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Rapid determination of Cl^- by light-absorption ratio variation approach using Cl^-–eosin Y–Ag^+ adsorptive precipitation

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Abstract

The adsorptive precipitation between eosin Y (EY) and AgCl colloids at pH 3.73 caused the sensitive color change of the solution. The reaction mechanism between EY and AgCl was analyzed and this reaction was used for determination of Cl^- in trace level by the light-absorption radio variation approach.

Keywords: Determination of chloride; Eosin Y; Adsorptive precipitation; Light-absorption ratio variation approach

It is well known that Cl^- concentration has been increasing in ground and surface water over the last decades due to human activities [1]. High concentration of Cl^- may destroy metal pipes and buildings, and has bad effect on human as well. There are some traditional methods to choose for determination of Cl^-, such as gravimetric method, titration method and electrochemical process. Recently, some new methods were developed, for instance capillary electrophoresis [2], isotope dilution mass spectrometry [3] and epithermal neutron activation [4]. Ion chromatography (IC) is most usually employed to determine the anions of chlorine, bromine and iodine [5]. However, the big devices and expensive monitoring cost limit their applications in some special conditions, for example field or *in-situ* analyses. In this work, eosin Y (EY) named chemically tetrabromofluorescein was found to sensitively interact with the growing AgCl particles at pH 3.73, similar to the Fajans reaction [6]. The color change of the solution occurred in the presence of AgCl. This ternary reaction combined with light-absorption ratio variation approach (LARVA) was used to determine Cl^- in natural water.

Effects of pH and Ag^+ concentration on the absorption spectra of the ternary reaction among EY, Cl^- and Ag^+ were carried out (Fig. 1). The peak and valley wavelengths of the reaction solution are located at 554 and 518 nm from Fig. 1A (Model Lambda-25, PerkinElmer Instruments, USA) with a spectrophotometer. The peak–valley interval becomes great with increase in acidity of solution. Possibly, the growth of AgCl particles becomes rapid with decrease of the acidity so that EY cannot be adsorbed immediately. From curves in Fig. 1B, the peak–valley interval approaches a constant maximum when the mass concentration of Ag^+ is over 40 times that of Cl^-. Thus, Cl^- could be precipitated completely. In this work, pH 3.73 buffer and 40 μg/mL Ag^+ were added. From curves in Fig. 2A, the different addition

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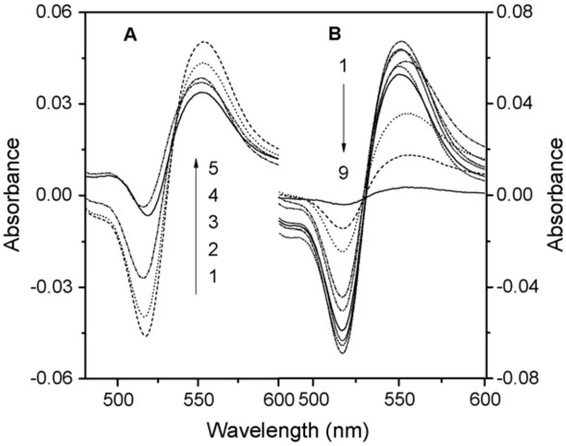

Fig. 1. Absorption spectra of reactions of Ag^+ (40.0 μg/mL), Cl^- (1.00 μg/mL) and EY (0.010 μmol/mL) at various pHs (A) and concentration of Ag^+ (B). A1–A5: pH values 3.73, 3.95, 4.52, 5.07 and 1.0. B1–B9: the absorption spectra of the solution containing Cl^- (1.0 μg/mL), EY (0.010 μmol/mL) at pH 3.73 and different concentration of Ag^+: 1.0, 3.0, 5.0, 10.0, 15.0, 50.0, 30.0, 20.0 and 40.0 μg/mL.

subsequence of three reactants affects the absorption spectra of the product, but the one of Cl^-–EY^{2-}–Ag^+ added in turn gives the highest reaction sensitivity (Fig. 2A, curve 1). In the addition subsequence Cl^-–Ag^+–EY^{2-}, AgCl particles are formed before the EY is added. EY is adsorbed only on the outer surfaces of the AgCl particles by colloidal electric double layers. Thus, only a slight light-absorption change is observed from curve 3. In the addition subsequence Ag^+–EY^{2-}–Cl^-, AgCl particles are formed rapidly when the Cl^- is added because the Ag^+ concentration (40 μg/mL) remained high. Thus, there is not enough time for EY to be adsorbed on the growing AgCl particles. In the first subsequence, only 1.00 mg/L Cl^- remained. When Ag^+ is added drop by drop, the Ag^+ concentration rises gradually from 0 to 40 μg/mL. The formation of AgCl particles becomes slow so that EY is adsorbed efficiently by the growing particles; moreover, it is embedded into them. To demonstrate the *in-situ* inclusion of EY, The precipitates were separated by centrifugation at 12,000 rpm (Model TG16-WS, Hunan Xiangyi Instruments, China), *N*,*N*-dimethylformamide (DMF) [7] was added to remove all the EY molecules adsorbed to the outer surfaces of the AgCl particles and ammonia solution was then added to dissolve them, releasing any embedded EY. The absorption spectra of the final ammonia solutions of the particles are shown in Fig. 2B. Comparison of curves 2 and 3 indicates that there is more EY in the first addition subsequence. From the chemical structure of EY, we know that EY anions can bind to Ag^+ in the double layer of AgCl colloids by electric interaction. Besides, the four –Br substitute groups of EY have the

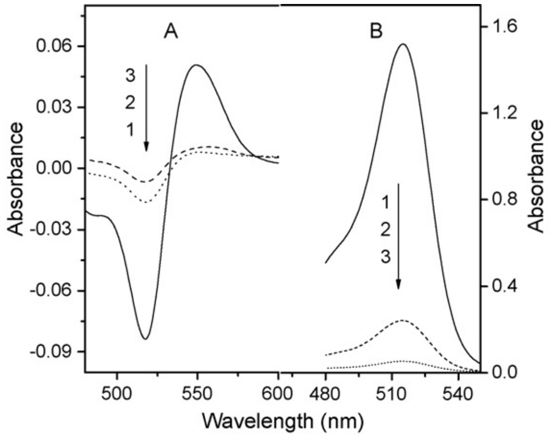

Fig. 2. Absorption spectra of reactions of Ag^+ (40.0 μg/mL), Cl^- (1.00 μg/mL) and EY (0.0100 μmol/mL) at pH 3.73. A1: the addition subsequence Cl^-–EY^{2-}–Ag^+. A2: Ag^+–EY^{2-}–Cl^- addition subsequence. A3: Cl^-–Ag^+–EY^{2-} addition subsequence. B1: EY (0.0100 μmol/mL) solution, B2: the absorption spectrum of the AgCl particles–ammonia solution formed in the first addition subsequence and then treated with DMF, B3: the same as B2 but in the third addition subsequence.

Table 1
Standard regression equation parameters and LOD for Cl^-

Line	EY (μmol/L)	Linear range Cl^- (mg/L)	p[a]	q[a]	R[b]	σ[c]	LOD[d] (mg/L)
1	1.00	0.10–0.40	0.117	−0.014	0.9973	0.013	0.03
2	1.50	0.15–0.60	0.0730	0.0060	0.9971	0.013	0.05
3	2.00	0.03–0.80	0.0575	−0.018	0.9976	0.0023	0.01
4	3.00	0.20–1.00	0.0427	−0.020	0.9956	0.0090	0.06

[a] The symbols p and q are the slope and intercept of the regression lines.
[b] Linear correlation coefficient.
[c] Standard deviation of 10 replicated blanks.
[d] Calculated by LOD = $3\sigma/p$.

strong affinity with Ag^+ according to the hard and soft acids and bases proven by Lewis in 1923. Thus, EY is embedded in the AgCl particles. The effect of temperature and electrolyte indicate that the absorbance is almost constant with different quantities of 2 mol/L $NaNO_3$, but decrease with the temperature increment. Therefore, this method is still suitable for direct determination of Cl^- in sea water, spring water or other environmental water.

The LARVA was proposed earlier with higher selectivity and sensitivity [8]. It is established on the basis that a sensitive variation of the light-absorption ratio of a reaction between a chromophore and a detected component in trace level. The sensitivity of LARVA increases as over 10 times as ordinary spectrophotometry. Using this color reaction, we can determine Cl^- in water by LARVA. The reaction among three reactants is complete in 10 min and the absorbances remain constant for at least 1 h.

The procedure detail was followed: a known volume of Cl^- sample, 1 mL of 1 mol/L sodium fluoride, 0.1 mL of pH 3.73 buffer and 0.2 mL of 0.10 mmol/L EY were added into 10 mL flask. Diluted to 10.0 mL and mixed well. 0.66 mL of 5.63 mmol/L $AgNO_3$ was added. After mixed for 10 min, the absorbances ($A_{554\,\mathrm{nm}}$ and $A_{518\,\mathrm{nm}}$) were measured at 554 (λ_2) and 518 nm (λ_1) against water. Simultaneously, a reagent blank without Cl^- was prepared and then measured $A^0_{554\,\mathrm{nm}}$ and $A^0_{518\,\mathrm{nm}}$. Thus, the light-absorption ratio variation (ΔA_r) of the product is calculated by the relation $\Delta A_r = A_{554\,\mathrm{nm}}/A_{518\,\mathrm{nm}} - A^0_{554\,\mathrm{nm}}/A^0_{518\,\mathrm{nm}}$. Plots ΔA_r vs. C_{M0} is linear where C_{M0} is the Cl^- concentration. Four standard series of Cl^- were prepared and their regression equations are given in Table 1. All plots ΔA_r vs. C_{M0} have good linearity. The limit of detection (LOD) of Cl^-, defined as the blank values plus three times of the standard deviation of 10 replicated blanks, was calculated and given in Table 1. A lower LOD could be achieved at a lower concentration of EY. However, a too low concentration of EY will cause the increase of fraction of noise of the optical signal. Thus, the precision of replicated blanks test will go poor at a too low concentration of EY. A suitable concentration of EY should be selected for the lowest LOD of Cl^-. In the present work, 2.00 μmol/L EY was added and the corresponding LOD is 0.01 mg/L Cl^-. Thus, the recommended method is sensitive.

None of the following species affect direct determination (error less than 5%): 40 mg/L SO_4^{2-}; 30 mg/L NO_3^-; 10 mg/L Mg^{2+}, NH_4^+ and Ca^{2+}; 2 mg/L Zn^{2+}; 1 mg/L Fe^{2+}, Ba^{2+} and PO_4^{3-} and 0.2 mg/L Mn^{2+}, Cu^{2+}, Al^{3+} and SO_3^{2-}. Sodium fluoride is used to mask Fe^{3+} in samples.

The quantitative detection of Cl^- in three samples was carried out: tap water, West Lake water and Tai Lake water. Their solutions were prepared, reacted and then measured according to the recommended procedures. The analytical

Table 2
Determination of Cl^- water samples

Sample from	Cl^- added (mg/L)	Cl^- found (mg/L)	Cl^- found in sample (mg/L)	R.S.D. (%)	Recovery (%)
Tap water	0	0.617 ± 0.040	6.17[a], 5.58[b]	0.60	104
	0.1	0.721			
West Lake	0	0.455 ± 0.21	4.55[a], 4.44[b]	4.6	101
	0.3	0.757			
Tai Lake	0	0.584 ± 0.18	5.44[a], 5.78[b]	3.1	97.7
	0.2	0.779			

[a] Average of three replicate determinations.
[b] One determination by IC.

results were given in Table 2. The recovery is between 97.7 and 104% with the relative standard deviation (R.S.D.) less than 4.6%. The three samples were measured by IC (Model ICS-1000, Dionex, USA) as well and the result is matched well. Therefore, this method is accurate.

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