

# Application of light-absorption ratio variation approach as an optimum spectrophotometry to determination of Mn(II) in $\text{ng ml}^{-1}$ level using a competitive replacement complexation

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## Abstract

The light-absorption ratio variation approach (LARVA) which produces an outstandingly increasing of analytical sensitivity was applied to the quantitative detection of ultramicro amounts of Mn(II) by light-absorption spectrometry using the competitive replacement complexation among 1,5-di(2-hydroxy-5-sulfophenyl)-3-cyanoformazan (DSPCF), Zn(II) and Mn(II) in the presence of *o*-phenanthroline (OPTL). Not only masks OPTL foreign metal ions but also seriously sensitizes the competitive complexation. All the binary and ternary complexes were characterized by the break point approach. Results have shown that the limit of detection ( $3\delta$ ) of Mn(II) is only  $0.7 \text{ ng ml}^{-1}$ . This method has been applied to analysis of water quality with satisfactory results.

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## 1. Introduction

Ultraviolet and light-absorption spectrometry is a most conventional method for trace analysis. Though the light-absorption spectrometry becomes inactive today because of the limited sensitivity and selectivity, it has a number of very important specificities, for example simple operation, low-priced instrument and wide owning all over the world. With the design and production of new-typical spectrophotometer with high-resolution and high-sensitivity and synthesis of highly sensitive chromophores, new techniques and calculations were proposed increasingly e.g. H-point standard-additions [1], dual-wavelength [2], kinetic [3,4], flow-injection [5], derivative [6], spectral correction [7]. Recently, a new technique named the light-absorption ratio variation approach (LARVA) has been just developed [8]. It may raise the spectrophotometric

sensitivity for over 10 times and especially it is fit to analysis of a micro-volume sample, e.g. biologic, wastewater, noble metal and drug. Both the deep-color chromophore and highly sensitive spectrophotometer supply LARVA with a hardware base. The chromophore, 1,5-di(2-hydroxy-5-sulfophenyl)-3-cyanoformazan (DSPCF) is one deep colorant. Early, it was used in determination of Ni(II) and  $\text{NO}_2^-$  [8,9]. Because it can coordinate many transition metals, e.g. Cu(II), Fe(II), Zn(II), Mn(II), Ni(II), Co(II), Al(III) and Pb(II), it was limited out of any metal analysis. However, the investigation showed that *o*-phenanthroline (OPTL) may sensitize the Zn-DSPCF and Mn-DSPCF complexations and it is able to also mask the other metal ions, e.g. Ni(II), Fe(II), Fe(III), Cu(II) and Co(II). In addition, trace amounts of Mn(II) can replace competitively Zn from the Zn-DSPCF-OPTL complex. Therefore, the application of both the competitive replacement complexation (CRC) [10,11] and LARVA will bring the quantitative detection of Mn(II) a high-sensitivity and a good selectivity. The composition ratios of the Zn-DSPCF-OPTL and Mn-DSPCF-OPTL complexes were determined by

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the break point approach (BPA) [12]. Results have shown that the complexes,  $\text{Zn}(\text{DSPCF})_3$ ,  $\text{Zn}(\text{DSPCF})(\text{OPTL})_2$  and  $\text{Mn}(\text{DSPCF})_4(\text{OPTL})_2$  were formed at pH 9.66. In this work, the break point approach (BPA) was still applied to the characterization of a reaction product instead of the classical methods, e.g. continuous variations [13] and equilibrium movements [14].

## 2. Principles

### 2.1. Description of LARVA

The LARVA is described and expressed as follows [8]:

$$\Delta A_r^{-1} = p' C_{M0}^{-1} + q' \quad (1)$$

or

$$\Delta A_r = p C_{M0}' + q \quad (\text{only } C_{M0}' \ll C_{M0}) \quad (2)$$

where

$$\Delta A_r = A_r - A_{r0} = \frac{A_{\lambda_2}}{A_{\lambda_1}} - \frac{A_{\lambda_2}^0}{A_{\lambda_1}^0} \quad (3)$$

The symbols  $A_{\lambda_1}$ ,  $A_{\lambda_2}$ ,  $A_{\lambda_1}^0$  and  $A_{\lambda_2}^0$  are the absorbances of the reaction solution and the blank solution measured at  $\lambda_1$  and  $\lambda_2$  against water reference.  $\Delta A_r$  indicates the absorbance ratio variation of the reaction solution.  $C_{M0}$  and  $C_{M0}'$  are the initial concentration of M but  $C_{M0}'$  should be much more than  $C_{M0}$ . All  $p'$ ,  $q'$ ,  $p$  and  $q$  are constants when  $\lambda_1$  and  $\lambda_2$  and the reaction conditions are fixed. Such two theoretical Eqs. (1) and (2) both can be directly used in the quantitative detection of M traces. This method is named as light-absorption ratio variation approach (LARVA). From the equation above, the sensitivity factor  $p$  is the inverse ratio to  $C_{L0}$ . Therefore, less L is added and higher the analytical sensitivity goes. Nevertheless, too low L will certainly bring an obvious error, e.g. increase of fraction of the instrument's noise signal. Therefore, both higher the light-absorptivity of a chromophore is and more sensitive the spectrometer is, lower the detection limit of a component goes by LARVA. According to the present cases, it is suggested for the addition of a chromophore to produce the peak absorbance between 0.05 and 0.2.

### 2.2. Break point approach

In the M–L reaction solution where L is being held a constant, the absorbance ratio of the solutions at two wavelengths decreases continuously down to a constant with increase of M molarity, which is sketched in Fig. 1. L is always to be bound completely with M at 1:1 when M is more than  $M_{P2}$ . The solutions consist of both ML and excess of M. On the contrary, the coordination number ( $n$ ) of L increases with decrease of M molarity from  $M_{P2}$ .  $n$  always remains a maximum ( $N$ ) when M is less than  $M_{P2}$

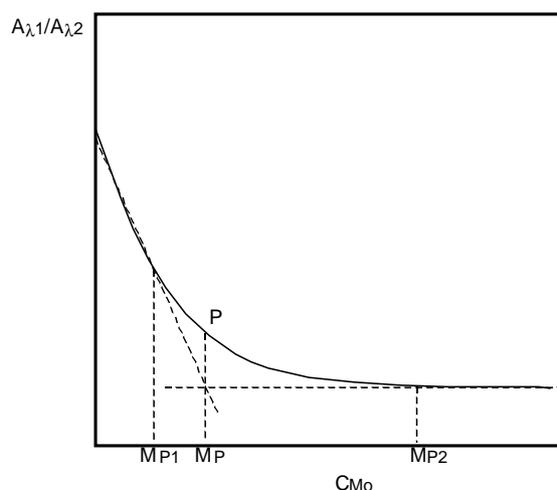


Fig. 1. Sketch for establishment of BPA by plot  $A_{\lambda_1}/A_{\lambda_2}$  vs.  $C_{M0}$ .

and the solutions consist of both  $ML_N$  and excess of L. Therefore,  $N$  corresponds to the point (P) of intersection of the two tangents as shown in Fig. 1, which is just the break point of the absorbance ratio curve. The BPA seems similar to the continuous variations method but is different from it because a deep-color chromophore will bring the latter a notable error. The BPA improves the classical characterization way. It may be applied to not only a complexation also ionic pair interaction and assembly of a macromolecule.

## 3. Experimental

### 3.1. Apparatus and reagents

Absorption spectra were recorded on a Model Lambda 25 spectrometer (Perkin–Elmer Instruments). The pH of the solution was measured with a Model pHs-25 meter (Shanghai). A Model BS110S electronic balance (Sartorius Instruments, Beijing) was used to accurately weight the standard substances and DSPCF. A Model PLA-SPEC ICP-AES (Leeman Instruments) was used to examine the quantitative result of Mn(II) obtained by LARVA.

Stock standard solutions of Zn(II) and Mn(II) ( $200 \text{ mg l}^{-1}$ ) was prepared by dissolving their metals in spectrometric purity in 20% hydrogen chloride and diluting with deionized water.  $0.100 \text{ mg l}^{-1}$  and  $1.00 \text{ mg l}^{-1}$  Mn(II) standard use solutions both were prepared daily by diluting the above solution. Standard DSPCF ( $0.800 \text{ mmol l}^{-1}$ ) solution was prepared by dissolving 243 mg of disodium 1,5-di(2-hydroxy-5-sulfophenyl)-3-cyanoformazan (content 80%, provided by Changke Reagents Institute of Shanghai) in 500 ml deionized water. It was used to complex Mn(II) and Zn(II). Standard OPTL solution ( $1.00 \text{ mmol l}^{-1}$ ) was prepared by dissolving 198.2 mg of *o*-phenanthroline hydrate (A.R., Shanghai Third Reagents Industry) in 10 ml of

absolute alcohol and then diluting to 1000 ml with deionized water. 1% OPTL was prepared according to the procedure above as well. They were used to bind the Zn-DSPCF and Mn-DSPCF complexes to form ternary complexes. The Zn-DSPCF complex ( $0.0400 \text{ mmol l}^{-1}$ ) solution was prepared by mixing 80 ml of  $200 \text{ mg l}^{-1}$  Zn(II), 25 ml of pH 9.66 buffer solution and 12.50 ml of  $0.800 \text{ mmol l}^{-1}$  DSPCF and then diluting to 250 ml with deionized water. It was used as a competitive replacement reagent and Mn(II) trace may substitute Zn from the Zn-DSPCF-OPTL complex.

### 3.2. General procedures

#### 3.2.1. Determination of composition of Zn-DSPCF-OPTL complex

Into ten 10-ml calibrated flasks were added all  $1.00 \text{ ml}$  of  $1.00 \text{ mmol l}^{-1}$  Zn(DSPCF) complex,  $1 \text{ ml}$  of pH 9.66 buffer solution and  $1.00 \text{ mmol l}^{-1}$  OPTL from  $0.50$  to  $5.00 \text{ ml}$  in  $0.50 \text{ ml}$  steps. The mixture was diluted to  $10 \text{ ml}$  with deionized water and mixed thoroughly. After  $10 \text{ min}$ , the absorbances were measured at  $625$  and  $570 \text{ nm}$  against water.

#### 3.2.2. Competitive replacement complexation and determination of composition of Mn-DSPCF-OPTL complex

Into fifteen  $10 \text{ ml}$  calibrated flasks were added all  $1 \text{ ml}$  of pH 9.66 buffer solution,  $5.00 \text{ ml}$  of  $0.040 \text{ mmol l}^{-1}$  Zn-DSPCF complex and  $0.5 \text{ ml}$  of 1% OPTL. Those solutions were diluted to about  $8 \text{ ml}$  and Mn(II) from  $0$  to  $50 \mu\text{g}$  was added into each solution. They were diluted to  $10 \text{ ml}$  with deionized water and mixed thoroughly. After  $10 \text{ min}$ , the absorbances,  $A_{500 \text{ nm}}$  and  $A_{625 \text{ nm}}$  were measured at  $500$  and  $625 \text{ nm}$  against water.

#### 3.2.3. Determination of ultramicro amounts of Mn(II) in water

Five milliliters of a water sample was added into  $10\text{-ml}$  flask. One milliliters of pH 9.66 buffer solution and  $0.5 \text{ ml}$  of 1% OPTL were added. After  $5 \text{ min}$ ,  $2.00 \text{ ml}$  of  $0.050 \text{ mmol l}^{-1}$  Zn-DSPCF complex were added. After  $10 \text{ min}$ , the light-absorption was measured against water. Simultaneously, a reagent blank without Mn(II) was prepared and measured as same as that above. Thus,  $\Delta A_r$  is calculated by the relation:

$$\Delta A_r = \frac{A_{500 \text{ nm}}}{A_{625 \text{ nm}}} - \frac{A_{500 \text{ nm}}^0}{A_{625 \text{ nm}}^0} \quad (4)$$

where  $A_{500 \text{ nm}}$  and  $A_{625 \text{ nm}}$  are the absorbances of the Mn-(DSPCF)-OPTL solution measured at  $500 \text{ nm}$  and  $625 \text{ nm}$  against water.  $A_{500 \text{ nm}}^0$  and  $A_{625 \text{ nm}}^0$  are the absorbances of the solution without Mn(II), respectively measured at  $500$  and  $625 \text{ nm}$  against water. From Eqs. (1) and (2),  $C_{\text{Mn}}$  in the sample was calculated.

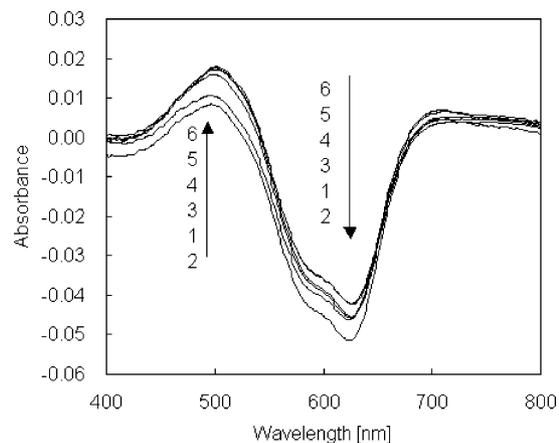


Fig. 2. Effect of pH on absorption spectra of the Zn-DSPCF-OPTL-Mn(II) solutions, all of which contained  $0.0080 \text{ mmol l}^{-1}$  Zn(DSPCF),  $0.05\%$  OPTL and  $0.050 \mu\text{g ml}^{-1}$  Mn(II) against the reagent blank. From curves 1–6: pH 8.99, 9.03, 9.27, 9.66, 9.79 and 10.07.

## 4. Results and discussion

### 4.1. Variation of absorption spectra with pH

The absorption spectra of the Zn(DSPCF)(OPTL)-Mn(II) solutions in various pH buffer mediums were shown in Fig. 2. From six curves, the competitive replacement complexation between Zn(DSPCF) and Mn(II) are very sensitive in the presence of OPTL. By comparing the absorbance difference between peak and valley, curve 4 is most suitable. If the solution is too basic, the precipitation of hydroxide will occur. On the contrary, the complexation between Zn(II) and DSPCF will become insensitive if pH is less than 9.0. Therefore, pH 9.66 was added in the reaction. From curve 4, the peak is located at  $500 \text{ nm}$  and the valley at  $625 \text{ nm}$ . Such two wavelengths were used in quantitative detection of Mn(II) trace.

### 4.2. Composition of the complexes

#### 4.2.1. Zn-DSPCF complex

At pH 9.66, the absorption spectra of DSPCF and Zn-DSPCF solutions were shown in Fig. 3(A). From curve 1, the absorption peak of DSPCF is located at  $557 \text{ nm}$  and its molar absorptivity is  $\epsilon^{557 \text{ nm}} = 1.47 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ . From the relative spectrum 3, the peak is located at  $620 \text{ nm}$  and the valley at  $481 \text{ nm}$ . The variation of the absorbance ratio of the Zn-DSPCF solution measured at  $481$  and  $620 \text{ nm}$  is shown in Fig. 3(B). The ratio,  $A_{481 \text{ nm}}/A_{620 \text{ nm}}$  approaches a minimum and remains constant when the addition of Zn(II) is more than 1 time of DSPCF. It is said that the DSPCF is almost complete to complex Zn(II) and only a color compound, Zn-DSPCF complex exists in the presence of enough excessive Zn(II). The absorption spectrum of the Zn-DSPCF complex solution is shown as curve 2 in Fig. 3(A). From curve 2, its peak is located at  $614 \text{ nm}$ . By comparing curves 1 and 2, the red shift of peak of the com-

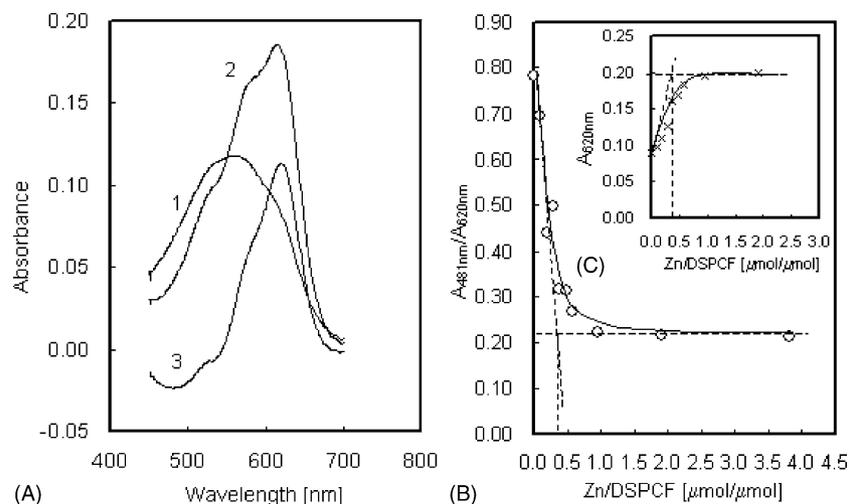


Fig. 3. Characterization of the Zn-DSPCF complex at pH 9.66. (A) Absorption spectra of the Zn-DSPCF solutions: (1)  $0.0080 \text{ mmol l}^{-1}$  DSPCF against water, (2)  $0.0080 \text{ mmol l}^{-1}$  DSPCF plus  $13 \mu\text{g ml}^{-1}$  Zn(II) against water and (3)  $0.0080 \text{ mmol l}^{-1}$  DSPCF plus  $0.50 \mu\text{g ml}^{-1}$  Zn(II) against the blank. (B) Variation of  $A_{481 \text{ nm}}/A_{620 \text{ nm}}$  with the molar ratio of Zn(II) (from 0 to  $2 \mu\text{g ml}^{-1}$ ) to DSPCF ( $0.0080 \text{ mmol l}^{-1}$ ) and (C) concentration variations for determination of composition ratio of Zn to DSPCF (variation of  $A_{620 \text{ nm}}$  with the Zn/DSPCF molar ratio).

plex is only 57 nm. It indicates the Zn-DSPCF coordination bond is not too strong and the molar structure of the complex is loose and simple. From the curve in Fig. 3(B), the peak point is located at about 0.35 of the molar ratio of Zn to DSPCF. Therefore, the maximal coordination number of DSPCF is 3. In addition, the conventional ligand concentration variation method was used to examine the composition ratio of the complex obtained by BPA. The curve shown in Fig. 3(C) indicates that the maximal coordination number of DSPCF is 3, too. In addition, such a coordination number was still confirmed by the spectral correction technique [7]. Comprehensively, the complex,  $\text{Zn}(\text{DSPCF})_3$  will be formed only in presence of enough DSPCF.

#### 4.2.2. Zn(DSPCF)-OPTL ternary complex

From the last paragraph, only Zn(DSPCF) complex (1:1) will be formed in a DSPCF solution containing enough excessive Zn(II) at pH 9.66. Fig. 4 shows effect of OPTL. From relative spectrum 2, the peak is located at 653 nm and the valleys at 562 and 609 nm. Here, both 653 and 562 nm were selected. Curve B shows the variation of the absorbance ratio of the Zn(DSPCF)-OPTL solutions measured at 562 and 653 nm against water. The ratio,  $A_{562 \text{ nm}}/A_{653 \text{ nm}}$  approaches a minimum and remains constant when the addition of OPTL is over FIVE times of total Zn(II). It is said that the Zn(DSPCF) is complete to bind OPTL and only a color compound, Zn(DSPCF)-OPTL ternary complex exists

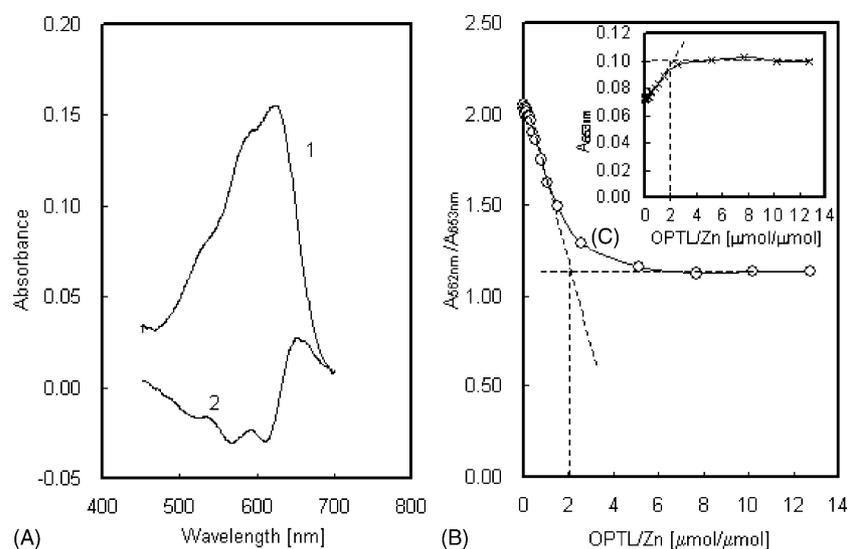


Fig. 4. Characterization of the Zn(DSPCF)-OPTL ternary complex at pH 9.66. (A) Absorption spectra of the Zn(DSPCF)-OPTL solutions: (1)  $0.0080 \text{ mmol l}^{-1}$  Zn(DSPCF) plus 0.05% OPTL against water, (2) same as 1 but against the blank. (B) Variation of  $A_{562 \text{ nm}}/A_{653 \text{ nm}}$  with the molar ratio of OPTL (from 0 to  $2.5 \mu\text{mol ml}^{-1}$ ) to total Zn (complexed Zn plus free  $\text{Zn}^{2+}$ ) and (C) concentration variations for determination of composition ratio of Zn to OPTL (variation of  $A_{653 \text{ nm}}$  with the OPTL/Zn molar ratio).

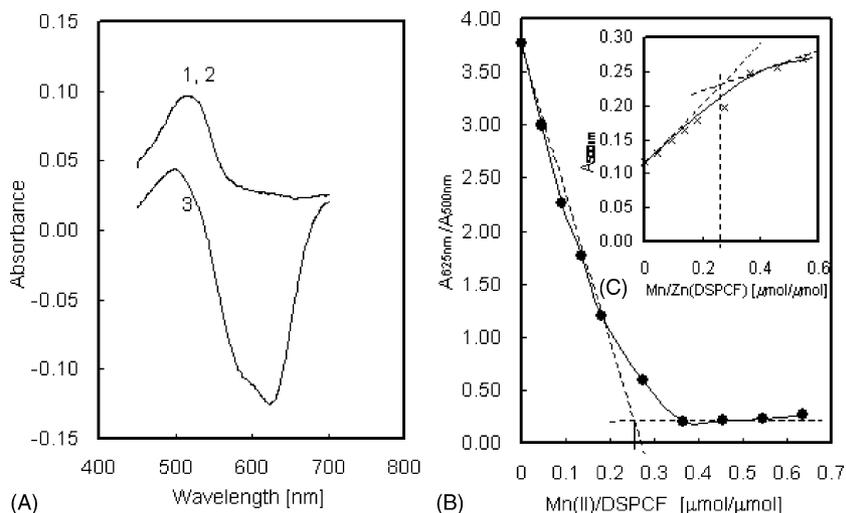


Fig. 5. Characterization of the Zn(DSPCF)(OPTL)<sub>2</sub>-Mn(II) competitive replacement complexation at pH 9.66. (A) Absorption spectra of the Zn(DSPCF)(OPTL)<sub>2</sub>-Mn(II) solutions: (1) 0.0080 mmol l<sup>-1</sup> DSPCF plus 0.05% OPTL and 0.700 μg ml<sup>-1</sup> Mn(II) against water, (2) 0.0080 mmol l<sup>-1</sup> Zn(DSPCF)(OPTL)<sub>2</sub> plus 0.700 μg ml<sup>-1</sup> Mn(II) against water and (3) same as (2) but against the blank. (B) Variation of  $A_{625\text{nm}}/A_{500\text{nm}}$  with the molar ratio of Mn(II) (from 0 to 0.700 μg ml<sup>-1</sup>) to DSPCF (0.0080 mmol l<sup>-1</sup>) and (C) concentration variations for determination of composition ratio of Mn(II) to DSPCF (variation of  $A_{500\text{nm}}$  with the Mn/Zn(DSPCF) molar ratio).

in the presence of enough excessive OPTL. The absorption spectrum of the ternary complex is shown as curve 1 in Fig. 4(A). From curve 1, its peak is located at 623 nm. From curve B in Fig. 5, the beak point is located at about 2.0 of the molar ratio of OPTL to Zn. Therefore, the maximal coordination number of OPTL is 2. In addition, the conventional ligand concentration variation method was used to examine the composition ratio of the complex obtained by BPA. Curve C shown in Fig. 3 indicates that the maximal coordination number of DSPCF is 2, too. Therefore, the ternary complex, Zn(DSPCF)(OPTL)<sub>2</sub> will be formed where 0.5 ml of addition of 1% OPTL is enough.

#### 4.2.3. Competitive replacement and Zn(DSPCF)(OPTL)<sub>2</sub>-Mn(II) complexation

At the same way above, into the Zn(DSPCF)(OPTL)<sub>2</sub> complex solutions, Mn(II) was added. Its absorption spectra are shown in Fig. 5(A). The peak of the relative spectrum 3 is located at 500 nm and the valley at 625 nm. Curve B shows the variation of the absorbance ratio of

the Zn(DSPCF)-OPTL-Mn(II) solutions measured at 500 and 625 nm against water. The ratio,  $A_{625\text{nm}}/A_{500\text{nm}}$  approaches a minimum and remains constant when Mn(II) is over 0.36 time of Zn(DSPCF) complex. It is said that only a color compound exists in the presence of enough excessive Mn(II). The absorption spectrum of the compound is shown as curve 2 in Fig. 5(A). Interestingly, it is coincident completely and exactly alike to curve 1. This states that the two solutions contain only an identical color complex, Mn(DSPCF). Therefore, Mn(II) replaced all Zn(II) in Zn(DSPCF)(OPTL)<sub>2</sub> complex in the solution containing enough Mn(II) to form a new Mn-DSPCF-OPTL complex. The color compound mentioned above is just this complex. The replacement reaction is illustrated in Fig. 6. From it, the visualized color change is observed from blue to red and trace amounts of Mn(II) has replaced sensitively Zn in the Zn(DSPCF) complex. From curve 1 or 2 in Fig. 5, the absorption peak of the complex is located at 515 nm. By comparing it with curve 1 in Fig. 5, the blue shift of absorption peak of the Mn-DSPCF-OPTL complex reaches

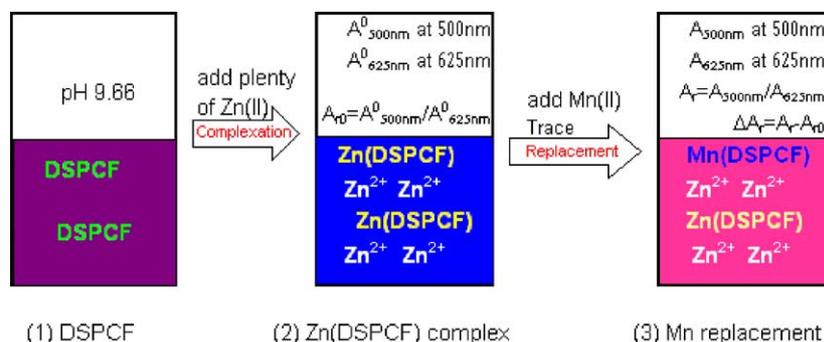


Fig. 6. Color change of the replacement complexation between Mn(II) and Zn(DSPCF) in the presence of OPTL at pH 9.66.

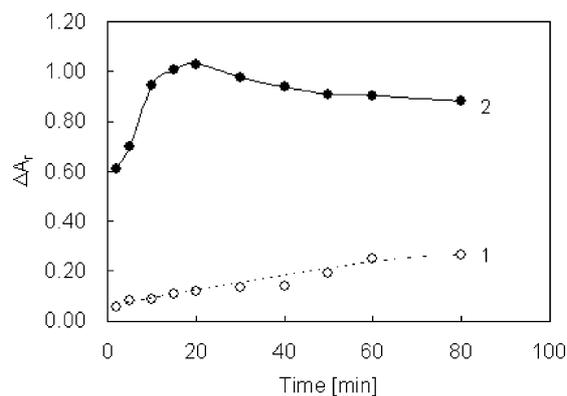


Fig. 7. Effect of time on  $\Delta A_r$  of the Zn(DSPCF)-Mn(II) solution at pH 9.66: (1)  $0.0040 \text{ mmol l}^{-1}$  Zn(DSPCF) plus  $0.050 \mu\text{g ml}^{-1}$  Mn(II) in the absence of 0.05% OPTL and (2) same as 1 but with 0.05% OPTL.

108 nm. From curve B, the beak point is located at about 0.25 of the molar ratio of Mn(II) to Zn(DSPCF). Therefore, the maximal coordination number of DSPCF is four. In addition, the conventional ligand concentration variation method was used to examine the composition ratio of the complex obtained by BPA. Curve in Fig. 5(C) indicates that the maximal coordination number of DSPCF is 4, too. Therefore, the complex,  $\text{Mn}(\text{DSPCF})_4$  will be formed in the presence of OPTL.

### 4.3. Application of LARVA to analysis of ultramicro amounts of Mn(II)

#### 4.3.1. Effect of time on $\Delta A_r$

From curve 4 in Fig. 2(A), both 500 and 625 nm have been selected as the measurement wavelengths. Effect of the replacement time on  $\Delta A_r$  is shown in Fig. 7. From curve 2, the replacement reaction is complete in 10 min in the presence of 0.05% OPTL. However, from curve 1 it will spend not only over 60 min to approach the replacement end in the absence of OPTL but also its  $\Delta A_r$  is much less than that of curve 2. Hence, the addition of OPTL sensitizes and catalyzes the replacement reaction between Mn(II) and Zn(DSPCF) complex. Moreover, OPTL masks Fe(II), Cu(II), Ni(II) and Co(II) so that the selectivity is improved in determination of Mn(II). From curve 2, the measurement of the replacement solution should be carried out between 15 and 40 min.

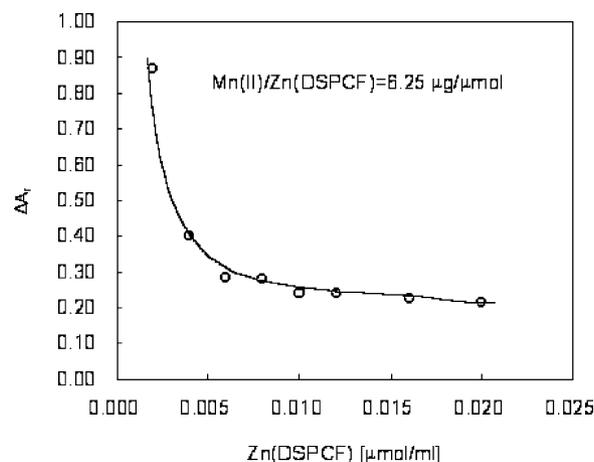


Fig. 8. Effect of addition of  $0.040 \text{ mmol l}^{-1}$  Zn(DSPCF) complex (from 0.50 to 5.00 ml) on  $\Delta A_r$  of the Zn(DSPCF)-Mn(II) solution in the presence of 0.05% OPTL at pH 9.66, where Mn(II) was added according to the constant ratio of Mn(II) to Zn(DSPCF) complex at  $6.25 \mu\text{g } \mu\text{mol}^{-1}$ .

Thus,  $\Delta A_r$  reaches a maximum. After 40 min,  $\Delta A_r$  decreases slowly. This is attributed to an enough diluted complex solution to fade when it exposes in air for a long time.

#### 4.3.2. Effect of addition of the Zn-DSPCF complex on $\Delta A_r$

From the variation (as shown in Fig. 8) of  $\Delta A_r$  of the solutions with the constant initial molar ratio of Mn(II) to Zn(DSPCF) at  $6.25 \mu\text{g}/\mu\text{mol}$ ,  $\Delta A_r$  approaches a minimal constant only when Zn(DSPCF) is more than  $0.010 \text{ mmol l}^{-1}$ .  $\Delta A_r$  increases rapidly when Zn(DSPCF) is less than  $0.0040 \text{ mmol l}^{-1}$ . The primary reason is that the self-aggregation of Zn-DSPCF complex will not occur in an extremely diluted solution. Though the analytical sensitivity goes higher and higher with dilution of the Zn(DSPCF) solution, the fraction of the instrumental noise will raise, especially when the absorbance is less than 0.020. Of course, a high-sensitive and low-noise spectrometer can overcome such a defect.

#### 4.3.3. Calibration linear equations and detection limit of mn(II)

Four series of standard Mn(II) between 0 and 0.050, 0 and 0.100, 0 and 0.200 and 0 and  $0.400 \mu\text{g ml}^{-1}$  were prepared and 1.00, 2.00, 3.00 and 5.00 ml of  $0.0400 \text{ mmol l}^{-1}$

Table 1  
Regression equations and detection limit of Mn(II)

Line	Mn(II) ( $\mu\text{g ml}^{-1}$ )	Zn(DSPCF), $0.040 \text{ mmol l}^{-1}$ (ml)	$p'$	$q'$	$\Delta A_r^{-1}$ vs. $C_{\text{Mn}}^{-1}$	$R^a$	$\sigma^b$	DT <sup>c</sup> ( $\text{ng ml}^{-1}$ )
1	0–0.050	1.00	0.0996	–1.17	$\Delta A_r^{-1} = 0.0996 C_{\text{Mn}}^{-1} - 1.17$	0.9980	0.00233	0.7
2	0–0.100	2.00	0.3625	–3.33	$\Delta A_r^{-1} = 0.3625 C_{\text{Mn}}^{-1} - 3.33$	0.9995	0.00180	2.0
3	0–0.200	3.00	0.4453	–1.44	$\Delta A_r^{-1} = 0.4453 C_{\text{Mn}}^{-1} - 1.44$	0.9892	0.00145	2.3
4	0–0.400	5.00	1.272	–5.42	$\Delta A_r^{-1} = 1.272 C_{\text{Mn}}^{-1} - 5.42$	0.9982	0.00170	6.5

<sup>a</sup> Linear correlation coefficient.

<sup>b</sup> Standard deviation of eight repetitive reagent blanks.

<sup>c</sup> Detection limit of Mn(II) was calculated by  $\text{DT} = 3 \times \sigma \times p'$ .

Zn(DSPCF) complex were added, respectively. The absorbances of each were measured.  $\Delta A_r$  of each solution was obtained. Their regression equations are given in Table 1 all with the good linearity. The limits of detection of Mn(II), defined as the blank values plus three times the standard deviation of eight replicated blanks, was calculated and given in Table 1, too. By comparing them, line 1 owns the lowest detection limit at only  $0.7 \text{ ng ml}^{-1}$ . In this work,  $1.00 \text{ ml}$  of  $0.040 \text{ mmol l}^{-1}$  Zn(DSPCF) complex was added into the replacement reaction solution for the sensitive determination of ultramicro amounts of Mn(II) in water samples.

#### 4.3.4. Effect of foreign ions

In the replacement reaction, plenty of Zn(II) was added. It will anticipate most of the other metal ions, e.g. Pb(II), Cd(II), Hg(II), Al(III) in micro-amount level to complex the complete DSPCF. Therefore, the presence of enough excessive Zn(II) prevents the interference of a number of metal ions possibly existing in water samples, except for Mn(II), Ni(II), Cu(II), Fe(II) and Co(II). The OPTL was added into the replacement reaction so as to reduce the influence of the metal ions except for Mn(II). The recommended procedure in "Section 2" was carried out. Seventeen of foreign ions were added into the Mn-Zn(DSPCF)-OPTL solutions and their effects on  $\Delta A_r$  were shown in Table 2. Cu(II) appears a high error over 10% only when its weight amount more than 2.5 times of Mn(II). Therefore, the replacement reaction between Zn(DSPCF) and Mn(II) in the presence of OPTL at pH 9.66 is selective and suitable for monitoring of natural water quality.

#### 4.3.5. Analysis of water samples

As a test of the method, Mn(II) in four water samples was determined. The results are listed in Table 3. The recovery rates of Mn(II) added are between 91.0 and 116.6% and the R.S.D. less than 3.36%. The analytical results were also compared with the results obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES) determination. Thus, the two methods obtained the anastomotic re-

Table 2

Effect of foreign ions on  $\Delta A_r$  of the solutions containing  $0.20 \mu\text{g}$  of Mn(II) and error showing

No.	Foreign ion	Added ( $\mu\text{g}/10 \text{ ml}$ )	$\Delta A_r$	Error <sup>a</sup> (%)
1	Mn(II)	0.20	0.1857	0.0
2	Ca(II) <sup>b</sup>	50.0	0.1980	6.6
3	Mg(II)	20.0	0.1980	6.6
4	Al(III)	5.0	0.1706	-8.1
5	Fe(II)	1.0	0.2024	9.0
6	Sn(II)	2.5	0.1690	-9.0
7	Pb(II)	5.0	0.1738	-6.4
8	Cr(III)	5.0	0.1760	-5.2
9	Cd(II)	5.0	0.1807	-2.7
10	Ba(II)	5.0	0.2020	8.8
11	Hg(II)	5.0	0.1915	3.1
12	Fe(III)	2.0	0.1881	1.3
13	V(V)	1.0	0.2006	8.0
14	Ge(IV)	2.0	0.1865	0.4
15	Ni(II)	1.0	0.1911	2.9
16	Co(II)	0.30	0.2024	9.0
17	Cu(II)	0.50	0.2080	12.0
18	SDS	20.0	0.2005	8.0

$$^a \text{ Error} = \frac{\Delta A_r^{\text{No.}x} - \Delta A_r^{\text{No.}1}}{\Delta A_r^{\text{No.}1}} \times 100 (\times \text{ from 2 to 18}).$$

<sup>b</sup> Added  $0.20 \mu\text{g}$  of Mn(II) into all the solutions from No. 2 to 18.

sults. Therefore, the LARVA is accurate in ultra-trace analysis.

## 5. Conclusion

In the present work, the basic physics of LARVA was described. In fact, lots of the present colorimetric reactions with deep-color chromogenic reagents may be improved obviously by LARVA. If the LARVA is applied to fluorophotometric analysis, it will further raise the sensitivity of trace analysis. Such a revolutionary technique has provided a strategic methodology for analytical science and it will bring a great and wide attention of a lot of spectroscopists and analysts. It is possible that the research of light-absorption spectrometry will again become active in the near future.

Table 3

Determination of Mn(II) in water samples

Sample no.	Sample from	Mn(II) added ( $\text{mg l}^{-1}$ )	Mn(II) found ( $\text{mg l}^{-1}$ )	R.S.D. (%)	Recovery (%)
1	Mine well	0.000	$0.0018 \pm 0.00005^a$ (0.0015) <sup>b</sup>	2.83	112.7
		0.020	$0.0243^c$		
2	Agricultural well	0.000	$0.0042 \pm 0.00009^a$ (0.0037) <sup>b</sup>	2.19	116.6
		0.020	$0.0275^c$		
3	Main-water	0.000	$0.0025 \pm 0.00007^a$ (0.0024) <sup>b</sup>	2.63	91.0
		0.020	$0.0207^c$		
4	Huaihe river	0.000	$0.0356 \pm 0.00120^a$ (0.0362) <sup>b</sup>	3.36	94.3
		0.020	$0.0544^c$		

<sup>a</sup> Average of four replicated determinations.

<sup>b</sup> One determination by ICP-AES after enrichment.

<sup>c</sup> Average of three replicated determinations.

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