Supplementary Material

Simultaneous determination of PMS, PDS and H_2O_2 concentrations by multi-step iodometric titration

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TEXT S1 Detailed statements on the procedures of multiple-step iodometric determination.

Generally, the multiple-step iodometric determination of PMS, PDS, and H_2O_2 concentrations in their mixed solution included 3 steps. Samples were divided into 3 equivalent parts. In Step I, the first part was treated by $NaHCO_3$ (with or without molybdate) buffered iodometry to obtain the total concentration of the three peroxides. Solid KI was dissolved in $NaHCO_3$ solution (6.6 $g \cdot L^{-1}$, with or without molybdate) before PMS, PDS, and H_2O_2 stock solutions were added in sequence. The solution was then allowed to react for a while (t_1) and then titrated by $Na_2S_2O_3$ (0.01 $mol \cdot L^{-1}$) after adding 3.3% (v/v) acetic acid. In Step II, the second part of mixed solution was treated by catalase and $NaHCO_3$ (with or without molybdate) buffered iodometry to obtain the sum of PMS and PDS concentrations. PMS, PDS, and H_2O_2 stock solutions were added in sequence to the solution containing phosphate buffer (composed of 0.39 $mmol \cdot L^{-1}$ HPO_4^{2-} and 0.70 $mmol \cdot L^{-1}$ $H_2PO_4^-$) and catalase 0.01 $g \cdot L^{-1}$. The solution was allowed to remain for 5 min. Then $NaHCO_3$ solution (with or without molybdate) and solid KI was added. And the following titration process was similar to Step I. In Step III, the third part of mixed solution was treated by catalase and revised acetate buffered iodometry to obtain PMS concentration. PMS, PDS, and H_2O_2 stock solutions were added in sequence to the solution containing phosphate buffer and catalase, and the solution was allowed for 5 min as Step II. Then 10 $g \cdot L^{-1}$ KI and 5 mL acetate buffer (0.98 $mol \cdot L^{-1}$ acetic acid and 0.017 $mol \cdot L^{-1}$ sodium acetate) were added, the solution was kept for 2 min before titrated by $Na_2S_2O_3$.

TEXT S2 General principle and detailed experimental procedure of revised acetate buffered iodometry.

a. Principle: PMS reacts with KI under acidic conditions will liberate free iodine from potassium iodide (KI) solutions (Equations S1 and S2) [1]. The liberated iodine is titrated with a standard solution of sodium thiosulfate ($Na_2S_2O_3$) (Equation S3) with starch as the indicator.

$$HSO_5^- + 2I^- \longrightarrow SO_4^{2-} + I_2 + OH^- \quad (S1)$$

$$I_2 + I^- \longleftrightarrow I_3^- \quad (S2)$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^- \quad (S3)$$

b. Procedure: Add appropriate amount of PMS to 100 mL Milli-Q water in the conical flask so that the consumed $Na_2S_2O_3$ (0.01 $mol \cdot L^{-1}$) will be no more than 20 mL and no less than 0.2 mL for the starch-iodide end point. Add 1 g KI and 5 mL acetic acid buffer (0.98 $mol \cdot L^{-1}$ acetic acid and 0.017 $mol \cdot L^{-1}$ sodium acetate). The solutions were allowed to stand for 2 min, and then titrated with $Na_2S_2O_3$ (0.01 $mol \cdot L^{-1}$) until the yellow color of the liberated iodine almost is discharged. Add 1 mL of 0.5% (*w*/*v*) starch indicator solution and titrate until blue color is discharged. Denote the consumed $Na_2S_2O_3$ volume after correction by blank titration as V. The concentration of PMS solution was calculated according to

equation S4.

$$c_{PMS} = \frac{c_{Na_2S_2O_3} \times V}{2 \times 100} \quad (S4)$$

Where c_{PMS} is the PMS concentration in 100 mL solution, mol·L^{-1}; $c_{Na_2S_2O_3}$ is the concentration of $Na_2S_2O_3$, mol·L^{-1}; and V is the consumed $Na_2S_2O_3$ volume after correction by blank titration, mL.

TEXT S3 General principle and detailed experimental procedure of $NaHCO_3$ buffered iodometry.

a. Principle: Free iodine is released during the reaction of PDS with KI in the presence of $NaHCO_3$ (Equations S2 and S5) [2]. The liberated iodine is titrated with a standard solution of sodium thiosulfate ($Na_2S_2O_3$) with starch as the indicator (Equation S3), and the concentration of PDS in the solution was calculated based on the volume of titrant consumed.

$$S_2O_8^{2-} + 2I^- \longrightarrow I_2 + 2SO_4^{2-} \quad (S5)$$

b. Procedure: Add the appropriate amount of PDS to 100 mL Milli-Q water so that the consumed $Na_2S_2O_3$ (0.01 mol·L^{-1}) will be no more than 20 mL and no less than 0.2 mL for the starch-iodide end point. Add 13.2g of KI and 0.66 g of $NaHCO_3$ to solution. The solution was allowed to stand for 15 min before adding 3.3 mL (v/v=3.3%) of acetic acid. Then titrate the solution with $Na_2S_2O_3$ (0.01 mol·L^{-1}) until the yellow color of the liberated iodine almost is discharged. Add 1 mL of 0.5% (*w*/*v*) starch indicator solution and titrate until blue color is discharged. Denote the consumed $Na_2S_2O_3$ volume after correction by blank titration as ***V***. The concentration of PDS solution was calculated according to equation S6.

$$c_{PDS} = \frac{c_{Na_2S_2O_3} \times V}{2 \times 100} \quad (S6)$$

Where c_{PDS} is the PDS concentration in 100 mL solution, mol·L^{-1}; $c_{Na_2S_2O_3}$ is the concentration of $Na_2S_2O_3$, mol·L^{-1}; and V is the consumed $Na_2S_2O_3$ volume after correction by blank titration, mL.

Figures

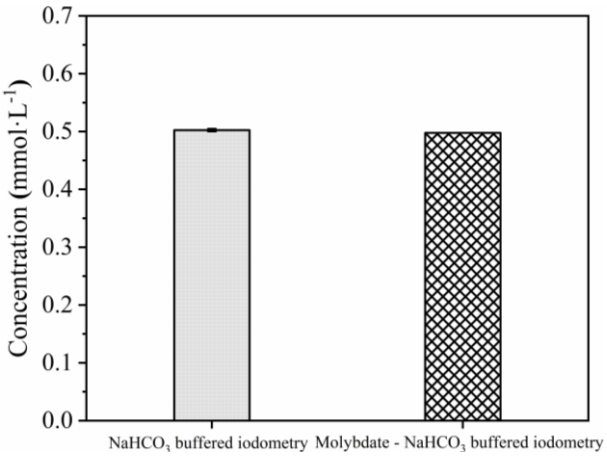

Figure S1. PDS concentrations titrated by $NaHCO_3$ buffered iodometry and molybdate - $NaHCO_3$ buffered iodometry. Conditions: [PDS]= 0.502 mmol·L^{-1}, [KI]=132 g·L^{-1}, t_1 =15 min, $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ =26.09 mg·L^{-1}.

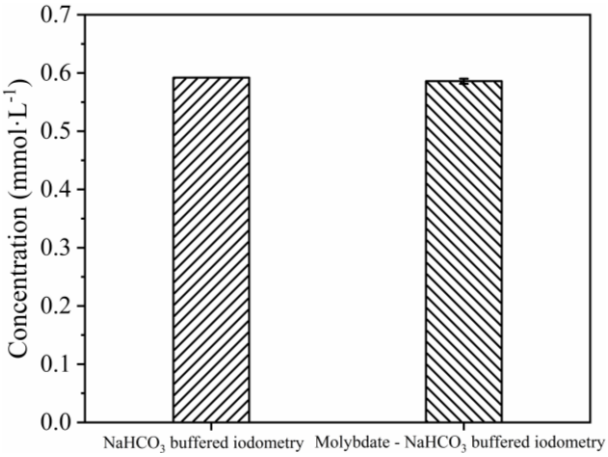

Figure S2. PMS concentrations titrated by $NaHCO_3$ buffered iodometry and molybdate - $NaHCO_3$ buffered iodometry. Conditions: [PMS]=0.592 mmol·L^{-1}, [KI]=132 g·L^{-1}, t_1 =15 min, $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ =26.09 mg·L^{-1}.

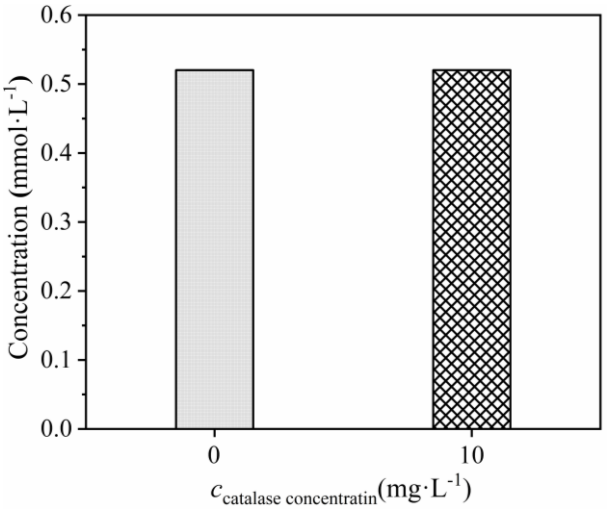

Figure S3. Influence of phosphate buffer and catalase on the detection of PDS by molybdate - $NaHCO_3$ buffered iodometry. Conditions: [PDS]=0.52 mmol·L^{-1}, [KI]=132 g·L^{-1}, [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$]= 26.09 mg·$L^{-1}$, t_1 =15 min, phosphate buffer= 1.1 mmol·L^{-1}.

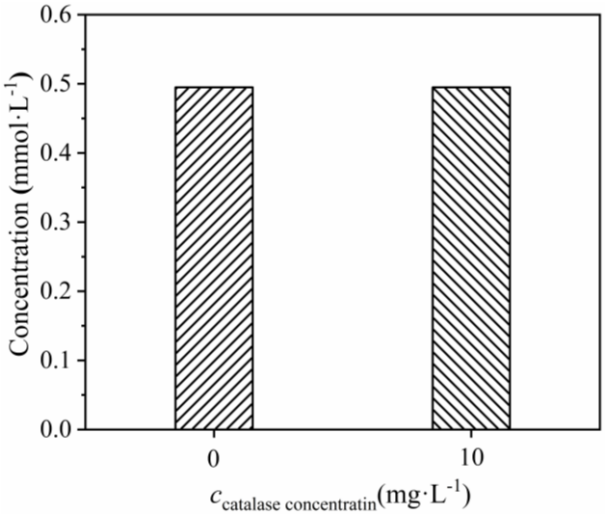

Figure S4. Influence of phosphate buffer and catalase on the detection of PMS by molybdate - $NaHCO_3$ buffered iodometry. Conditions: [PMS]=0.495 mmol·L^{-1}, [KI]=132 g·L^{-1}, [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$]= 26.09 mg·$L^{-1}$,$t_1$ =15 min, phosphate buffer= 1.1 mmol·L^{-1}.

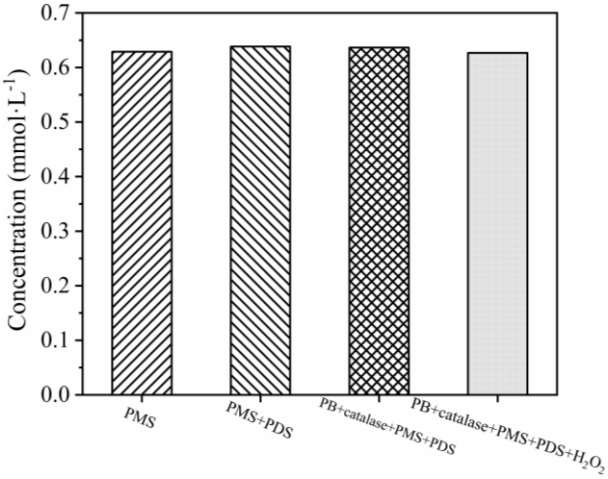

Figure S5. Influence of phosphate buffer and catalase on the detection of PMS by revised acetate buffered iodometry. Conditions: [PMS]=0.629 mmol·L^{-1}, [PDS]=0.500 mmol·L^{-1}, [H_2O_2]=0.634 mmol·L^{-1}, [catalase]= 10 mg·L^{-1}, phosphate buffer= 1.1 mmol·L^{-1}.

Tables

Table S1 Recovery rates of peroxides in separate solutions by iodometric titration.

Method	H_2O_2			PDS			PMS		
	Theoretical concentration (mmol·L^{-1})	Recovery rate (%)	Standard deviation (%)	Theoretical concentration (mmol·L^{-1})	Recovery rate (%)	Standard deviation (%)	Theoretical concentration (mmol·L^{-1})	Recovery rate (%)	Standard deviation (%)
$NaHCO_3$ buffered iodometry	0.62	87.03	3.66	1.01	100	0	1.30	102.38	0
Revised acetate buffered iodometry	NA	NA	NA	1.01	1.34	0.09	1.26	99.44	0

Note: NA means that the value cannot be determined accurately.

Table S2 Determination of peroxide concentrations in the three peroxide mixtures by the combination of revised acetate buffered iodometry and $NaHCO_3$ buffered iodometry with catalase.

Scenarios	H_2O_2			PDS			PMS		
	Theoretical concentration ($mmol \cdot L^{-1}$)	Recovery rate (%)	Standard deviation (%)	Theoretical concentration ($mmol \cdot L^{-1}$)	Recovery rate (%)	Standard deviation (%)	Theoretical concentration ($mmol \cdot L^{-1}$)	Recovery rate (%)	Standard deviation (%)
1	0.634	27.43	0.34	0.500	99.31	0	0.630	99.82	0.30
2	0.186	30.00	0	0.196	98.73	0.52	0.177	100.00	0.03

Table S3. Levels of factors in orthogonal experiments of molybdate - $NaHCO_3$ buffered iodometry.

Levels	Factors		
	KI dosage ($g \cdot L^{-1}$)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ concentration ($mg \cdot L^{-1}$)	Time (min)
1	10	0	5
2	60	26.09	15
3	132	46.15	30

Table S4. Results of orthogonal experiments.

Serial number	KI ($g \cdot L^{-1}$)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ($mg \cdot L^{-1}$)	Time (min)	H_2O_2 detection rate (%)
1	10	0	5	0
2	10	26.09	15	0
3	10	46.15	30	0
4	60	0	15	25.42
5	60	26.09	30	80.63
6	60	46.15	5	65.37
7	132	0	30	30.00
8	132	26.09	5	92.36
9	132	46.15	15	94.76
k_1	0	55.42	157.73	
k_2	171.42	172.99	120.18	
k_3	217.12	160.13	110.63	
R	72.37	39.19	15.70	

Table S5 The pH values of $NaHCO_3$ buffered samples to be titrated by molybdate - $NaHCO_3$ buffered iodometry in Step I of multi-step iodometric titration.

Scenarios	Ca^{2+} ($mg \cdot L^{-1}$)	Mg^{2+} ($mg \cdot L^{-1}$)	Na_2CO_3 ($g \cdot L^{-1}$)	peroxide concentration ($\mu mol \cdot L^{-1}$)			pH
				PMS	PDS	H_2O_2	
1	0	0	0	166	177	222	8.35
2	100	0	0	166	177	222	8.03
3	100	0	1.06	166	177	222	8.59
4	0	100	0	166	177	222	8.22
5	0	100	1.06	166	177	222	8.83

Table S6 Water quality parameters of the real water samples.

Sample	Cl^- ($mg \cdot L^{-1}$)	F^- ($mg \cdot L^{-1}$)	NO_3^- ($mg \cdot L^{-1}$)	SO_4^{2-} ($mg \cdot L^{-1}$)	TOC ($mg \cdot L^{-1}$)	pH	Hardness (as $CaCO_3$, $mg \cdot L^{-1}$)	UV_{254}
Tap water	9.70	0.03	4.03	10.91	3.52	7.29	29.03	0.021
Surface water	21.10	0.39	7.82	29.38	6.80	7.20	126.13	0.150
Groundwater	1.75	0.11	0.93	10.60	12.04	8.56	384.38	0.035

References

1. Güpta, Y. K. Iodometric determination of persulphate in sulphuric acid solution. Fresenius' Journal of Analytical Chemistry 1961, 180(4): 260-265.
2. Liang, C., Huang, C.-F., Mohanty, N., Kurakalva, R.M. A rapid spectrophotometric determination of persulfate anion in ISCO. Chemosphere 2008, 73, 1540-1543.