obtained with this very method (see Experimental). However, when this result is compared with the apparent HP concentration in the Stock Solution 1:1 diluted with methanol it fully confirms that the over-consumption of permanganate is attributable to the presence of methanol and that the relative over-consumption decreases, but that its absolute value increases, with increasing HP concentration.

On these grounds the evaluation of the performance of the DS catalysts requires great care when the reaction is carried out in hydro-alcoholic solution and the HP concentration is assessed by permanganometry. Under these circumstances over-estimation of the HP concentration is to be expected, from large (a few tens %) for relatively concentrated mixtures to severe (several hundred %) for the relatively diluted ones.

Figure 6 shows the results of the iodometric and the permanganometric analyses on the same methanol samples collected during a real catalytic run, carried out over a Pd/C eggshell catalyst (1% w/w metal loading) in a semi-continuous reactor as described elsewhere.^[78]

The volume of the methanol phase of the reaction mixture was 300 mL, so that the final plateau concentration of H_2O_2 was below 2 mM. As discussed above, for the iodometric titrations of these samples low acidity conditions are the most recommendable ones (Figure 6, red diamonds). In agreement with the results of the titrations of the model solutions Titr1-Titr5, both iodometry under high acidity conditions gave under-estimated

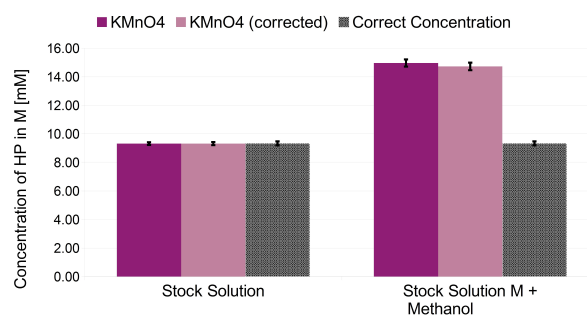


Figure 5. Titration with 0.2 mM KMnO_4 of a standard 1 mL M H_2O_2 aqueous solution (left) and after the addition of 1 mL of methanol (right). The concentration estimated with the titration, after the correction by KMnO_4 consumption of the pure solvent and the expected value are reported in purple, pink and black colors, respectively.

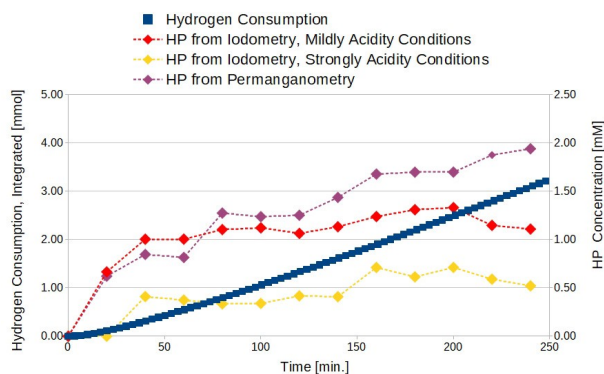


Figure 6. Permanganometric (purple diamond) and iodometric (under both mildly and strongly acidic conditions, red and yellow diamond, respectively) of samples of the methanol reaction mixture collected during a catalytic test of DS.

values of HP concentrations and permanganometry over-estimated ones. At the end of the test the gap between the result of permanganometry surpassed by at least 50% the result of iodometry under optimized conditions.

In the example illustrated above these differences would be reflected in the assessment of the selectivity of the catalyst (not a very selective indeed): based on the results of permanganometric, iodometric (low acidity) and iodometric (high acidity) it would turn out to be respectively ca 10%, 5.5% and ca 3%.

In conclusion our opinion is that whenever possible methods different from permanganometry should be employed for the analysis of H_2O_2 in hydro-alcoholic solutions. In line with this it can be appreciated that among the titrimetric techniques (Figure 1) this is already the less popular.

Cerimetric titration

In cerimetric titrations, HP is oxidized to O_2 by a standard solution of cerium (IV) sulfate under acidic conditions (in the order of 0.4–3 M of nitric or hydrochloric acid or 0.2–1.5 M of sulfuric acid), with ferroin as the indicator.^[89,98] After the end point excess cerium (IV) oxidizes the indicator turning the solution to colorless. In this work, five methanol solutions of H_2O_2 , as well as the Stock Solution, as prepared and with the addition of methanol, were analyzed with cerimetric titration. As for the other titrations, only 1 mL of each solution was analyzed, because samples from the reaction mixture during the DS are generally small, especially in continuous testing with several withdrawals in which it is important not to change too much the ratio between the amounts of the liquid and the solid phases. The small size of the samples (and of the amounts of HP to be titrated) is more relevant here, because color change of the indicator requires the consumption of additional cerium (IV), and for very diluted samples could be the cause of inaccuracy. In this work one drop of ferroin was used per mL of solution to be titrated. Hence the amount of cerium(IV) needed to oxidize one drop of ferroin in 1 mL of either methanol or

water was measured in order to evaluate the extent of the possible interferences, if any.

Unfortunately, ferroin is not very deeply colored and appreciating its color change with only one drop of indicator per mL of solution of the analyte is hard. On the other hand, a larger quantity is not recommended at all. In fact, the titration of this small amount of the indicator in blank solution consumed, both in water and methanol, an amount of cerium (IV) sulfate corresponding to an apparent HP concentration of ca 0.2 mM. Moreover, ferroin could be slowly oxidized by HP: this was qualitatively confirmed by the complete fading, in 1 h under magnetic stirring, of 5 mL of the solution Titr5 to which five drops of ferroin had been added. In view of these circumstances cerimetric titration of very diluted HP solutions could be particularly challenging, if not even little reliable.

The results of the titrations of the five hydro-alcoholic HP solutions (Titr1-Titr5, Table 1) and of a blank sample in methanol (only indicator, no HP) are illustrated in Figure 7.

The orange bars in Figure 7 represent the raw results of the titrations. For the most diluted solutions (Titr1, 0.093 mM; Titr2, 0.186 mM) the results are higher than the expected ones, but somewhat smaller than the blank. In these two cases the effect of the oxidation of the indicator is quite apparent. If this is taken into account by subtracting the blank from the raw results of all the samples (yellow bars) a systematic under-estimation of HP is apparent. It should be appreciated that also the raw results for Titr3-Titr5 gave concentrations somewhat lower than the known ones. The extent of under-estimation gets relatively smaller as the HP concentration increases and amounts to “only” 15% for Titr5 (1.86 mM), but for Titr4 it already approaches 35%.

The results of the titrations of the Stock Solution are illustrated in Figure 8. In this case the Stock Solution was analyzed not only as described above (1 mL as such and after the addition of 1 mL of methanol), but also after the addition of the alcohol to 2 mL of the solution. The latter titration confirmed that the higher the amount of HP to be titrated the more accurate is the result. In fact, the cerimetric method still underestimate the HP concentration, but with a double volume

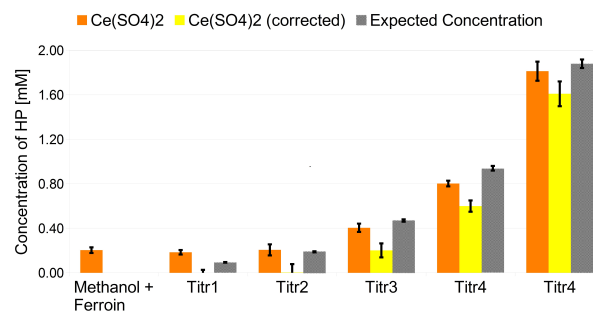


Figure 7. Results of cerimetric titrations of H_2O_2 methanol solutions. The result of the titration of the indicator is reported as the reference. The raw results of the titrations (orange bar) are reported along with those corrected by the amount of titrant consumed by the indicator (yellow bar) and those expected from the dilution ratio (black bar).

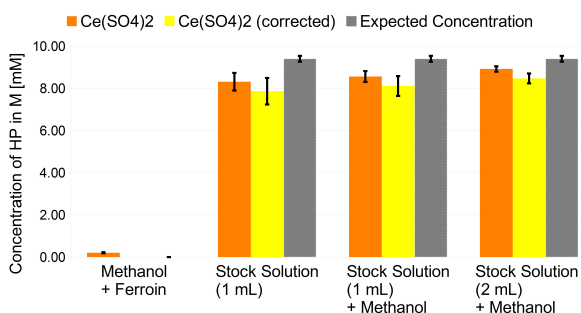


Figure 8. Results of cerimetric titrations of the H₂O₂ aqueous Stock Solution, as prepared and after addition of methanol (1 mL). The result of the titration of the indicator is reported as the reference. The raw results of the titrations (orange bar) are reported along with those corrected by the amount of titrant consumed by the indicator (yellow bar) and those expected from the dilution ratio (black bar).

of stock solution titrated the gap was 7%, the smallest achieved in this work.

As to the results of the titration of 1 mL of the straight Stock Solution and after the addition of 1 mL of methanol the latter was only 3% higher than the former. This shows that methanol oxidation by cerium(IV) does not interfere too much.

In conclusion, the cerimetric titration appears suitable for the quantitative analysis of methanol solutions HP, provided their concentration is higher than 2 mM or large amounts are available. In any case some underestimation should be expected, which is only partially balanced by a small overconsumption of cerium(IV) due to limited oxidation of methanol and to the amount required to oxidize ferroin and produce its appreciable color change. The latter is the main source of error in the titration of diluted solutions (< 2 mM).

Spectrophotometric analysis with titanium oxysulfate

The fourth method commonly reported in the literature for the analysis of reaction mixtures of the DS^[27,32] is the indirect measure of the concentration of HP by the spectrophotometric analysis of the peroxidic complex [Ti(O₂)OH(H₂O)₃]⁺_{aq}.^[99,100] This is obtained upon reacting H₂O₂ with an aqueous solution of TiOSO₄.^[101] For the evaluation of the method, alcoholic solutions with different H₂O₂ concentration and containing the same amount of methanol and of an acidic solution of titanium oxysulfate were analyzed.

The water/methanol ratio is important because the position of the absorption peak of [Ti(O₂)OH(H₂O)₃]⁺_{aq} significantly depends on the solvent. In this work the maximum of absorbance occurred at 409 nm.

The absorbance (A) at this wavelength was measured for hydro-alcoholic solutions of known concentration (Vis1-Vis9, Table 2) ranging from 4.675 μM (Vis1) to 1.866 mM (Vis9). A linear dependence of A on the HP concentration was observed in this range (Figure 9). With a further point from a 4.6 mM solution included (A = 3.24) the linear fit was still excellent (R² =

Solution	Concentration [mM]	Preparation
Vis1	0.00467 ± 0.00016	0.3967 g of Solution Titr1
Vis2	0.0093 ± 0.0005	1 mL of Solution Titr1
Vis3	0.0187 ± 0.0008	1 mL of Solution Titr2
Vis4	0.0467 ± 0.0018	1 mL of Solution Titr3
Vis5	0.093 ± 0.004	1 mL of Solution Titr4
Vis6	0.187 ± 0.007	1 mL of Solution Titr5
Vis7	0.467 ± 0.014	5 mL of Solution Titr4
Vis8	0.933 ± 0.019	1 mL of Stock Solution + 1 mL MeOH
Vis9	1.87 ± 0.05	2 mL of Stock Solution + 1 mL MeOH

[a] 0.5 mL of titanium oxysulfate solution have been added to each sample, prepared according to the reported information, before dilution to 10 mL with water. Concentrations refer to the final 10 mL solution, determined with spectrophotometric analysis at 409 nm.

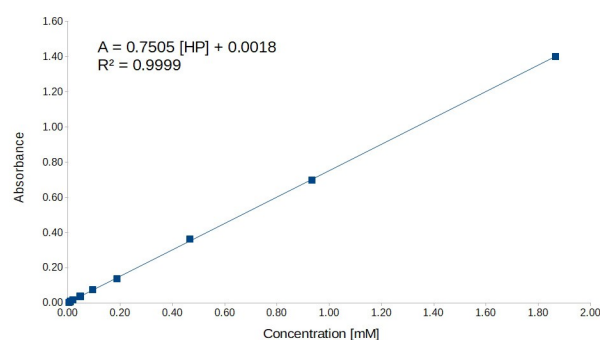


Figure 9. Absorbance at 409 nm of the Vis1-Vis9 solutions (Table 2).

0.9989). Accordingly, this method could be suitable for the analysis of HP in a concentration range wider than three orders of magnitude (more concentrated solutions can be simply diluted to achieve measurable absorbance values).

Interestingly in this work no modification of the UV-Vis spectra or precipitation of titanium dioxide was observed in solutions of [Ti(O₂)OH(H₂O)₃]⁺_{aq} stored at 4 °C for 24 hours or more. Therefore, in case of need they can be stored in a fridge for later analysis. The precipitation of TiO₂ is matter of concern not only because it would decrease the concentration of [Ti(O₂)OH(H₂O)₃]⁺_{aq}, but also because suspended solids would scatter the radiation and interfere with the spectrophotometric measure.

Although Ti(IV) hydrolysis does not appear to be an issue, suspended solids could be present in the DS reaction mixtures as the result of mechanical erosion of the catalyst, depending on its nature and on the design of the experimental set-up. As the fines more effectively scatter light when their size is comparable to the radiation wavelength, their presence cannot be appreciated simply at glance. Figure 10 shows the pictures of three different DS reaction mixtures, after addition of TiOSO₄ solution, collected at different times during a real catalytic run, carried out over a palladium catalyst supported on mesoporous ion-exchange resin, in a semi-continuous reactor, as described elsewhere.^[78] Each of them was syringe-filtered with a Teflon filter (cut-off 450 μm), but nevertheless to the naked eye they appear the same as before filtration.

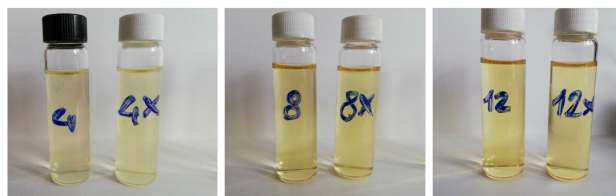


Figure 10. Samples of reaction mixture at different reaction time, after the addition of TiOSO_4 solution, as collected (4, 8 and 12) and after filtration on Teflon syringe filters (4x, 8x and 12x).

In spite of this the results of their spectrophotometric analyses are different and clearly affected by light scattering (Figure 11). Due to the overestimation of the absorbance at 409 nm of the unfiltered solutions, the measured amount of H_2O_2 produced in the reaction (Figure 11, blue line) was overestimated as well, by about 40%, in comparison with the filtered solution (Figure 11, yellow line).

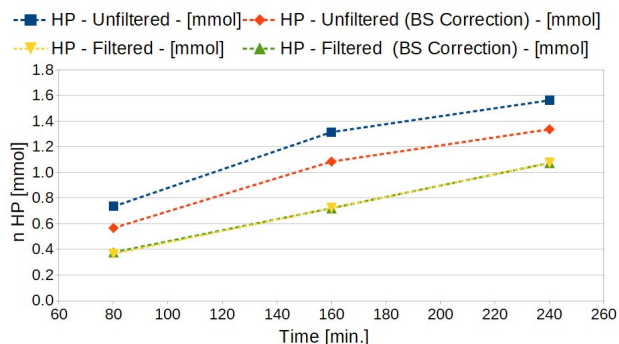


Figure 11. Moles of H_2O_2 determined with spectrophotometric analysis at 409 nm of the as collected samples of reaction mixture (blue curve) and after correction with the absorbance at 800 nm (red curve, see text). As the reference, the results of the spectrophotometric analysis of the samples after filtration are also presented (yellow curve).

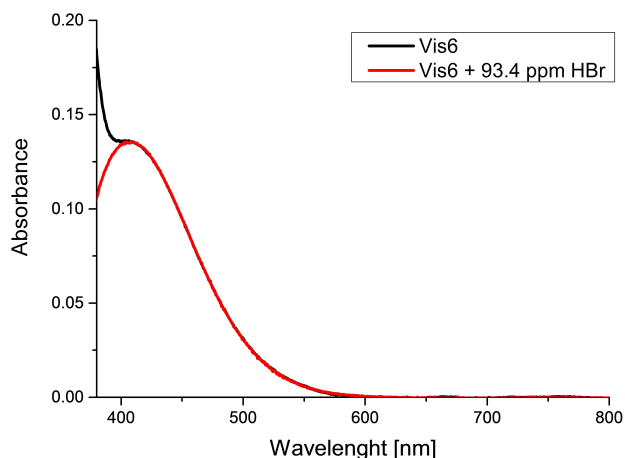


Figure 12. Absorption spectra of H_2O_2 Solution Vis6 as prepared and with 93.4 ppm HBr.

The red line of Figure 11 was obtained upon subtraction of the absorbance of the $[\text{Ti}(\text{O}_2)\text{OH}(\text{H}_2\text{O})_3]^+_{(\text{aq})}$ solutions at 800 nm from the absorbance at 409 nm. This correction would work if the effect of light scattering were the same at every wavelength. This is apparently not the case and the filtration of the solutions is recommended prior the spectrophotometric analysis. If the same subtraction is made on the spectrum of the filtered solution no change in the values of H_2O_2 as a function of the time reaction is observed (Figure 11, green and yellow lines). This implies that the filtration is enough to completely remove from the solution scattering particles so that the apparent absorbance at 800 nm is practically equal to zero.

To investigate the possible interference arising from the presence of HBr (as mentioned above a commonly employed promoter in the DS) the Solution Vis6 was also analyzed in the presence of 93.4 ppm of hydrobromic acid and no difference in the absorbance at 409 nm was observed (Figure 12).

In conclusion, spectrophotometric analysis appears a very reliable method for the quantification of alcohol solutions of HP. It is applicable in a large range of HP concentrations and is not affected by interferences arising from the presence of methanol or hydrobromic acid. However, when the design of the experimental set-up or the mechanical properties of the catalyst allow for the formation of suspended fines filtration of the samples to be analyzed is recommended to prevent light scattering.

Conclusion

With all the titrimetric methods commonly employed in the analysis of H_2O_2 in aqueous methanol solutions, mimicking reaction mixtures of its direct synthesis, the results deviate more or less from the known values of its concentration within a representative range.

The most seriously affected method is the permanganometric titration, with a systematic over-estimation mostly due to the oxidation of methanol. This is very severe when the concentration of hydrogen peroxide is relatively low. Blank correction is ineffective because with increasing concentration of H_2O_2 the absolute value of over-consumed KMnO_4 increases, although its relative values decreases. With this method relative deviations as high as 50%, or larger at very low concentration, should be expected. Our results only confirm the very well-known interference from methanol in this method, which appears not well suited for this kind of analysis.

Iodometry and cerimetry are not affected by the presence of the alcohol and give better results. However, cerimetry does not provide reliable results when the concentration of H_2O_2 is low (< 0.4 mM), because the amount of Ce^{IV} consumed in its oxidation is lower than the amount required for changing the color of the indicator. If this is measured in blank titration and the results of the titrations are corrected accordingly the estimate of the concentration is fair provided it is close to 2 mM or higher. Under these circumstances this method underestimates the concentration of H_2O_2 by ca 15%-to-7% (the higher the concentration, the better), which could be accept-

able to define a *lower* limit of catalytic performance. Iodometry can give both under- or over-estimated values of the concentration of H₂O₂. This depends on both the acidity of the solution and the concentration of H₂O₂. In relatively little acidic mixtures HP concentration is somewhat over-estimated below 2 mM and under-estimated around 2 mM, with deviations limited to less than 10–15%. Above 2 mM under-estimation, and much more severe (ca 75% around 10 mM), is always observed. By contrast if the mixture is strongly acidic the iodometric method provides always under-estimated values and, in this case, the higher the concentration of H₂O₂ the better. Only from ca 2 mM up the deviations are less than ca 15%.

It is clear, in any case, that all the titrimetric methods can be little reliable for the detection of very low concentrations of hydrogen peroxide in aqueous methanol solutions. This could be the case of samples collected in catalytic runs when the yield of H₂O₂ is low. Titrimetric methods, apart permanganometry and iodometry under little acidic conditions, are therefore more appropriate when the concentration of H₂O₂ is relatively high.

The spectrophotometric analysis of the Ti^{IV}/H₂O₂ adduct, in conclusion, is apparently the best suited single method. It is not affected by the presence of methanol or hydrogen bromide (selectivity enhancer) and gives a strictly linear response of the absorbance at 409 nm as a function of the concentration of H₂O₂ in the whole investigated range which spans two orders of magnitudes (from ca 10⁻¹ to 10 mM). Deviations of the results implying an over-estimated concentration of H₂O₂ can arise from light-scattering produced by suspended fines released from the solid catalyst. However, they can be easily removed upon simple syringe-filtration of the samples, which is suitable also for small volumes of liquid and restores a correct response.

Experimental Section

All the titrations were performed with a Brand bottle-top Burette Titrette[®], with a nominal volume of 25 mL and an accuracy of 18 μL. Every titration was repeated three times (N=3) and the concentration of HP was determined from the mean value of the end points of the three titrations.

Preparation of the solutions for the titrations. The Stock Solution of HP was obtained by the dilution of 1 mL of concentrated HP (30% v/v, EMPROVE[®] ESSENTIAL Ph Eur, BP, USP) into 1 liter of deionized water. The concentration of the Stock Solution is exactly determined by titration with potassium permanganate 0.02 M Normex (Titolchimica) of 50 mL of HP solution to which 20 mL of H₂SO₄ 3.6 M (dil. 1:5 in water) (Sigma-Aldrich) had been added.^[102] No indicators are needed for this method. The solutions for the titrations (Titr1-Titr5, Table 1) were obtained upon dilution of the stock solution with methanol (HPLC PLUS Gradient, Carlo Erba), with different dilution ratios (from ca. 1:5 to 1:100 vol). All the solutions were prepared using Class A glassware. After the preparation all the solution were stored at 4°C until the measurement.

Titration with potassium permanganate. For the titration of the HP solution in methanol 1 mL of the sample was added to 2.5 mL of H₂SO₄ 5 M, and then titrated with KMnO₄ 0.002 M Normex. After the addition of the first drops of titrating solution a pale pink color is

formed, but differently from the titration of aqueous solutions of H₂O₂, it disappears after a few seconds.

Iodometric titration. The iodometric titration of the solutions of HP was performed in either a mildly acidic or a strongly acidic one. For both cases, a solution of Na₂MoO₄ (0.13 g/L, Carlo Erba) in aqueous H₂SO₄ 10⁻³ M (solution A), and a solution of KI 10 g/L (Sigma-Aldrich) (solution B) were prepared by dissolving the solid reagents. For the titration under mildly acidic condition, 2 mL of the solution A and 3 mL of the solution B were added to 1 mL of the sample. The formed triiodide is titrated with a standard solution of sodium thiosulfate 0.001 M (Titolchimica). Starch, added to the solution when the yellow color of triiodide disappeared, was used as the indicator. For iodometric titration under strongly acidic conditions, 1 mL of a sample was treated with 2 mL of solution A, 2.5 mL of 5 M H₂SO₄ and 3 mL of solution B.

Titration with cerium (IV) sulfate. 1 mL of the sample was titrated with a 0.2 mM Ce(SO₄)₂ solution in 0.2 M H₂SO₄, prepared by dilution of a 0.1 M cerium sulfate standard solution (Tritipur[®], Supelco). A 0.1% w/w aqueous solution of ferroin (Sigma-Aldrich) was used as the indicator.

Spectrophotometric detection with titanium oxysulfate. 0.5 mL of titanium (IV) oxysulfate solution (~5% Ti basis, in H₂SO₄ 27–31%, Sigma-Aldrich) were added to 1 mL of the sample in a 10 mL volumetric flask and diluted with deionized water. All the solutions were prepared using Class A glassware. The UV-Vis absorption spectrum was recorded, from 355 nm to 800 nm, with a double beam spectrometer Varian Cary 100 Bio with a scan rate of 200 nm/min and using a water solution (0.5 mL of TiOSO₄ solution and 1 mL of methanol diluted to 10 mL with deionized water) as the reference. For the analysis of concentrated samples (above 20 mM of HP) the solution can be diluted up to 1:5 vol with deionized water without no precipitation of TiO₂. In this investigation we prepared nine samples (Vis1-Vis9, Table 2), prepared by dilution, from the solutions Titr1-Titr5 and M reported in Table 1.

Determination of the errors.^[103] The error of the titration volume (ΔV_{tit}) is calculated from the standard deviation of the mean ($\sigma N^{1/2}$ with a Student's $t=4.303$ and $N=3$), considering a confidence interval of 95% [Eq. (7)]:

$$\Delta V_{tit} = t \cdot \sigma / \sqrt{N} \quad (7)$$

The error in the mean concentration is obtained with the propagation of the maximum error for a function $f(x)$, using the general [Eq. (8)],

$$\Delta f(x) = \sum |(\partial f(x) / \partial x)| \cdot \Delta x \quad (8)$$

with $\Delta f(x)$ the propagated uncertain of the final function and Δx the uncertain in the variables that define the function. While the errors of the volume of the samples and in the titrating solution are negligible, the error of the mean concentration is calculated according to [Eq. (9)]:

$$\Delta C_{sample} = [(C_{tit} \cdot V_{tit} / V_{sample}) \cdot v_{stech}] \cdot \Delta V_{tit} \quad (9)$$

with C_{tit} concentration of the titrating solution, V_{tit} volume of the titrating solution, V_{sample} volume of the titrated sample and v_{stech} a coefficient to take into the account the stoichiometry of the reaction (5/2 in case of permanganometry and 1/2 for both iodometry and cerimetry). The errors solutions Titr1-Titr5 are determined from the error of the concentration of the aqueous Stock Solution, determined with permanganometry, using the

propagation of the maximum error [Eq. (8)]. In the case of the solutions Titr1-Titr5, prepared by dilution of the Stock Solution, and the solutions Vis1-Vis9, obtained by diluting the solutions Titr1-Titr5, the concentration is obtained with the [Eq. (10)]:

$$C_{fin} = (C_{in} \cdot V_{in}) / V_{fin} \quad (10)$$

hence, the error of the final concentration is calculated according to [Eq. (11)]:

$$\Delta C_{fin} = (C_{in}/V_{fin}) \cdot \Delta V_{in} + (V_{in}/V_{fin}) \cdot \Delta C_{in} + (C_{in} \cdot V_{in}/V_{fin}^2) \cdot \Delta V_{fin} \quad (11)$$

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Hydrogen Peroxide · Direct Synthesis · Titrimetric Analysis · Permanganometry · Spectrophotometric Analysis

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