

Simulation Analysis on Determination Technology of Catalytic Discoloring Spectrophotometry of Photometric of Trace Selenium in Marine Organisms by Catalytic Discoloring

^{1,a} Tao Weiran

¹ Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering, Tianjin University of Science and Technology, Tianjin 300457, China
^a.16566345@qq.com

Keywords: Marine Organism ; Catalytic Spectrophotometric Determination of Trace; Simulation; Determination of Trace.

Abstract. As the improvement of people's living standard, the content of trace elements in food more and more attract the attention from people. In this paper, I integrate all the analysis situation from Catalytic Kinetic Spectrophotometry to trace elements in the food over the past ten years. Through the NH₃-NH₄Cl, Se has the inhibitory effect on fading reaction of hydrogen peroxide oxidation G, and develop one new method to stop fading spectrophotometric method and determine trace element Se, the best reaction conditions and the environmental water can be determined by experiments.

Introduction

Catalytic kinetic analysis has been widely used in the quantitative determination of trace elements, the character is high sensitivity (10 ~ 12g/mL), the equipment is simple, so the analysis of trace substances is very often to be seen in in high purity materials, high purity materials, biological samples and environmental samples. The catalytic kinetic spectrophotometric method is Kinetic analysis method which is based on the quantitative relation between the concentration of measurements reaction and reaction rate, taking spectrophotometer, fluorescence spectrophotometer as measurement means. It is different from the traditional thermodynamic methods, the unique of the reaction can measure, and therefore the scope of available chemical reaction can be expanded and the weakness of the traditional photometry can be overcome, making spectrophotometric method a new development. It is not only an important quantitative analysis method, but also one of the important tools to study on the mechanism of catalytic and kinetics reaction[1,5].

Compared with the thermodynamics method, the kinetics method has the following strong points: ① The selection in the reaction is very good, and is suitable for simultaneous determination in the mixture with properties that are very similar to each other (such as isomers and homologues in organic compound); ② The Catalytic Kinetic Analysis method has high sensitivity; ③ Expanding the scope of available chemical reaction, because it does not require a complete reaction, only needs the data at the very beginning of the reaction. ④ Because the dynamic analysis method takes the time as variable, which is convenient for the automation of the on-line use of computer and analysis equipments, and is easy to control the process, to determine the sample, to collect and process the data [6-7]. Se is an essential trace element for human beings, and plays an important role on the anti-cancer, anti-aging and other aspects. The main intake of selenium for human is from food, and marine organisms are publically recognized which is enriched if Se. Therefore, the determination of the Se content is very important.

Se is a rare element, the average abundance value in the earth's crust is 0.2mg/kg, the concentration in natural water is less than 1μg/L. As the continuous mining of antimony, continuous development and widely use of its products, antimony is omnipresent around us, but until now no evidence can approve that antimony is the essential elements for human, however, antimony and its compounds have been recognized as one of the toxic elements by American Environmental Protection Organization (USEPA) and the European Union (EU). The research shows that with different form, the toxicity of antimony is also different, Se (III) as a form of antimony with great toxicity has

attracted more and more attention from people, therefore, it is important to establish an effective, rapid, sensitive determination method to determine Se (III) in the environment. At present, the main testing method for Sb (III) including spectrophotometry, atomic absorption spectrometry, ICP-OES, neutron activation analysis, atomic fluorescence spectrometry, chemical luminescence method, electrochemical method. Compared with above analysis methods, catalytic spectrophotometric method has high sensitivity and good selectivity with simple equipment. So it attracts much attention from people. Especially in recent years, as the new chromogenic agent appears, surface active agent has been used in the solubilization, sensitization of color (fading), which makes the catalytic kinetic spectrophotometric method have a new breakthrough. Because the kinetic spectrophotometric method has high sensitivity, and instrument reagent is easy to have, and the operation is simple and fast, it is widely used in the analysis of trace Se in recent years [8, 9]. Observed from the experiments, Se can significantly catalyze the potassium bromate methyl violet fading reaction in acidic medium, so develop a new method to catalytic kinetic spectrophotometric determine trace Se, and it has been used in the determination Se content in kelp, oysters and other marine biological samples and which has good results.

Experiment

Instruments and reagents: We choose spectrophotometer with 200 type (Shanghai Unique Instrument Co. Ltd); acidity meter with pHS-3C type (Shanghai Precise Science Instrument Co Ltd); SYZ-B type quartz sub boiling distiller (Jiangsu Qinhu Glass Instrument Factory); FA2004N electronic analytical balance (Shanghai Precision Instrument Factory); SC-501 type super constant temperature water bath (Shanghai Jinping Instrument Company); Sb(III) standard solution: potassium antimony tartrate 0.2743g added into 250mL beaker, add into 20mL sulfuric acid, heating to dissolve, cooling, moved into 1000mL volumetric flask (with 160mL (volume ratio of 1: 1) sulfate inside), dilute it with water, shake, it will be standard stock solution with 0.10mg/mL, dilute to working solution with 5 μ g/mL; H₂O₂ solution (6%): put 30% of H₂O₂ 50mL to into volumetric flask in 250mL, dilute and constant volume. Solution orange G (OG): 1.0×10^{-3} mol/L; NH₃-NH₄Cl buffer solution: pH = 11.05; all the reagents are analytically pure, and water is two times distilled water.

The Experimental Method: We take two pieces tube in 25 mL, one with some Se inside (catalytic reaction, absorbance is A), another without Se (non-catalytic reaction, absorbance is A₀); and then separately add into 3 mL buffer solution, 1 mL KBrO₃ solution and 3 mL Methyl violet solution, dilute with water, shake, at the same time, put into water in 90°C with continuous temperature for 6 min, quickly take the colorimetric tube out, cooling with running water for 5 min, when it is the same as room temperature, compared with distilled water, at wavelength of 590 nm, measuring A₀ and A, calculate the catalytic reaction rate $\Delta A(A_0 - A)$.

Results and Discussion

Absorption Curve: The experiment method, measure absorbance A and A₀ of inhibitory system and non-inhibitory system in the range of 400 ~ 530nm, drawing a absorption spectrum, as shown in Figure 1, the maximum absorption wavelength of the two curves were located at 475nm, no displacement, but the peak increases, we can determine that Sb (III) has inhibitory effect on H₂O₂ oxidation on orange G fading, so we select 475nm as the measuring wavelength.

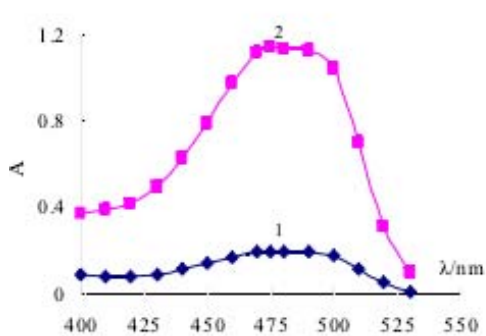


Figure 1 The absorption spectrum of methyl violet

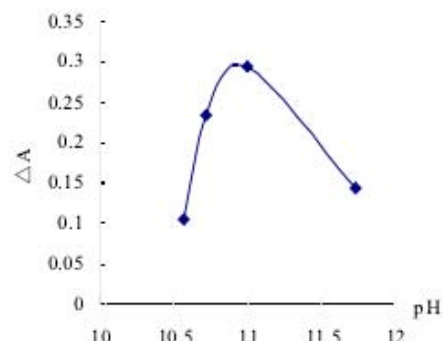


Figure 2 Effect from PH

The Choose of Experiment Conditions: After testing different reaction media, we find that when take the $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution as reaction medium, the system selectivity and sensitivity is better. compared different $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution with different acidity, the experimental results as shown in Figure 2, when pH is 11.05 ΔA value is with maximum number, so in the experiment, we choose the $\text{NH}_3\text{-NH}_4\text{Cl}$ 11.05 buffer solution with pH 11.05 to control the acidity of the system.

According to the test method, when test from changing the consumption of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution of pH 11.05 on sensitivity, the results shown in Figure 3, shows that when the buffer solution concentration is 0.10mL, ΔA is with maximum value, so in the experiment we use 0.10mL.

Effect of the Consumption of Orange G and H_2O_2 : Orange G is as indicators solution in the system, and has impact on the determination of the sensitivity and linear range. The results of the study on the effect of the dosage of sensitivity are shown in Figure 4, with the consumption of orange G increasing, the value of A, A_0 and ΔA are also increasing constantly, sensitivity of the system has been increased, but the absorbance is too big, and the accuracy decreased, in order to ensure the A value is around 1, we choose orange G in 1.80mL.

In this experiment we choose H_2O_2 as the oxidant, according to the test method, we make the test with 6% H_2O_2 (Figure 5), the results show that with the increase of the consumption, the ΔA is also increasing and when it is around 4.00 ~ 6.00mL, ΔA is with the maximum value and stable, so in the experiment, we choose 5.00mL.

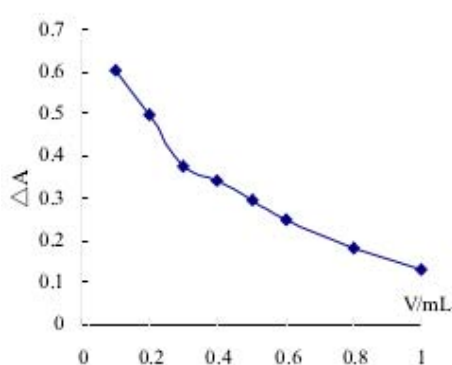


Figure 3 Influence of dosage of $\text{NH}_3\text{-NH}_4\text{Cl}$

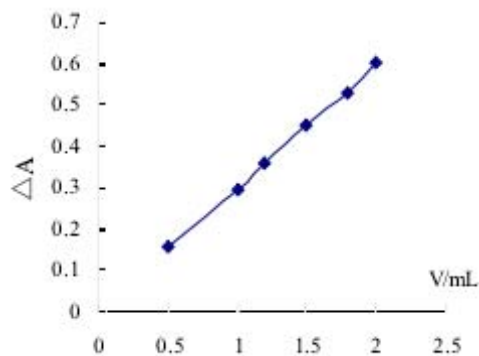


Figure 4 Effect from the indicator

Effect from Reaction Temperature: Fixing the other conditions during the experiment process, only change the reaction temperature, determining of ΔA value under different temperature, the results are shown in Figure 6, when the temperature is lower than 50 C, the fading reaction of inhibition system and non-inhibitory system are not obvious, so we can use running water to cool and stop the reaction. When the temperature is higher than 50 C, with the increasing of the temperature Delta ΔA value is gradually increasing, in order to get a higher sensitivity and convenient to operate, we choose boiling water to heat and running water to stop the reaction.

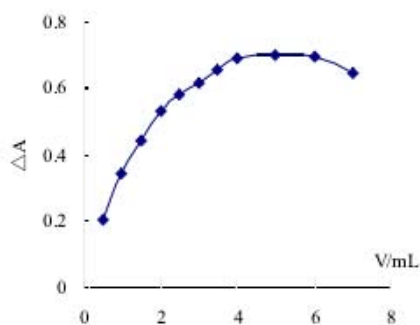


Figure 5 Effect from oxidant

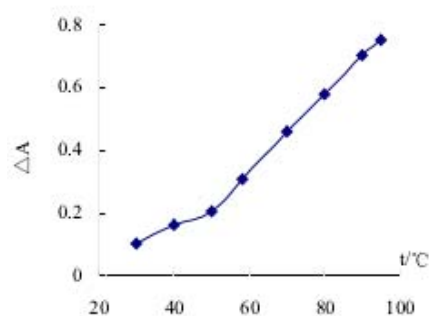


Figure 6 Effect from reaction temperature

Working Curves and Detection Limits of the Method: Under the selected experiment conditions, when the the concentration of Se is in 0~8.0 $\mu\text{g L}$ and it has good linear relationship with ΔA , the regression equation was: $\Delta A=0.0069C_{\text{se}}(\mu\text{g L})+0.0075(r=0.9983)$. According to $b=1\text{ cm}$, $\Delta A =0.001[2]$, we can get that this method for the detection limit of Se is 0.14 $\mu\text{g L}$, equivalent to fluorescence spectrophotometry of DAN.

Influence and Elimination of Coexisting Ions: The determination of 0.1 $\mu\text{g Se}$ also tests some effect from some common ions. The results showed that: when the relative error is within $\pm 5\%$, 5000 times of K^+ , Na^+ , Ca^{2+} , NO_3^- , Cl^- , 2000 times of Mg^{2+} , Zn^{2+} , Ni^{2+} , SO_4^{2-} , 1000 times of Al^{3+} , Co^{2+} , Ti , Mo , Se , 200 times of Mn^{2+} , 100 times of NO_2^- , I^- and 10 times of Fe^{3+} , Cu^{2+} does not influence the determination. When take the natural sea water instead of distilled water in the experiments, we further analyzes the comprehensive effect of coexisting ions. Table 1 show that the high concentration of Fe^{3+} , Mn^{2+} and Cu^{2+} in the marine environment has serious interference on the experiment. In the 6 mol HCl medium, when methyl isobutyl ketone (MIBK) has been extracted, the recovery rate is 96.8%, shows that the influence from coexisting components are effectively eliminated.

Table 1 Effect from sea water to the determination of Se

System	Distilled water	Sea water	MIBK extracted sea water
ΔA	0.062,0.067,0.063 (0.064,4.1%)	-0.070,-0.055,-0.078 (-0.068%,17%)	0.064,0.061,0.058 (0.061,4.9%)

Analysis on the Samples: Water samples needs to be filtered quickly by the filter paper, to remove the insoluble impurities, absorbed filtrate needs to be separated by cation exchange resin to separate and remove Co^{2+} , Cu^{2+} , Fe^{3+} and other cation, take exchange liquid 30mL, and add into 6mol/L with 3mL, 10% sulfate with 4.5mL, heating in a boiling water for 30min, reduce the Sb (V) in water to Sb (III), after cooling, use deionized water to constant volume to 50mL. Get processed solution with 10mL, measuring according to experiment method, and do the recovery experiments at the same time, results are shown in table 2.

Table 2 analytical results of sample antimony (III) and recoveries rate(n=6)

Samples	Determination value of water ($\mu\text{g/mL}$)	Determination value of solution($\mu\text{g}/10\text{mL}$)	Added scalar ($\mu\text{g}/10\text{mL}$)	Measurement results ($\mu\text{g}/10\text{mL}$)	Recovery rate (%)	RSD (%)
Spring water	0.0250	0.150	1.0	1.109	95.9	3.4
River water	0.0541	0.324	1.0	1.302	97.8	2.5

Processing of Biological Samples Before the Treatment: Experiments show that, under selected conditions, Se can catalyzed potassium bromate oxidation of methyl violet fading, other forms of Se do not have this function. Therefore, to determine the total Se in biological samples, we need to separate them at the same time, transfer all the form into Se. Wet digestion is a commonly used decomposition method. Considering the recovery rate and sensitivity, mixed acid $\text{HNO}_3\text{-HClO}_4$ is a perfect digestion solution, and only can transfer the organic Se and Se^0 oxidize to Se and Se will not

change. Therefore, the sample digested by mixed acid HNO₃-HClO₄, still need to further oxidize to Se.

This paper we choose to soaked samples with nitric acid for the whole night, when most organic matter has been decomposed, add into mixed acid HNO₃-HClO₄ (4: 1) with low temperature (<200 C) to heat and decompose. Test organic Se with containing 0.1 g Se according to this, the recovery rate is in 95.2% ~ 99.7%, shows a complete conversion, and no volatilization loss. In order to simplify the operation, in this paper we adopts the same medium with MIBK extraction and purification of digestion solution. Experiment shows that: in 6 mol L HCl medium, use boiling water to heat for 10 min, the conversion rate is 96%; Heating above 30 min, Se will have a loss, so in this paper we choose a boiling water for 20 min.

Conclusion

In buffer solution of NH₃-NH₄Cl medium, Se has the inhibitory effect of on hydrogen peroxide oxidation orange G fading reaction, and establish a new method to determinate Fading Spectrophotometric method of trace Se, the best reaction conditions are determined by experiments, and the environmental water samples were determined.

References

- [1] Lai Haitao, Bai Yue. Using Methylene Blue Catalytic Kinetic Spectrophotometric for the Determination of Trace Selenium in foods (IV) [J]. Food and Fermentation Industry, 2006,32 (2): 102-105.
- [2] Dong Binggang, Liu Yu, Sang Demin. Determination of Trace Selenium in food by Spectrophotometry [J]. Trace Elements and Health Research, 2006,23 (4): 43-46. 2006,23 (4): 43-46.
- [3] Ni Xiuzhen, Wang Xiaojun. Determination of Trace Iodine by Sixteen Alkyl Bromide Catalytic Kinetic Spectrophotometry Method in Food [J]. Food Science and Technology, 2008,33 (5): 226-228.
- [4] Zhang Dong, Yu Ping, Zhao Guangsheng. Determination of Trace Two Aniline by Inhibitory Catalytic Kinetic Photometry [J]. Physical and Chemical Inspection (chemical), 2007, 43 (8): 680-681.
- [5] Chen Yahong, Wu Zhihao, Luo Danming. B Determination of Hemoglobin Bleaching [J]. Chemical Reagent, fading method 2007, 29 (3): 151-153
- [6] Song Xuesheng. Orcein Fading Spectrophotometric method for the determination of trace copper [J]. Metallurgical Analysis, 2006, 26 (3): 62-64.
- [7] Chen Yujing. The Determination of Trace Cr(VI) of Catalytic Zinc Enrichment Separation of Corn by Glutene enrichment Catalytic Spectrophotometric Method [J]. Analysis Laboratory, 2006, 25 (2): 66-68
- [8] Fang Xia. Determination of Trace Formaldehyde in beverage by Catalytic kinetics of potassium bromate - azuro I photometric system [J]. Food and Science, 2009,30 (6): 199-202.
- [9] Cai Xiangwen. Determination of Trace Copper in Food by spectrophotometry [J]. Guangzhou chemical, 2009,37 (4): 141-144..
- [10] Wang Hongfu, Determination of Trace Chromium Cr (VI) -H₂O₂-4,5- Dibromo Fluorescein System for Catalytic Spectrophotometric Method, [J]. Metallurgy 2007, 27 (6): 55-57