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A Prolegomena to Chemiluminescence Determination of Manganese in Water

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Abstract

A new prolegomena to chemiluminescent determination of manganese in water was proposed. Initially Mn(II) is oxidized by periodate in acetate buffer with concentration not more 10mM and pH near neutral. Then intrinsic chemiluminescence of chemiexcited Mn(II) ions is registered in the reaction of Mn(IV) with lactic acid in the sulfuric acid solutions. The linear range of determination of manganese is 10-500 ppm. The possibility of manganese determination in presence of great excess of cobalt and iron is demonstrated.

Introduction

It is known that the consumption of water with high content of manganese adversely affects on the human health. The maximum admissible concentration of manganese in drinking water is 50μg /L (1μM) in European Union, US, Canada, Japan, Finland and 100mg/L in Chine, Australia, Russian Federation. High manganese content in groundwater, water springs and wells are typical for many regions. In this context, the task of rapid determination of manganese in natural waters in non-laboratory (field) conditions is important and interesting.

Manganese in the water may be determined by spectrophotometer, atomic absorption, neutron activation, luminescent, kinetic and other methods [1,2]. Kinetic method based on the catalytic oxidation of chromogenic substrate by potassium periodate in a neutral medium has detection limit about 10ng/L [3-5]. This is one of the most sensitive reactions for detection of manganese, however, a laboratory conditions are necessary. A simple way of manganese determination based on its oxidation in the acidic medium by $NaBiO_3$, $(NH_4)_2S_2O_8$ or KIO_4 to the permanganate, which has a characteristic vibronic spectrum at the 480-580 nm and a characteristic color. But the assessment of the concentration of permanganate based on color at concentration 1-2μM and lower is unreliable; it cannot be made without a high-quality spectrophotometer. A chemiluminescence (CL) analysis has the most simple and affordable instrumentation, and so the emergence of CL methods for determination of manganese looks quite natural. The most popular idea of CL determination of manganese (as well as of other transition metal ions) is based on their catalytic effect in reactions of chemiluminophores: like of luminol with H_2O_2 [6-10], luminol with KIO_4 [11-12], luminol with dissolved oxygen in a highly concentrated solution of NaCl [13], lucigenin with H_2O_2 [14], and lucigenin with dissolved oxygen [15]. Typically, not only the Mn(II) ion but other transition metal ions have catalytic effects on the CL reaction of luminol and lucigenin. Their interference is reduced to some level by various ways. In addition to the well-studied chemiluminophores as luminol and lucigenin, the multicomponent CL reagent based on 7,7,8,8-tetracyanoquinodimethan, didodecyldimethylammonium bromide and Eosin-Y was used for the determination of manganese [16-18]. Realization of this technique is quite complicated because it requires flow system. The use of inorganic CL systems was described in [19-20]. In these cases, Mn(II) was oxidizing to permanganate, which is determined in reaction with carbonate and siloxen.

The intrinsic CL of manganese ions is the most studied now [21]. CL is observed in the reduction reactions of manganese in oxidation states III, IV and VII at acidic medium. A catalytic effect of Mn(II) on the development of the CL reaction of permanganate with diacetyl was used in [22]. In this case, the manganese concentration was determined based on the time required to reach maximum intensity of CL. In this approach, many of organic and inorganic (Fe(II), Br^-) substances are the potential interferences. They quickly reduce permanganate to Mn(II) and, as a result, they have the same effect on reaction progress as Mn(II).

Reduction reactions of manganese ions in oxidation states III and IV in sulfuric acid solutions by lactic acid have high chemiexcitation yield of Mn^{2+} [23, 24]. In these reactions (in contrast to reactions of permanganate in the same conditions) CL observed immediately after mixing the reagents. Importantly, only some substances, besides manganese, possess CL in sulfuric acid solutions: U (IV) ions at oxidation by xenon difluoride [25], curium(IV) and terbium(IV) ions [26] at reduction, and siloxen at oxidation [27]. Potentially, these compounds may be active interferences for manganese determination based on its CL, but these possibilities can be ignored in most cases because of their rarity. Thus, the CL of manganese ions, which is observed in reduction reactions in sulfuric acid solutions, coupled with preliminary oxidation of Mn(II) to Mn(III) and Mn(IV) can be quite useful for manganese determination in natural water. This paper presents the physicochemical foundation of this approach.

Experimental

Reagents

The following chemicals were used: $MnSO_4 \cdot 5H_2O$, $CoSO_4 \cdot 7H_2O$, $FeSO_4 \cdot H_2O$ of the analytical grade, concentrated sulfuric acid of the special purity grade, lactic acid and glacial acetic acid of the reagent grade, standard sample solutions of manganese(II) ions: state standard sample 7266-96 (solution in 1M HNO_3) and 8056-94 (solution in 0.1M H_2SO_4), deionized water.

Apparatus

CL was recorded with a chemiluminometer assembled on the basis of a H7360-3 photon counting head (Hamamatsu, Japan), a CNT-202 counting unit (Spetspribor, Belarus), and a personal computer. Photo detector has sufficiently high sensitivity in the red spectral region (600-800 nm) for registration of light emitted in the reaction. A noise - background signal of photo detector was taken into account when finding of light-sum.

Spectral ratio was used as a spectral characteristic of CL [28]. It equals to the ratio of the amount of light measured during reaction in the presence and absence of light filter in optical channel. Filter (type KS-19) cuts off the light with the wavelength below 660 nm. Absorption spectra were recorded on a PerkinElmer Lambda 25 spectrophotometer. Manganese content in the $CoSO_4 \cdot 7H_2O$, $FeSO_4 \cdot H_2O$ was determined in The Central analytical laboratory of The Vernadsky institute on iCAP-6500 Duo ICP emission spectrometer (Thermo Scientific, UK).

Procedures

CL experiments were performed in 2mL polypropylene micro tubes. Prior to the experiment, portions (50µL) of a buffer solution, 20mM solution of KIO_4, and water with Mn^{2+} were added into micro tube. Within 1-2 minutes, the micro tube was placed in cuvette holder of chemiluminometer. During the experiment a CL was initiated by injection of 100 µL of a 0.05M lactic acid solution in 2.3M H_2SO_4 into microtube located in the cuvette holder in front of the photo detector using a lightproof dispenser. Experiments were conducted at 20-23°C.

Results and Discussion

Oxidation of Mn(II) by Potassium Periodate

Mn(III), Mn(IV) and permanganate anion are the products of the oxidation of Mn(II) by a periodate. It is known that the proportion between them may change over time and depends from the reaction medium and from the presence of ligands. In a strongly acidic medium main product is permanganate, its quantitative yield is obtained at heating the reaction mixture. This is a relatively slow autocatalytic process at room temperature [29].

The kinetics of the oxidation of Mn(II) by periodate was studied in [4,5,30,31] under conditions when the medium was close to neutral. According to [30] the main product (yield from 60 to 99%) is permanganate in ammoniac buffer at pH 4-9 and a concentration of buffer about 1M. But, according to [4,5,31], the main product is Mn(IV) in the presence of acetate (pH 4.2-5.8) and borate buffers. A rate constant of the reaction:

$$\mathrm{Mn\ (II)} + IO_4^- \xrightarrow{k} \mathrm{Mn\ (IV)} + IO_3^-,$$

is increased from 50 to 300 $M^{-1}s^{-1}$, when pH is increased from 5.5 to 7.5 [5]. And thus, the formation of Mn(IV) will occur during the mixing of the reactants at concentration KIO_4 -20mM (close to the solubility KIO_4 in water).

Kinetics of the CL reactions of Mn(III), Mn(IV) and Mn(VII) is quite different: Mn(III) and Mn(IV) have fast kinetics, permanganate has slowed one. The usage of reaction demands unambiguity in the product yield. But there is dramatic discrepancy between the data obtained in [30] and [4,5,31]: in one case there is a quantitative yield of permanganate, and in another permanganate not observed in the products.

The experiments indicate that ionic strength of solution is significant factor influencing on the formation of permanganate. Figure 1 shows the spectra of the products of oxidation Mn(II) by periodate in acetate buffer, pH 6.2. The vibronic spectrum in the range 480-580 nm, which is like identity card for permanganate anion, is absent in 10mM buffer, exists in 86mM buffer and is significantly enhanced in 29mM buffer with 0.66M NaCl.

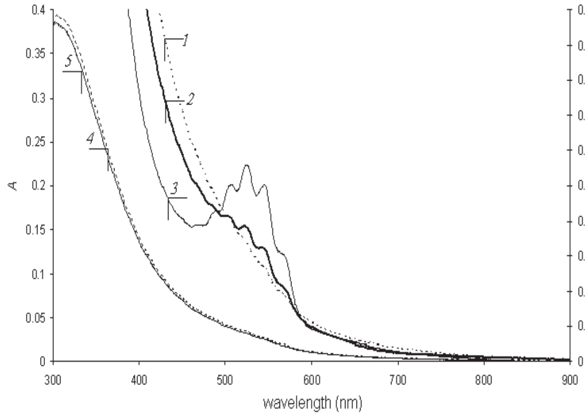

Figure 1: Spectra of the products of oxidation of Mn^{2+} by periodate in acetate buffer at a concentration of the buffer 10 (1, 4, 5), 86 (2) and 29mM with 0.66M NaCl (3) in a minute (5) and a half hour (1 - 4) after mixing of reactants. Initial concentrations: $MnSO_4$, 46µM; KIO_4, 10mM.

Hence, acetate buffer at concentration 10mM was selected for the medium of oxidation Mn(II) by periodate. Figure 1 (lines 4 and 5) shows the absorption spectra of the oxidation product at these conditions in a minute and a half hour after mixing of reactants. It can be seen that spectra changed quite slightly, so the oxidation product formed in less than one minute. The spectra agree with those obtained in [4, 32] for solutions of colloidal forms of Mn(IV). It is to be noted that solutions of the oxidation product possess of appreciable light scattering like other solutions of colloidal forms of Mn(IV) [24]. Based on these facts, it may be assumed that the reaction product is colloidal form of Mn(IV).

Chemiluminescence of Product in Sulfuric Acid Solutions of Lactic Acid

Figure 2 shows the kinetics of CL at mixing of solution of the oxidation product with solution of lactic acid in H_2SO_4. CL intensity has maximum during the mixing of the reactants. Variations in mixing have minimal effect on a value of a light-sum obtained during the reaction. A light-sum accumulated in the first 30 seconds (S30) was used as a parameter. Figure 3 (line 1) shows the dependence of S30 on Mn^{2+} concentration in aliquot of solution which was been taken for oxidation. The dependence is close to linear function at the Mn^{2+} concentration within 0.2-10µM that at lower limit is less and at upper limit is greater than maximum admissible concentration of manganese in drinking water. This means that the proposed approach is suitable for solving the problem.

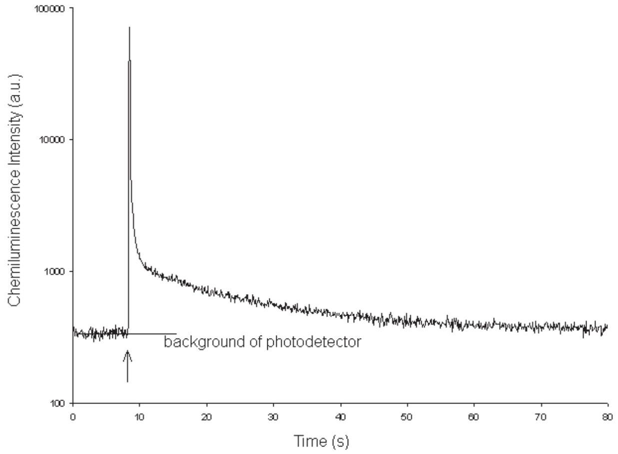

Figure 2: Kinetics of CL at mixing oxidation product with lactic acid solution in H_2SO_4. Mixing of the reactants is indicated by an arrow. Concentration of Mn^{2+} in aliquot is 10 µM.

In the study of the interference effects of Fe(II) and Co(II) to determine the manganese, we found that there is no such influence at their concentrations comparable to the concentrations of manganese. However, at much higher concentrations, CL has been detected even in the absence of manganese. Figure 3 (lines 2 and 3) shows the dependence of S30 on concentrations of $CoSO_4.7H_2O$ and $FeSO_4.H_2O$. In these cases, the CL has the same spectral and kinetic characteristics, as in the presence of manganese. That suggests that CL of manganese is registered, and manganese is present in used chemicals: $CoSO_4.7H_2O$ and $FeSO_4.H_2O$. Estimation of manganese content on the level of S30=10000 (Figure 3) is 0.002 and 0.0007 mol/mol for cobalt and iron chemicals, respectively. To test this assumption, the manganese content was determined by ICP-AES at Vernadsky institute, and was found that the manganese content in $CoSO_4.7H_2O$ and $FeSO_4.H_2O$ is 0.05 and 0.03%, respectively, or 0.0026 and 0.00093 and mol/mol. Hence, this data confirmed suggestion about manganese content in used chemicals. This means that the proposed approach is operated at 400 to 1000-fold excess of cobalt and iron, which is inaccessible to all the known methods of CL determination of manganese.

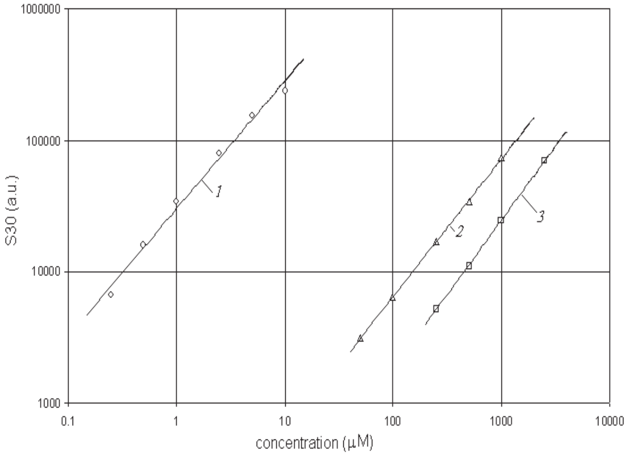

Figure 3: Dependence of S30 on concentration of Mn^{2+} (1), $CoSO_4$•$7H_2O$ (2) and $FeSO_4$•H_2O (3) in water.

Conclusion

A new prolegomena to chemiluminescent determination of manganese in water was proposed. The first step of this way is oxidation of Mn(II) by the periodate in acetate buffer with concentration not more 10mM and pH near neutral. A product of this reaction is colloidal form of Mn(IV). The second step is chemiluminescent reaction of Mn(IV) with lactic acid in H_2SO_4. Proposed scheme has great interference immunity to iron and cobalt content in matrix.

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