

Spectrophotometric method for determination of trace aluminum with application of Alizarin Red S

F. Leng^{1*}, Y. Jing¹, Q. Wei¹, Y. Wang¹, Y. Lv¹, X. Wang^{2*}, X. Zhu²

¹School of Life Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, China

²Lanzhou Institute of Husbandry and Pharmaceutical Sciences of CAAS, P. R. China

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Chromogenic agent alizarin red S was applied as complexant for the quantitative determination of trace aluminum by ultraviolet spectrophotometer. The experimental parameters (pH of the aqueous solution, temperature and the reaction time), interference in the measurement was optimized. The maximum absorbance of the reaction system was 490 nm further than the one of alizarin red S itself. The calibration curve was linear over the concentration range 0.04~0.14 mg·mL⁻¹ of aluminum with good precision as well as accuracy and the variance reached to 0.9803. The detection limit was down to 0.004 mg·mL⁻¹. Method Validation showed that: Fe³⁺ and Cu²⁺ had some influence on determination of Al³⁺, while K⁺, Na⁺ had little interference. The recoveries were 82%~108%. Results from experiments indicated that the proposed method was easy for operation with great selection, reproductivity and comparison as well as board range of detecting concentration.

Keywords: Alizarin Red S, Spectrophotometry, Aluminum(III) Ion, Determination

INTRODUCTION

Aluminum is a familiar metallic element which is up to 8.8% (by weight) in the earth's crust, just lower than oxygen and silicon. The main existence form of aluminum is compound silicate or weathering products. As a broad-spectrum metal, aluminum has great number purposes in the realm of industries and other fields of life[1]. Early before the 1970S, it's universal that aluminum is not absorbed and digested by human body. Therefore, aluminum is widely used as food additives, water treatment agent[2], drug, structural material in the construction[3], etc. It also used to make tableware and food packaging. But in recent years, studies have shown that aluminum is toxicological effect on health of the public concluding the human beings, animals and plants[4, 5]. Aluminum accumulated in the body can produce great number of illnesses, Alzheimer disease, dialysis encephalopathy, Guam dementia Parkinson's syndrome and so on[6]. Aluminum accumulated in the brain could cause central nervous system dysfunction. Aluminum cumulative in bone tissue may result in bone pathology. The activity of many enzymes system can be affected by aluminum, which produce toxicity to the hematopoietic system. In addition, aluminum has significant inhibitory effects on immune function. Aluminum

also does damage to embryo. Meanwhile, Aluminum could inhibit the elongation and division of plant root tip cell. Taking into account all evidence offered above, determination of aluminum content accurately and rapidly is the premise to ensure the safety of food and then the health of human beings.

Currently, the common measurement methods of trace aluminum contain EDTA complexometric titration, high performance liquid chromatography (HPLC)[7] and Inductively coupled plasma atomic emission spectrometry (ICP-AES)[8] and inductively coupled plasma mass spectrometry (ICP-MS)[9], graphite furnace atomic absorption spectrophotometry[10], fluorescence spectrometry and polarography and so on. However, all these methods have some limitations. For example, EDTA complexometric titration is easily influenced by other interfering ions; UV-Visible absorption spectrum is greatly influenced by the medium; Mass spectrometry instruments is much expensive

Alizarin red S (Alizarin sodium sulfonate, Alizarin S, ARS) is a kind of hydroxyl anthraquinone reagent applied widely in photometric analysis as chromogenic agent[11] and complexing agent[12]. It is the organic material extracted from a natural product called anthraquinone[13]. It can form a number of water-soluble complexes with lots of metal ions[14], mainly for the determination of Al³⁺, Ga³⁺, In³⁺ and rare earth elements ion. In this experiment, the absorbance of materials being tested was measured

* To whom all correspondence should be sent:
E-mail: lff0928@sina.com; wangxiaoli6578@sina.com

using spectrophotometric method at particular wavelength or a certain range of wavelength, therefore, the material was qualitative and quantitative analysis. Alizarin red S and aluminum can produce color reaction under certain conditions. The maximum absorption peaks of complex produced by alizarin red S and aluminum was determined using spectrophotometer. Under the maximum absorption peak, the optimal conditions of of aluminium content the determination was evaluated by controlling variables method, concluding temperature, acidity and reaction time. Four interfering ions and recoveries were used to confirm the feasibility of the experiment. By UV spectrophotometer, a new and simple method is created with high sensitivity, good selectivity for the determination of trace aluminum.

EXPERIMENTAL

Apparatus

A ultraviolet spectrophotometer (Cary50, Varian, USA) equipped with 1.0 cm quartz cells was used to collect all the spectral data at room temperature. All the reagents were weighed by an analytical balance (0.0001g, Mettler-Toledo Instruments, USA). Digital electronic constant temperature water-bath (HY-4, Guohua Electrical Instruments, China) was use to control the temperature. The pH of the solution was measured by a pH meter (PHS-3D, Shanghai Precise Instruments, China).

Reagents

All the reagents used were of chemical purity or analytical grade. The solutions were prepared with distilled water or deionized water, and working solutions were obtained by appropriate dilution.

Alizarin red moderate S ($0.25 \text{ mg}\cdot\text{mL}^{-1}$) solution was prepared by dissolving 0.0500 g of alizarin red moderate S in 100 ml absolute ethyl alcohol and then diluted to 200 ml with distilled water. The Al^{3+} standard solution ($1 \text{ mg}\cdot\text{mL}^{-1}$) was prepared by dissolving 8.9000 g of $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ in 100 ml distilled water and 10 ml of $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl, and then diluted to 1000 ml in volumetric flask on 1000 ml with distilled water. Disodium hydrogen phosphate solution ($0.2 \text{ mol}\cdot\text{L}^{-1}$) was prepared by dissolving 17.9 g of disodium hydrogen phosphate in 100 ml distilled water and subsequently diluted to 250 ml in volumetric flask on 250 ml with distilled water. Citric acid solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$) was prepared by dissolving 5.2500 g of Citric acid in 100 ml distilled water and diluted to 250 ml in volumetric

flask on 250 ml with distilled water. Interferential ions solutions ($0.25 \text{ g}\cdot\text{L}^{-1}$) was prepared by dissolving 0.0500 g of FeCl_3 , $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, KCl, NaCl, respectively, in 100 ml deionized water and then diluted to 200 ml with deionized water.

PROCEDURES

Adsorption preparation and dosage determination

1.5 ml of alizarin red S solution was diluted to 5 ml with distilled water. 0.7 ml of standard solution of aluminum together with 1.5 ml of alizarin red S solution were measured accurately into a test tube, and then 7 another test tubes were prepared similar to the aforementioned. An aliquot of solution of phosphate hydrogen phosphate-citrate buffer (0.0~5.0 ml), separately, were added into the 8 test tubes, and finally diluted to 5 ml with distilled water. 0.15 ml of disodium hydrogen phosphate-citrate buffer solution (pH=4.5, determined optimum finally) and 1.5 ml of alizarin red s solution as well as the aluminum standard solution (0.0~0.7 ml) were taken into graduated test-tubes, and diluted to 5 ml with distilled water. Various amounts of color reagent and 0.15 ml buffer (pH=4.6) together with a certain volume of standard solution of aluminum (0.2~0.7 ml, respectively) were added into 6 test tubes, and then diluted to 5 ml.

The solution above was put in a 1.0 cm quartz cell, respectively. The absorption curve as well as the maximum absorbance of all the aquas were measured by ultraviolet spectrophotometer at room temperature.

Determination of the optimum condition

1.5 ml alizarin red S solution and 0.7 ml aluminum standard solution together with disodium hydrogen phosphate-citrate buffer solution with different pH values were added into the above tubes, water was added until the volume is 5 ml, absorbance values of the solutions were determined at the room temperature. 1.5 ml alizarin red S solution and 0.7 ml aluminum standard solution in conjunction with 0.15 ml disodium hydrogen phosphate-citrate buffer solution (pH=4.6) were put into a test tube(5 ml), absorbance measured at different temperatures. Solution similar to the second one was left to stand for diverse time (10~60 min) with absorbance detection.

Method Validation

The stability test of recommended method was assess by the addition of interfering ions in the reaction system. The interference of foreign ions

(Na⁺, Fe³⁺, Cu²⁺, K⁺) were measured with various concentration of aluminum standard solution (pH=4.6). The accuracy and precision of the proposed method was evaluated with the standard curve and the recoveries.

RESULTS AND DISCUSSION

Dosage determination

The studies indicated that utilize of alizarin red S for determination of trace aluminum was feasible and precise. Without anything others, absorption response of alizarin red S itself appeared at 420 nm (Fig. 1a). Within disodium hydrogen phosphate-citrate buffer solution, absorption wavelength as well as Abs value of the reaction system increased with its volume. The absorption wavelength ranges from 420 nm to 490 nm (Fig. 1b). The range of the

absorption wavelength was wide and the sensitivity was accurate with 0.15 ml buffer solution (Fig. 1c). In addition, together with the aluminum standard solution, absorption peak increased with its dosage to 490 nm because of the complexation between aluminum and alizarin red S. The Abs also rised with its volume until the volume was equal to 0.7 ml (Fig. 1d, 1e). In conjunction with various dosage of aluminum standard solution, Abs grew with the volume of the Alizarin red S. The Abs had large extent and great accuracy when the volume of Alizarin red S was from 1.5 ml to 1.8 ml (Fig. 1f). From the point of cost-saving and result-precise, the dosage of disodium hydrogen phosphate-citrate buffer solution, aluminum standard solution and Alizarin red S were 0.15 ml, 0.2-0.7 ml and 1.5 ml, respectively

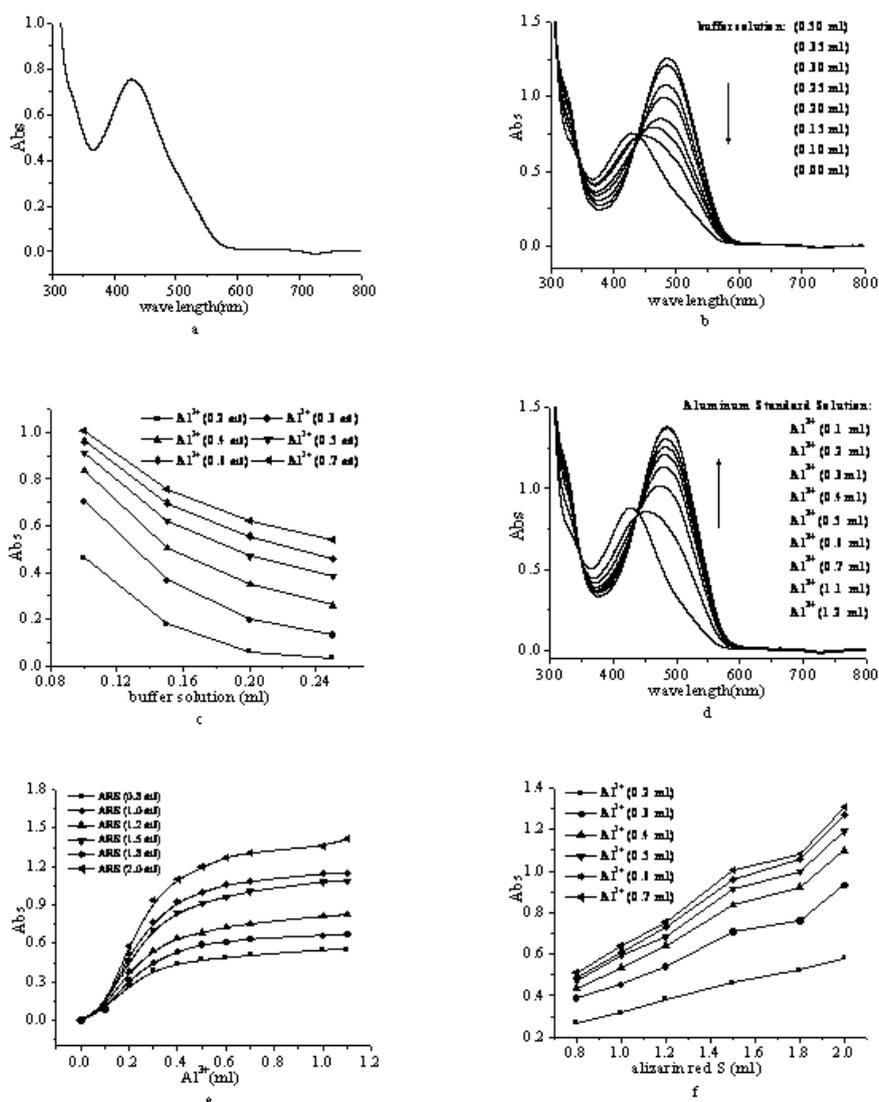


Fig. 1. Reagents dosage determination: (a) absorption spectrum of alizarin red S, (b) influence of buffer solution's volume, (c) buffer solution's volume determination, (d) absorption spectrum of aluminum standard solution, (e) absorbance of aluminum standard solution, (f) absorbance of Alizarin red S.

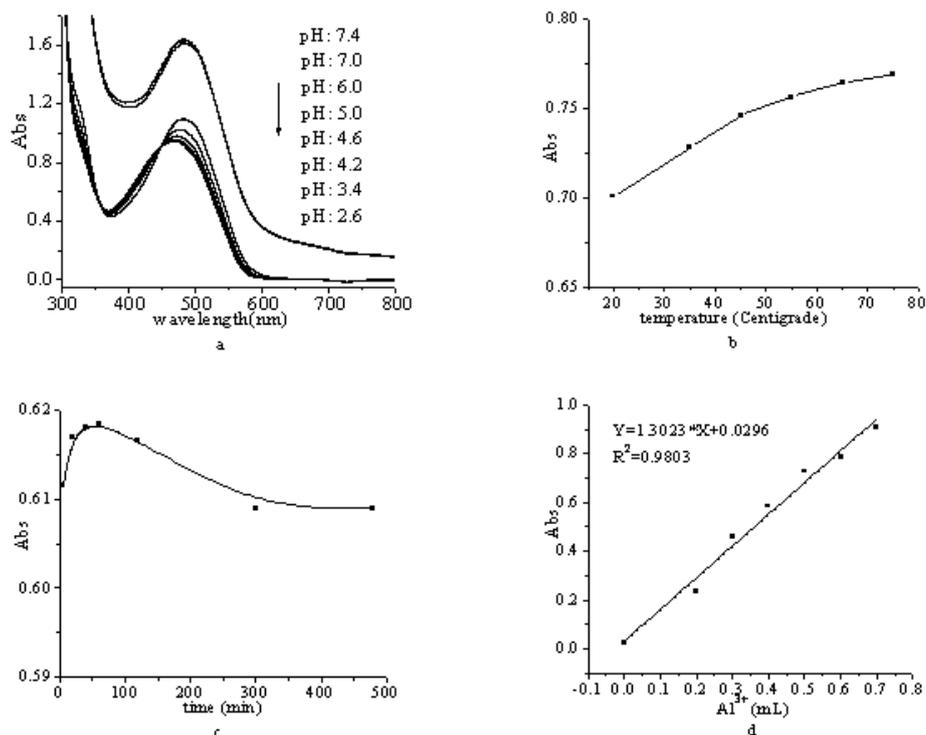


Fig. 2. The optimum condition: (a) influence of the pH value, (b) impact of the temperature, (c) effect of the reaction time, (d) standard curve.

The effects of reaction variables

The pH value of alizarin red S itself was 4.67. In order to achieve better sensitivity, the reaction should be carried out in a weakly acidic medium. When the pH value was lesser than 4.0, the maximum absorption peak was about 470 nm. There was sediment in the reaction system when the pH value was greater than 7.0. The absorption peak was approximate 490 nm (Fig. 2a). So the Abs should be measured when the pH was 4.6 at 490 nm. The value of Abs increased with temperature in only a slight degree (Fig. 2b). For cost-effective and easy-to-control, the experiments were operated at room temperature. The absorbance fluctuated as the reaction time in a small range. The reaction system can keep stable for about 6 h with correlation index of the standard curve equal to 0.9803 (Fig. 2c, 2d).

Method Validation

This study took interfering ions and recovery into consideration to discuss feasibility of this method. For the interfering ions, the Na⁺, K⁺, Fe³⁺, Cu²⁺ were chosen to be tested. The absorbance as well as maximum absorption peak were nearly invariant with Na⁺ or K⁺ whether there is Al³⁺ in the system (Fig. 3a, 3b, 3c, 3d). But for Fe³⁺ and Cu²⁺,

the Abs value rised with their concentration to some extent (Fig. 3e, 3f, 3g, 3h). The recovery and precision were tested for accuracy. The result is between 82%~108%, which illustrated the method feasible (Tab. 1).

Table 1. Recovery test results of determination of aluminum.

Number	Background values (μg)	Addition values (μg)	Absorbance	Recovery (%)
1	0.15	0.1	0.2981	82
2	0.15	0.2	0.5302	108
3	0.15	0.3	0.6691	107
4	0.15	0.4	0.7475	99
5	0.15	0.5	0.8005	90

CONCLUSIONS

The results showed that the appropriate use of alizarin red S allowed determining trace aluminum exactly. Alizarin red S was employed as complexing agent. To ensure satisfactory results, some conditions such as pH of the aqueous solution, temperature, the reaction time of the reaction system were optimized. The application of spectrophotometer provided a very simple and relatively rapid determination of aluminum. The linear range was relatively wide within general concentration range of 0.04~0.14 mg·mL⁻¹.

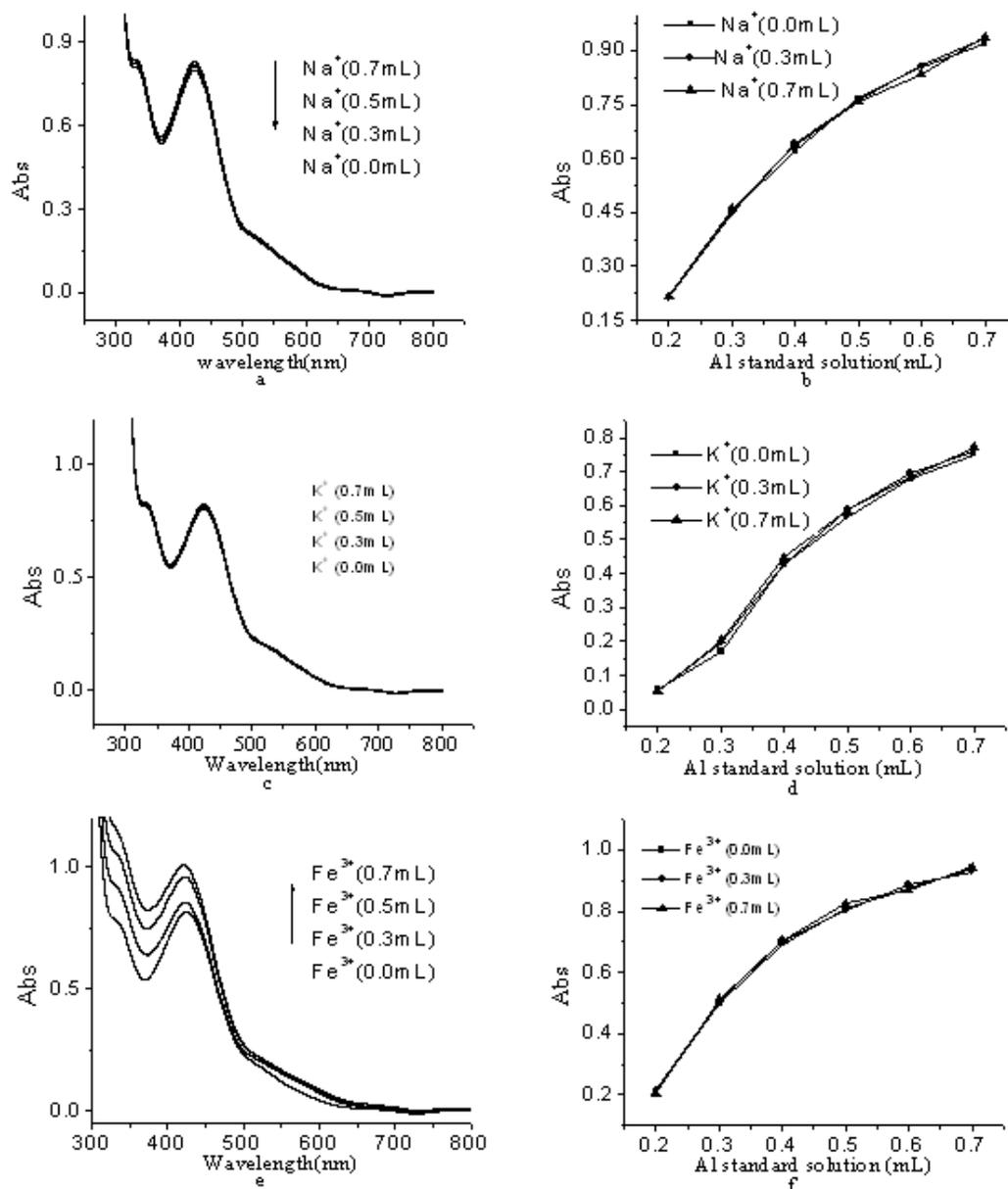


Fig. 3. the influence of interfering ions: (a, c, e, g) Reaction between Alizarin Red S and different quantity of Na^+ , K^+ , Fe^{3+} , Cu^{2+} , (b, d, f, h) Influence of Na^+ , K^+ , Fe^{3+} , Cu^{2+} on absorbance determination of reaction system.

The method recommended was precise, less cumbersome, easy to operate and sensitive when the volume of disodium hydrogen phosphate-citrate buffer solution, aluminum standard solution and alizarin red S were respectively 0.15 ml, 0.2~0.7 ml and 1.5 ml with pH equal to 4.6 at room temperature in conjunction with wavelength of 490nm. Method validation concluding influence of interfering ions and recovery indicated that the recommended method was of great veracity and stability. As a consequence, alizarin red S represents a possible new alternative which surpasses the methods known from literature in

many aspects. It may be a new test tool for determination of aluminum.

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СПЕКТРОФОТОМЕТРИЧЕН МЕТОД ЗА ОПРЕДЕЛЯНЕ НА СЛЕДИ ОТ АЛУМИНИЙ С ПРИЛАГАНЕ НА АЛИЗАРИНОВО ЧЕРВЕНО S

Ф. Лен^{1*}, И. Джин¹, П. Уей¹, И. Уан¹, И. Лв¹, Кс.Уан^{2*}, КсХ. Жу²

¹ Училище за науки за живота и инженерство, Технологичен университет в Ланджоу, Ланджоу 730050, Китай

² Ланджоу институт за селско стопанство и фармацевтични науки на СААС, Китай

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(Резюме)

Хромогенния агент ализариново червено S се прилага като комплексобразувател за количествено определяне на следи от алуминий с ултравиолетов спектрофотометър. Експерименталните параметри (рН на водния разтвор, температура и време на реакция), смущенията в измерването са оптимизирани. Максималната абсорбция на реакционната система е с 490 нм отдалечена от тази на самото ализариново червено S. Калибрационната крива е линейна в диапазон на концентрации 0.04 ~ 0.14 мг/мл алуминий с добра точност, както и прецизността и вариацията достигна до 0.9803. Границата на откриване е 0.004 мг/мл. Валидирането на метода показва, че Fe³⁺ и Cu²⁺ имат известно влияние върху определянето на Al³⁺, докато K⁺, Na⁺ имат малко влияние. Нивата на възстановяване са 82% ~ 108%. Резултатите от експериментите показват, че предложеният метод е лесен за работа, с голяма селективност, повторямост, както и широк диапазон на определяни концентрации.