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Simultaneous Determination of PMS, PDS, and H_2O_2 Concentrations with Multi-Step Iodometry

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Abstract: Peroxodisulfate (PDS), peroxymonosulfate (PMS), and hydrogen peroxide (H_2O_2) might coexist in a persulfate system. It leads to the mutual interference in concentration determination due to their similar structures. Simultaneous detection of the three peroxides involves limited reporting. Herein, a multi-step iodometry was established to simultaneously determine the concentrations of PDS, PMS, and H_2O_2 coexisting in a solution. Firstly, molybdate–$NaHCO_3$-buffered iodometry was proposed to uplift the overall detection of peroxides since the recovery rate of H_2O_2 was unexpectedly lower in the peroxide mixture than in the single H_2O_2 solution with reported $NaHCO_3$-buffered iodometry. Then, multi-step iodometry was proposed based on the established molybdate–$NaHCO_3$-buffered iodometry using the combination with catalase and revised acetate-buffered iodometry (pH 3). The multi-step iodometry determined the coexisting PMS, PDS, and H_2O_2 with the recovery rate of 95–105% and a standard deviation of ≤7% of two replicates at the individual centration of 13–500 μmol·L^{-1}. The recovery rates of peroxides were within 95–105% at pH 3–11 and within 90–110% in the presence of Cl^- (0–150 mg·L^{-1}), F^- (0–1.5 mg·L^{-1}), SO_4^{2-} (0–150 mg·L^{-1}), or NO_3^- (0–20 mg·L^{-1}). The recovery rate of H_2O_2 was lowered down to 91% or 87% in the sample containing 100 mg/L Ca^{2+} or Mg^{2+}, respectively, but was lifted up to 100% or 93% once pretreated by adding 0.11–1.06 g·L^{-1} Na_2CO_3. In the background of tap water, surface water, and ground water, peroxides were all detected in 90–110%, which indicates the applicability of multi-step iodometry in real waters.

Keywords: peroxodisulfate; peroxymonosulfate; hydrogen peroxide; iodometric titration; advanced oxidation

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1. Introduction

Peroxodisulfate (PDS)- and peroxymonosulfate (PMS)-based advanced oxidation processes (AOPs) have attracted great interest due to the production of highly reactive radicals ($SO_4^{\bullet-}$ and $HO^{\bullet}$) and their effectiveness in degrading various pollutants [1,2]. Accompanying the increasing use of persulfate (PMS and PDS) for remediation of contaminated soil and water, the on-site/off-site detection of persulfate concentration is inevitable and necessary in the theoretical analysis on decontamination mechanisms or oxidant efficiency assessment in applications.

In persulfate-based systems, $SO_4^{\bullet-}$ and $HO^{\bullet}$ usually coexist [3]. Mutual quenching of the radicals would produce PDS, PMS, and H_2O_2 in a single solution. In the case of PMS-based AOPs, PDS could also be formed from the decay of the peroxymonosulfate radical ($SO_5^{\bullet-}$), which was produced from PMS by the attack of radicals (including $SO_4^{\bullet-}$, $HO^{\bullet}$, the chlorine atom ($Cl^{\bullet}$), and the dichloride radical ($Cl_2^{\bullet-}$)) [4]. Meanwhile, PDS was hydrolyzed to PMS and subsequent H_2O_2 under alkaline or strong acidic conditions [5,6]. Therefore, during PMS- or PDS-related decontamination processes, it is possible that the three peroxides, H_2O_2, HSO_5^-, and $S_2O_8^{2-}$, are present in a solution simultaneously. Recently, the coupling of peroxides was used as a way to produce reactive oxidants in

decontamination. The combination of PDS and H_2O_2 was investigated for the in situ remediation of ortho-nitrochlorobenzene in soil with $SO_4^{\bullet -}$ and $HO^{\bullet}$ as reactive species [7]. The mixing of PMS and H_2O_2 mutually accelerated their decomposition and produced the oxidative species singlet oxygen [8]. PMS, PDS, and H_2O_2 have a similar structure to the -O-O- bond, which leads to the mutual interference in concentration determination when coexisting. Additionally, the development of methods to simultaneously determine the concentrations of peroxides in their mixture deserves attention.

Previous studies mainly focused on the detection of a single oxidant. A single PMS solution was determined with acetate-buffered iodometry [9], the ABTS method [10], ion chromatography [6], liquid chromatography [11], and BA fluorometry [12]. PDS was measured with $NaHCO_3$-buffered iodometry [13] and sulfate acid iodometry [5]. Hydrogen peroxide (H_2O_2), a similar peroxide, was measured with molyadate–iodide spectrophotometry [14], $KMnO_4$ titration [14], the titanate complex method [15], and DPD spectrometry [16].

For the determination of mixed peroxides, research has touched upon the determination of the mixture containing two peroxides. In the solution containing PDS and H_2O_2, H_2O_2 concentration was quantified photometrically using the complexation with titanium sulfate while the concentration of PDS was obtained with subtracting the H_2O_2 concentration from the total concentration, which was determined by iodometric titration [6]. Similarly, the detection of PMS and H_2O_2 in their mixture was realized with the combination of the ABTS method and horseradish peroxidase. The PMS concentration was measured with the ABTS method alone while H_2O_2 was determined with the difference between the two measurements using the ABTS method in the presence and absence of horseradish peroxidase [8]. For the mixture of PMS, PDS, and H_2O_2, ion chromatography [6] and BA fluorometry [12] were used to measure the concentration of PMS in the mixture without the determination of PDS and H_2O_2. The available method for simultaneous determination of the concentrations of PMS, PDS, and H_2O_2 was established by Boudeville (1983) based on thermometric titrimetry [17]. PMS, PDS, and H_2O_2 concentrations were measured within the range of 100–1000 $\mu mol \cdot L^{-1}$. The titration was operated under strongly acidic conditions (4–5 $mol \cdot L^{-1}$ H_2SO_4). Under the conditions, PDS would hydrolyze to PMS [5], which should be considered during the determination.

In this work, a method based on iodometric titration was developed for the simultaneous determination of PMS, PDS, and H_2O_2 coexisting in a solution. Firstly, the unexpectedly low overall detection of peroxides in the mixture was observed with reported $NaHCO_3$ buffered iodometry, and was further uplifted by increasing the KI dosage or adding molybdate. Additionally, molybdate–$NaHCO_3$-buffered iodometry was further proposed by optimizing the reaction time, KI, and molybdate dosages. Secondly, the multi-step iodometric titration was proposed based on the established molybdate–$NaHCO_3$-buffered iodometry using the combination with catalase (from a bovine liver) and revised acetate-buffered iodometry. Additionally, the detection ranges and detection limits were further determined. Finally, the detection of peroxides (PMS, PDS, and H_2O_2) simultaneously existing in a single solution with the multi-step iodometry was performed in the presence of common ions, under various pH conditions, or in the background of real waters.

2. Materials and Methods

2.1. Chemicals and Reagents

Peroxymonosulfate ($KHSO_5 \cdot 0.5\ KHSO_4 \cdot 0.5\ K_2SO_4$, PMS), peroxodisulfate ($K_2S_2O_8$, PDS), sodium bicarbonate, catalase (from bovine liver), sodium dihydrogen phosphate anhydrous, sodium phosphate dibasic, and potassium hydroxide were purchased from Sigma-Aldrich (Shanghai, China). Hydrogen peroxide (H_2O_2, 35% *w*/*w*) was purchased from Alfa Aesar (Haverhill, MA, USA). Calcium chloride anhydrous, magnesium sulfate anhydrous, ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), and starch were purchased from Tianjin Tianli Chemical Reagent Co., Ltd. (Tianjin, China). Acetic acid was purchased from Tianjin Kemeo Chemical Reagent Co., Ltd. (Tianjin, China). Other

chemicals were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals and reagents were of analytical grade and used without any further purification. Solutions were prepared in Milli-Q water produced by the Milli-Q® Biocel (Millipore, Billerica, MA, USA) water system unless otherwise stated.

2.2. Experimental Procedures

All experiments were carried out in a 250 mL conical flask with a total solution volume of 100 mL at 25 ± 2 °C. Predetermined volume of 0.1 mol·L^{-1} H_2SO_4 or NaOH solution was added to imitate the scenarios of different pH samples of the mixed peroxide (PMS, PDS, and H_2O_2) solution if needed. The mixture of PMS, PDS, and H_2O_2 was simulated by the sequential addition of PMS, PDS, and H_2O_2 stock solutions. Generally, the multi-step iodometric determination of PMS, PDS, and H_2O_2 concentrations in the peroxide mixture included 3 steps. Sample was divided into 3 equivalent parts. In Step I, the first part was treated with $NaHCO_3$ (with or without molybdate)-buffered iodometry to obtain the total concentration of the three peroxides. In Step II, the second part of sample was treated with catalase and $NaHCO_3$ (with or without molybdate)-buffered iodometry to obtain the sum of PMS and PDS concentrations. In Step III, the third part of sample was treated with catalase and revised acetate-buffered iodometry to obtain PMS concentration. Experiments were performed at least in duplicate and error bar represents the standard deviation of replicates. For details, see Supplementary Text S1.

2.3. Analytical Methods

Concentration of PMS stock solution was standardized with acetate-buffered iodometric titration with reaction time of 5 min for KI and PMS [9]. For revised acetate-buffered iodometry used in Step III of multi-step iodometry, everything was kept unchanged except that the reaction time was set as 2 min. For detailed experimental procedure, see Supplementary Text S2. PDS stock solution was quantified with $NaHCO_3$-buffered iodometry with 132 g·L^{-1} KI [13]. For details, see Supplementary Text S3. Molybdate–$NaHCO_3$-buffered iodometry used in Steps I and II of multi-step iodometry was established in the current work based on $NaHCO_3$-buffered iodometry with introduction of molybdate as described in Section 3.3.1. Concentration of H_2O_2 stock solution was standardized based on spectrophotometric iodometry with $\varepsilon(I_3^-)$ = 25,800 M^{-1}·cm^{-1} at λ = 351 nm [14]. The concentrations of anions in real waters were determined with ion chromatography (Metrohm 930, Metrohm, Herisau, Switzerland) with the eluent composed of 3.2 mmol·L^{-1} Na_2CO_3 and 1.0 mmol·L^{-1} $NaHCO_3$. Dissolved organic carbon (DOC) was measured with a Vario TOC analyzer (Elementar, Langenselbold, Germany). Tap water was collected from the laboratory in Northeast Agricultural University. Surface water was obtained from Songhua River in Harbin City (45°48′13.59″ N, 126°32′5.88″ E) and ground water was collected from a ground water well in Harbin City (45°37′20.9″ N, 126°32′59.8″ E).

3. Results and Discussion

3.1. Unexpected Low Recovery Rate of H_2O_2 in Peroxide Mixture

The recovery rates of H_2O_2, PDS, and PMS in their separate solution with $NaHCO_3$-buffered iodometry (132 g·L^{-1} KI) were 87.03 ± 3.66%, 100.00 ± 0%, and 102.38 ± 0%, respectively (Table S1). Meanwhile, PDS and PMS were detected at 1.34 ± 0.09% and 99.44 ± 0%, respectively, with revised acetate-buffered iodometry in their solo solutions. The concentration of H_2O_2 could not be accurately determined with the revised acetate-buffered iodometry due to the indistinguishable end point of titration. This may be due to the low reaction rate of H_2O_2 with KI and the slow release of I_2/I_3^- under the condition of the acetic acid solution.

The almost complete detection of peroxides with $NaHCO_3$-buffered iodometry in their individual solutions and rare detection of PDS with revised acetate-buffered iodometry indicated that the feasibility of H_2O_2, PDS, and PMS in their mixed solution could be determined with the combination of revised acetate-buffered iodometry and $NaHCO_3$

buffered-iodometry with catalase (from a bovine liver) as the process of the multi-step iodometric determination described in Experimental Procedures. H_2O_2, in the mixed solution, was decomposed by catalase in Steps II and III. It was expected that the H_2O_2 concentration would be quantified by the difference of the peroxide concentrations titrated in Step I and Step II. The PDS concentration was the concentration difference between Step II and Step III. The PMS concentration was the value of the peroxide concentration determined in Step III.

The recovery rate of H_2O_2 was just 27.43 ± 0.34% in the mixture of 0.634 mmol·L^{-1} H_2O_2, 0.500 mmol·L^{-1} PDS, and 0.630 mmol·L^{-1} PMS (Scenario 1, Table S2). It was much lower than 87.03 ± 3.66% in the single H_2O_2 solution (Table S1). When the total peroxide concentration (0.559 mmol·L^{-1}) in the mixture was lowered down to less than the concentration of the single H_2O_2 solution (0.62 mmol·L^{-1}), the recovery rate of H_2O_2 in the mixed solution was still 30.00 ± 0% (Scenario 2, Table S2). Under the two conditions, PDS and PMS were well detected in the range of 98–100% (Table S2). It excluded the possibility that the depletion or insufficiency of KI led to the low detection of H_2O_2 in the mixture. Huang et al. (2018) also observed that the addition of H_2O_2, whether alone or together with PDS, eliminated the absorbance of the PMS solution at 352 nm in KI spectrophotometry, making the analytical method inoperable [12]. Furman et al. (2010) reported that PDS could react with H_2O_2 to generate $SO_4^{\bullet-}$ [6]. Meanwhile, Yang et al. (2018) found that PMS could react with H_2O_2 to generate O_2 [8]. In addition, the self-decomposition of PMS proceeded through a transition state of the intermediate complexes from its monovalent anion (HSO_5^-) and divalent anion (SO_5^{2-}), and then generated O_2 [18]. It is inferred that the low detection of H_2O_2 in the peroxide mixture may be due to the complexation of H_2O_2 with PDS and PMS in the mixture. Additionally, the complexation might slow down the reaction between peroxides and KI, resulting in the low overall conversion of peroxides into I_2/I_3^- in the mixture in Step I.

3.2. Elevating the Recovery Rate of H_2O_2 in Peroxide Mixture

3.2.1. Increasing KI Dosage

The effect of the KI dosage in $NaHCO_3$-buffered iodometry (Step I and Step II) on the detection of peroxides in the mixture was further studied. The overall recovery rate of PDS and PMS was 99–102% at KI dosage ≥ 132 g·L^{-1} (Figure 1a). The recovery rate of H_2O_2 increased with the KI dosage and reached 101.37 ± 3.29% at 300 g·L^{-1} KI. The increase in the KI dosage might accelerate the reaction between free peroxides and I^-, and consequently promote the dissociation of PDS/PMS and H_2O_2 complexes, thereby facilitating the reactions between peroxides and I^- to form I_2/I_3^- in the mixed solution. The high recovery rates of peroxides at 300 g·L^{-1} KI indicate the almost complete conversion of peroxides into I_2/I_3^-. Furthermore, the recovery rates of PMS and PDS were measured as 100.53 ± 0% and 102.89 ± 3.86%, respectively, with combing the $NaHCO_3$-buffered iodometry (300 g·L^{-1} KI) and catalase with revised acetate-buffered iodometry (Figure 1b).

3.2.2. Adding Molybdate

Molybdate was used as a catalyst in H_2O_2 determination with molybdate–iodide spectrophotometry [14]. Additionally, it might enhance the conversion of peroxides into I_2/I_3^- by accelerating the reaction between I^- and H_2O_2 and consequent dissociation of PDS/PMS and H_2O_2 complexes. Therefore, ammonium molybdate was added in the measurements of peroxides with $NaHCO_3$-buffered iodometry (molybdate–$NaHCO_3$-buffered iodometry). An orthogonal experimental design with three factors and three levels was used to determine the optimal parameters of molybdate–$NaHCO_3$-buffered iodometry with the H_2O_2 recovery rate in the mixture as the objective. The factors and levels are given in Table S3. The addition of molybdate increased the H_2O_2 recovery rate from 30.00 ± 0% with $NaHCO_3$-buffered iodometry (132 g·L^{-1} KI and t_1 = 15 min) (Table S2) to 94.76 ± 0.04% with molybdate–$NaHCO_3$-buffered iodometry (132 g·L^{-1} KI, 46 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, and t_1 = 15 min) (Table S4). The R value in Table S4 indicates

that H_2O_2 detection was affected by the factors in the sequence of KI dosage > molybdate concentration > reaction time. The optimal recovery rate of H_2O_2 in the peroxide mixture was obtained at the condition of 132 g·L^{-1} KI, 26 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, and t_1 = 5 min with molybdate–$NaHCO_3$-buffered iodometry. Under the suggested conditions, the recovery rate of H_2O_2 was 92.36%.

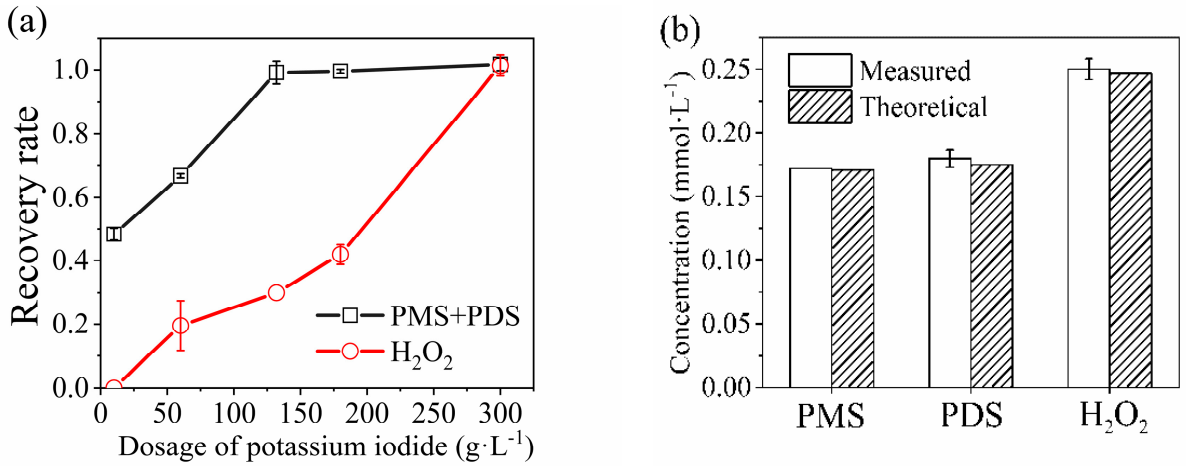

Figure 1. Determination of peroxides in their mixture with the combination of $NaHCO_3$-buffered iodometry and catalase at various KI dosages (**a**). Determination of PMS, PDS, and H_2O_2 with the combination of $NaHCO_3$-buffered iodometry (300 g·L^{-1} KI) and catalase with revised acetate-buffered iodometry (**b**). Conditions: [PMS] = 171 µmol·L^{-1}, [PDS] = 175 µmol·L^{-1}, and $[H_2O_2]$ = 247 µmol·L^{-1}.

3.3. Establishment of Multi-Step Iodometric Titration

3.3.1. Optimization of Operation Parameters in Molybdate–$NaHCO_3$-Buffered Iodometry

PDS and PMS were simultaneously detected with molybdate–$NaHCO_3$-buffered iodometry along with H_2O_2 in Step I or alone in Step II of multi-step iodometric titration. Therefore, the operation parameters in molybdate–$NaHCO_3$-buffered iodometry were further investigated, considering both H_2O_2 detection and the overall detection of PMS and PDS. The reaction time barely changed the recovery rates of peroxides at $t_1 \geq 15$ min (Figure 2a). The optimal dosages of KI were obtained at KI ≥ 132 g·L^{-1} (Figure 2b). The recovery rate of H_2O_2 stayed in the range of 94–98% at 18–46 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, with the highest value corresponding to 97.64% obtained at 26 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. Meanwhile, the addition of molybdate had almost no effect on the overall recovery rate of PDS and PMS at 0–46 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, which was stable around 100% (Figure 2c). Figures S1 and S2 also show that molybdate had little effect on the detection of the PMS or PDS single solution with molybdate–$NaHCO_3$-buffered iodometry. Thus, 132 g·L^{-1} KI and 26 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were added into the determination of peroxides with molybdate–$NaHCO_3$-buffered iodometry with t_1 = 15 min.

3.3.2. Calibration Coefficient for PMS Concentration Determination with Molybdate–$NaHCO_3$-Buffered Iodometry Referring to Revised Acetate-Buffered Iodometry

There existed a slight deviation in the PMS concentration measured with molybdate–$NaHCO_3$-buffered iodometry from that measured with revised acetate-buffered iodometry. Agreement between the two methods required a calibration coefficient. Additionally, the calibration coefficient was determined to be α = 1.04 via the linear regression analysis of PMS concentrations measured with molybdate–$NaHCO_3$-buffered iodometry versus those with revised acetate-buffered iodometry in the PMS theoretical concentration range of 5–1000 µmol·L^{-1} (Figure 3).

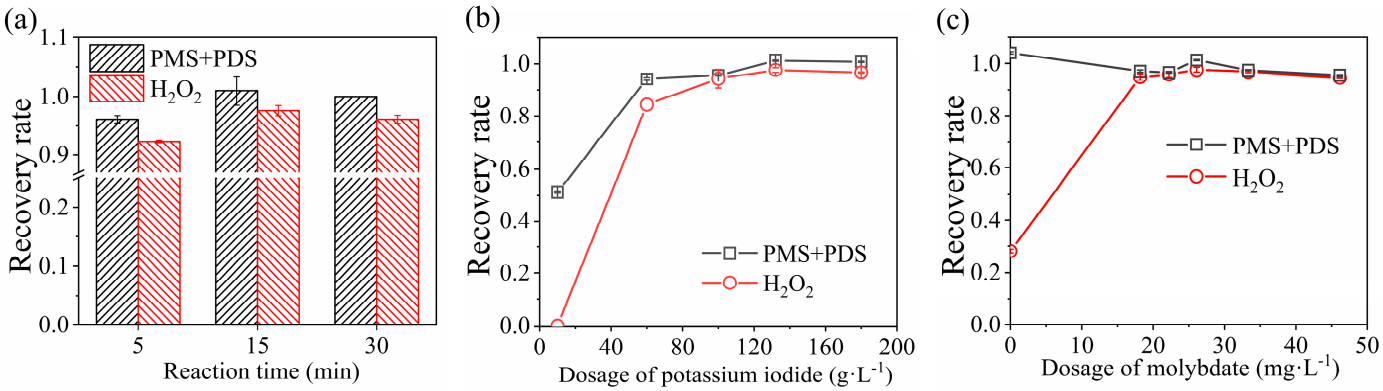

Figure 2. Recovery rate of H_2O_2 and overall recovery rate of PDS and PMS in peroxide mixture versus reaction time (**a**), KI dosage (**b**), and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ dosage (**c**). Conditions: [PDS] = 185 μmol·L^{-1}, [PMS] = 185 μmol·L^{-1}, [H_2O_2] = 225 μmol·L^{-1}, [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] = 26 mg·$L^{-1}$, [KI] = 132 g·$L^{-1}$, and t_1 = 15 min, unless otherwise stated in figures.

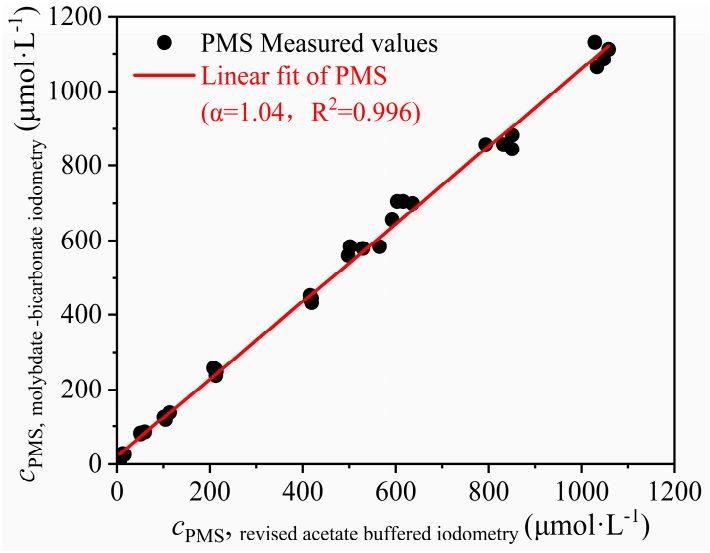

Figure 3. PMS concentrations measured with molybdate–$NaHCO_3$–buffered iodometry versus those with revised acetate-buffered iodometry.

3.3.3. Procedure of Multi-Step Iodometric Titration

Based on the above results, multi-step iodometry was established by combining catalase with molybdate–$NaHCO_3$-buffered iodometry and revised acetate-buffered iodometry. It was also checked that the phosphate buffer and catalase had little effect on the determination of PDS and PMS with molybdate–$NaHCO_3$-buffered iodometry or revised acetate-buffered iodometry (Figures S3–S5).

The multi-step iodometric determination of PMS, PDS, and H_2O_2 concentrations included three steps. Accordingly, the titrated sample ($3V_{sample}$) was divided into three equivalent parts (V_{sample}). Blank titration was performed by substituting Milli-Q water for the sample during each step. In Step I, the first part was treated with molybdate–$NaHCO_3$-buffered iodometry to obtain the total value of the three peroxide concentrations. In total, 13.2 g KI, 0.66 g $NaHCO_3$, and 15 mL 0.17 g·L^{-1} $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ stock solutions were added to the samples (V_{sample} = 100 mL) so that their concentrations in the solutions were 132 g·L^{-1}, 6.6 g·L^{-1}, and 26 mg·L^{-1}, respectively. The solutions were allowed to stand for 15 min, and then titrated with $Na_2S_2O_3$ (0.01 mol·L^{-1}) after adding 3.3 % (*v*/*v*) acetic acid until the yellow color of the liberated iodine was almost discharged. We added 1 mL of a 0.5% (*w*/*v*) starch indicator solution and titrated until the blue color was discharged. We denoted the consumed $Na_2S_2O_3$ volume after correction by blank titration as V_1. In

Step II, the second part of the sample was treated with catalase and molybdate–$NaHCO_3$-buffered iodometry to obtain the sum of PMS and PDS concentrations. We added 1 mL of a phosphate buffer (composed of 0.039 mol·L^{-1} HPO_4^{2-} and 0.070 mol·L^{-1} $H_2PO_4^-$) and 0.2 mL 5 g·L^{-1} catalase to the sample. The solution was allowed to remain for 5 min. Then, solid KI, $NaHCO_3$, and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ stock solutions were added. Additionally, the following titration process is similar to Step I. We denoted the consumed $Na_2S_2O_3$ volume after correction by blank titration as V_2. In Step III, the third part of the sample was treated with catalase and revised acetate-buffered iodometry to obtain the PMS concentration. A phosphate buffer and catalase were added to the sample, and the solution was left for 5 min as Step II. Then, 10 g·L^{-1} KI and 5 mL acetate buffer (0.98 mol·L^{-1} acetic acid and 0.017 mol·L^{-1} sodium acetate) were added. We let the solution stand for 2 min before titrating with $Na_2S_2O_3$. We denoted the consumed $Na_2S_2O_3$ volume after correction by blank titration as V_3. The concentrations of PMS, PDS, and H_2O_2 could be calculated as Equations (1)–(3).

$$c_{\mathrm{PMS}} = \frac{c_{\mathrm{Na_2S_2O_3}} \times V_3}{2 \times V_{\mathrm{sample}}} \quad (1)$$

$$c_{\mathrm{PDS}} = \frac{c_{\mathrm{Na_2S_2O_3}} \times (V_2 - \alpha V_3)}{2 \times V_{\mathrm{sample}}} \quad (2)$$

$$c_{\mathrm{H_2O_2}} = \frac{c_{\mathrm{Na_2S_2O_3}} \times (V_1 - V_2)}{2 \times V_{\mathrm{sample}}} \quad (3)$$

where $c_{\mathrm{Na_2S_2O_3}}$ is the concentration of the $Na_2S_2O_3$ titrant, V_{sample} is the sample volume in each step (100 mL), α is the calibration coefficient for PMS concentration determination with molybdate–$NaHCO_3$-buffered iodometry referring to revised acetate-buffered iodometry (1.04). c_{PMS}, c_{PDS}, and $c_{\mathrm{H_2O_2}}$ are the concentrations of PMS, PDS, and H_2O_2 in the sample, respectively.

3.4. Detection Limits and Detection Range of Multi-Step Iodometric Titration

The method detection level (MDL) was determined according to Equation (4) [19]. The MDLs of PMS, PDS, and H_2O_2 were 6.45 μmol·L^{-1}, 12.90 μmol·L^{-1}, and 10.60 μmol·L^{-1}, respectively, based on the determination of seven replicates containing 20.28 μmol·L^{-1} PMS, 20.20 μmol·L^{-1} PDS, and 29.64 μmol·L^{-1} H_2O_2. The concentrations of PMS, PDS, and H_2O_2 in the replicates were one to five times those of the respective MDLs, meeting the requirement of MDL determination.

$$\mathrm{MDL} = 3.14\delta \quad (4)$$

where δ is the standard deviation of seven replicates.

The detection range of multi-step iodometry was further evaluated under 15 scenarios of different individual peroxide concentrations covering 10–720 μmol·L^{-1}. The recovery rates of peroxides were in the range of 95–105% with standard deviation (SD) $\leq$ 7% at the individual peroxide concentration of 13–500 μmol·L^{-1} (Table 1). It indicates the measured concentrations are statistically close to the theoretical values. It should also be noted that the sample with PMS concentration <10 μmol·L^{-1} was not titratable although the single PMS solution was still detectable even at 5 μmol·L^{-1} (Figure 3). The higher threshold of the detectable PMS concentration in the peroxide mixture (about 10 μmol·L^{-1}) than in the single PMS solution might indicate the interference between peroxides.

3.5. Influence of Water Matrix on the Determination of Peroxides Coexisting in Sample with Multi-Step Iodometric Titration

3.5.1. Influence of pH

Detection of PMS, PDS, and H_2O_2 in the scenarios of a different sample pH was performed to explore the applicable pH range of multi-step iodometry. Figure 4 shows that the recovery rates of the three peroxides were all in the range of 95–105% at pH 3–11. There

is no obvious deviation between theoretical and experimental values. It indicates that the multi-step iodometry is applicable in simultaneous determination of PMS, PDS, and H_2O_2 concentrations in the sample pH range of 3–11.

Table 1. Recovery rates of peroxides in the mixture under various concentration scenarios measured in duplicate.

	H_2O_2			PDS			PMS		
Scenarios	**Theoretical Concentration (μmol·L^{-1})**	**Recovery Rate (%)**	**Standard Deviation (%)**	**Theoretical Concentration (μmol·L^{-1})**	**Recovery Rate (%)**	**Standard Deviation (%)**	**Theoretical Concentration (μmol·L^{-1})**	**Recovery Rate (%)**	**Standard Deviation (%)**
1	13.40	97.83	3.37	10.49	102.54	4.31	10.78	100.00	0.00
2	17.00	97.81	5.32	13.93	101.75	<0.01	14.17	99.28	0.00
3	20.10	104.99	4.50	15.74	101.60	5.74	16.17	98.87	0.00
4	28.20	100.40	3.23	20.54	103.76	4.99	21.88	101.47	2.08
5	70.50	103.60	1.44	51.35	100.42	2.04	54.70	98.82	1.66
6	137.05	99.31	1.77	101.36	98.02	1.65	103.59	102.47	1.31
7	252.71	97.64	0.89	184.88	101.55	1.76	162.56	100.71	1.38
8	320.93	98.82	1.57	255.00	101.00	1.78	253.40	100.63	0.00
9	718.57	99.85	0.31	545.65	105.00	0.47	503.60	99.53	0.45
10	507.00	99.65	0.63	52.33	103.44	4.32	47.96	99.99	0.00
11	55.86	97.31	5.72	52.33	96.00	6.22	527.59	100.30	0.42
12	55.86	103.03	<0.01	549.97	98.22	0.43	47.96	96.66	4.71
13	0.00	0.00	0.00	52.33	97.33	4.32	47.96	99.99	0.00
14	55.86	100.17	4.04	52.33	97.76	0.00	0.00	0.00	0.00
15	55.86	97.31	4.05	0.00	0.00	0.00	47.96	96.67	4.71

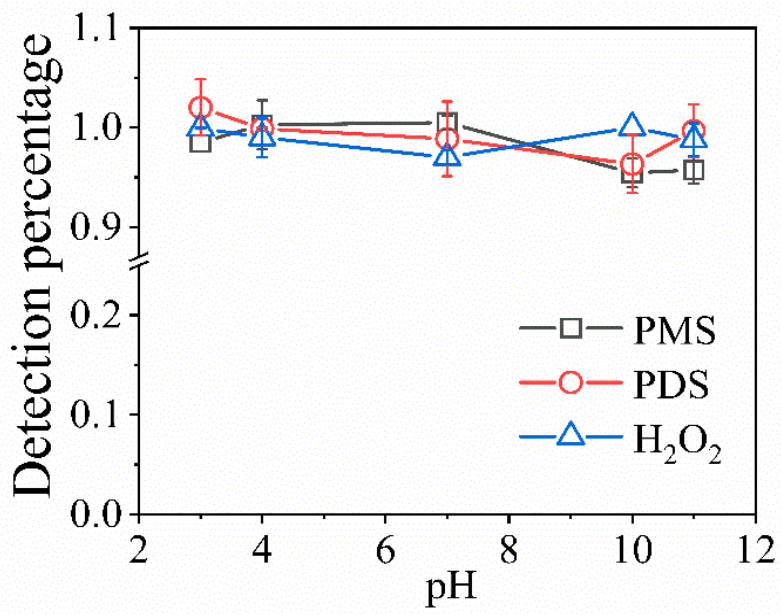

Figure 4. Influence of solution pH on the recovery rates of peroxides in mixture. Conditions: [PMS] = 155 μmol·L^{-1}, [PDS] = 159 μmol·L^{-1}, and [H_2O_2] = 324 μmol·L^{-1}.

3.5.2. Influences of Anions

The interferences of the anions and cations, commonly found in practical water bodies, were also investigated in determining peroxide concentrations with multi-step iodometry. This was assessed by the recovery rates of peroxides in the mixture by adding individual anions or cations at various regular concentrations. NO_3^-, Cl^-, F^-, and SO_4^{2-} showed a negligible effect on PMS and PDS determination that the recovery rates of PMS and PDS were in the respective ranges of 97–102% and 95–102% at the investigated anionic concentrations. The four anions all showed a negative effect on H_2O_2 determination. Recovery rates of H_2O_2 fell down to 92.16%, 92.29%, 92.54%, and 91.24% at the individual concentrations of 20 mg·L^{-1} NO_3^-, 150 mg·L^{-1} Cl^-, 1.5 mg·L^{-1} F^-, and 150 mg·L^{-1} SO_4^{2-}, respectively (Figure 5a–d). However, the recovery rates of H_2O_2 were all above 90%.

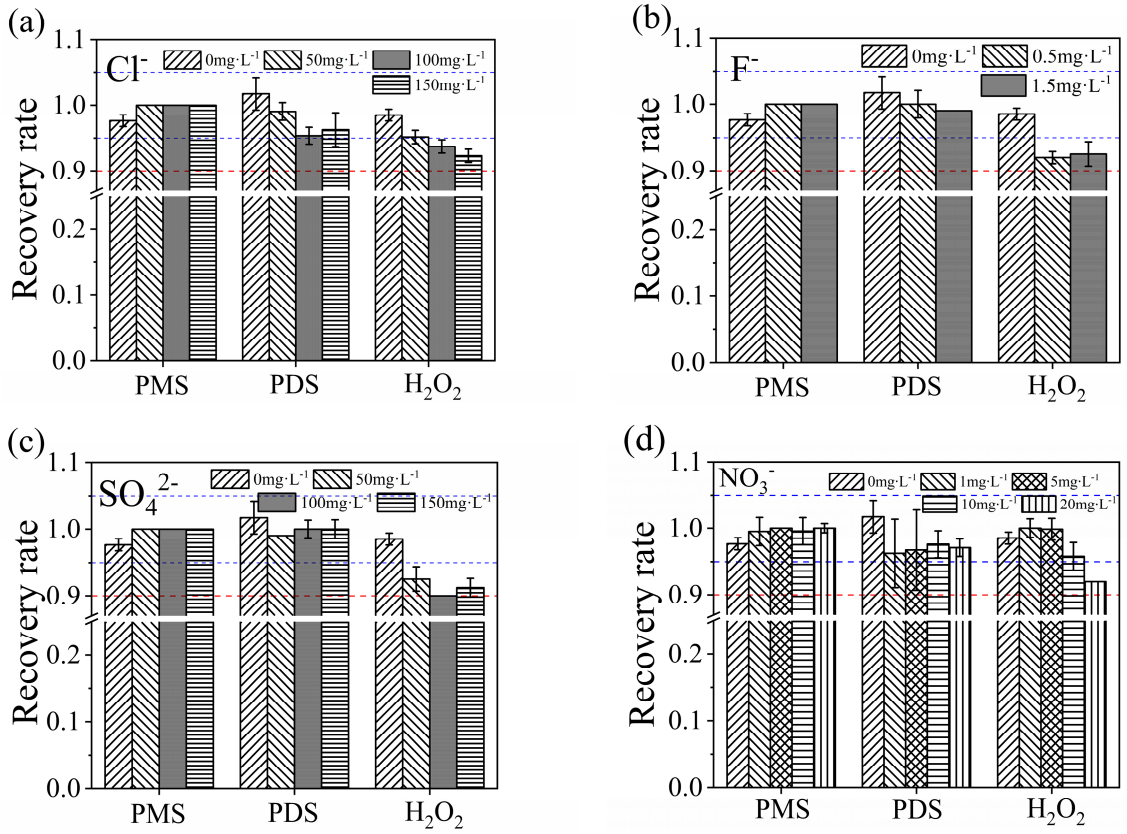

Figure 5. Influence of Cl^- (**a**), F^- (**b**), SO_4^{2-} (**c**), and NO_3^- (**d**) on the recovery rates of peroxides in mixture. Conditions: [PMS] = 160 μmol·L^{-1}, [PDS] = 167 μmol·L^{-1}, and [H_2O_2] = 243 μmol·L^{-1}.

Bicarbonate, a major constituent of alkalinity in practical water, is not discussed here. The quantity of $NaHCO_3$ (6.6 g·L^{-1}, 78 mmol·L^{-1}) added in the measurement process (Steps I and II) of multi-step iodometry was much larger than the concentrations in real waters (10–500 mg·L^{-1} as $CaCO_3$) [20–22]. Additionally, the influence of bicarbonate was therefore not considered.

3.5.3. Influences of Ca^{2+} and Mg^{2+}

Ca^{2+} and Mg^{2+} had a negligible effect on PMS and PDS determination but an obvious adverse effect on the detection of H_2O_2 (Figure 6a,b). The recovery rate of H_2O_2 decreased to 91.97 ± 1.78% at 1 mg·L^{-1} Ca^{2+}, and remained decreased to 90.71 ± 3.56% at 100 mg·L^{-1} Ca^{2+}. In the presence of Mg^{2+}, the recovery rate of H_2O_2 went down below 90% at 20 mg·L^{-1} Mg^{2+}, and was 86.93 ± 1.78% at 100 mg·L^{-1} Mg^{2+}. The addition of 100 mg·L^{-1} Ca^{2+} or 100 mg·L^{-1} Mg^{2+} lowered the pH value of the $NaHCO_3$-buffered sample to 8.03 and 8.22 (Table S5), respectively, from the original value of 8.35 in the presence of peroxides (c_{PMS} = 166 μmol·L^{-1}, c_{PDS} = 177 μmol·L^{-1}, and $c_{H_2O_2}$ = 222 μmol·L^{-1}). As discussed above in the scenarios of a different sample pH, the pH values of $NaHCO_3$-buffered solutions were in the range of 8.2–8.4, corresponding to samples containing peroxides at pH 3–11. It indicates that the slight pH decrease induced by Mg^{2+} addition would not be the origin for low H_2O_2 determination while the obvious decrease in pH induced by Ca^{2+} addition might be sound for the decreased recovery rate of H_2O_2 in the presence of Ca^{2+}. Ca^{2+} complexed or reacted with molybdate to form an insoluble precipitate [23]. Mg^{2+} might also complex with molybdate since it has a similar electronic structure with Ca^{2+}. This would lower the concentration of free molybdate and diminish the catalysis on the reaction between H_2O_2 and KI, resulting in the decreased conversion of peroxides into I_2/I_3^-. Furthermore, Ca^{2+} might react with H_2O_2 under alkaline conditions to form CaO_2 [24], reducing the formation of I_2/I_3^-.

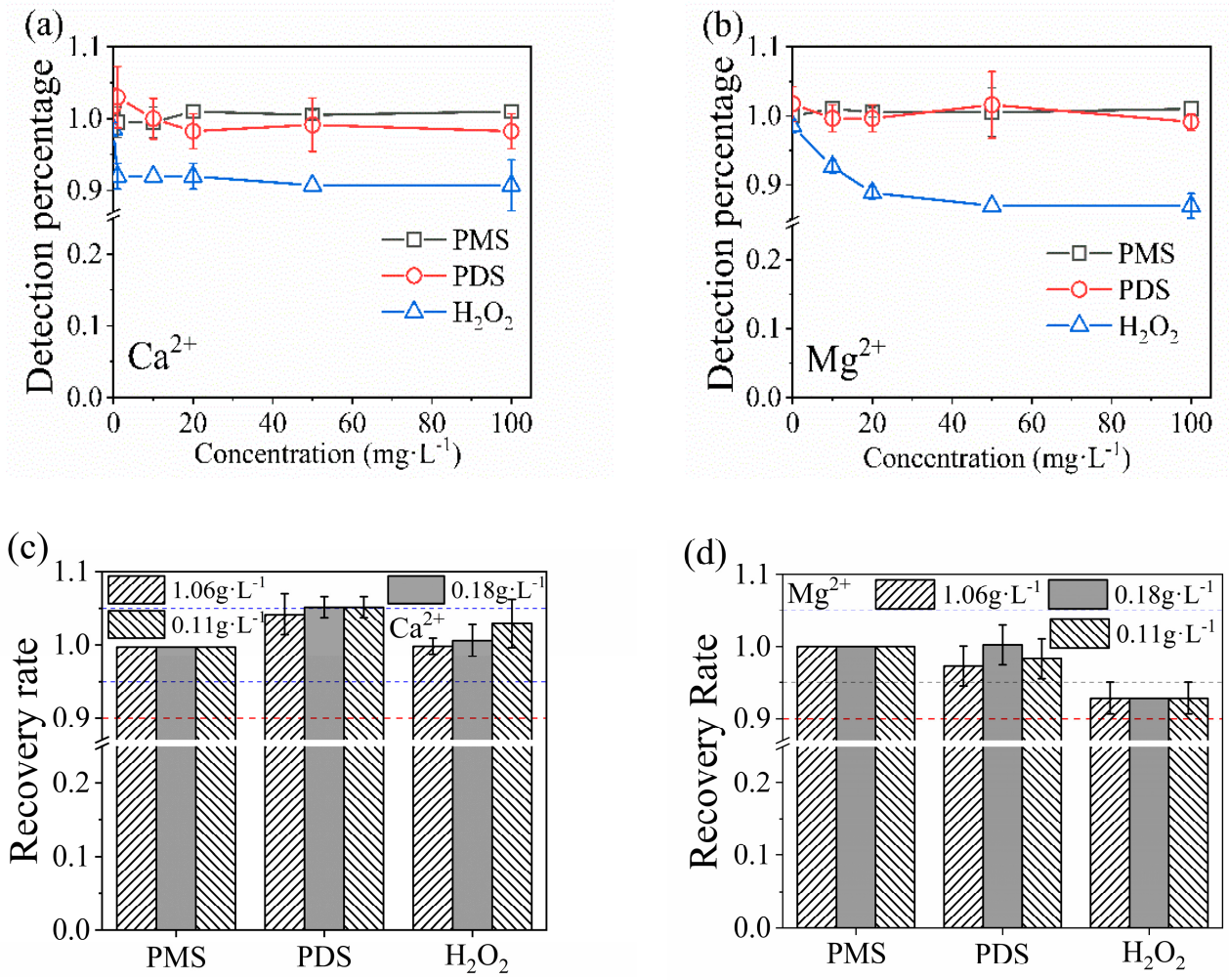

Figure 6. Influences of Ca^{2+} (**a**) and Mg^{2+} (**b**) on the detection of peroxides coexisting in sample. Effect of Na_2CO_3 addition on the detection of peroxides in the sample containing 100 mg·L^{-1} Ca^{2+} (**c**) or Mg^{2+} (**d**). Conditions: [PMS] = 163 μmol·L^{-1}, [PDS] = 185 μmol·L^{-1}, and [H_2O_2] = 253 μmol·L^{-1} for (**a**,**b**); [PMS] = 160 μmol·L^{-1}, [PDS] = 163 μmol·L^{-1}, and [H_2O_2] = 206 μmol·L^{-1} for (**c**,**d**).

Na_2CO_3, a common precipitant, was added to the sample (in Step I) as pre-treatment to precipitate Ca^{2+} and Mg^{2+}. The recovery rate of H_2O_2 was then lifted to 99.80 ± 1.09% by adding 1.06 g·L^{-1} Na_2CO_3 to the sample containing 100 mg·L^{-1} Ca^{2+}. It was stable within 95–105% even at the low Na_2CO_3 concentration of 0.11 g·L^{-1} (Figure 6c). The recovery rate of H_2O_2 was increased to around 93% by adding 0.11–1.06 g·L^{-1} Na_2CO_3 to the sample containing 100 mg·L^{-1} Mg^{2+} (Figure 6d). The addition of Na_2CO_3 led to an increase in pH in the $NaHCO_3$-buffered sample. The pH value was elevated to 8.59 or 8.83 by adding 1.06 g·L^{-1} Na_2CO_3 to the sample containing 100 mg·L^{-1} Ca^{2+} or Mg^{2+}, respectively (Table S5). The amelioration of H_2O_2 determination by adding Na_2CO_3 might be due to the increased pH of the titrated sample and the reduced free Ca^{2+} or Mg^{2+} to react with peroxides or occupy molybdate, which functioned as a catalyst for the reaction between H_2O_2 and I^-. At the Na_2CO_3 dosage of 0.11–1.06 g·L^{-1}, the recovery rates of PMS and PDS were all in the range of 95–105% (Figure 6c,d). The addition of Na_2CO_3 did not adversely obviously affect the determination of PMS and PDS concentrations. It can be seen that the multi-step iodometric titration, coupled with Na_2CO_3, could determine the peroxide concentrations with error ≤ 7% at the cationic concentration as high as 100 mg·L^{-1} for Ca^{2+} (equivalent to 250 mg·L^{-1} $CaCO_3$) or Mg^{2+} (equivalent to 417 mg·L^{-1} $CaCO_3$).

3.6. Choice of Buffer

$NaHCO_3$, in molybdate–$NaHCO_3$-buffered iodometry (Steps I and II in multi-step iodometry), was used to keep the solution under a neutral pH condition. When it was substituted by a 0.1 mol·L^{-1} phosphate buffer, PMS, PDS, and H_2O_2 were still well detected in the background Milli-Q water that the recovery rates of PMS, PDS, and H_2O_2 were 100.00 ± 1.41%, 100.00 ± 2.28%, and 96.90 ± 1.87%, respectively (Figure 7). However, in the sample containing 50 mg·L^{-1} Ca^{2+} or Mg^{2+}, the recovery rate of H_2O_2 decreased to 84.58 ± 4.12% or 82.39 ± 5.15% while PDS was detected as 92.76 ± 2.43% or 90.97 ± 0.10% (Figure 7). Ca^{2+} and Mg^{2+} might have precipitated with phosphate [25], and then decreased the pH of the titrated sample. Meanwhile, the two cations would also complex with molybdate and lower the effective molybdate concentration as discussed above. These factors might be the main reasons for the poor determination of peroxides. Thus, a phosphate buffer could be used as a substituent for $NaHCO_3$ in the background of Milli-Q water but not for samples containing Ca^{2+} or Mg^{2+} in molybdate–$NaHCO_3$-buffered iodometry (Steps I and II in multi-step iodometry).

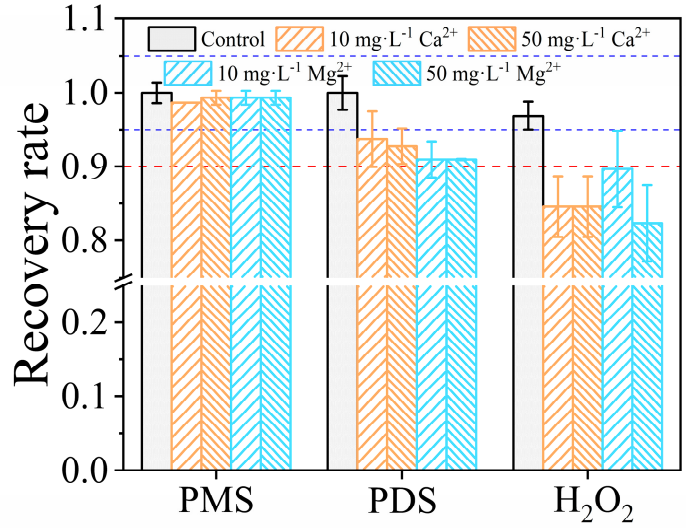

Figure 7. Recovery rates of peroxides in the sample with/without Ca^{2+} and Mg^{2+} with bicarbonate buffer substituted by phosphate buffer in molybdate–$NaHCO_3$-buffered iodometry. Conditions: [PMS] = 160 μmol·L^{-1}, [PDS] = 174 μmol·L^{-1}, and [H_2O_2] = 240 μmol·L^{-1}.

3.7. Applicability in Real Waters

To assess the applicability of multi-step iodometry in real water samples, determination of PMS, PDS, and H_2O_2 concentrations was performed in the background of tap water, surface water, and ground water. Figure 8 shows that the recovery rates of PMS, PDS, and H_2O_2 were 100.48 ± 2.53%, 100.56 ± 2.37%, and 101.66 ± 4.84% in tap water; 102.01 ± 2.82%, 99.95 ± 2.88%, and 104.56 ± 2.12% in surface water; and 92.67 ± 3.54%, 94.00 ± 1.27%, and 89.89 ± 0% in ground water, respectively. The recovery rates of the three peroxides in ground water were all lower than those in surface water and tap water. By comparing the water quality parameters of real waters (Table S6), the high hardness might be sound for the low detection of H_2O_2 in ground water while the low anion concentrations and near neutral pH would not be the original reason for the low detection of peroxides. It might be ascribed to the presence of reduced chemicals (such as Fe^{2+}) in ground water, which can consume peroxides. The recovery rates of the peroxides in the real waters were all around or above 90%, indicating the applicability of multi-step iodometry to determine the concentrations of PMS, PDS, and H_2O_2 simultaneously existing in natural water.

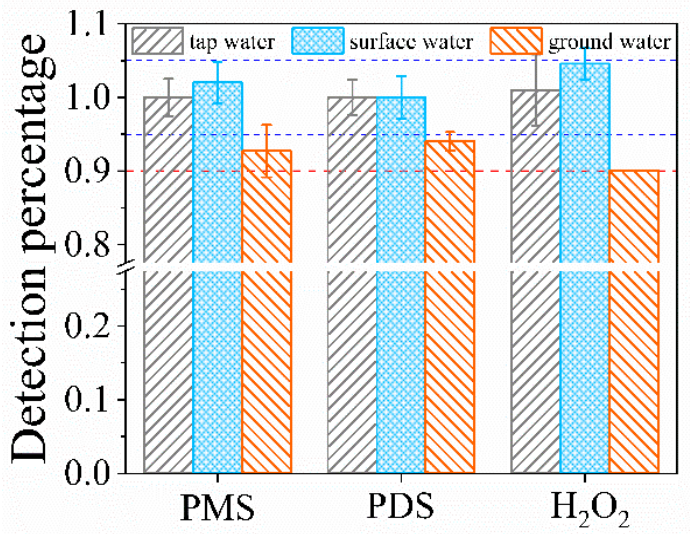

Figure 8. Detection of peroxides in real waters with multi-step iodometry. Conditions: [PMS] = 155 μmol·L^{-1}, [PDS] = 174 μmol·L^{-1}, and [H_2O_2] = 181 μmol·L^{-1}.

4. Conclusions

A simple multi-step iodometry was established to determine the concentrations of PMS, PDS, and H_2O_2 simultaneously existing in water. The recovery rate of H_2O_2 in the peroxide mixture was found to be unexpectedly low with the combination of $NaHCO_3$-buffered iodometry and catalase. Additionally, the low formation of I_2/I_3^- from the reaction between overall peroxides and I^- in the mixture could be enhanced by increasing the KI dosage (300 g·L^{-1}) or adding molybdate (26 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$)). Molybdate–$NaHCO_3$-buffered iodometry was then proposed with the optimized parameters as the reaction time of t_1 = 15 min, 130 g·L^{-1} KI, and 26 mg·L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. Furthermore, multi-step iodometry was established by combining molybdate–$NaHCO_3$-buffered iodometry and revised acetate-buffered iodometry with catalase. The multi-step iodometric titration could determine the concentrations of PMS, PDS, and H_2O_2 coexisting in the sample in the individual peroxide centration range of 13–500 μmol·L^{-1} with various ratios of peroxides, obtaining the recovery rates of 95–105% and a precision of SD ≤ 7% of two replicates. The recovery rates of PMS, PDS, and H_2O_2 were within 95–105% in the sample pH range of 3–11 and within 90–110% in the presence of Cl^- (0–150 mg·L^{-1}), F^- (0–1.5 mg·L^{-1}), SO_4^{2-} (0–150 mg·L^{-1}), or NO_3^- (0–20 mg·L^{-1}). The presence of 100 mg·L^{-1} Ca^{2+} and Mg^{2+} lowered the recovery rate of H_2O_2. The addition of Na_2CO_3 (0.11–1.06 g·L^{-1}) obviously alleviated the adverse effect of Ca^{2+} and Mg^{2+} and increased the recovery rate of H_2O_2. In the background of tap water, surface water, and ground water, the recovery rates of PMS, PDS, and H_2O_2 were all within 90–110%. It indicates multi-step iodometry would be applicable to the determination of peroxides coexisting in actual water bodies. Meanwhile, the multi-step iodometric titration is theoretically simple and easy to operate, with no special requirements on equipment.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15122190/s1, Text S1: Detailed statements on the procedures of multi-step iodometric determination. Text S2: General principle and detailed experimental procedure of revised acetate-buffered iodometry. Text S3: General principle and detailed experimental procedure of $NaHCO_3$-buffered iodometry. Figure S1: PDS concentrations titrated with $NaHCO_3$-buffered iodometry and molybdate–$NaHCO_3$-buffered iodometry. Figure S2: PMS concentrations titrated with $NaHCO_3$-buffered iodometry and molybdate–$NaHCO_3$-buffered iodometry. Figure S3: Influence of phosphate buffer and catalase on the detection of PDS with molybdate–$NaHCO_3$–buffered iodometry. Figure S4: Influence of phosphate buffer and catalase on the detection of PMS with molybdate–$NaHCO_3$-buffered iodometry. Figure S5: Influence of phosphate buffer and catalase on the detection of PMS with revised acetate-buffered iodometry. Table S1: Recovery rates of peroxides in separate

solutions with iodometric titration. Table S2: Determination of peroxide concentrations in the three peroxide mixtures by the coupling of revised acetate-buffered iodometry and $NaHCO_3$-buffered iodometry with catalase. Table S3: Levels of factors in orthogonal experiments of molybdate–$NaHCO_3$-buffered iodometry. Table S4: Results of orthogonal experiments. 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. Table S6: Water quality parameters of the real water samples. (References [5,13] are cited in the Supplementary Materials).

Author Contributions: M.W.: Data curation; Formal analysis; Investigation; Methodology; Writing—original draft. Y.Z.: Investigation; Formal analysis; Validation. S.Y.: Investigation; Validation. X.J. (Xinxin Jiang): Writing—review and editing; Validation. X.J. (Xue Jiang): Writing—review and editing. Z.X.: Writing—review and editing. Y.G.: Conceptualization; Data curation; Resources; Supervision; Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data will be made available on request.

Conflicts of Interest: The authors declare no conflict of interest.

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