Determination of aluminum ion at ng mL^{-1} level in natural water using trimethoxyphenylfluorone by light-absorption ratio variation approach

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Abstract

The complexation between trimethoxyphenylfluorone (TMPF) and Al^{3+} is sensitive at pH 10.98 in the presence of both cetyltrimethylammonium bromide (CTAB) and acetone. CTAB was used as a sensitizer to bind TMPF and acetone as a stabilizer to inhibit the oxidation of the TMPF-Al complex. The masking reagent, ethylenediaminetetraacetic acid (EDTA) is helpful to improve the selectivity of the complexation. The spectral correction technique was applied to characterize the Al-TMPF complex and the formation of Al $(TMPF)_2$ complex. The light-absorption ratio variation approach (LARVA) is used for quantitative detection of Al^{3+} using complexation in a range from of 2 to 50 ng mL^{-1} of Al^{3+}. The light-absorption ratio difference in this range is linear. The limit of detection (3σ) of Al^{3+} by the LARVA is only 2 ng mL^{-1}. Trace amounts of Al^{3+} in natural water has been determined with satisfactory results.

Keywords: aluminum, light-absorption ratio variation approach, metal complex, spectrophotometry, trimethoxyphenylfluorone

Résumé

La complexation entre le triméthoxyphénylflurone (TMPF) et Al^{3+} est sensible à pH 10.98, et ce en présence du bromure de cétyltriméthylammonium (CTAB) et de l'acétone, lorsque CTAB est utilisé pour lier TMPF et l'acétone en un agent stabilisant qui empêche l'oxydation du complexe TMPF-Al. L'agent masquant, acide éthylènediaminetétraacetique (EDTA) sert à améliorer la sélectivité de la complexation. Nous avons utilisé la technique de correction spectrale pour caractériser le complexe Al-TMPF et le complexe $Al(TMPF)_2$ a été formé. Nous avons utilisé l'approche de la variation du rapport de l'absorption de lumière (LARVA) pour la détection quantitative de Al^{3+} en se servant de la complexation, dans la gamme 2 à 50 ng mL^{-1} en Al^{3+}. La différence du rapport absorption de lumière est linéaire dans cette gamme. La limite de détection (3σ) de Al^{3+} par l'approche LARVA est de 2 ng mL^{-1} seulement. Nous avons mesuré des quantités traces de Al^{3+} dans les eaux naturelles et obtenu des résultats satisfaisants.

Introduction

Aluminum (Al) exists widely in nature e.g. rocks, soil but it is often low in concentration in natural water. A series of environmental problems, e.g. water acidification, waste discharge, soil extract from acidic rain due to human activities, a large amount of Al has been released into natural water and its presence has significantly increased. The maximum permissible content of Al^{3+} in drinking water is only 0.2 mg/L (1). Abnormally high Al levels are linked to socially relevant pathologies (2) and therefore the biological effects of Al have received much attention. There is little doubt that Al reactivity and bioavailability depend on the existing form. Al^{3+} that is more significant to the environment than its oxide, and complexes, because of its bioavailability and toxicity (3). It is still very important to establish simple, sensitive and selective ways for the determination of Al^{3+} although many methods have been reported, such as spectrophotometry (4-6), spectrofluorimetry (7, 8),

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*Author to whom correspondence should be addressed: hwgao@mail.tongji.edu.cn; Tel/Fax: +86-21-6598-8598 graphite furnace atomic absorption spectrometry (GF-AAS) (9), inductively coupled plasma atomic emission spectrometry (ICP-AES) (10), and high performance liquid chromatography (HPLC) (11). The GF-AAS, ICP-AES and HPLC equipments are more expensive. Spectrophotometry has advantages such as low cost, simple operation, and wide applications. It is still currently being used extensively, particularly in the developing countries. Because of a number of limitations in on-line and real-time analysis, automation, miniaturization and multi-components detection, many improvements has been proposed, for example, the development of new instruments, application of chemometric methods (12,13) and the combination of instrumentation. Furthermore, numerous sensitive chromophores are frequently synthesized (14, 15) and can be used for metal determination. The light-absorption ratio variation approach (LARVA) was established as a novel and sensitive method (16). It is different from the traditional absorbance ratio applied to determine the purity of an organic compound e.g. protein (17) and analysis of drug structure (18). The light-absorption ratio variation approach (LARVA) can improve the sensitivity 10 times higher than with the ordinary method. Trimethoxyphenylfluorone (TMPF), one of the phenylfluorone derivatives, has a high molar absorptivity. It was synthesized and applied to the sensitive determination of Ge (IV) (19). In the present work, it has been used for the spectrophotometric determination of Al^{3+}. The TMPF is sensitive to Al^{3+} complexes in the presence of the cationic surfactant, cetyltrimethylammonium bromide (CTAB) and acetone and is selective in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA). The molar absorptivity of TMPF is $\varepsilon_{506nm}=2.02\times10^4$ L·mol^{-1}·cm^{-1} at pH 10.98, therefore, it is suitable for the application of LARVA. The calibration graph for the determination of Al^{3+} is linear between 2 and 50 ng/mL. In addition, the complexation was characterized by the spectral correction technique (20), which was confirmed to be useful in the elimination of excess color reactant.

Principle and calculation

Description of the Spectral Correction Technique (20)

A metal (M)–ligand (L) complexation is often used for the analysis of trace M. The reaction equilibrium is expressed as follows:

	$N\mathbf{L}$	+	$\mathbf{M}$	$\rightleftharpoons$	$\mathbf{ML}_N$
Initial state	C_{Lo}		C_{Mo}		0
Corresponding to	$A^L{}_{\lambda1}$ and $A^L{}_{\lambda2}$				
Equilibrium	C_L		~0		C_{Mo}
Corresponding to	$(1-\eta)A^L{}_{\lambda1}$ and $(1-\eta)A^L{}_{\lambda2}$				A_c

The symbols C_{L0} and C_{M0} are the initial molarities of L and M. η is the effective fraction of L to complex M and A_c is the practical absorbance of ML complex at wavelength λ_2. Both $A^L{}_{\lambda1}$ and $A^L{}_{\lambda2}$ are the absorbances of L solution, respectively measured at the wavelengths λ_1 and λ_2 against a water reference. *N* is the maximal coordination number of L to M.

In a complex solution, an excessive ligand (L) is always added to complex M. Eventually, the solution contains two color compounds in which there is excessive L and ML complexes formed. Thus, the excessive L will affect the measurement of the absorbance of ML complex. The spectral correction technique can eliminate the effect of the absorption of light by excess L. The practical light-absorption or absorbance (A_0) of ML complex is calculated by the relations:

$$A_c = \frac{A_{\lambda2} - \beta A_{\lambda1}}{1 - \alpha\beta} \quad \text{..........................} (1)$$

where

$$\beta = \frac{A^L{}_{\lambda2}}{A^L{}_{\lambda1}} \quad \text{.................................} \ (2)$$

and

$$\alpha = \frac{A^{ML}{}_{\lambda1}}{A^{ML}{}_{\lambda2}} \quad \text{...............................} (3)$$

and

$$\gamma = \eta \times \frac{C_{L0}}{C_{M0}} \quad \text{...............................} (4)$$

where

$$\eta = \frac{A_c - A_{\lambda2}}{A^L{}_{\lambda2}} + 1 \quad \text{............................} (5)$$

Both β and α are the correction constants, γ is the complexation number of L to M. $A_{\lambda1}$ and $A_{\lambda2}$, $A^{ML}{}_{\lambda1}$ and $A^{ML}{}_{\lambda2}$ are the absorbances of the M–L and ML complex solutions, respectively measured at λ_1 and λ_2 against a water reference. From Equation 4, γ increases with increase of L and then remains constant.

LARVA (16)

The main equations of LARVA are given below:

$$\Delta A_r^{-1} = p'C_{M0}^{-1} + q' \tag{6}$$

or

$$\Delta A_r = pC'_{M0} + q \qquad (\text{only } C'_{M0} << C_{M0}) \tag{7}$$

where

$$\Delta A_r = A_r - A_{r0} = \frac{A_{\lambda 2}}{A_{\lambda 1}} - \frac{A^L{}_{\lambda 2}}{A^L{}_{\lambda 1}} \tag{8}$$

The symbols $A_{\lambda 1}$, $A_{\lambda 2}$, $A^L{}_{\lambda 1}$ and $A^L{}_{\lambda 2}$ have the same meanings as the above equations. ΔA_r indicates the absorbance ratio variation of the reaction solution. C'_{M0} also refers to the initial concentration of M but it should be much less than C_{M0}. All *p'*, *q'*, *p* and *q* are constants when λ_1 and λ_2 and the reaction conditions are selected. Such two equations can be directly used in the quantitative detection of trace M. From the equation above, the sensitivity factor *p* is the inverse ratio to C_{L0}. Therefore, the less L is added and higher the analytical sensitivity goes. However, too few L will cause measurement errors to increase due to instrumental noise.

Experimental

Apparatus and reagents

The absorption spectra of the TMPF and its metal complex solutions were recorded with a Perkin-Elmer Model Lambda -25 spectrometer. The spectrometer was computer controlled using a UV WinLab software (Version 2.85.04). The pH of solution was measured with a Model pHS-25 acidity meter (Shanghai Precise Sci. Instrum., China).

1000 µg/mL Al^{3+} standard solution (National Standard, No. GSB G 62006-90) in 10% HCl was purchased from Department of Research and Development of Standard Samples, Shanghai Institute of Materials. Both 1.00 and 10.0 µg/mL Al^{3+} solutions were prepared by diluting the above solution. 0.250 mmol/L TMPF was prepared by dissolving 51.7 mg of trimethoxyphenylfluorone (provided by Changke Reagents Institute of Shanghai) in 250 mL of ethanol (AR, Shanghai Zhenxing Chemicals) and then it was diluted to 500 mL with deionized water. It was used as the chromophore ligand to react with Al^{3+}. The ammonia buffer solutions of pH 9.24, 9.43, 10.0, 10.48, 10.98, 11.53 and 11.88 were prepared with ammonia and ammonium chloride and they were used to adjust the solution pH accordingly. 2.0 mmol/L CTAB was prepared by dissolving cetyltrimethylammonium bromide (purchased from Shanghai Chemical Reagents Co.) in deionized water and it was used to expedite the Al-TMPF complexation. Acetone (AR, Shanghai Zhenxing Chemicals) was used as the terminal reaction reagent when the Al-TMPF complexation is complete in the presence of CTAB. 0.1 M ethylenediaminetetraacetic acid disodium salt (EDTA, purchased from Shanghai Chemical Reagents Co.) was used to chelate most of the metals.

General Procedures

Characterization of Al-TMPF complex. Into a series of 10-mL volumetric flasks, 1 mL of pH 10.98 buffer solution, 0.5 mL of 2 mmol/L CTAB and 0.500 µg of Al^{3+} were added. They were all diluted to about 5 mL with deionized water. Then, 0.250 mmol/L TMPF was added from 0.050 to 1.50 mL and they were mixed well. After 5 min, 2.5 mL of acetone was added at once and the solutions were diluted to 10 mL with deionized water. After 5 min, the absorbances were measured at 560 and 512 nm against the blank without Al^{3+}. The factors β, A_0, η, γ and ε were calculated by using the equations above.

Determination of Al^{3+}. A water sample (5 mL) was transferred into a 10-mL volumetric flask. 0.5 mL of 2 mmol/L CTAB, 1 mL of pH 10.98 buffer solution, 1 mL of 0.1 M EDTA and 0.200 mL of 0.250 mmol/L TMPF were added and was mixed well. After 5 min, 2.5 mL of acetone were added and it was diluted to 10 mL at once. After 5 min, the absorbances (A_{512nm} and A_{560nm}) were measured at 512 (λ_2) and 560 nm (λ_1) against water. Simultaneously, a reagent blank without Al^{3+} was prepared and then measured at $A^0{}_{512nm}$ and $A^0{}_{560nm}$. Thus, ΔA_r is calculated by the relation:

$$\Delta A_r = \frac{A_{512nm}}{A_{560nm}} - \frac{A^0{}_{512nm}}{A^0{}_{560nm}} \quad \text{.......................}(9)$$

From Equation (6) or (7), C_{Al} in the sample was calculated.

Results and Discussion

pH Dependence of Al-TMPF complexation

The absorption spectra of the Al-TMPF solutions in various pH mediums are shown in Fig. 1. From the in-

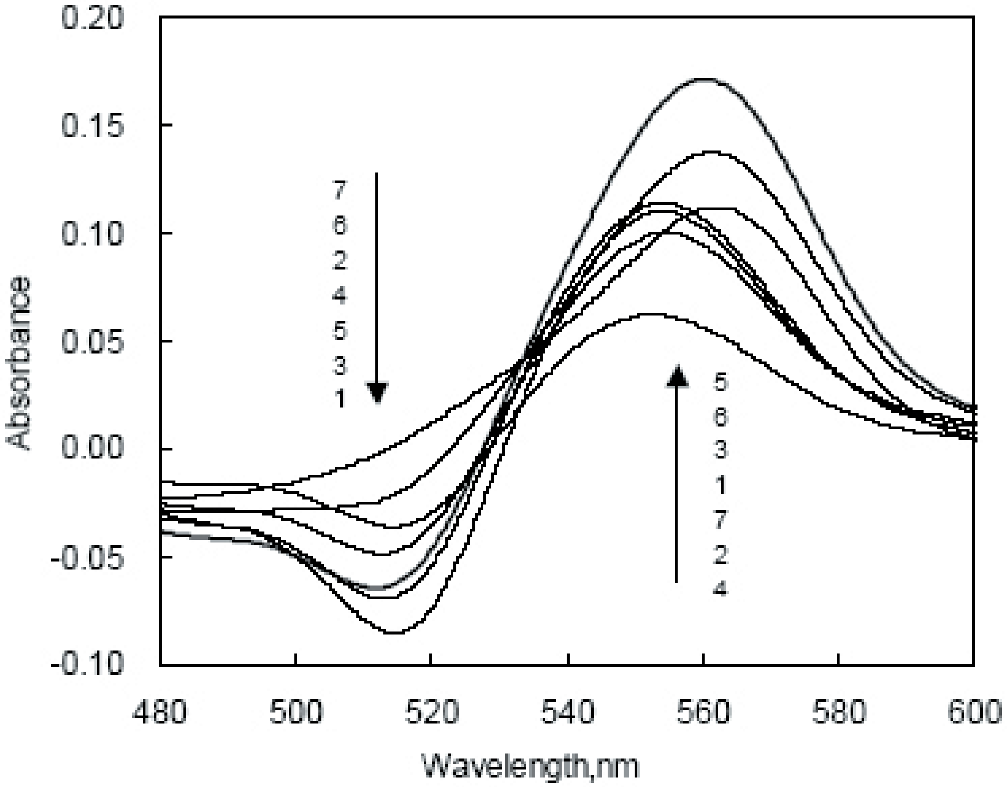

Figure 1. Effect of pH on absorption spectra of the Al-TMPF complexation solutions, which contained 0.010 mmol/L TMPF, 0.050 mg/L Al^{3+}, 0.050 mmol/L CTAB and 25% acetone, all against the reagent blank without Al^{3+}. From graph 1 to 7: pH 9.24, 9.43, 10.00, 10.48, 10.98, 11.53 and 11.88.

terval difference between peak and valley of all spectra, we can deduce that the complexation between TMPF and Al^{3+} is sensitive in basic media. However, the oxidation of TMPF will be accelerated in strongly basic media and the absorption spectrum of TMPF changes. The presence of other metal ions in the water sample will cause the formation of hydroxides. On the contrary, the Al-TMPF complexation is slow when pH is less than 11. Spectrum 7 gives the highest absorption peak and a maximum peak-valley interval. This explains why pH 10.98 ammonia buffer solution was added. The absorption peak of the solution is located at 560 nm and the absorption valley at 512 nm. Such two wavelengths were used in the following experiments.

Effect of CTAB and acetone on Al-TMPF complexation

The spectral red shift (SRS) in Fig. 2, graph 1, 2 and 3 shows that CTAB and acetone can react with TMPF at pH 10.98. From graph 1, the peak of TMPF-H_2O complex is at 506 nm and its molar absorptivity $\varepsilon^{506\,nm} = 2.02\times10^4$ L·mol^{-1}·cm^{-1}. From graph 2, the peak of CTAB-TMPF complex is at 524 nm (SRS is only 18 nm) and its molar absorptivity $\varepsilon^{524\,nm} = 3.01\times10^4$ L·mol^{-1}·cm^{-1}. From graph 3 in the same figure, the peak of TMPF-acetone complex is at 516 nm (SRS is only 10 nm) and its molar absorptivity $\varepsilon^{516\,nm} = 3.02\times10^4$ L·mol^{-1}·cm^{-1}. This is attributed to the fact that the interactions of TMPF with CTAB and acetone belong to non-covalent binding (21). The former interacts by the electrostatic attraction between $TMPF^{2-}$ and $CTAB^+$ and the latter by hydrophobic forces and hydrogen bonds. From graph 4, the addition of acetone into the CTAB-TMPF complex solution results in the spectral shift of the solution from 524 to 516 nm. Apparently, the CTAB-TMPF-acetone complex was formed by non-covalent bonds. From graph 5, the peak of the Al-TMPF complex solution is located at 566 nm and the

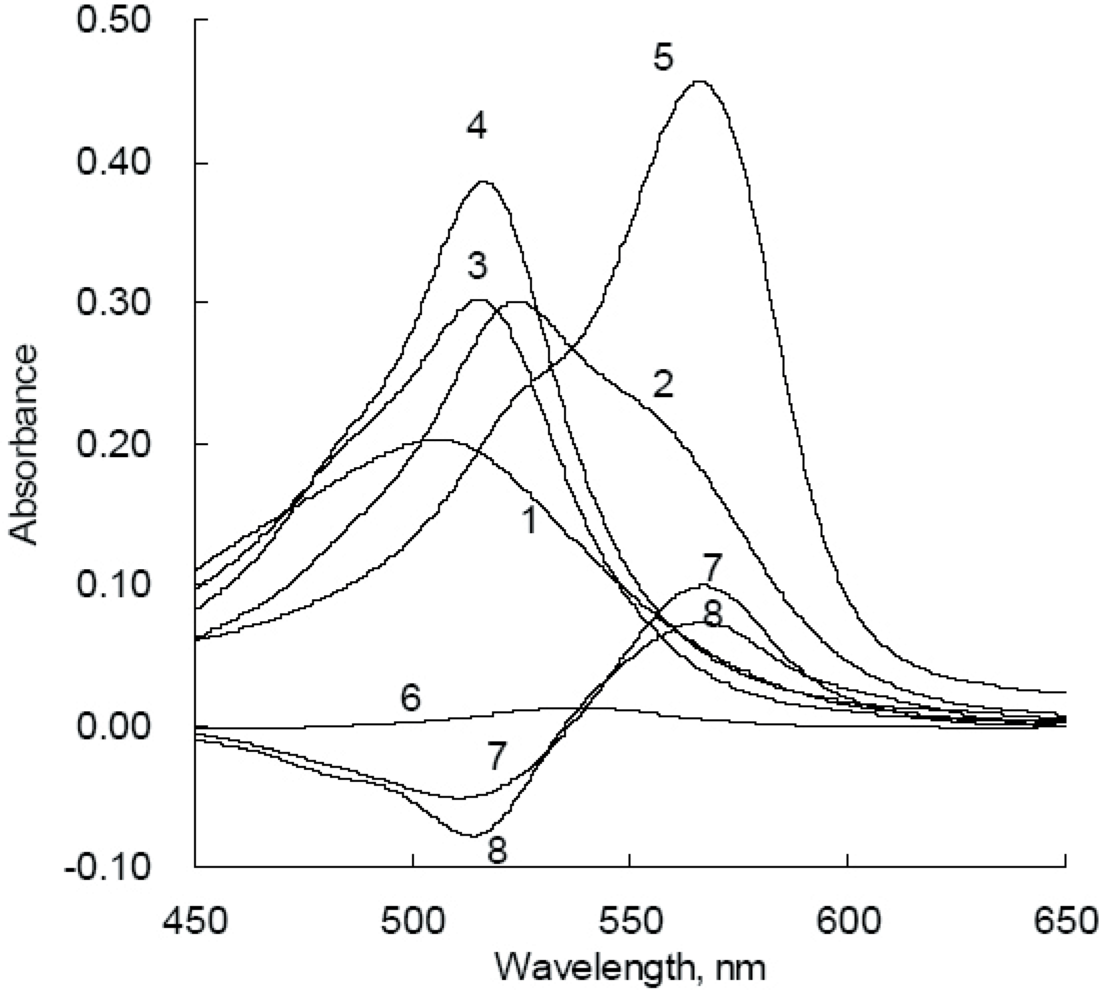

Figure 2. Absorption spectra of TMPF in the presence of complexation agents and Al^{3+} at pH 10.98: (1) 0.010 mmol/L TMPF; (2) 0.010 mmol/L TMPF - 0.30 mmol/L CTAB complexation; (3) 0.010 mmol/L TMPF in 25% acetone medium; (4) 0.010 mmol/L TMPF - 0.10 mmol/L CTAB complexation in 25% acetone medium; (5) 0.010 mmol/L TMPF - 0.10 mmol/L CTAB - 3.0 mg/L Al complexation in 25% acetone medium; (6) 0.010 mmol/L TMPF - 0.050 mg/L Al complexation in absence of CTAB; (7) same as 6 but in the presence of 0.10 mmol/L CTAB and (8) same as 7 in 25% acetone medium. In (1) to (5), water was used as reference. In the others, the corresponding blank was used.

spectral red shift of the solution is 50 nm by comparison of curve graph 5 with 4. Undoubtedly, the Al-TMPF interaction is a coordination reaction. The comparison of graphs 6 with 7 shows that CTAB is useful to accelerate the formation of Al-TMPF complex and to increase the sensitivity. Because the interval between peak and valley changes little when graph 8 is compared with 7, the addition of acetone will not affect the sensitivity of Al-TMPF complexation.

From graph 1 in Fig. 3(A), A_{r0} of the TMPF-CTAB complex solution always increases with reaction time. Thus, the precision of the replicated blanks and the linearity of the calibration series will become poor when measured at any reaction time. It is unfavorable to the LARVA. However, the effect of the reaction time can be improved when acetone was added. From graph 2 in Fig. 3(A), A_{r0} remains almost constant. The reason is that acetone joins in the complexation so as to inhibit the oxidation of Al-TMPF complex in basic media. From Fig. 3(B), the TMPF-Al complexation approaches completion in 5 min. 2.5 mL of acetone was added when the TMPF-Al reaction lasts for 5 min in the presence of CTAB.

Characterization of Al-TMPF complex

Variation of the absorbance ratio, A_{560nm}/A_{512nm} of the Al-TMPF solutions is shown in Fig. 4. The ratio approaches a minimum and remains constant at 0.380 when the concentration of Al^{3+} is greater than TMPF. When TMPF reacts completely with Al^{3+} only one color compound exists, which is the Al-TMPF complex. The absorption spectrum of such a solution is shown as graph 5 in Fig. 2. The correction constant α of the Al-TMPF

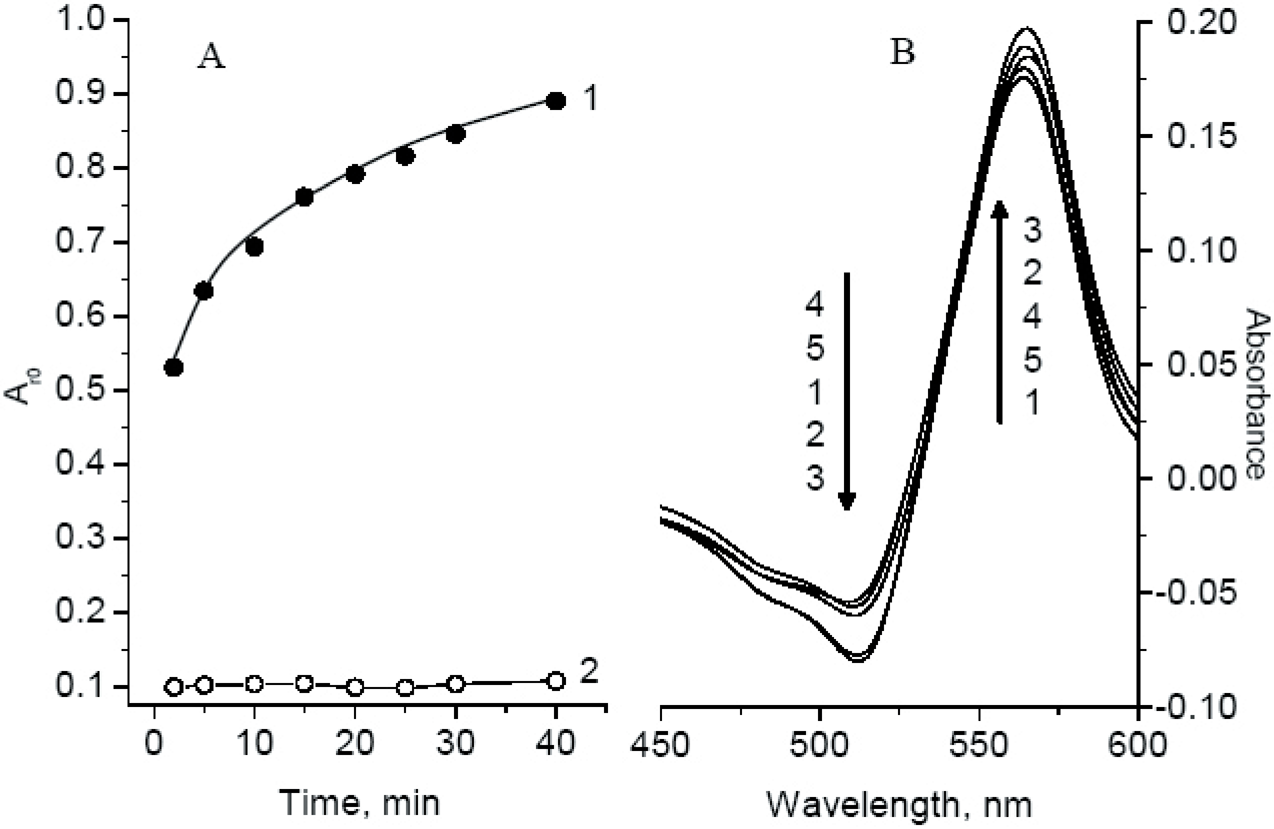

Figure 3. Effect of the reaction time on Ar$_0$ (A) of TMPF solutions : (1) 0.010 mmol/L TMPF - 0.10 mmol/L CTAB complexation in 0.01 M EDTA medium; (2) same as 1 but 2.5 mL of acetone was added on time and on the absorption spectra (B) of the Al-TMPF complexation at pH 10.98: (1)-(5): at 2, 5 10, 15 and 20 min where 0.050 mg/L Al^{3+}, 0.010 mmol/L TMPF and 0.10 mmol/L CTAB were contained in the presence of 0.01 M EDTA. 2.5 mL of acetone was added on time.

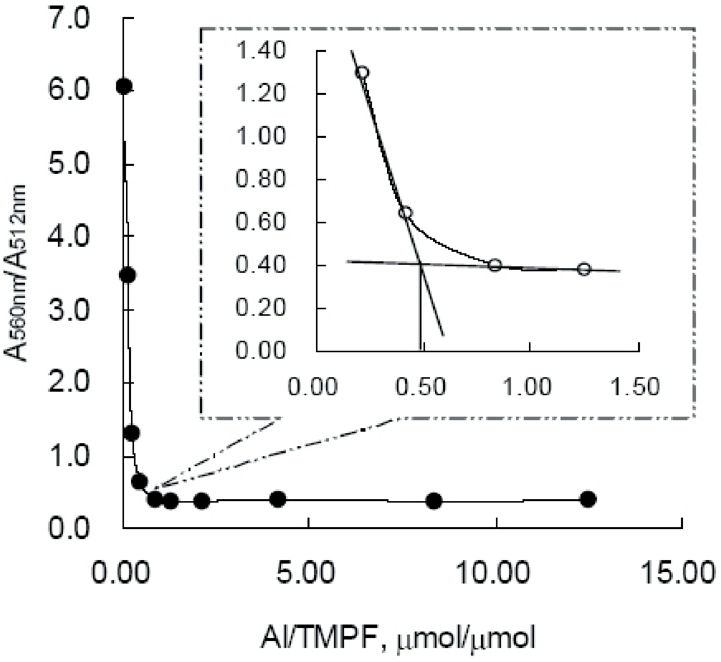

Figure 4. Variation of A_{560nm}/A_{512nm} of the Al-TMPF solutions with the molar ratio of Al^{3+} (from 0 to 3.00 mg/L) to TMPF (constant molarity at 0.010 mmol/L) in the presence of 0.10 mmol/L CTAB and 25% acetone at pH 10.98. The solutions were measured at 560 and 512 nm against water reference.

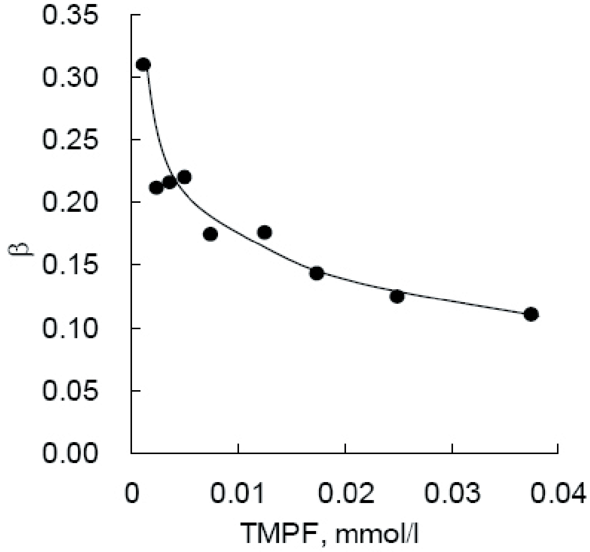

Fig. 5 Variation of β with TMPF molarity at pH 10.98. The solutions contained 0.050 μg/ml Al^{3+} and TMPF from 0.00125 to 0.0375 μmol/mL in the presence of 0.10 mmol/L CTAB.

complex is calculated to be 0.380. From the partial enlarged detail in Fig. 4, the break point of curve corresponds to 0.5 of Al^{3+} to TMPF. Therefore, the complex containing 1 Al to 2 TMPF is determined by the break point approach (21). It will still be confirmed by the spectral correction technique as described below.

The solutions containing 0.050 mg/L of Al^{3+} and TMPF were measured. β, A_0, η and γ were calculated. Variation of β is shown in Fig. 5. β decreases with increase of TMPF. It is attributed to the formation of TMPF dimer in case of high concentration. From A_0 of the Al-TMPF complex, the molar absorptivity ($\varepsilon^{566\text{ nm}}$) of the complex was computed to be 1.16×10^5 $L\cdot mol^{-1}\cdot cm^{-1}$. It denotes that the complexation is highly sensitive. Variations of both η and γ are shown in Fig. 6. From graph 1, η decreases to less than 50% when the concentration of TMPF is greater than 0.01 mmol/L. Thus, over half of TMPF has not reacted with Al^{3+}. Indeed, the excess TMPF will affect the measurement of the absorbance of only the Al-TMPF complex. Thus, an ordinary spectrophotometry is unfit to characterize such a reaction. From graph 2, γ increases with increase of TMPF molarity and then ap-

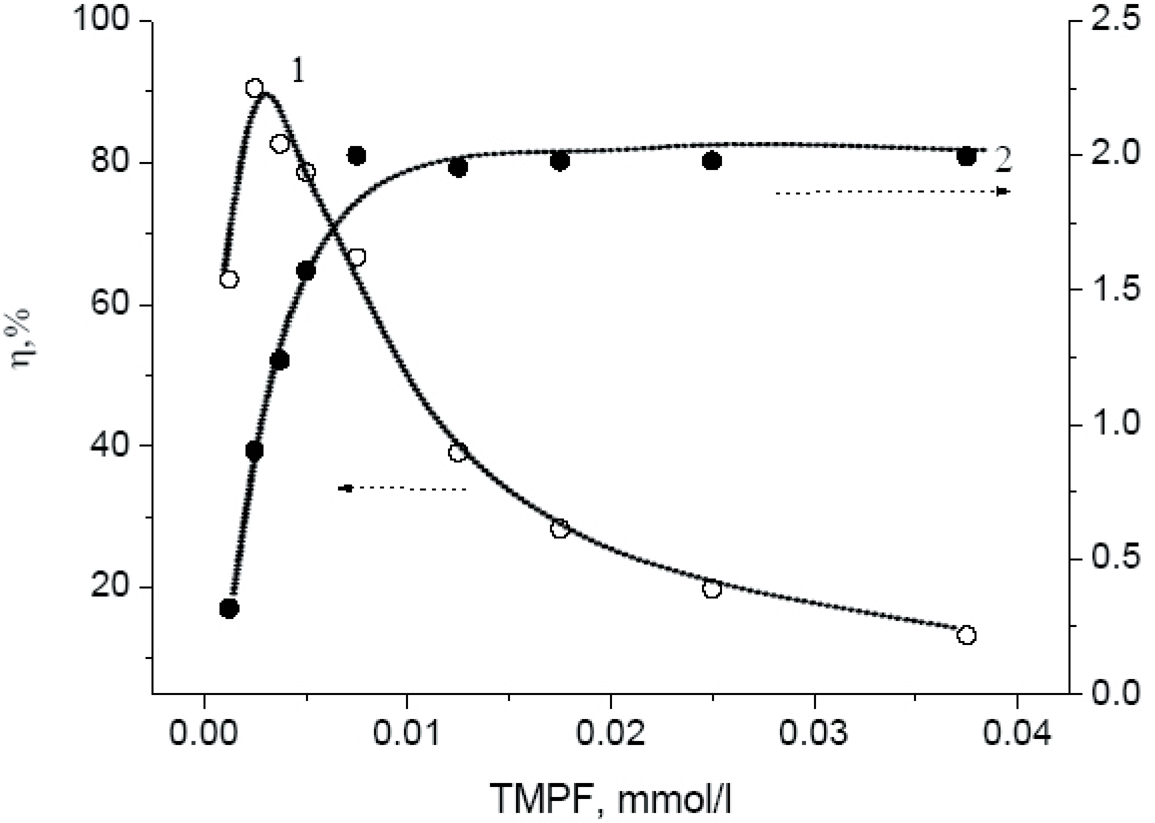

Figure 6. Variation of η (1) and γ (2) with TMPF molarity at pH 10.98. The solutions contained 0.050 μg/mL Al^{3+} and TMPF from 0.00125 to 0.0375 μmol/mL in the presence of 0.10 mmol/L CTAB.

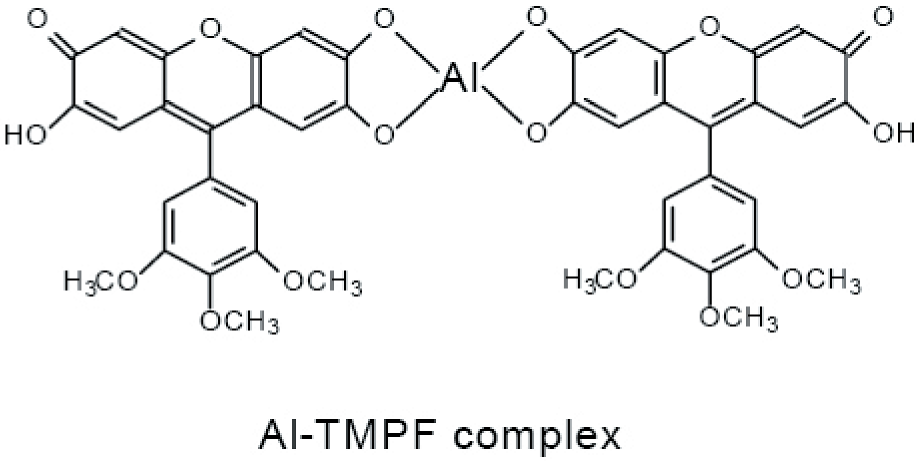

Figure 7. The possible chemical structure of complex $Al(TMPF)_2$ formed.

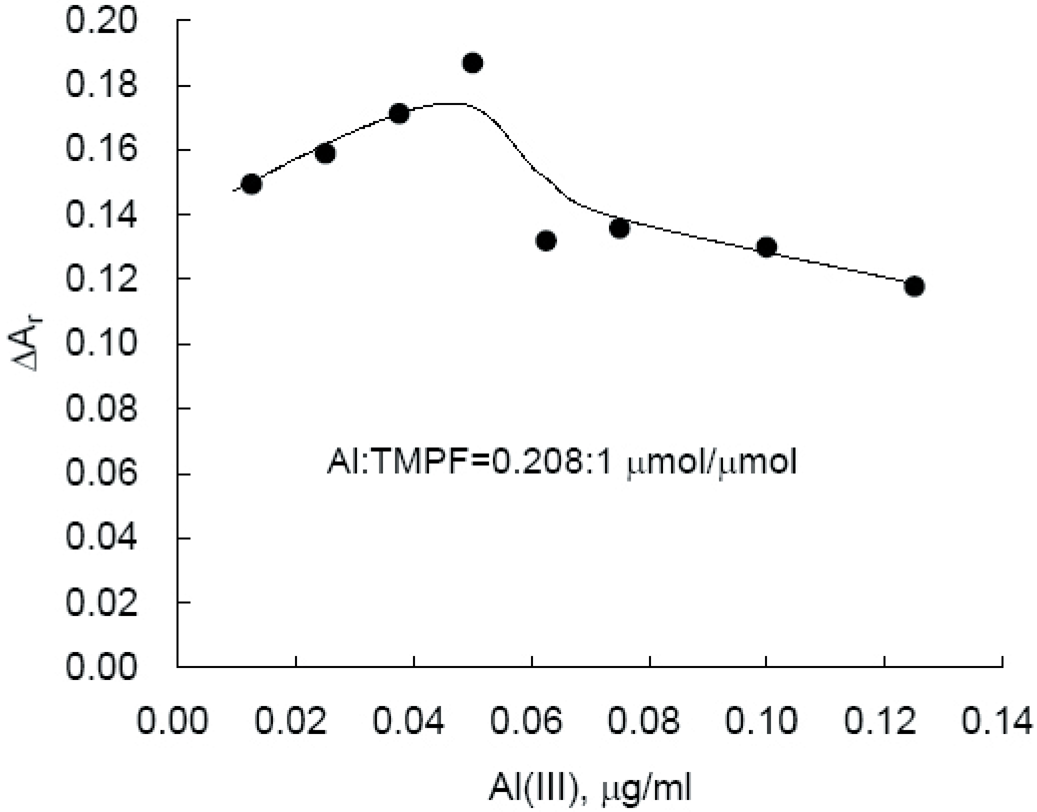

Figure. 8 Effect of Al^{3+} and TMPF molarity on ΔA_r of the solutions at pH 10.98 initially containing TMPF from 0.00250 to 0.0250 μmol/mL and Al^{3+} from 0.1250 to 0.125 μg/mL. The initial molar ratio of Al^{3+} to TMPF always remained constant at 0.208:1 μmol/μmol and 0.010 M EDTA and 0.1 mmol/L CTAB were contained. 2.5 mL of acetone was added on time.

proaches a maximal maximum constant at 2. Therefore, the formation of complex Al(TMPF)$_2$ was confirmed and its chemical structure is shown in Fig. 7.

Effect of TMPF on ΔA_r

From the variation (Fig. 8) of ΔA_r of the solutions with the constant molar ratio of Al^{3+} to TMPF at 0.208:1 μmol/μmol in the presence of EDTA, CTAB and acetone, ΔA_r increases with increase of Al^{3+} between 0.01 and 0.05 mg/L and then begins to decrease when Al^{3+} is over 0.05 mg/L. ΔA_r changes between 0.1178 and 0.1867. The detection of Al^{3+} decreases with the decrease in concentration of TMPF. Of course, the fraction of the instrumental noise will increase seriously if the absorbance is too low. Thus, the absorbance between 0.01 and 0.2 is suggested.

Calibration Graphs and Limit of Detection

Three series of standard Al^{3+} solutions containing 0-0.040, 0-0.100 and 0-0.150 μg/mL Al^{3+} were prepared and 0.100, 0.200 and 0.400 mL of 0.250 mmol/L TMPF were added, respectively. Their color reactions were investigated according to the recommended procedures. The absorbance of the solutions were measured at 560 and 512 nm and ΔA_r was calculated using Equation 9. The regression equations are given in Table 1 with the linear scope of Al^{3+} determination. The limit of detection of Al^{3+}, defined as the blank values plus 3 times of the standard deviation of the replicated blanks, was calculated and listed in Table 1. Series 2 is the most adaptable because of the lower detection limit of Al^{3+}, larger linear range and higher precision. Therefore, 0.200 mL of 0.250 mmol/L TMPF is added for the determination of Al^{3+}.

Effect of Foreign Ions

EDTA was added to mask the other metal ions and it was found not to complex with Al^{3+} in the presence of

Table 1. Regression equations and limit of detection of Al^{3+}.

Series	μg/10 mL Al^{3+}	mM of TMPF	*p*	ΔA_r vs. C_{Al}	R[1]	σ[2]	LOD[3], ng/mL
1	0-0.30	0.0025	0.9662	ΔA_r=0.9662C_{Al}+0.0065	0.9983	0.0524	2.0
2	0-0.50	0.0050	0.4406	ΔA_r=0.4006C_{Al}-0.0068	0.9985	0.00291	2.0
3	0-0.70	0.0100	0.2150	ΔA_r=0.2150C_{Al}-0.0007	0.9977	0.00401	6.0

1) Linear correlation coefficient

2) Standard deviation of 10 repetitive blanks

3) Limit of detection of Al^{3+} was calculated by LOD=3σ/*p*.

Table 2 Errors of ΔA_r resulting from 17 kinds of foreign ions mixed into 0.500 μg/10 mL Al^{3+}.

No.	Foreign ion	Added, μg/10 mL	Error in ΔA_r %
1	Ca^{2+}	20.0	9.5
2	Mg^{2+}	10.0	3.9
3	Co^{2+}	5.00	0.6
4	Fe^{2+}	1.00	-7.7
5	Zn^{2+}	1.00	-0.7
6	Sn (IV)	1.00	7.1
7	Pb^{2+}	1.00	-2.0
8	Cd^{2+}	1.00	5.1
9	Cu^{2+}	1.00	0.1
10	Fe^{3+}	0.50	11
11	V (V)	1.00	-5.8
12	Ni^{2+}	1.00	-7.9
13	Mn^{2+}	2.00	5.0
14	Ge (IV)	1.00	-7.4
15	Cr^{3+}	0.50	1.3
16	Mo (VI)	1.00	2.1
17	As (III)	0.50	8.3

Table 3. Determination of Al^{3+} in water.

Source of sample	**Al^{3+} added, µg/L**	**Al^{3+} found, µg/L**	**Recovery %**
Lake	0	15.9 ± 2.4 $^{1)}$	
	40	55.3 ± 3.6 $^{1)}$	89.2-107.5 $^{2)}$
Underground water $^{3)}$	0	319 ± 13.7 $^{1)}$	
	400	697 ± 15 $^{1)}$	90.7-98.2 $^{2)}$
River	0	50.7 ± 3.5 $^{1)}$	
	100	157 ± 7.5 $^{1)}$	99.3-114.3 $^{2)}$

$^{1)}$ average of five replicated determinations

$^{2)}$ e.g. 89.2%=(51.6-15.9)/40.0 × 100%

$^{3)}$ sample from Jin Shan in Shanghai (in the seaside, high concentration of Al^{3+})

TMPF. Seventeen foreign metal ions were added in the Al^{3+} solutions and their effects on A_r are shown in Table 2. There are 7 metals which have errors of over 7% such as Ca^{2+}(2.0 mg/L), Fe^{2+}(0.1 mg/L), Fe^{3+}(0.05 mg/L), Ni^{2+}(0.1 mg/L), Sn(0.1 mg/L), Ge(0.1 mg/L) and As(0.05 mg/L). Using EDTA, metals like Ca^{2+}, Ni^{2+}, Sn(IV) and Fe^{2+} can be masked, and As^{3+}, Ge(IV) can be masked by adding sodium tartrate to the solution. If $[Fe^{3+}]$ is equal to $[Al^{3+}]$, a high error of over 10% results. Consequently, Fe^{3+} must be transformed into Fe^{2+} by adding both hydroxylamine hydrochloride and 5% phenanthroline (PRL). The Fe-PRL complex solution may be considered as the reference instead of water.

Analysis of Samples

To validate this method, Al^{3+} in natural water was determined. The results are listed in Table 3. The recovery rates of Al^{3+} are between 89.2 and 114.3%. The method is simple in operation and accurate. Because the recommended method is highly sensitive, only micro-volume of a sample, e.g. 0.100 mL of a biological or food sample, is required.

Conclusion

LARVA is an important contribution to spectrophotometric method in ultra-trace analysis. Also, it will notably improve numerous present spectrophotometric methods so that they will become more useful in the direct detection of trace components in natural water. However, LARVA often requires that the chromophore should have a high molar absorptivity and the spectrometer should have a low noise signal. Thus, it will make the analytical sensitivity as over 10 times high as the traditional method. For characterizing a chemical reaction, the spectral correction technique is more suitable than the other classical methods such as continuous variations and equilibrium movements because of the strong absorbance of the excessive chromophore in the complexation solution.

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