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A colorimetric method for rapid and selective quantification of peroxodisulfate, peroxomonosulfate and hydrogen peroxide

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Redox colorimetric tests have been devised for the rapid analysis of the individual components of aqueous mixtures of peroxodisulfate, peroxomonosulfate and hydrogen peroxide; providing a convenient and selective method for the determination of these industrially relevant oxidants, which are known to inter-convert in solution.

Peroxomonosulfate (SO_5^{2-}) and peroxodisulfate ($S_2O_8^{2-}$) anions are some of the strongest oxidants with important industrial applications in chemical synthesis, water treatment, pulp and paper, textiles, electronics and metal finishing industries.[1] To circumvent the potential hazards associated with handling these reactive oxidants (peroxosulfates are respiratory irritants and sensitizers), our group and others have been developing lab-scale reactors for the on-site, on-demand electrochemical generation of ammonium peroxodisulfate [$(NH_4)_2S_2O_8$] solutions for applications in chemical synthesis.[2–4]

Aqueous solutions of $S_2O_8^{2-}$ are known to decompose (eqn 1 and 2) to form SO_5^{2-} and hydrogen peroxide (H_2O_2).[5] In recent work, we observed that the efficacy and reproducibility of oxidation reactions were highly dependent on the quality of the peroxosulfate solution.[6] Consequently, we needed a method that can be used to determine the precise composition of a electrochemically-generated peroxosulfate solution before it can be deployed in a reaction process.

$$S_2O_8^{2-} + H^+ + H_2O \rightarrow HSO_5^- + H_2SO_4 \quad (1)$$

$$HSO_5^- + H_2O \rightarrow H_2O_2 + HSO_4^- \quad (2)$$

Analysis of a mixture of these oxidants can be problematic – most redox titrations (e.g. iodometry) are non-selective and provide only the total oxidant content ($[Ox]_{tot}$). While certain redox titrants can be used for the specific quantification of $S_2O_8^{2-}$, SO_5^{2-}, or H_2O_2 (Table 1), these are tedious to perform, and generate large quantities of aqueous waste containing toxic arsenic, vanadium and manganese salts. Alternatively, quantitative methods based on polarography[7] or ion chromatography[8,9] had been reported, which will require access to dedicated analytical instruments. Furthermore, analysis of $S_2O_8^{2-}$ by ion chromatography is particularly challenging, requiring special measures to elute the large and highly polar anion.[10,11]

Herein, we will report an expedient approach to the rapid analysis of these oxidants by using UV-Vis spectroscopy, which can be easily automated for high-throughput reaction analysis using readily accessible laboratory equipment (Fig. 1). Rapid quantification of peroxosulfate ions can be achieved for the first time,[12,13] either individually, or as a mixture with H_2O_2.

This work was inspired by the observation of colourful transitions during the process of using a $VOSO_4$ titration to determine the concentration of HSO_5^- in a solution of peroxodisulfate.[14] In a typical analysis, a sample (0.5 mL) of the peroxosulfate solution is treated with an excess (20 mL) of the blue $VOSO_4$ solution at room temperature, and the remaining VO^{2+} then quantified by titration against a standardised $KMnO_4$ solution. The distinct colour changes involved during these processes subsequently prompted us to develop a colorimetric assay, whereby samples of the oxidant (25 µL) were diluted with 0.2 M $VOSO_4$ solution (475 µL) at room temperature. The blue VO^{2+} ion was oxidised by SO_5^{2-} to form yellow VO_2^+ (Fig. 1B); giving rise to a distinct absorption peak at 360 nm which can be used directly in the quantification of the oxidant (eqn 3).

$$SO_5^{2-} + 2VO^{2+} + H_2O \rightarrow SO_4^{2-} + 2VO_2^+ + 2H^+ \quad (3)$$

In this work, the analysis was automated by utilising an HPLC system fitted with an autosampler: the chromatographic column is removed from the instrument, so that the flow from the injector passes directly to the diode array detector. With a mobile phase consisting of water flowing at 0.2 mL.min^{-1}, each sample was monitored for 1 min, with a complete cycle of injection, analysis, and software processing completing within 3 min. The peak areas at selected wavelengths were then used to determine oxidant concentrations, in accordance with Beer-Lambert Law.

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Table 1. Comparison of methods used in the analysis of peroxosulfate solutions.

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Method	Measures	Oxidant Selectivity	Readily Available Equipment	Rapid Analysis (<5 min)	Small Sample Volumes (< 100 µL)	Minimal Waste (< 1 mL)
iodometric titration[15,16]	$[Ox]_{tot}$	✗	✓	✗	✗	–
Fe(II) titration[17]	$[Ox]_{tot}$	✗	✓	✗	✗	–
As(V) (back-titration[18,19]	$[SO_5^{2-}]$	✓	✓	✗	✗	✗
V(IV) back-titration[14]	$[SO_5^{2-}]$	✓	✓	✗	✗	✗
Ce(IV) titration[15]	$[H_2O_2]$	✓	✓	✗	✗	–
polarography[7,17]	$[S_2O_8^{2-} + SO_5^{2-}]$	–	✗	✓	✗	–
ion chromatography[8–11]	$[SO_5^{2-}]$, $[S_2O_8^{2-}]$	✓	✗	✗	✓	✓
$TiOSO_4$ redox colorimetry[12,13]	$[H_2O_2]$	✓	✓	✓	✓	✓
redox colorimetry array (this work)	$[SO_5^{2-}]$, $[S_2O_8^{2-}]$, $[H_2O_2]$, $[Ox]_{tot}$	✓	✓	✓	✓	✓

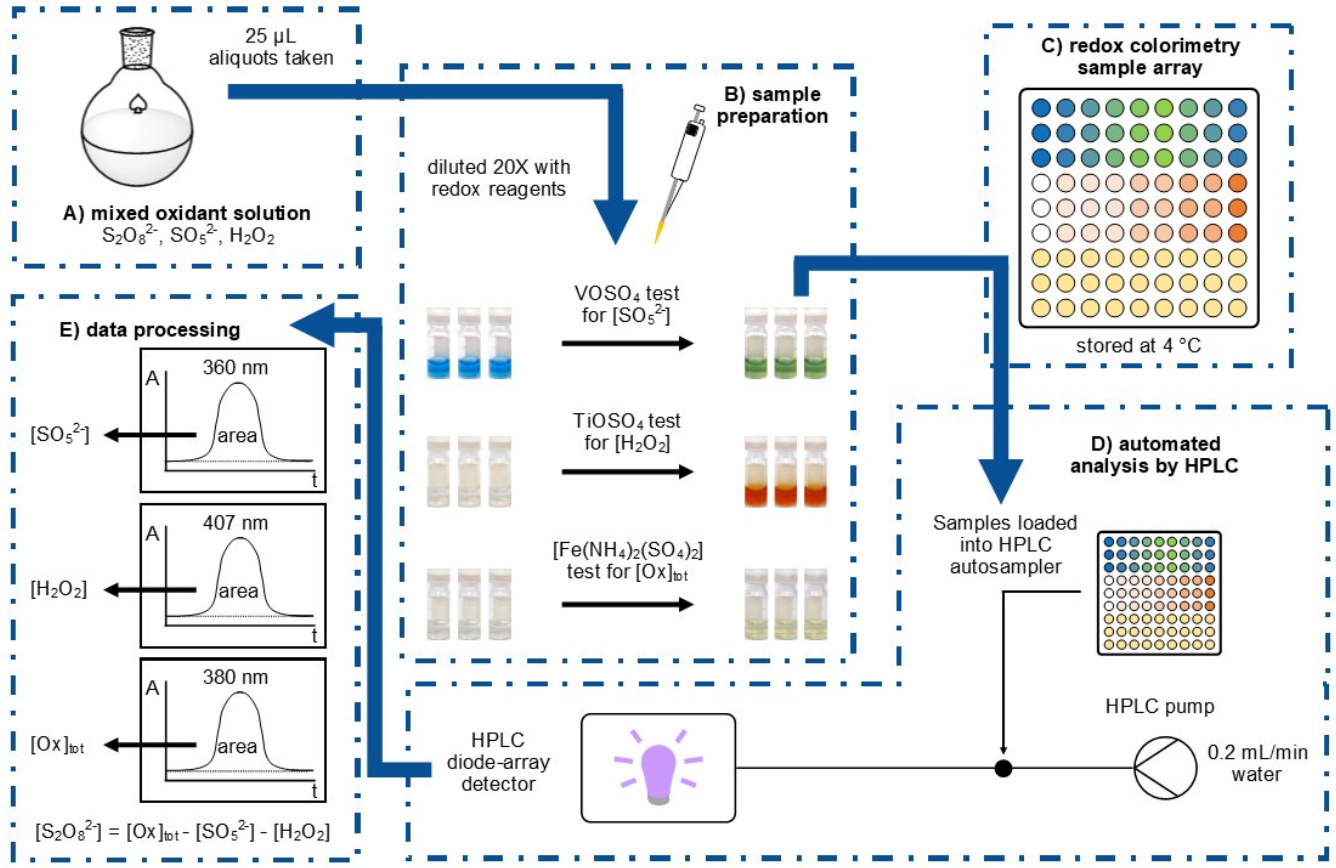

Fig. 1 Systematic determination of $S_2O_8^{2-}$, SO_5^{2-}, and H_2O_2 by redox colorimetry. (A) Aliquots were taken from mixed peroxosulfate solutions by autopipette and (B) diluted with redox colorimetry reagents to effect colour changes in response to specific oxidants. (C) Sample arrays were refrigerated before (D) being submitted to automated analysis using an HPLC system with diode array detection. (D) The specific oxidant concentrations were calculated from the peak areas after calibration.

This automated process requires minimal user intervention, eliminating the need to employ $KMnO_4$ as an additional titrant (with associated errors), thus greatly improving the workflow as well as accuracy of the analysis. In principle, further increases in the throughput could be realised by use of a microplate photometer (if this is accessible). Another key advantage of the spectroscopic analysis over the titration method is a substantial reduction in the volumes of aqueous manganese and vanadium waste: Each analysis generates only 0.5 mL of waste, compared to the 40 to 50 mL generated in each titration analysis. This reduction in volumes greatly extends the number of analyses that can be performed using a single batch of $VOSO_4$ solution

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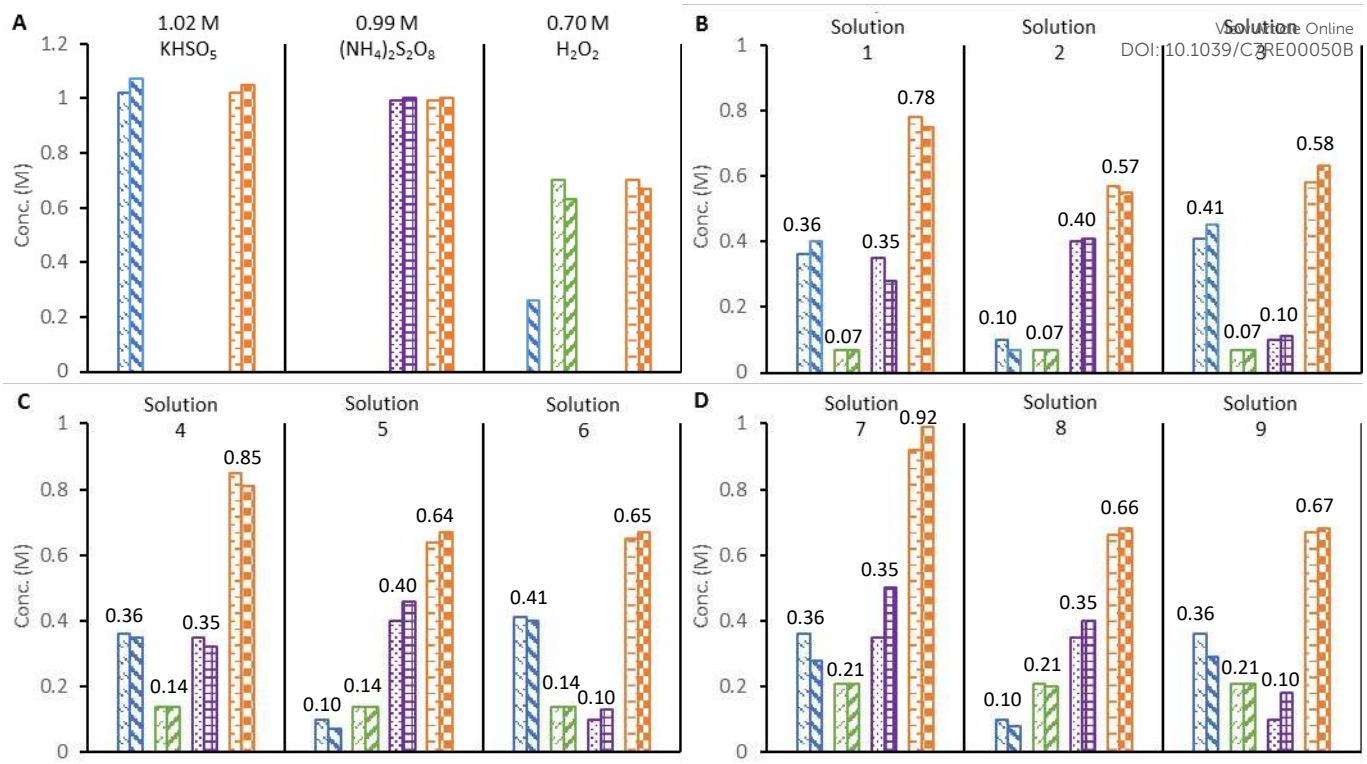

Fig. 2 Validation of redox colorimetry tests against oxidant mixtures of known composition. **A**) standardised solutions of single oxidants, **B**) mixed oxidant solutions with 0.07 M H_2O_2, **C**) mixed oxidant solutions with 0.14 M H_2O_2, **D**) mixed oxidant solutions with 0.21 M H_2O_2. Key to bar charts: $[SO_5^{2-}]$ by titration, $[SO_5^{2-}]$ by colorimetry, $[H_2O_2]$ by titration, $[H_2O_2]$ by colorimetry, $[S_2O_8^{2-}]$ by titration, $[S_2O_8^{2-}]$ by colorimetry, $[Ox]_{tot}$ by titration, $[Ox]_{tot}$ by colorimetry, numbers above bars are the expected concentrations in M.

(2,000 colorimetric analyses, compared to 48 titrations per litre of the titrant).

Calibration of the automated $VOSO_4$ assay provided a linear response (R^2 = 0.9993) for SO_5^{2-} concentrations between 0.20 and 1.00 M, which is a synthetically relevant concentration range required for our research work. For more dilute solutions, treatment of a larger sample (100 µL) with 0.2 M $VOSO_4$ solution (400 µL) allows the quantitation of $[SO_5^{2-}]$ at concentrations as low as 0.05 M. The sensitivity of the redox colorimetry test for low level $[SO_5^{2-}]$ analysis can also be further enhanced by increasing the injection volume used in the analysis, and a reduction in the concentration of the $VOSO_4$ reagent solution. For the current method, an injection volume of only 1 µL has been employed to provide a linear response over the concentration range required for our research purposes.

Electrochemically generated peroxosulfate solutions may contain $S_2O_8^{2-}$, SO_5^{2-}, and H_2O_2 and it is this complexity which negates the use of simpler analysis methods which can only determine the total oxidant concentration. To complement our colorimetric test for SO_5^{2-} we also explored options for the colorimetric measurement of H_2O_2 in peroxosulfate solutions. The formation of yellow titanic acid has been previously used as a colorimetric test for H_2O_2 (eqn 4).[12,13] In the present procedure, samples (25 µL) were treated with acidified 0.1 M $TiOSO_4$ solution (475 µL) and the resultant absorbance at 407 nm was measured using the automated HPLC process (Fig. 1B). The calibration curve was linear (R^2 = 0.997) for the analysis of H_2O_2 concentrations between 0.01 and 0.80 M.

$$H_2O_2 + TiO^{2+} + H_2O \rightarrow H_2TiO_4 + 2H^+ \quad (4)$$

Colorimetric assays for the determination of $S_2O_8^{2-}$ were also investigated. Despite its strong oxidising potential (E° = 2.01 V), we are not aware of any colorimetric or titration methods which are specific to this oxidant. For peroxosulfate solutions it is assumed that the total oxidant concentration $[Ox]_{tot}$ is equivalent to the sum of $[S_2O_8^{2-}]$, $[SO_5^{2-}]$ and $[H_2O_2]$. Hence, we assume that $[S_2O_8^{2-}]$ can be determined from measurements of $[Ox]_{tot}$, $[SO_5^{2-}]$ and $[H_2O_2]$.

The determination of $[S_2O_8^{2-}]$ has previously been achieved by iodometry,[16] although the titration is not specific to $S_2O_8^{2-}$. Initial attempts to develop a colorimetric test for $[Ox]_{tot}$ based on the oxidation of aqueous KI proved unsuccessful, as the reaction of I^- with $S_2O_8^{2-}$ was found not to be quantitative. In contrast, a uniform response to all three oxidants can be achieved when an acidic solution of $[Fe(NH_4)_2(SO_4)_2]$ (Mohr's salt) was used as the reductant (eqns 5, 6 and 7). In our colorimetric measurement of $[Ox]_{tot}$, samples (25 µL) were treated with acidified 0.3 M $[Fe(NH_4)_2(SO_4)_2]$ solution (475 µL) and the absorbance was measured at 380 nm (Fig. 1B). The calibration curve was linear (R^2 = 0.994) for the analysis of total oxidant concentrations between 0.1 and 2.0 M.

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+} \quad (5)$$

$$SO_5^{2-} + 2Fe^{2+} + 2H^+ \rightarrow SO_4^{2-} + 2Fe^{3+} + H_2O \quad (6)$$

$$H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2H_2O + 2Fe^{3+} \quad (7)$$

Next, the application of the colorimetric redox tests to the study of a mixture of oxidants was demonstrated by the analysis

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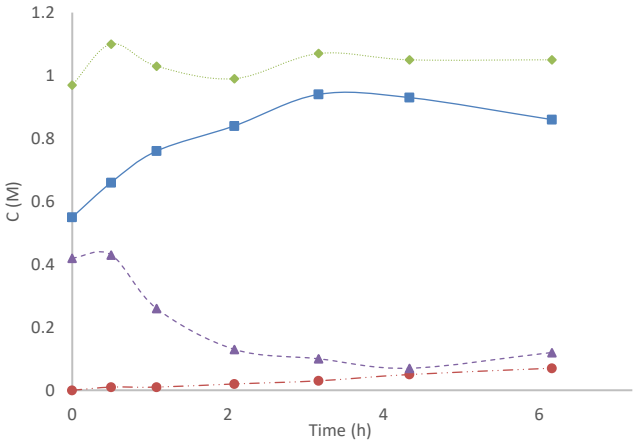

Fig. 3 Changes in the oxidant composition of an electrochemically generated acidic peroxosulfate solution heated at 50 °C were followed using the colorimetric redox assays. Key to chart: ■ $[SO_5^{2-}]$, ● $[H_2O_2]$, ◆ $[Ox.]_{tot}$, ▲ $[S_2O_8^{2-}]$.

of standardised solutions of 0.99 M $(NH_4)_2S_2O_8$, 1.02 M potassium peroxomonosulfate triple salt [$KHSO_5$. ½$KHSO_4$. ½K_2SO_4], and 0.70 M H_2O_2 (Fig. 2A). As expected, the $(NH_4)_2S_2O_8$ solution only furnished a positive response in the [$Fe(NH_4)_2(SO_4)_2$] total oxidant test, while the [$KHSO_5$. ½$KHSO_4$. ½K_2SO_4] solution gave positive responses in both the total oxidant and $VOSO_4$ test. The 0.70 M H_2O_2 solution gave a positive response using both the total oxidant and $TiOSO_4$ tests; however, it also underwent a reaction with the $VOSO_4$ reagent to produce a dark green colour, giving a measurable absorbance at 360 nm. This colour change is thought to indicate the formation of oxoperoxo vanadium complexes,[20] which can limit the applicability of the $VOSO_4$ assay to solutions containing high concentrations of H_2O_2. Finally, distilled water was subjected to the same redox colorimetry tests in a control experiment, which returned a nil response in every case.

The three standardised oxidant solutions were subsequently combined in varying quantities to create 9 test solutions of known compositions, which were analysed in triplicate by redox colorimetry (Fig. 2 B-D). Analysis of solutions containing 0.07 or 0.14 M of H_2O_2 gave oxidant compositions in good agreement with the expected results (solutions 1-6).

Mixed peroxosulfate systems with low levels (< 0.2 M) of H_2O_2 can be characterised by the redox colorimetry assay with an acceptable level of accuracy. However, when the mixed oxidant solutions contained a higher concentration of H_2O_2 (0.21 M), the formation of the dark green (oxoperoxo) species interfered with the measurement of $[SO_5^{2-}]$, which was found to be consistently lower (approximately 20%) than expected (solutions 7-9). Since $[S_2O_8^{2-}]$ is derived from the redox colorimetric measurement of the $[SO_5^{2-}]$, its measurement is also affected by the undesired reaction of $VOSO_4$ with H_2O_2. In the original redox titration employing $VOSO_4$, the H_2O_2 was first removed from the sample by a titration against $Ce(SO_4)_2$ at 0 °C.[14] In this work, addition of a small portion of MnO_2 rapidly decomposed H_2O_2 to O_2 in a peroxosulfate solution at room temperature, while the $S_2O_8^{2-}$ and SO_5^{2-} were unaffected. Hence, redox colorimetric analysis performed before and after quenching with MnO_2 allows the concentrations of $S_2O_8^{2-}$ and SO_5^{2-} to be determined in peroxosulfate solutions containing H_2O_2 (details in SI).

The experimental uncertainty in the colorimetric redox tests was estimated by performing six repeat analyses of the mixed oxidant solutions (1, 4 and 7 from Fig. 2). The uncertainty in $[SO_5^{2-}]$ and $[S_2O_8^{2-}]$ are both estimated to be ±0.05 M, while $[H_2O_2]$ could be determined to within ±0.01 M. The uncertainty in $[Ox]_{tot}$ is estimated to be ±0.02 M (note: these uncertainty estimates apply to the measurement of peroxosulfate solutions with $[H_2O_2] < 0.2$ M).

Samples treated with the $VOSO_4$ and $TiOSO_4$ reagents should be analysed immediately or stored at reduced temperatures (3–4 °C). In our ongoing research into applications of peroxosulfates, we have observed that the $[SO_5^{2-}]$ and $[H_2O_2]$ measured by redox colorimetry will increase over a period of 1-2 h when samples are stored in a reasonably warm laboratory (> 25 °C). This could be due to the interconversion of the oxidants (eqns 1 and 2), or slow reaction of off-target oxidants with the redox reagent. We have found that refrigeration of the treated samples stabilises them for at least 4 h, during which time any change in the measured oxidant concentrations is within the limits of uncertainty.

In an application of these redox colorimetric tests we have followed the decomposition of $S_2O_8^{2-}$ into SO_5^{2-} and H_2O_2 in an electrochemically-generated acidic peroxosulfate solution (Fig. 3): The solution (containing 0.42 M $S_2O_8^{2-}$ and 0.55 M SO_5^{2-}) was heated at 50 °C and aliquots were analysed by redox colorimetry. The expected conversion of $S_2O_8^{2-}$ into SO_5^{2-} was observed to progress over 3 h with the formation of only 0.03 M of H_2O_2. After 3 h, $[SO_5^{2-}]$ reached a maxima and proceeded to decrease, with a concomitant increase in $[H_2O_2]$. After 25 h, the solution contained a mixture of 0.59 M SO_5^{2-} and 0.38 M H_2O_2 (determined using MnO_2 to quench H_2O_2). This application demonstrates the utility of these assays for characterising the specific concentrations of oxidants in peroxosulfate solutions.

Conclusions

To summarise, we have developed novel colorimetric redox assays for the selective determination of $S_2O_8^{2-}$, SO_5^{2-} and H_2O_2 where they co-exist in solution. These assays are now being routinely employed in our ongoing investigation into synthetic applications of electrochemically generated solutions of peroxosulfates. In this application we have automated the analysis of redox colorimetry samples, which were collected manually by autopipette in this study. Going forward, automated liquid handling and sampling technologies can be utilised to achieve an uninterrupted workflow; from sample collection to analysis and processing (refer to SI for design details of an automated sampling system). Implementation of these technologies in future work will make redox colorimetry an attractive tool for characterisation and quality control of processes involving peroxosulfates.

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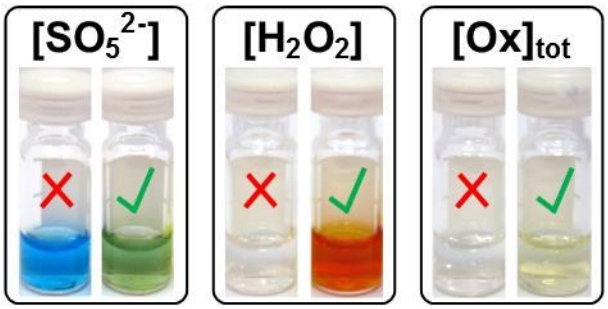

A convenient and selective method for the determination of peroxodisulfate, peroxomonosulfate and hydrogen peroxide in mixed oxidant systems.