

NOVEL METHOD FOR RAPID DETERMINATION OF OCTADECYLAMINE USING UV SPECTROPHOTOMETRY**

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A new, rapid UV spectrophotometry method (UV) for the determination of octadecylamine using ninhydrin as a chromogenic reagent was developed. The solution pH, concentration of ninhydrin, temperature, heating time and coexisted ions have been optimized. Under the optimal conditions, the linear regression equation was $A = 0.0108c - 0.0179$, and the calibration curve demonstrated linearity over a concentration range of ~1.0–50 mg/L with a correlation coefficient (R^2) of 0.9970. The developed method with a high degree of precision and accuracy, good repeatability and cost effectiveness, can be successfully applied for the detection of octadecylamine in the samples of any stage of the potassium flotation process from the salt lake brine.

Keywords: octadecylamine, concentration, UV-visible spectrophotometry, ninhydrin.

**УФ-СПЕКТРОФОТОМЕТРИЧЕСКИЙ ЭКСПРЕСС-МЕТОД
ОПРЕДЕЛЕНИЯ ОКТАДЕЦИЛАМИНА**

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Разработан быстрый УФ-спектрофотометрический метод определения октадециламина с использованием нингидрина в качестве хромогенного реагента. Оптимизированы pH раствора, концентрация нингидрина, температура, время нагревания и сосуществующие ионы. При оптимальных условиях уравнение линейной регрессии $A = 0.0108c - 0.0179$, калибровочная кривая линейна в диапазоне концентраций ~1.0–50 мг/л с коэффициентом корреляции (R^2) 0.9970. Разработанный метод с высокой точностью, хорошей повторяемостью и экономичностью может быть успешно применен для обнаружения октадециламина в пробах на любой стадии флотации калия из рапы соленых озер.

Ключевые слова: октадециламин, концентрация, УФ-видимая спектрофотометрия, нингидрин.

Introduction. Octadecylamine (ODA), as a cationic surfactant, can generate hydrophobic groups in water to reduce the surface tension of the solution, so it is widely used in the preparation of mineral flotation agents, hydrophobic materials [1] and chemical fertilizer anti-caking agents. Compared with other amines, it

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has the advantages of high thermal stability, low thermal destruction, minimum toxicity, and biological degradability [2]. With the preceding advantages, octadecylamine has become the main flotation reagent for the industrial preparation of potassium chloride. As an important fertilizer, potassium chloride came mainly from salt lake brine in China, especially from Qinghai Province. With the increasing exploitation of the salt lake resources, the yield of potassium chloride increased year by year, and the demand for ODA in the flotation process also increased accordingly. However, the dosage of octadecylamine is not accurate in the production process and is mainly based on previous production experience. In order to obtain high efficiency, excess ODA was used, and excessive addition will cause waste and might adversely affect the products including KCl and other products [3]. Additionally, the residual octadecylamine will be discharged into the natural environment of the salt pans with the wastewater, which could destroy the delicate ecological environment of salt lakes. An accurate measuring of ODA does not only reduce the dosage of ODA but can also decrease adverse effects on products and the ecological environment. Therefore, the quick and simple accurate determination of ODA concentration has great significance for the development of KCl in salt lake brine.

Nowadays, the concentration of ODA can be determined by gas chromatography [4, 5] and spectrophotometry [6–14]. Gas chromatography has good selectivity, high separation efficiency and detection sensitivity, but needs the addition of internal standards applied, and requires specific equipment, which causes inconvenient operation for many laboratories. Comparatively, spectrophotometry is more suitable for the routine quantitative determination of ODA due to its uncomplicated instruments, simple operation and rapid measurement. The spectrophotometric determination of ODA can be divided into two types: extraction method and direct method. For the extraction method, the extraction process is crucial, and organic extractants, including toxic reagents such as chloroform, were necessary. Moreover, octadecylamine suffers from incomplete extraction, leading to low assay results, which limit the application of the extraction method in the practical process. Direct determination is more rapid and convenient, and this procedure involves adding appropriate chromogenic agents, such as methyl orange and bromocresol green, which can react with ODA to form colored compounds [13, 14], whereby the concentration of ODA can be obtained by a spectrophotometer. However, due to the low solubility and poor hydrophilicity of octadecylamine, a large quantity of soluble inorganic salts has a serious impact on the determination results, particularly in the flotation process of potassium chloride. Current methods cannot provide a quick and accurate measurement of ODA.

A rapid and accurate method for the determination of ODA by spectrophotometry was established using ninhydrin as a chromogenic reagent. By the direct method, the concentration of ODA in various salt solutions such as NaCl, KCl, and $MgCl_2$ were measured systematically. The results show that this method is successful in measuring ODA in salt solution and has high accuracy and validity.

Experimental. The quantitative principle of this method is based on Lambert Beer's law. Under heating conditions, ODA can react with ninhydrin to form a blue-violet complex in the pH 4–6, which produces characteristic absorption peaks in the 500–600 nm region [15]. According to the linear relationship between the absorbance value and the concentration of octadecylamine in the solution under certain conditions, the concentration of octadecylamine can be determined.

All absorbance measurements were performed on a TU-1810PC spectrophotometer equipped with 1 cm matched quartz cells. All chemicals and reagents used were of analytical or pharmaceutical grade and distilled water was used throughout the experiment.

0.20 g of ODA was accurately weighed and dissolved in 3 mL of hydrochloric acid. The solution was heated to 80°C and 500 mL of water (80°C) was added to ensure complete solubilization. After cooling to room temperature, the solution pH was adjusted to ~2.0 with hydrochloric acid. Then the solution was transferred to a 1000 mL volumetric flask and diluted to volume with deionized water.

The acetate buffers (pH 3.6–6.0) were prepared from 1.0 mol/L acetic acid and 1.2 mol/L sodium acetate as shown in Table 1. And the buffer with pH 6.5 was prepared by dissolving 3.4 g dipotassium phosphate into 7.6 mL of 1 mol/L sodium hydroxide solution, then diluted to 500 mL with deionized water. A 2% ninhydrin solution was prepared by dissolving 2 g ninhydrin in 100 mL water.

ODA solution and buffer solution were placed in a glass bottle and capped, then 2% ninhydrin solution was added and diluted to 20 mL with deionized water, shaken and heated for 20 min. After cooling to room temperature, the solution was spectrally scanned using a quartz cuvette with deionized water as a blank.

The analytical conditions for determining the ODA concentration were optimized by a single-factor experiment. First, two factors were considered: the pH of the buffer solution varying between 3.6 and 6.5, and the ODA concentration between 0 and 50 mg/L, UV absorbance scanning was performed in the range of 300–800 nm to determine the maximum absorbance and find the wavelength and the optimal pH. Then, un-

der the determined optimal pH and maximum absorption wavelength, the amount of chromogenic agent (0.5–4 mL), water bath temperature (50–90°C) and time (5–40 min) in the analytical solution with an ODA concentration of 50 mg/L were examined in each case. Three parallel experiments were carried out and expressed as A_1 , A_2 , and A_3 . Finally, the effects of sodium chloride, potassium chloride and magnesium chloride were investigated under the optimized experimental conditions.

TABLE 1. The Preparation of Acetate – Sodium Acetate Buffer Solution

Buffers	pH	1.2 mol/L sodium acetate/mL	1.0 mol/L acetic acid/mL
1	3.6	20.8	229.2
2	5.0	156.2	93.8
3	5.5	206.6	43.4
4	6.0	234.2	15.3

Absorbance values of 0, 5, 10, 20, 30, 40, and 50 mg/L octadecylamine at 566 nm were determined under optimal conditions: pH 6.0 sodium acetate-acetic acid buffer solution of 8.0 mL, 2% ninhydrin chromogenic agent of 2.0 mL, water bath temperature of 80°C, the heating time of 20 min. The corresponding equation parameters were obtained according to Lambert Beer's law.

The performance of the method was evaluated based on reproducibility and accuracy. Seven ODA solutions with different concentrations were accurately prepared and added to the buffer solution and indicator. Each sample was tested 6 times in parallel to evaluate repeatability. By comparing the actual value of ODA solutions with the calculated value, the relative error was calculated to test the accuracy of the method.

Results and discussion. The effect of pH on the UV-Vis spectrum of octadecylamine was investigated from pH 3.6 to 6.5 as shown in Fig. 1a. A strong absorption band with a maximum at 556 nm can be seen in the absorption spectrum for octadecylamine-ninhydrin (Fig. 1a) in weakly acidic media (pH 6.0–6.5), while there is no maximum absorption peak in the solution pH range of 3.6–5.5. This is probably because of interactions between ODA and ninhydrin, which indicates that the absorbance was no longer simply additive. The maximum absorption intensity decreased with the increase of pH from 6.0 to 6.5. In Fig. 1b, the absorbance of the solution with pH 6.0 is in the measured wavelength range and symmetrically distributed in the wavelength range of 500–600 nm. It can be seen that the absorbance value reaches the maximum value at 566 nm, which is similar to the results obtained in the previous conditional experiment.

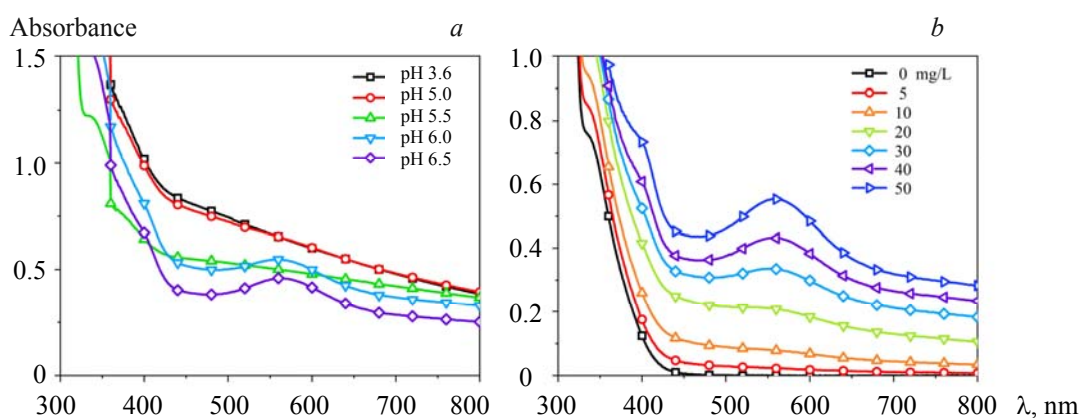


Fig. 1. UV-Vis absorption spectra of octadecylamine solution at different (a) pH and (b) concentrations.

In order to determine the effect of the chromogenic reagent, 2.0–4.0 mL of 2% ninhydrin was added, and the absorbance value of the solution at 566 nm was measured and repeated 3 times. As shown in Fig. 2a, the repeatability in parallel cubic times (A_1 , A_2 , A_3) was good, and 2 mL was selected as the adding quantity of ninhydrin; the molar ratio of ninhydrin to octadecylamine was 26.67:1. Figure 2b shows the effect of the water bath temperature on the absorbance at 566 nm in the range of 50–90°C, where it can be seen that the absorbance is highest at 80°C, while it is lower in the range of 50–70°C and the repeatability was poor, due to incomplete reaction at lower temperatures. And when the temperature is set to 90, the absorbance decreases, owing to the decomposition of the octadecylamine-ninhydrin complex formed at high temperatures.

Therefore, 80°C was chosen as the optimal water bath temperature. The influence of the heating time on the absorbance at 566 nm in the range of 5–60 min was presented in Fig. 2c. The reaction was found to be complete in 15 min from 80°C and then the absorbance decreased slowly from 20–60 min, which may be caused by the decomposition of the octadecylamine-ninhydrin complex upon prolonged heating. Therefore, a heating time of 20 min was specified for the determination of octadecylamine.

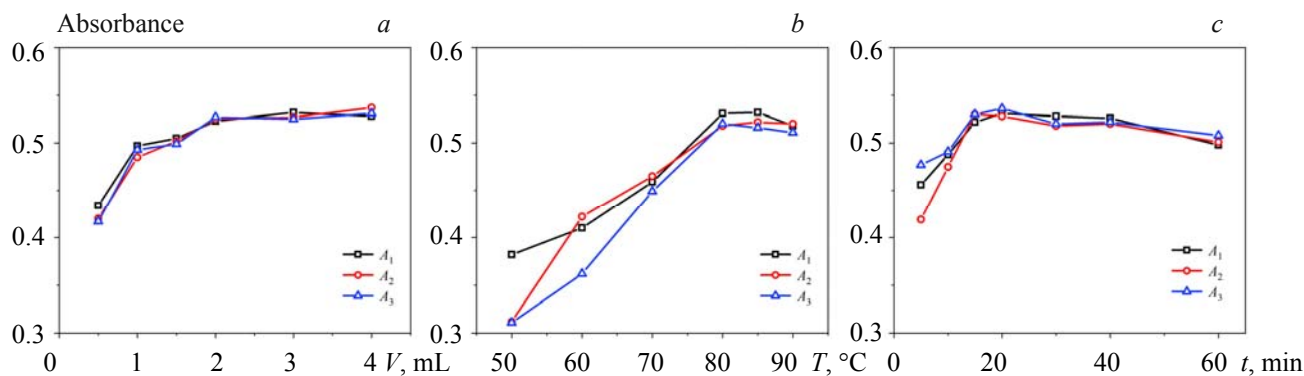


Fig. 2. Effect of chromogenic agent addition (a), temperature (b), heating time (c) on the absorbance of the octadecylamine system.

The influence of NaCl, KCl, and MgCl₂ in the solution on the UV-visible absorption spectrum of octadecylamine is shown in Fig. 3 shows the effects of NaCl, KCl, and MgCl₂ concentrations on the absorption values of 50 mg/L octadecylamine solutions at 566 nm. K⁺, Na⁺, Mg²⁺, and Cl⁻ have no absorption in the region with a wavelength longer than 300 nm [16, 17], and K⁺, Mg²⁺ and Cl⁻ at different concentrations had a negligible effect on the absorbance value at 566 nm of the octadecylamine solution. The absorbance value at 566 nm decreased when the NaCl concentration was higher than 150 g/L. Sodium ions do not react with ninhydrin. The possible explanation for this phenomenon is that the formation of octadecylamine-ninhydrin complexes is impaired when the sodium ion concentration exceeds 150 g/L.

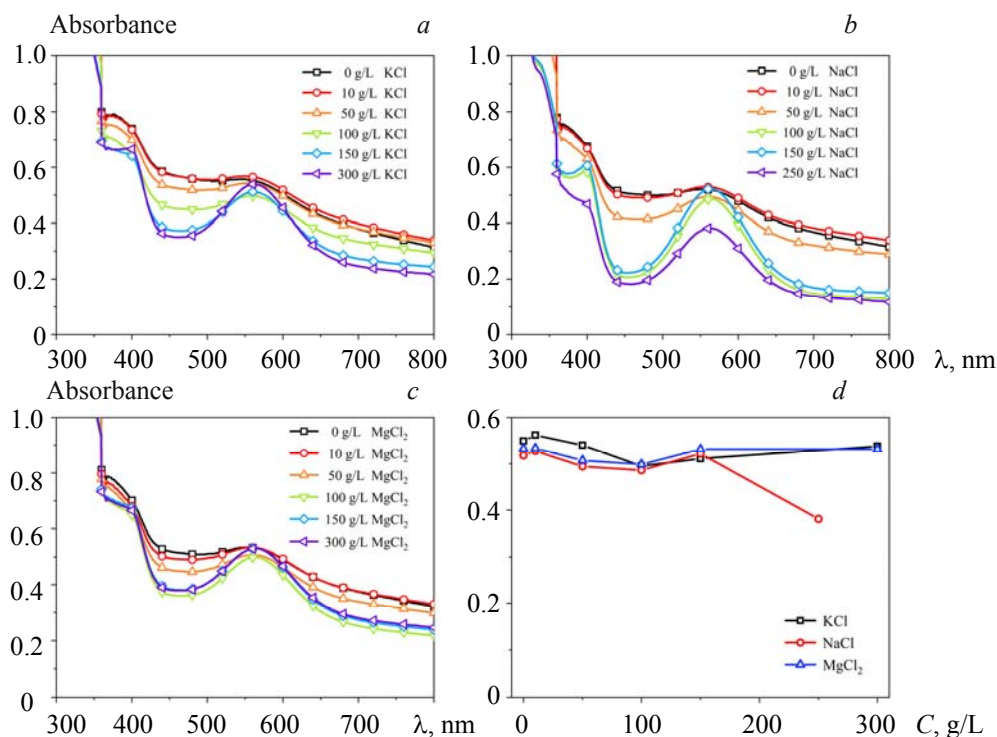


Fig. 3. Effect of chloride concentration on the UV-Vis absorption spectra of octadecylamine solutions.

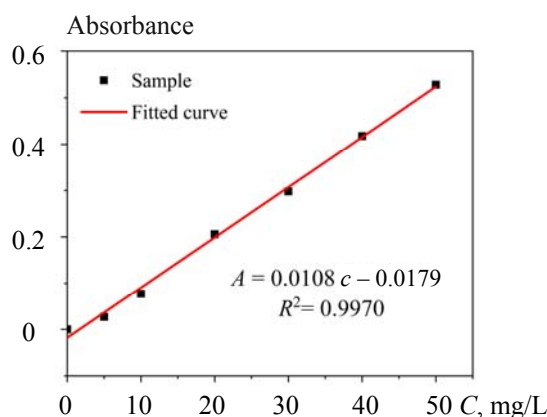


Fig. 4. Standard equation.

The standard curve (Fig. 4) shows that a concentration of octadecylamine is in the range of 1.0–50 mg/L, with a good linear relationship between concentration and absorbance at 566 nm. The linear equation is $A = 0.0108c - 0.0179$ and the correlation coefficient R^2 reached 0.9970.

To determine the minimum detection limit of the method, the standard deviation of the absorbance of the blank solution was calculated by 20 consecutive absorbance measurements and the detection limit formula $D.L. = 3\sigma/r$ (r is the slope of the standard curve) recommended by IUPAC. The detection limit of the standard curve was calculated to be 8.74×10^{-2} mg/L.

A series of octadecylamine solutions were prepared, and buffer solution and indicator solution were added, each sample was measured 6 times in parallel, and the measurement results are shown in Table 2. The relative standard deviation for determining the octadecylamine concentration was between 0.05 and 0.15%. The comparison between the measured and sample concentrations is shown in Table 3, with a relative error from –3.0 to +1.0%, and the average relative error is 1.51%.

TABLE 2. Repeatability of Standard Equation

Sample	A						RSD, %
1	0.066	0.065	0.067	0.065	0.065	0.066	0.132
2	0.082	0.082	0.080	0.081	0.083	0.083	0.129
3	0.154	0.153	0.153	0.152	0.152	0.154	0.145
4	0.202	0.201	0.200	0.204	0.202	0.202	0.121
5	0.254	0.254	0.255	0.256	0.255	0.255	0.068
6	0.386	0.385	0.383	0.385	0.385	0.386	0.134
7	0.452	0.451	0.453	0.452	0.452	0.454	0.094

N o t e. RSD: Relative standard deviation.

TABLE 3. Accuracy and Relative Error of ODA Concentration

Sample	Real value, mg/L	A	Measured value, mg/L	RE, %
1	9.98	0.087	9.71	–2.7
2	25.18	0.251	24.90	–1.1
3	50.08	0.529	50.45	+0.7

N o t e. RE: Relative error.

Conclusions. The absorbance of the solution and its concentration in the range of 1.0–50 mg/L obey Beer's law, and KCl, MgCl₂, and NaCl ($C_{NaCl} < 150$ g/L) solution have little influence on the determination of the octadecylamine concentration. The linear equation $A = 0.0108c - 0.0179$, R^2 is 0.9970. The average relative deviation of the measured samples was 1.51%. The method has the advantages of convenient operation, high accuracy, good repeatability, and low analysis cost. It can be used for the rapid determination of octadecylamine in the aqueous and salt solution.

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