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

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General

Potassium permanganate (>99%), titanium oxysulfate (technical grade), potassium iodide (99%), starch were purchased from Sigma-Aldrich. Sulfuric acid, sodium sulfite and hydrogen peroxide (30%) were purchased from VWR. Ammonium metavanadate (99.5%), ammonium iron(II) sulfate (>99%) and ammonium persulfate (98%) were purchased from Acros. Potassium monopersulfate triple salt was purchased from Merck and sodium thiosulfate was purchased from Fisher Scientific. All chemicals and solvents were used without further purification unless otherwise stated.

Reference Half-Cell Equations

$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

$H_2TiO_4 + 4H^+ + 2e^- \rightarrow TiO^{2+} + 3H_2O$

$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$

$SO_5^{2-} + 2H^+ + 2e^- \rightarrow SO_4^{2-} + H_2O$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Preparation of Solutions

0.0196 M $KMnO_4$ Solution for Redox Titrations

Potassium permanganate (3.1511 g, 19.9 mmol) was made up to 1 L with distilled water. The solution was sonicated for 30 min and then filtered to remove any solid residues. The filtered solution was stored at room temperature in a sealed bottle covered in foil to exclude light.

The potassium permanganate solution was standardized in triplicate. Measured quantities of disodium oxalate (0.1 g) were dissolved in distilled water (50 mL). 2 M sulfuric acid (15 mL) was then added and the solution heated to 70 °C on a hot plate. The hot disodium oxalate solution was titrated against the potassium permanganate solution until the end-point was indicated by persistence of a pale pink color for 1 min. The concentration of potassium permanganate was measured to be 0.0196 M ± 0.0001 M.

Note that the redox reaction can be slow during the early stages of the titration (particularly if the disodium oxalate solution is not sufficiently warm) and it may appear that permanganate ion is not being reduced by the disodium oxalate. Standing the sample on a 70 °C hot plate for up to a minute will result in the solution returning to its colorless state. As the titration progresses the transition from pink/purple to colorless will accelerate until the end-point is reached and an excess of permanganate ion is present in the solution.

An example calculation is:

Mass of disodium oxalate = 0.0994 g ± 0.0004 g (0.4%)

$n_{oxalate} = \frac{m}{M} = \frac{0.0994\ g}{133.999\ g/mol}$ = 0.0007417 mol ± 0.4%

The redox half cell reactions are

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

therefore

$n_{permanganate} = \frac{2}{5}$ x $n_{oxalate}$ = 0.0002966 mol ± 0.4%

Volume of $KMnO_4$ solution titrated was 15.18 mL ± 0.05 mL (0.3%)

$C_{permanganate} = \frac{n}{V} = \frac{0.2966\ mmol}{15.18\ mL}$ = 0.0195 mol/L ± 0.0001 mol/L (0.7%)

0.09 M $VOSO_4$ Solution for Redox Titrations

Based on the method reported by Berry.[1]

Concentrated sulfuric acid (100 mL) was added to water (300 mL) to form a 25% v/v solution of sulfuric acid. Ammonium metavanadate (10 g, 85 mmol) was added to the diluted sulfuric acid to form an orange solution. After dissolution was complete the solution was diluted by the addition of water (600 mL). The vanadate was reduced by the addition of sodium sulfite (12.9 g, 102 mmol) to form a deep blue solution of $VOSO_4$. The solution was refluxed for a minimum of 30 min to expel SO_2 gas. The $VOSO_4$ was stored at room temperature in a sealed bottle and was found to be stable over several months of use.

The concentration of $VOSO_4$ was determined by titration of triplicate samples (20 mL) against a standardized solution of potassium permanganate (0.0196 M ± 0.0002 M). A color transition from pale yellow to pale pink indicated the end-point of the titration. The concentration of $VOSO_4$ was measured to be 0.0922 M ± 0.0009 M.

An example calculation is:

Volume of $KMnO_4$ solution titrated was 18.82 mL ± 0.05 mL (0.3%)

$n_{permanganate} = C_{permanganate}$ x $V_{permanganate}$ = 0.0196 mol/L x 0.01882 L = 0.3688 mmol ± 1%

The redox half cell reactions are

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$

therefore

$n_{vanadyl} = 5 \times n_{permanganate} = 1.844$ mmol ± 1%

Volume of $VOSO_4$ solution analysed was 20.00 mL ± 0.08 mL (0.4%)

$C_{vanadyl} = \frac{n}{V} = \frac{1.844 \text{ mmol}}{20.00 \text{ mL}} = 0.0922$ mol/L ± 0.0009 mol/L (1%)

0.2 M $VOSO_4$ Solution for Redox Colorimetry

Adapted from the method reported by Berry.[1] This higher concentration solution was prepared for use in redox colorimetry.

Concentrated sulfuric acid (25 mL) was added to water (75 mL) to form a 25% v/v solution of sulfuric acid. Ammonium metavanadate (5.8 g, 50 mmol) was added to the diluted sulfuric acid to form an orange solution. After dissolution was complete the solution was diluted by the addition of water (150 mL). Vanadate was reduced by the addition of sodium sulfite (6.6 g, 52.5 mmol) to form a deep blue solution of $VOSO_4$. The solution was refluxed for a minimum of 30 min to expel SO_2 gas. The $VOSO_4$ was stored at room temperature in a sealed bottle and was observed to be stable over several months of use.

The prepared solution can be used for redox colorimetric analysis without accurate determination of the concentration of $VOSO_4$.

2 M H_2SO_4 Solution

Concentrated sulfuric acid (109 mL) was added to a stirring bottle of distilled water (891 mL) which was immersed in an ice bath. The diluted sulfuric acid was allowed to cool to room temperature before use.

0.1 M $TiOSO_4$ Solution for Redox Colorimetry

2 M Sulfuric acid solution (250 mL) was added to titanium oxysulfate (25 mmol, 3.998 g) and ultrasound was applied until the suspended white solid had dissolved completely. The resulting solution was used in redox colorimetric tests without further treatment or analysis. The colorless $TiOSO_4$ solution was stored at room temperature in a sealed bottle and was observed to be stable over several months of use.

0.3 M $Fe(NH_4)_2(SO_4)_2$ Solution for Redox Colorimetry

2M Sulfuric acid solution (200 mL) was added to Mohr's salt (ammonium iron(II) sulfate) (75 mmol, 29.4 g). After the salt had dissolved completely the solution was made up to 250 mL by the addition of 2M Sulfuric acid solution. The resulting solution was used in redox colorimetric tests without further treatment or analysis. The pale green Fe(II) solution was stored at 4 °C in a sealed bottle and was observed to be stable for up to one week.

Starch Solution for Iodometric Titration

Based on the method described in Vogel's Textbook of Quantitative Chemical Analysis.[2]

Distilled water (100 mL) was added to soluble starch (0.1 g). The starch solution was then heated with stirring until it had boiled for at least 1 min. The solution was then allowed to cool before potassium iodide (2.0 g) was added.

The resulting solution was stored at room temperature and used in iodometric titrations over a period of 3 days.

0.1 M $Na_2S_2O_3$ Solution for Iodometric Titration

Based on the method described in Vogel's Textbook of Quantitative Chemical Analysis.[2]

Sodium thiosulfate (24.88 g) was made up to 1 L with distilled water using volumetric glassware. Chloroform (3 drops) and sodium carbonate (0.13 g) were added to the solution to prolong the shelf life of the solution. The solution was stored at room temperature in a sealed bottle covered in foil to exclude light.

The thiosulfate solution was standardized in triplicate. Potassium iodate (0.14 - 0.15 g) was weighed accurately then dissolved in cold distilled water (25 mL). Potassium iodide (2.0 g) was then added followed by 2 M sulfuric acid (2.5 mL). The liberated iodine was then titrated with the thiosulfate solution, with the flask being constantly shaken. When the solution had become pale yellow it was then diluted by the addition of distilled water (170 mL) and starch solution (2 mL). The thiosulfate titration was then continued until the color changed from blue to colorless.

The concentration of $Na_2S_2O_3$ was measured to be 0.1011 M ± 0.0005 M.

An example calculation is:

Mass of potassium iodate = 0.1462 g ± 0.0004 g (0.3%)

$n_{iodate} = \frac{m}{M} = \frac{0.1462\ g}{214.00\ g/mol}$ = 0.00068317 mol ± 0.3%

The iodate and iodide react to liberate iodine

$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

therefore

$n_{iodine} = 3 \times n_{iodate}$ = 0.0020495 mol ± 0.3%

For the reaction of iodine with thiosulfate the redox half cell reactions are

$I_2 + 2e^- \rightarrow I^-$

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

Therefore

$n_{thiosulfate} = 2 \times n_{iodine}$ = 0.0040990 mol ± 0.3%

Volume of $Na_2S_2O_3$ solution titrated was 40.50 mL ± 0.08 mL (0.2%)

$C_{thiosulfate} = \frac{n}{V} = \frac{4.0990\ mmol}{40.50\ mL}$ = 0.1012 mol/L ± 0.0005 mol/L (0.5%)

0.4 M $FeCl_3$ Solution for Iodometric Titration

Based on the method reported by Wahba, Asmar and Sadr.[3] This solution was used as a catalyst for iodometric titrations of peroxosulfate solutions.

Dissolved water (50 mL) and 2 M sulfuric acid (50 mL) was added to Iron(III) chloride hexahydrate (10 g, 37 mmol) to form an orange solution. The resulting solution was used to catalyze iodometric titrations without further treatment or analysis. The orange Fe(III) solution was stored at room temperature in a sealed bottle and was observed to be stable over one month of use.

Peroxomonosulfate Determination by Redox Titration

Based on the method reported by Berry.[1]

Titrations were performed in duplicate. Samples (0.5 mL) of the peroxosulfate solution were reacted with a measured excess (20.00 mL ± 0.08 mL) of 0.0922 M $VOSO_4$ solution at room temperature. Under ambient conditions VO^{2+} was oxidized selectively by SO_5^{2-}. The remaining VO^{2+} was then determined by titration against a standardized solution of potassium permanganate (0.0196 M ± 0.0002 M). A color transition from pale yellow to pale pink indicated the end-point of the titration. The molar difference between the VO^{2+} added to the sample and that measured by permanganate titration was used to determine the moles of SO_5^{2-} in the sample.

An example calculation is:

Volume of $KMnO_4$ solution titrated was 13.64 mL ± 0.05 mL (0.4%)

$n_{permanganate} = C_{permanganate} \times V_{permanganate} = 0.0196 \text{ mol/L} \times 0.01364 \text{ L} = 0.2673 \text{ mmol} \pm 1\%$

The redox half cell reactions are

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$

therefore

$n_{remaining\ vanadyl} = 5 \times n_{permanganate} = 1.336 \text{ mmol} \pm 0.01 \text{ mmol} (1\%)$

Volume of $VOSO_4$ solution analysed was 20.00 mL ± 0.08 mL (0.4%)

Therefore

$n_{intial\ vanadyl} = C_{vanadyl} \times V_{vanadyl\ sulfate} = 0.0922 \text{ M} \times 0.02000 \text{ L} = 1.844 \text{ mmol} \pm 0.02 \text{ mmol} (1\%)$

$n_{peroxomonosulfate} = 0.5 \times (n_{intial\ vanadyl} - n_{remaining\ vanadyl}) = 0.5 \times (1.84 - 1.34) = 0.25 \text{ mmol} \pm 0.015 \text{ mmol} (6\%)$

therefore

$[SO_5^{2-}] = \frac{n}{V} = \frac{0.25 \text{ mmol}}{0.500 \text{ mL}} = 0.500 \text{ mol/L} \pm 0.03 \text{ mol/L} (6\%)$

Measurement of Total Oxidant Concentration of Peroxosulfate and Hydrogen Peroxide Solutions by Iodometric Titration

Based on the method described in Vogel's Textbook of Quantitative Chemical Analysis[2] with the addition of $FeCl_3$ catalysis as described by. Wahba, Asmar and Sadr.[3]

Iodometric titrations were performed in triplicate. 1 M sulfuric acid (100 mL) was added to a sample (1.00 mL) of the oxidant solution. Potassium iodide (2 g) and 0.4 M $FeCl_3$ catalyst solution (1 mL) were added and then the solution was covered and allowed to stand at room temperature for 15 min. During this time the solution turned brown as iodine formed. The solution of liberated iodine was then uncovered and rapidly titrated with standardized 0.1011 M $Na_2S_2O_3$ solution. When the solution had become pale yellow it was then diluted by the addition of distilled water (170 mL) and starch solution (2 mL). The thiosulfate titration was then continued until the color changed from blue to colorless.

An example calculation is:

Volume of $Na_2S_2O_3$ solution titrated was 20.13 mL ± 0.05 mL (0.2%)

$n_{thiosulfate} = C_{thiosulfate} \times V_{thiosulfate} = 0.1011$ mol/L x 0.02013 L = 2.0351 mmol ± 0.7%

For the reaction of iodine with thiosulfate the redox half cell reactions are

$I_2 + 2e^- \rightarrow 2I^-$

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

Therefore

$n_{iodine} = 0.5 \times n_{thiosulfate} = 1.0175$ mmol ± 0.7%

For the reaction of iodide with peroxomonosulfate the redox half cell reactions are

$SO_5^{2-} + 2H^+ + 2e^- \rightarrow SO_4^{2-} + H_2O$

$2I^- \rightarrow I_2 + 2e^-$

Therefore

$n_{peroxomonosulfate} = n_{iodine} = 1.0175$ mmol ± 0.7%

Volume of oxidant solution analysed was 1.000 mL ± 0.008 mL (0.8%)

Therefore

$$[SO_5^{2-}] = \frac{n}{V} = \frac{1.0175 \text{ mmol}}{1.000 \text{ mL}} = 1.02 \text{ mol/L} \pm 0.02 \text{ mol/L (1.5\%)}$$

Oxidant Determination by Redox Colorimetry

General Comments about setup of HPLC for analysis

High throughput UV/visible spectrophotometric analysis was performed using an Agilent 1100 series HPLC system consisting of a pump, autosampler and photodiode array detector. To setup the HPLC for spectrophotometry the autosampler unit was connected to the detector using a straight union where the HPLC column would typically be installed. The mobile phase was 0.2 mL/min of water (HPLC grade), the injection volume was 1 µL and the run time was 1 min. In all redox colorimetry tests the

sample eluted as a peak between 0.1 and 0.5 min. The peak areas at 360, 380 and 407 nm were used to calculate specific oxidant concentrations.

It was observed in our laboratory that the diode array detector generated significant amounts of heat during operation, causing the sample tray to be at temperatures between 30 to 40 °C during warm days (room temperature > 25 °C). Thus, the use of a dedicated Peltier-based sample cooler is recommended. In the absence of an available sample cooler, effects of this heating were minimized by installing an insulating air space between the diode array detector and the autosampler unit. A 6-inch fan was also deployed to actively cool the detector, autosampler and the insulating gap.

Instrument Calibration

$VOSO_4$ Redox Colorimetry Test for Peroxomonosulfate Concentration

The UV-visible spectrophotometric measurement of monopersulfate was calibrated using standard solutions of VO_2^+ which were prepared by treatment of the $VOSO_4$ solution with known quantities of potassium permanganate. Potassium permanganate was selected as the oxidant due to its ability to cleanly oxidize the vanadyl anion, and because it is commercially available in analytically pure (> 99%) material. Potassium monopersulfate triple salt (Oxone) was briefly considered as a potential oxidant but its limited purity meant that the monopersulfate standardized would need to be standardized by iodometric titration.

Three 0.1 M VO_2^+ stock solutions were prepared by reacting potassium permanganate (0.5 mmol, 79 mg) with 0.2 M $VOSO_4$ solution and making up to 25 mL in volumetric glassware. The three 0.1 M VO_2^+ stock solutions were then diluted with 0.2 M $VOSO_4$ solution to make a series of fifteen standards. The standard concentrations and the absorption peak area at 360 nm are reported in Table S1 and Figure S1.

Table S1. Calibration data for the $VOSO_4$ redox colorimetry test for peroxomonosulfate.

$[VO_2^+]$ (M)	**Area at 360 nm**
0	152.9
0.0010	128.5
0.0050	125.0
0.0102	165.2
0.0203	326.4
0.0299	559.7
0.0407	826.6
0.0507	1051.1
0.0598	1318.8
0.0712	1604.4
0.0811	1851.9
0.0898	2086.0
0.1.08	2369.8
0.1014	2357.5
0.0997	2377.8

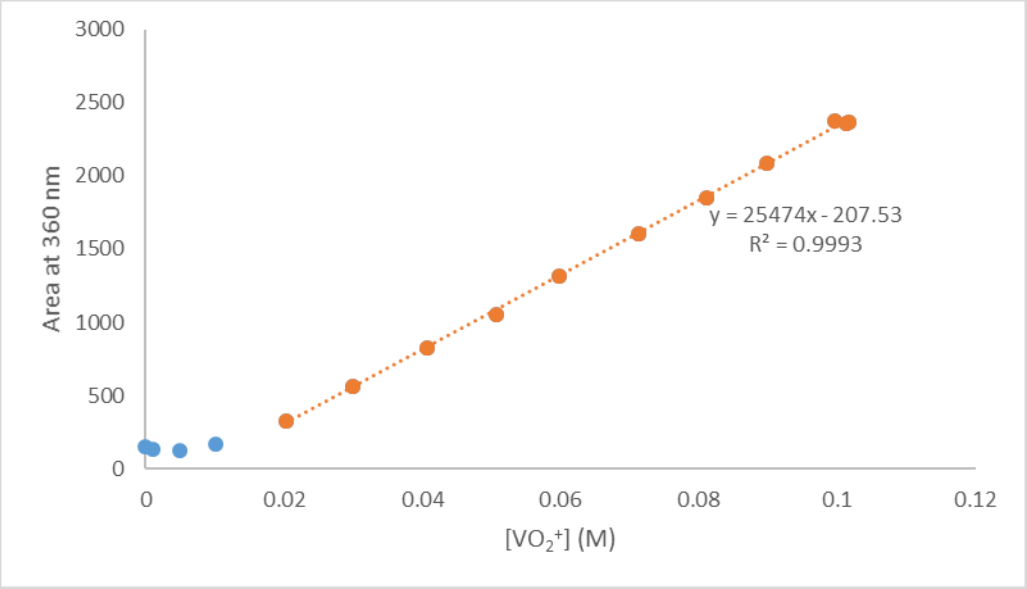

Figure S1. Calibration curve for the $VOSO_4$ redox colorimetry test for peroxomonosulfate.

From the calibration curve a straight line was obtained for the region between 0.02 M and 0.1 M. Below 0.02 M VO_2^+ the concentration could not be quantified due to low level background absorbance by the $VOSO_4$ solution.

The following calculations were used to convert peak area at 360 nm into a measurement of $[SO_5^{2-}]$ for the peroxosulfate solution.

Area(360 nm) = 25474 x $[VO_2^+]$ – 207.53

$$[VO_2^+] = \frac{\text{Area}(360\text{ nm}) + 2207.53}{25474}$$

$[SO_5^{2-}]$ in the reaction sample is determined by multiplying $[VO_2^+]$ by a stoichiometry factor (1:2 SO_5^{2-} / VO_2^+) and a dilution factor (25 µL diluted to 500 µL).

$[SO_5^{2-}]$ = $[VO_2^+]$ x stoichiometry factor x dilution factor = $[VO_2^+]$ x 0.5 x 20 = $[VO_2^+]$ x 10

This calculation is valid for peroxosulfate solutions which have 0.20 < $[SO_5^{2-}]$ < 1.00 M.

Note: for determining $[SO_5^{2-}]$ at levels below 0.2 M it is necessary to prepare more concentrated sample solutions. Samples (100 µL) treated with $VOSO_4$ solution (400 µL) would use the equation:

$[SO_5^{2-}]$ = $[VO_2^+]$ x 0.5 x 5 = $[VO_2^+]$ x 2.5

The $VOSO_4$ redox colorimetry test gave different colored solutions depending on the $[SO_5^{2-}]$ of the sample (Figure S2). Over the calibrated range the redox tests appeared blue with a green tint at high end of the calibration. Samples with $[SO_5^{2-}]$ outside the calibration range (> 1.0 M) turned the solution

progressively more green and then yellow. This color change can be used as a qualitative test that the samples are high in SO_5^{2-} and may require a different dilution factor for quantitation.

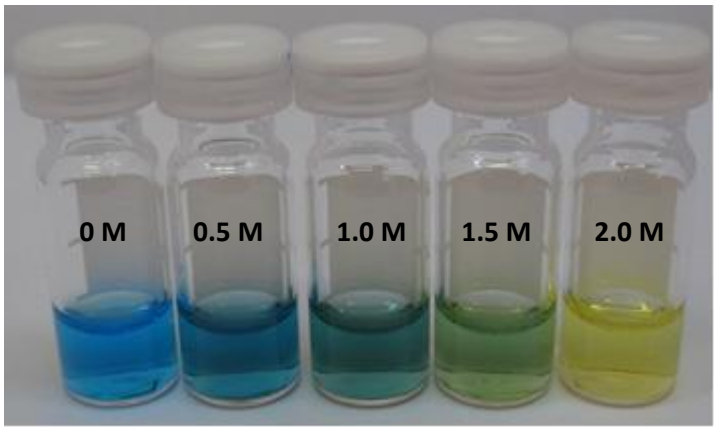

Figure S2. The color changes of the $VOSO_4$ redox colorimetry test for peroxomonosulfate. The numbers indicate the [SO_5^{2-}] of the sample (at a 20x dilution factor).

$TiOSO_4$ Redox Colorimetry Test for Hydrogen Peroxide Concentration

This method is a modification of the spectrophotometric method reported by David Graves.[4]

The redox colorimetric test for H_2O_2 was calibrated by treatment of a series of hydrogen peroxide solutions (concentrations ranging from 0.01 to 1.00 M) with 0.1 M $TiOSO_4$ solution. A 0.1 M solution of H_2O_2 was prepared by dilution of 30% v/v H_2O_2 (280.8 µL) with distilled water to make a 25 mL solution. The accurate concentration of our 30% v/v H_2O_2 was previously determined to be 8.9 M ± 0.2 M by titration with standardized potassium permanganate solution. Further dilution of the 0.10 M solution of H_2O_2 with distilled water provided 6 standards with [H_2O_2] ranging from 0.01 to 0.10 M. A 1.00 M solution of H_2O_2 was also prepared by dilution of 30% v/v H_2O_2 (2.808 mL) with distilled water to make a 25 mL solution. Further dilution of the 1.00 M solution of H_2O_2 with distilled water provided 7 standards with [H_2O_2] ranging from 0.10 to 1.00 M.

Samples (25 µL) of the H_2O_2 standards were treated with 0.1 M $TiOSO_4$ solution (475 µL) to create a series of H_2TiO_4 standards for calibration. A sample of distilled water was subjected to the same treatment to create a 0 M H_2TiO_4 standard. The H_2TiO_4 standards were subjected to spectrophotometric analysis at 407 nm using the automated HPLC method.

The standard concentrations and the absorption peak area at 407 nm are reported in Table S2 and Figure S3.

Table S2. Calibration data for the $TiOSO_4$ redox colorimetry test for hydrogen peroxide.

$[H_2O_2]$ (M)	Area at 407 nm
0	29.8
0.010	61.3
0.020	136.4
0.040	288.0
0.060	440.9
0.080	589.3
0.10	714.5
0.10	742.1
0.20	1458.9
0.30	2170.3
0.40	2959.5
0.60	4251.2
0.80	5291.4
1.00	6325.8

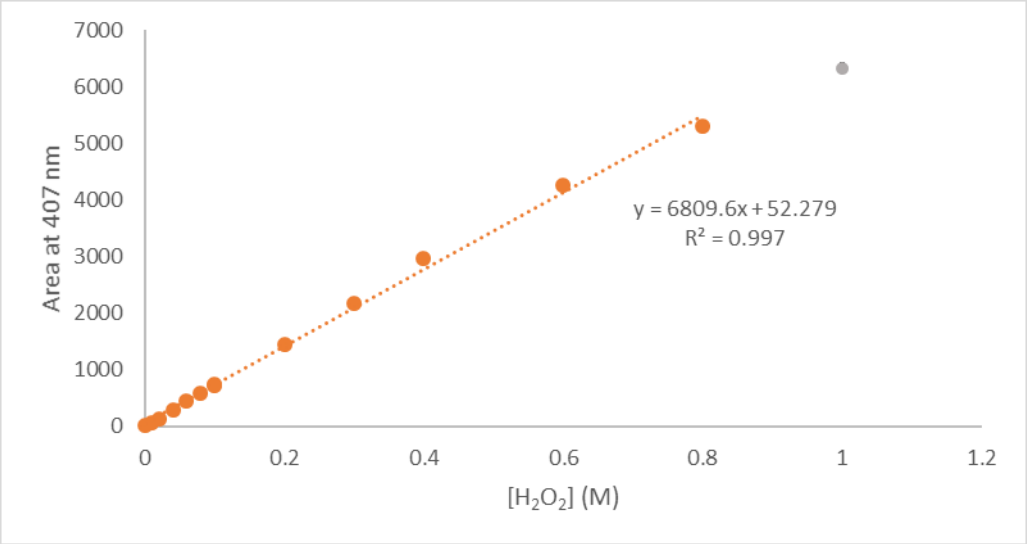

Figure S3. Calibration curve for the $TiOSO_4$ redox colorimetry test for hydrogen peroxide.

From the calibration curve a straight line was obtained for $[H_2O_2]$ between 0.01 M and 0.80 M.

Area(407 nm) = 6809.6 x $[H_2O_2]$ + 52.279

$$[H_2O_2] = \frac{\text{Area}(407\text{ nm}) - 52.279}{6809.6}$$

These calculations are valid for peroxosulfate solutions which have $0.01 < [H_2O_2] < 0.80$ M.

The $TiOSO_4$ redox colorimetry test gave different colored solutions depending on the $[H_2O_2]$ of the sample (Figure S4). Over the calibrated range the redox tests resulted in a distinctive colour change with the clear $TiOSO_4$ solution changing to yellow or orange depending on the $[H_2O_2]$.

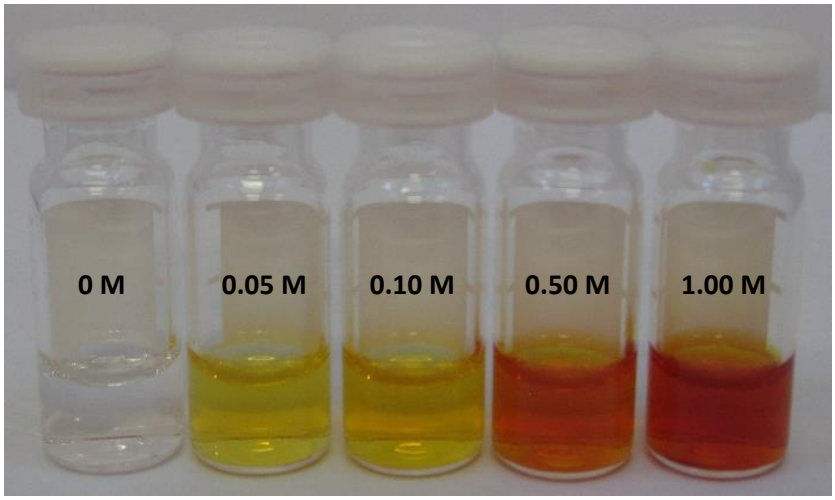

Figure S4. The color changes of the $TiOSO_4$ redox colorimetry test for hydrogen peroxide. The numbers indicate the $[H_2O_2]$ of the sample.

Fe(II) Redox Colorimetry Test for Total Oxidant Concentration

The redox colorimetric test for total oxidant concentration was calibrated by treatment of a series of $(NH_4)_2S_2O_8$ solutions (concentrations ranging from 0.09 to 1.99 M) with 0.3 M $Fe(NH_4)_2(SO_4)_2$ solution.

A 1.99 M solution of $(NH_4)_2S_2O_8$ was prepared by dissolving $(NH_4)_2S_2O_8$ (11.6082 g, 50.87 mmol) with distilled water to make a 25 mL solution. Further dilution of the 1.99 M solution of $(NH_4)_2S_2O_8$ with distilled water provided 8 standards with $[S_2O_8^{2-}]$ ranging from 0.09 to 1.99 M

Samples (25 µL) of the $(NH_4)_2S_2O_8$ standards were treated with 0.3 M $Fe(NH_4)_2(SO_4)_2$ solution (475 µL) to create a series of Fe(III) standards for calibration. A sample of distilled water was subjected to the same treatment to create a 0 M Fe(III) standard. The Fe(III) standards were subjected to spectrophotometric analysis at 380 nm using the automated HPLC method.

The standard concentrations and the absorption peak area at 380 nm are reported in Table S3 and Figure S5.

Table S3. Calibration data for the Fe(II) redox colorimetry test for total oxidant concentration.

$[S_2O_8^{2-}]$ (M)	**Area at 380 nm**
0	215.9
0.0997	627.4
0.1994	1131.4
0.4985	2565.3
0.7976	4043.9
0.9970	4961.6
1.1964	5676.5
1.3958	6635.9
1.9940	8580.6

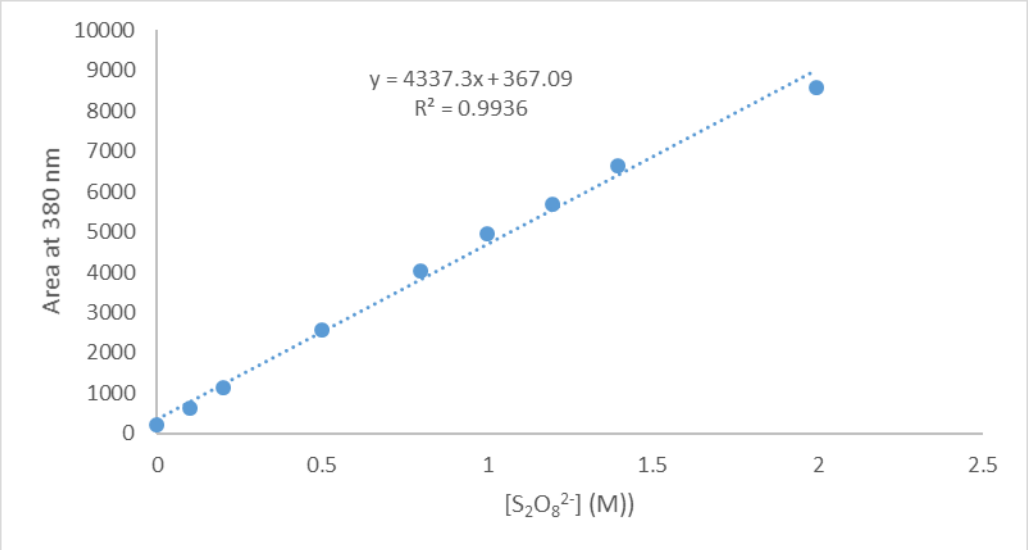

Figure S5. Calibration curve for the Fe(II) redox colorimetry test for total oxidant concentration.

From the calibration curve a straight line was obtained for the region between 0.10 M and 2.00 M.

Area(380 nm) = 4337.3 x $[S_2O_8^{2-}]$ + 367.09

therefore

$$[Ox]_{tot} = \frac{\text{Area}(380\text{ nm}) - 367.09}{4337.3}$$

These calculations are valid for reactions which have $0.1 < [Ox]_{tot} < 2.0$ M

The color change in the Fe(II) redox colorimetry test was less visually distinct than the other two redox colorimetry tests (Figure S6). The presence of an oxidant in the sample was indicated by a colour change from pale green to pale yellow.

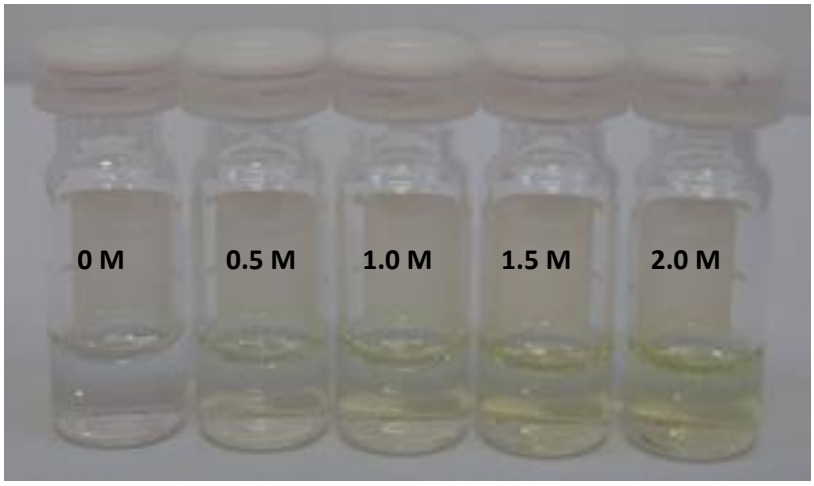

Figure S6. The color changes of the Fe(II) redox colorimetry test for total oxidant concentration. The numbers indicate the $[Ox]_{tot}$ of the sample.

Determination of Peroxodisulfate by Redox Colorimetry

The concentration of peroxodisulfate in solution was determined by a calculation using the results of the three redox colorimetric tests.

$[S_2O_8^{2-}] = [Ox]_{tot} - [SO_5^{2-}] - [H_2O_2]$

Sample Preparation and Analysis

Samples (25 µL) of peroxosulfate solutions were added to HPLC vials containing the redox colorimetry reagent solution (475 µL). Each of the three redox colorimetry tests (Table S4) were performed in triplicate for each sample. After the HPLC vials had been capped and inverted to mix the reagents, they were transferred to a fridge (4 °C) for storage prior to analysis using the automated HPLC method. Samples were analysed in batches within 4 h of their preparation.

Table S4. Summary of the redox colorimetric assays.

Spectrophotometric Reagent	Wavelength for Analysis	Species Measured
$VOSO_4$	360 nm	SO_5^{2-}
$TiOSO_4$	407 nm	H_2O_2
Fe(II)	380 nm	SO_5^{2-}, H_2O_2, $S_2O_8^{2-}$

During the development of this assay it was observed that the first HPLC measurement of $[SO_5^{2-}]$ in any analysis batch was typically larger than subsequent measurements. Batches were ran on the HPLC in sets of 9 with the 3 $[SO_5^{2-}]$ tests being analysed first, followed by the $[H_2O_2]$ tests, and then the $[Ox]_{tot}$ tests. The first of the $[SO_5^{2-}]$ analyses was typically larger than the subsequent measurements and repeated analyses of the same $[SO_5^{2-}]$ test sample would show the same behavior. To investigate this further a mixed peroxosulfate solution was subjected to the three redox colorimetry tests. In each test, a single treated sample was analysed ten times on the HPLC (Table S5). In the repeated determination of $[SO_5^{2-}]$ a value of 0.974 M was obtained from the first measurement. This first measurement was outside the range of the subsequent 9 measurements (0.860 to 0.925 M) and was suspected to be an outlier. The Grubbs' outlier test was applied to the measurements at a significance level of 5% and it was found that the Grubbs' test value (Z) for the first measurement (Z = 2.39) was larger than the critical value of 2.29 for a sample size of 10.[5] Outliers were not detected in the repeated analyses of the $[H_2O_2]$ and $[Ox]_{tot}$ samples (Table S5).

The inflation of the first $[SO_5^{2-}]$ measurement appears to be an artifact in the absorbance measurement by the HPLC. To correct for this the effect, the first redox colorimetry test sample in each batch was analysed twice on the HPLC, with the first measurement being discarded.

Table S5. Grubbs' outlier test showing that the first [SO_5^{2-}] test measurement in a batch of sample analyses is an outlier.

analysis	[SO5(2-)] (M)	Z	[H2O2] (M)	Z	[Ox]tot (M)	Z
1	0.974	**2.39**	0.021	0.97	0.832	1.77
2	0.902	0.33	0.019	1.54	0.845	1.26
3	0.884	0.17	0.021	1.08	0.863	0.54
4	0.867	0.64	0.022	0.67	0.906	1.18
5	0.873	0.47	0.026	0.23	0.906	1.21
6	0.925	0.98	0.026	0.44	0.863	0.51
7	0.872	0.52	0.029	1.11	0.885	0.37
8	0.868	0.63	0.030	1.38	0.884	0.31
9	0.875	0.42	0.026	0.31	0.882	0.23
10	0.860	0.85	0.028	0.78	0.895	0.77
mean	0.890		0.025		0.876	
standard deviation	0.035		0.004		0.025	

Validation of the Redox Colorimetry Tests Against Peroxosulfate Solutions of Known Composition

Aqueous oxidant solutions were prepared as follows, and standardized by iodometric titration for validation of the redox colorimetry tests. The comparison of the redox colorimetric and the iodometric titration results are reported in Table S6, and also Figure 2A of the article.

[$KHSO_5$.0.5$KHSO_4$.0.5K_2SO_4] (8.95 g, 25 mmol) was made up to 25 mL with distilled water. The salt was not completely soluble at this concentration (note: the K_2SO_4 and $KHSO_4$ salts precipitate before the $KHSO_5$). The excess solid material was removed by filtration. The oxidant concentration of the solution was found to be 1.02 M by iodometric titration (Table S6, entry 2).

30% v/v H_2O_2 (1.966 mL, 17.5 mmol) was made up to 25 mL with distilled water. The oxidant concentration of the solution was found to be 0.70 M by iodometric titration (Table S6, entry 4).

$(NH_4)_2S_2O_8$ (5.72 g, 25 mmol) was made up to 25 mL with distilled water. The oxidant concentration of the solution was found to be 0.99 M by iodometric titration (Table S6, entry 3).

Mixed oxidant solutions were created by the combination of the standardized oxidant solutions above, along with water, in different volume proportions. The compositions reported in table S6 were calculated based on the dilutions used to prepare the mixed oxidant solutions. The redox colorimetric analyses of these mixed solutions are reported in Table S7, and also in Figure 2B-D of the article.

Table S6. Validation of redox colorimetry tests against aqueous oxidant solutions which were also analysed by iodometric titration.

		iodometric titration				redox colorimetry											
		[oxidant] (M)				[SO5(2-)] (M)				[H2O2] (M)				[Ox]tot (M)			
entry	oxidant	1	2	3	mean	1	2	3	mean	1	2	3	mean	1	2	3	mean
1	distilled water					<0.2	<0.2	<0.2	**<0.2**	<0.01	<0.01	<0.01	**<0.01**	<0.1	<0.1	<0.1	**<0.1**
2	potassium peroxymonosulfate ammonium	1.018	1.045	0.994	**1.019**	1.078	1.065	1.067	**1.070**	<0.01	<0.01	<0.01	**<0.01**	1.022	1.026	1.053	**1.034**
3	peroxydisulfate	0.985	0.995	0.979	**0.986**	<0.2	<0.2	<0.2	**<0.2**	<0.01	<0.01	<0.01	**<0.01**	0.969	1.006	1.012	**0.996**
4	hydrogen peroxide	0.678	0.724	0.701	**0.701**	0.286	0.260	0.243	**0.263**	0.656	0.661	0.680	**0.666**	0.668	0.670	0.681	**0.673**

Table S7. Validation of redox colorimetry tests against aqueous oxidant mixtures of known composition.

	oxidant composition (M)				redox colorimetry												
					[SO5(2-)] (M)				[H2O2] (M)				[Ox]tot (M)				[S2O8(2-)]
solution	[SO5(2-)]	[H2O2]	[S2O8(2-)]	[Ox]tot	1	2	3	mean	1	2	3	mean	1	2	3	mean	(M)
1	0.36	0.07	0.35	0.78	0.419	0.397	0.396	**0.404**	0.055	0.067	0.069	**0.064**	0.745	0.751	0.766	**0.754**	**0.286**
2	0.10	0.07	0.40	0.57	0.073	0.072	0.071	**0.072**	0.065	0.068	0.072	**0.068**	0.539	0.549	0.566	**0.551**	**0.411**
3	0.41	0.07	0.10	0.58	0.452	0.452	0.454	**0.453**	0.060	0.072	0.075	**0.069**	0.606	0.637	0.648	**0.630**	**0.109**
4	0.36	0.14	0.35	0.85	0.364	0.347	0.352	**0.354**	0.130	0.149	0.149	**0.143**	0.798	0.813	0.821	**0.811**	**0.314**
5	0.10	0.14	0.40	0.64	0.0682	0.0638	0.0659	**0.066**	0.1342	0.1486	0.1461	**0.143**	0.66	0.6714	0.681	**0.671**	**0.462**
6	0.41	0.14	0.10	0.65	0.4181	0.3892	0.386	**0.398**	0.1279	0.1474	0.1524	**0.143**	0.6554	0.6769	0.6834	**0.672**	**0.132**
7	0.36	0.21	0.35	0.92	0.31	0.294	0.284	**0.296**	0.206	0.228	0.232	**0.222**	0.88	0.902	0.906	**0.896**	**0.378**
8	0.10	0.21	0.35	0.66	0.0795	0.0755	0.0749	**0.077**	0.1966	0.2145	0.2267	**0.213**	0.6636	0.6796	0.6859	**0.676**	**0.387**
9	0.36	0.21	0.10	0.67	0.3046	0.2868	0.2836	**0.292**	0.2009	0.2163	0.2279	**0.215**	0.6646	0.6836	0.6952	**0.681**	**0.174**

Estimation of the Uncertainty Levels in the Redox Colorimetric Tests

Solutions 1, 4 and 7 (Table S7) were analysed six times by the redox colorimetric tests. The results shown in Tables S8, S9 and S10 were used to estimate the experimental uncertainty in the redox colorimetric tests. The standard deviation of the six measurements has been taken as the absolute error in each test.

The standard deviation for a given test varied depended on the solution that was being analysed. The largest standard deviations have therefore been used in our research. It was also noted that the [$S_2O_8^{2-}$], obtained by calculation using the three redox colorimetric tests, was measured with more precision than [SO_5^{2-}] in this instance. We have increased the uncertainty in [$S_2O_8^{2-}$] to ±0.05 M to better reflect that this measurement is derived from the less precise [SO_5^{2-}] measurement.

Table S8. Estimation of the uncertainty level in the redox colorimetric analysis of mixed peroxosulfate solution 1 [0.36 M SO_5^{2-}, 0.07 M H_2O_2, 0.35 M $S_2O_8^{2-}$, 0.78 M Ox_{tot}].

	concentration by redox colorimetry (M)			
sample	**[SO5(2-)]**	**[H2O2]**	**[Ox]tot**	**[S2O8(2-)]**
1	0.419	0.055	0.745	0.270
2	0.397	0.067	0.751	0.287
3	0.396	0.069	0.766	0.301
4	0.402	0.060	0.738	0.276
5	0.389	0.062	0.756	0.305
6	0.398	0.070	0.760	0.292
mean	0.400	0.064	0.753	0.289
range	0.030	0.015	0.028	0.034
standard deviation	0.010	0.006	0.010	0.014
abs. error	0.01	0.006	0.01	0.01
% error	3%	9%	1%	5%

Table S9. Estimation of the uncertainty level in the redox colorimetric analysis of mixed peroxosulfate solution 1 [0.36 M SO_5^{2-}, 0.14 M H_2O_2, 0.35 M $S_2O_8^{2-}$, 0.85 M Ox_{tot}].

	concentration by redox colorimetry (M)			
sample	**[SO5(2-)]**	**[H2O2]**	**[Ox]tot**	**[S2O8(2-)]**
1	0.364	0.130	0.798	0.304
2	0.347	0.149	0.813	0.317
3	0.352	0.149	0.821	0.321
4	0.315	0.137	0.778	0.326
5	0.277	0.149	0.771	0.345
6	0.233	0.154	0.772	0.386
mean	0.315	0.145	0.792	0.333
range	0.131	0.023	0.050	0.082
standard deviation	0.051	0.009	0.022	0.029
abs. error	0.05	0.009	0.02	0.03
% error	16%	6%	3%	9%

Table S10. Estimation of the uncertainty level in the redox colorimetric analysis of mixed peroxosulfate solution 1 [0.36 M SO_5^{2-}, 0.14 M H_2O_2, 0.35 M $S_2O_8^{2-}$, 0.92 M Ox_{tot}].

	concentration by redox colorimetry (M)			
sample	**[SO5(2-)]**	**[H2O2]**	**[Ox]tot**	**[S2O8(2-)]**
1	0.310	0.206	0.880	0.363
2	0.294	0.228	0.902	0.379
3	0.284	0.232	0.906	0.390
4	0.299	0.216	0.866	0.351
5	0.285	0.231	0.885	0.369
6	0.290	0.239	0.899	0.370
mean	0.294	0.225	0.889	0.371
range	0.026	0.032	0.040	0.038
standard deviation	0.010	0.012	0.015	0.013
abs. error	0.01	0.01	0.02	0.01
% error	3%	5%	2%	4%

Limits of Detection and Quantitation for the Redox Colorimetry Tests

Samples of distilled water were analysed by redox colorimetry five times to determine the limits of detection and quantitation. The peak areas measured in the tests are reported in Table S11. The limits of detection have been defined as the mean zero measurements plus 3X the standard deviation in the zero measurements. The limits of detection have similarly been defined as the mean zero measurements plus 10X the standard deviation in the zero measurements. The limits are reported as both peak areas and also as $mol.L^{-1}$ (M) values using the calibration curves for each redox test.

The limits of detection for the $TiOSO_4$ and Fe(II) tests in $mol.L^{-1}$ (M) values were both determined to be negative values. This is due to the calibration curves not passing through zero. The limit of quantitation for the Fe(II) test in $mol.L^{-1}$ (M) was also negative due to this effect. It is therefore recommended that the only peak areas of the redox colorimetry assays should be considered when determining if results are above the limits of detection or quantitation. The limits of quantitation determined in this was equivalent to, or less than the lower limits of the calibrations ranges used in our research.

Table S11. Measurement of the limits of detection and quantitation for the redox colorimetry tests.

	redox colorimetry peak area			
	VOSO4 at 360 nm		TiSO4	Fe(II)
sample	(20x dilution)	(5x dilution)	at 407 nm	at 380 nm
1	166	129	27	292
2	151	136	18	294
3	141	131	17	296
4	114	156	18	293
5	120	109	18	289
mean	138	132	19	293
range	52	47	9	7
standard deviation	22	17	4	3
LOD (peak area)	203	183	31	301
LOD (M)	0.16	0.04	-0.003	-0.02
LOQ (peak area)	354	301	59	319
LOQ (M)	0.22	0.05	0.001	-0.01

It should be noted that the Fe(II) reagent solution becomes oxidized by atmospheric oxygen over time. In our research we have used the reagent over a period of one week (with storage at 4 °C) with a small but measurable increase in the zero measurement of the reagent being observed. In our research the effect of this background oxidation has not been problematic as it is below the limits of our calibration range. For applications were the total oxidant concentration must be determined accurately at low levels it is recommended that freshly prepared and calibrated Fe(II) reagent solution be used.

Quenching H_2O_2 in Peroxosulfate Solutions with MnO_2

An $(NH_4)_2SO_5$ solution was prepared by the addition of an excess of $(NH_4)_2SO_4$ (0.6 mol) to a saturated solution (75 mL) of $[KHSO_5.0.5KHSO_4.0.5K_2SO_4]$ (0.2 mol) in water. After filtration to remove the excess sulfate salts, the $(NH_4)_2SO_5$ was diluted with water (25 m) and stored in the refrigerator. The oxidant composition was determined to be 1.24 M SO_5^{2-} with less than 0.01 M of H_2O_2, by redox colorimetry.

A mixed oxidant solution of known composition was prepared by combining aqueous solutions of H_2O_2 (0.93 M, 3 mL), $(NH_4)_2SO_5$ (1.24 M, 5 mL) and $(NH_4)_2S_2O_8$ (1.25 M, 2 mL) in measured volumes. The expected composition of the mixed oxidant solution was 0.62 M SO_5^{2-}, 0.28 M H_2O_2 and 0.25 M $S_2O_8^{2-}$ (Table S12).

The mixed oxidant solution was analysed by redox colorimetry before a sample (0.5 mL) was added to MnO_2 (10 mg) and left to react at room temperature for 1 h. After the sample stopped effervescing it was analysed by redox colorimetry to determine the oxidant composition without the interference effects of H_2O_2 (Table S12).

The redox colorimetric analysis before MnO_2 treatment provided a measurement of [H_2O_2] which agreed with the expected value within the uncertainty limits of ± 0.01 M (Table S12). The [SO_5^{2-}] and [$S_2O_8^{2-}$] measured before MnO_2 treatment differed from the expected values due to the interference effects of H_2O_2 in the $VOSO_4$ assay. After treatment of the sample with MnO_2 the redox colorimetric assays provided measurements of [SO_5^{2-}] and [$S_2O_8^{2-}$] which agreed with the expected values within the uncertainty limits of ± 0.05 M.

Table S12 Redox colorimetric analysis of a peroxosulfate and H_2O_2 solution before, and after quenching of the H_2O_2 by MnO_2.

	concentration by redox colorimetry (M)							
	before MnO2 treatment				after MnO2 treatment			
sample	**[SO5(2-)]**	**[H2O2]**	**[Ox]tot**	**[S2O8(2-)]**	**[SO5(2-)]**	**[H2O2]**	**[Ox]tot**	**[S2O8(2-)]**
1	0.40	0.24	1.14	0.49	0.69	0.02	0.88	0.18
2	0.42	0.28	1.14	0.44	0.66	0.02	0.89	0.21
3	0.43	0.30	1.18	0.46	0.63	0.02	0.90	0.25
mean	0.42	0.27	1.15	0.46	0.66	0.02	0.89	0.21
expected	0.62	0.28	1.15	0.25	0.62	0.00	0.87	0.25

Analysis of the Decomposition of Peroxodisulfate into Peroxomonosulfate and Hydrogen Peroxide

2 M sulfuric acid (50 mL) was added to $(NH_4)_2S_2O_8$ (11.4 g, 50 mmol) in a magnetically stirred EasyMax 102 reactor (supplied by Mettler-Toledo). The reactor was stirred at room temperature until all the solid had dissolved, and then a sample of the solution was analysed by redox colorimetry. The reactor temperature was then increased to 50 °C over 2 min. Samples (0.5 mL) were taken from the reactor at intervals, rapidly cooled by immersion in a cold water bath, and then analysed by redox colorimetry using our standard method. The redox colorimetry results are reported in Table S13 and Figure S7.

Table S13. Redox colorimetric reaction analysis of the decomposition of peroxodisulfate in an acidic solution at 50 °C.

	concentration by redox colorimetry (M)			
time (h)	**[SO5(2-)]**	**[H2O2]**	**[Ox]tot**	**[S2O8(2-)]**
0	<0.05	<0.01	0.87	0.87
0.6	0.43	<0.01	0.86	0.43
1	0.56	<0.01	0.94	0.38
1.5	0.69	0.01	0.92	0.22
2.1	0.77	0.02	0.91	0.12
4.5	0.77	0.08	0.90	0.05
7	0.72	0.13	0.89	0.04

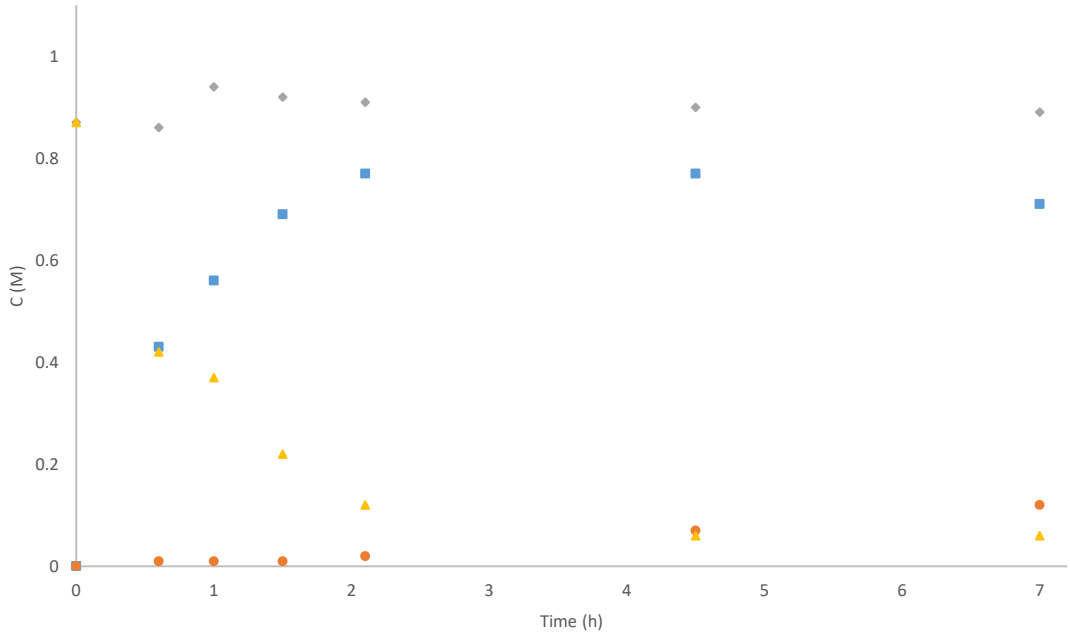

Figure S7 Changes in the oxidant composition of a 1 M $(NH_4)_2S_2O_8$ solution in 2 M H_2SO_4 heated at 50 °C were followed using the colorimetric redox assays. Key to chart: ■ $[SO_5^{2-}]$, ● $[H_2O_2]$, ◆ $[Ox]_{tot}$, ▲ $[S_2O_8^{2-}]$.

Analysis of the Decomposition of an Electrochemically Generated Peroxosulfate Solution

Peroxosulfate solutions were generated electrochemically using a method we have reported previously.[6]

A 2 M solution (100 mL) of $(NH_4)_2SO_4$ (11.4 g, 50 mmol) in 2 M sulfuric acid was recirculated (200 mL/min) through the anodic cell in batch recycle mode. The electrochemical reactor was operated under galvanostatic conditions (150 mA/cm^2 current density) for 10 h. The electrolytic flow cell was cooled by circulation of an ice water bath. After the peroxosulfate solution was electrochemically generated it was stored in a sealed bottle inside a refrigerator (3-4 °C).

A portion of the peroxosulfate solution (50 mL) was magnetically stirred in a EasyMax 102 reactor (supplied by Mettler-Toledo). A sample of the solution was analysed by redox colorimetry. The reactor temperature was then increased to 50 °C over 2 min. Samples (0.5 mL) were taken from the reactor at intervals, rapidly cooled by immersion in a cold water bath, and then analysed by redox colorimetry using our standard method. The sample collected after 25 h was analysed by redox colorimetry before and after quenching the H_2O_2 by addition of MnO_2 to the sample. The redox colorimetry results are reported in Table S14 and Figure 3.

Table S14. Redox colorimetric reaction analysis of the decomposition of an electrochemically generated peroxosulfate solution at 50 °C.

	concentration by redox colorimetry (M)			
time (h)	[SO5(2-)]	[H2O2]	[Ox]tot	[S2O8(2-)]
0	0.55	<0.01	0.97	0.42
0.5	0.66	0.01	1.10	0.43
1.1	0.76	0.01	1.03	0.26
2.1	0.84	0.02	0.99	0.13
3.2	0.94	0.03	1.07	0.10
4.3	0.93	0.05	1.05	0.07
6.2	0.86	0.07	1.05	0.12
25	0.59	0.38	0.98	0.01

Design of an Automated Sampling System

In this work we have employed manual sampling using an autopipette to dilute aliquots with the redox colorimetric reagents. In future applications, we envisage that an liquid handling and analysis system might be constructed to enable the fully automated and continuous analysis of reactions by redox colorimetry. The HPLC photodiode array detector could feasibly be replaced with low cost LED based absorbance detectors.[7–9] Figure S8 and S9 detail how such a platform might be constructed for the continuous monitoring of flow and batch processes employing peroxosulfate oxidants.

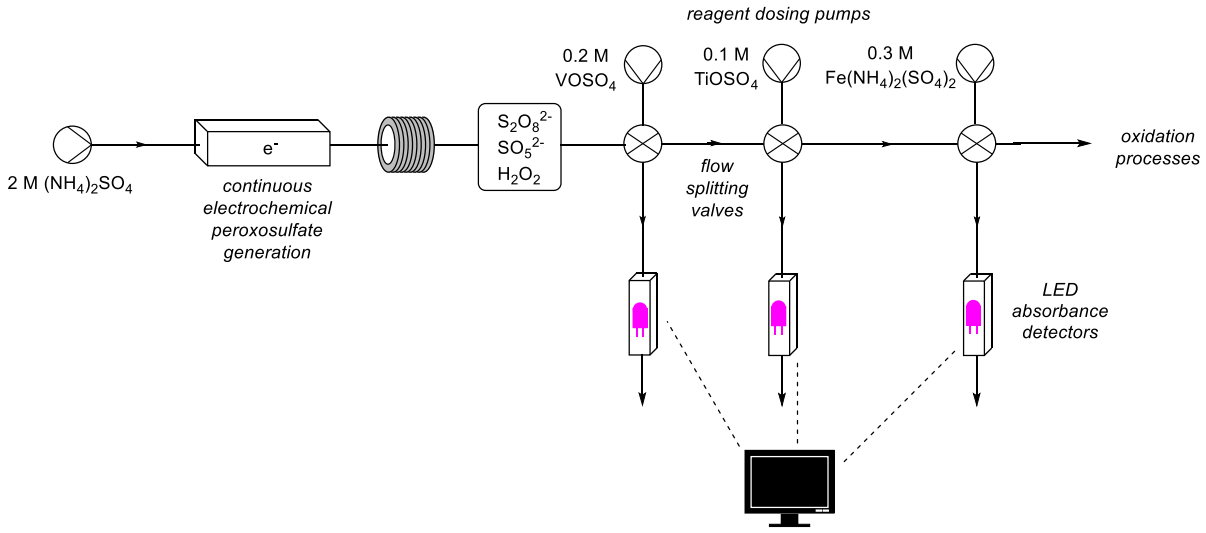

Figure S8 Design of an automated sampling and analysis platform for the continuous redox colorimetric analysis of a electrochemical flow reactor system for the generation of peroxosulfate oxidants.

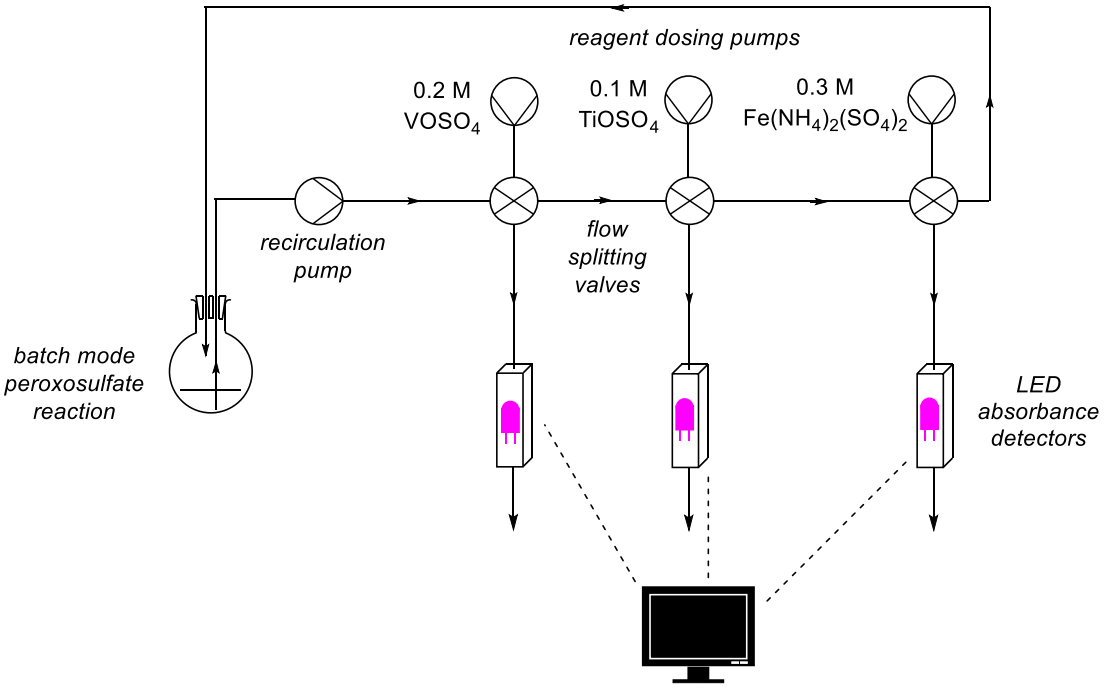

Figure S9 Design of an automated sampling and analysis platform for the continuous redox colorimetric analysis of a batch reaction involving peroxosulfate oxidants.

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