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Microwave digestion coupled with spectrophotometry for rapid analysis of the total aluminum in polyaluminum solutions

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Abstract

The traditional measurement methods of 3 kinds of aluminum species and the total aluminum content in polyaluminum solutions are Al-Ferron timed complex spectrophotometry and EDTA chelatometry respectively. But each

of these methods has different deficiencies. In this paper, microwave digesting technical had be coupled with the radiate Ferron spectrophotometry to rapid mensurate the concentration of total aluminum Al_T in polyaluminum solutions. Test results show that: (1) it has a very great influence on the measured value whether the Ferron mixed chromogenic solutions after deploys different time or not, but it can been put into use immediately after microwave digested 30 s, which overcomes the weakness that must set 5 days at the traditional method; (2) Proved at the same time that it can assay quantitatively the total aluminum content in some water treatment reagents of polyaluminum solutions conveniently by microwave digesting 2 min for the mixed solutions of the Ferron mixed chromogenic solutions and the polyaluminum solutions. The feasibility of this method has been verified by modified Al-Ferron timed complex spectrophotometry at the same time.

Keywords: Polynuclear aluminum, Microwave digesting, Spectrophotometry

1. Introduction

Because polymeric aluminum species in nano-size have many industrial applications [1], e.g., as coagulants in potable and waste water treatments, chemistry reaction catalyst, clay stabilizing agent in oilfield, oil/water separating agent, cement quick condensation agent, binding agent of fire-resistant material, and the cloth anti-fold agent etc, people have studied the species of hydrolysis-polymerization of Al widely and deeply for a century. Many analytical methods have been used in characterizing and quantifying polynuclear Al. But, up to now, due to the complexity of reaction dynamics of Al, the multiplicity of reaction conditions, the utilization of different experimental methods or approaches, and the effect of some complex anions [2], all of the factors make people can't judge the total aluminum correctly, and also make the conclusions exist some arguments even paradox [3].

Now, according to National Standards of P.R.C [4], the total aluminum content in water treatment reagents of polyaluminum is still widely assayed by the traditional methods [3, 5]:

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acidify the sample of polyaluminum (filter if necessarily); complex with excessive and quantitative EDTA ($C_{10}H_{14}O_8N_2Na_2$); boil 1 min; cool; dilute; fix the volume; adjust the pH value for 6~7; Take xylenol orange as visual indicator, than back titrate the residual EDTA by zinc chloride standard solution. This trivial process makes greater error in the assaying result. The use of ICP-AES analysis for total aluminum requires a long acidolysis process, is costly, and is prone to interference by other ions [6]. The Al-Ferron timed complex spectrophotometry is widely used to determine the distribution of aluminum species in polyaluminum, However, in order to make the solubility of Ferron reagent biggest, the Ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid) mixed chromogenic solution must be equilibrated for 5 days and must be used within 25 days [7-14]. This 5 day equilibration period makes it difficult for uninterrupted industrial production and scientific research; it can also bring great troubles to experiments and industrial controls. This paper couples a microwave-radiated technology with timed complex spectrophotometry to rapidly survey the total aluminum content of polyaluminum solutions.

2. Experimental

2.1. Reagents

Stock solutions of 0.5 mol L^{-1} $AlCl_3$ and 1 mol L^{-1} NaOH were prepared with corresponding reagents in double-deionised water that had been thoroughly purged with high purity N_2. Their standard operating solutions were both diluted from their corresponding stock solutions. All standard solutions were freshly prepared. Ferron mixed buffer spectrophotometer solution (following abbreviation as mixed chromogenic solution) was prepared following the procedure proposed by Jardine and Zelazny [15], which requires the following solutions: 0.2 % Ferron aqueous solution; 0.01% O-phenanthroline aqueous solution; 2.0 mol L^{-1} sodium acetate solution; 0.54 mol L^{-1} HCl solution; 1.0 mol L^{-1} $NH_2OH.HCl$ aqueous solution. In which, the molar concentration of Ferron is 4.1×10^{-3} mol L^{-1}, and the pH measured finally is 5.2. All reagents used were of analytical reagent grade and CO_2-free doubly deionized water was used in all experiments.

2.2. Instruments

The 752 type UV-Vis spectrophotometer (Shanghai) was used in the Ferron timed complexation spectrophotometry experiment. The pH was measured with pHS-3C acidimeter. The NN-S570 MFS type variable-frequency microwave oven (Nanjing) revamped by National type oven was put into use in this experiment. All experimental vessels are made from polyethylene material, and each vessel must be acid-soaked more than 24 hours in the 10 % HNO_3 solution.

2.3. Preparation of polyaluminium

Polyaluminum solution, which the mole ratio of OH^- to Al^{3+} (namely OH/Al, termed as ñ) is about 2.0, was prepared by the method of homoeothermic micro-drop base according to the documents [6], and then standby after aging for 24 hours.

2.4. Option of microwave power

It is linchpin to choose the microwave power and digesting time in surveying the total aluminum content of polyaluminum solutions by microwave digesting timed complex spectrophotometry. The optimal microwave digesting power was selected as 280 W by orthogonally experiment. For the limitation of initial working condition of permatron and for the consideration of the benefit to the depolymerization and complexation reaction of

polyaluminum, it takes the on-off control program (duty ratio mode), that is to say, being on for 17 s and being off for 5s. Its code is 280×17/22. There are two categories of determining the optimum microwave- digesting time in the experiment. One is the time of digesting the mixed chromogenic solution, the other is the time of digesting the mixed chromogenic solution and polyaluminum solution together.

2.5. Operating procedure of microwave digesting timed complex spectrophotometry

The experimental method of Al-Ferron timed complex spectrophotometry and the fraction of 3 kinds of aluminum species (Al_a: Monomer species, Al_b: Polymerization species, and Al_c: Sol or gel polymer $Al(OH)_3$ species) are refer to documents [6, 7, 10, 16, 17]. These species are distinguished from one another by their differences in rates of reaction with Ferron. The total alumnum, namely, $Al_T = Al_a + Al_b + Al_c$. Experimental temperature is (25 ± 2 °C). In the experiment, the mole ratio of Ferron / Al^{3+} is greater than or equal to 50. Timing immediately was from the point while the polyaluminum solution and the mixed chromogenic solution were mixed, and the microwave digesting time was included in this interval. Following the pseudo-first-order dynamic reaction [6, 8], $[Al_a]$, $[Al_b]$ and $[Al_c]$ can be calculated according to document [6]. Surveying A-t (absorbance to time) curve of two copies polynuclear aluminum solutions every time at the same time, one is digested by microwave for some time; the other is not.

3. Result and discussion

3.1. Mixed chromogenic solution after radiated by microwave could be used at once and need not to store for 5 days

Only digested the Ferron mixed chromogenic solution by microwave, the experimental results show in Table 1. It indicates that: (1) if the mixed chromogenic solution of 5th day is radiated by microwave, the contents of Al_a, Al_b and Al_c are similar to that of the 5th day's mixed chromogenic solution which have not radiated. It means that there is little effect to the 5th day's mixed chromogenic solution when radiated by microwave (see row 7 and row 5 in Table 1), therefore, the mixed chromogenic solution is basically steady. It reveals also that the traditional method of storing 5 days for mixed chromogenic solution is reasonable; (2) whether the solution stored or not has a great influence on the surveying result. If the test result of the 5th day's mixed chromogenic solution is taken as a relative standard, the content of Al_a will be inclined to bigger,

Table 1
The comparison of experimental results in the first day to digest some time by microwave with that of 5d after deploying Ferron mixed chromogenic solutions (ñ =2.0, $Al_T = 1\times10^{-4}$ mol·L^{-1}).

Serial number	the handling condition of Ferron mixed chromogenic solutions	Al_a (%)	Al_b (%)	Al_c (%)
1	1st day, not microwave radiated	46.80	47.60	5.59
2	1st day, microwave radiated 10 s	40.21	51.85	7.94
3	1st day, microwave radiated 30 s	34.47	55.35	10.18
4	1st day, microwave radiated 2 min	35.13	53.52	11.35
5	5th day, not microwave radiated	34.20	56.51	9.29
6	10th day, not microwave radiated	33.70	57.61	8.69
7	5th day, microwave radiated 2 min	33.18	57.23	9.59

and that of Al_b will be inclined to smaller in the case that the mixed chromogenic solution newly-prepared is directly used without storage (compared the row 1 with the row 5 in Table 1); (3)

The first day's mixed chromogenic solution (take 25 mL) was radiated by microwave for 30 s, which has the very similar results with that of the 5th day's mixed chromogenic solution without being radiated. That is to say, it can be used at once if digested for 30s by microwave, and needs not storing for 5-10 days, which can largely shorten the test period.

3.2. Rapid survey the total aluminum content of polyaluminum solutions by microwave digesting timed complex spectrophotometry

On the first day and the 5th day of the Ferron mixed chromogenic solution prepared, do the same tests respectively, namely, digested the mixed solution of polyaluminum solutions and Ferron chromogenic solution by microwave, experiments show from Fig.1 and Table 2 that: under the same condition, The longer the time of microwave handling, the bigger the Al_a % value, the smaller the Al_b % and the Al_c % value (Table 2); Having been digested for 70 s by microwave, Al_b has almost complete in depolymerizing and complexing (Table 2); Having been digested for 2 mins by microwave, the A-t curve seems to a straight line paralleling with abscissa and nearly overlapping the photometric absorption curve of $AlCl_3$ whose content of aluminum is the same to Al_t of polyaluminum (Fig. 1). So it is thought that the surveying result after digesting by microwave for polynuclear aluminum is the total aluminum content in fact. Besides, the same result can be got from the data in Table 2.

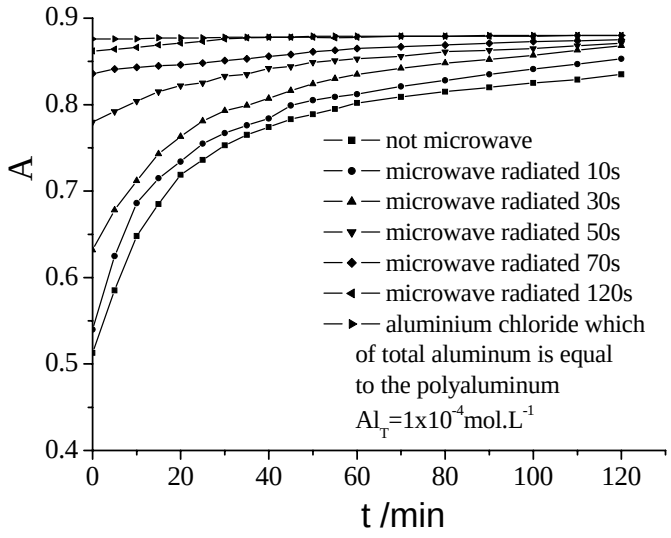

Fig. 1 The comparison of the alteration of A *vs.* time curve when polyaluminium solutions was radiated different time by microwave (ñ=2.0, $Al_T = 1\times10^{-4}$ mol L^{-1})

3.3. Analysis of the principle of microwave digesting timed complex spectrophotometry

Microwave is a kind of electromagnetic waves with very high frequency. It has strong penetrating power. Now, there are two explanations [18] as for microwave accelerating the chemical reaction: One viewpoint says that microwave can accelerate the speed of the chemical reaction by making the material's deep layer heated, thereby accelerating the speed of the molecular movement. Meanwhile, the infliction of microwave can raise the temperature and reduce the viscosity of polyaluminum solution, which can speed the collision probability between the Ferron molecules and aluminum ions, and then accelerate the depolymerization speed of Al_b; The other standpoint thinks that the radiation of microwave not only has the heating function, but also has nonheating function which is caused by temperature.

Table 2
The comparison of the content distribution among Al_a, Al_b, Al_c when digested the mixed solution of polyaluminum solutions and Ferron chromogenic solution by microwave in different time (ñ=2.0, $Al_T=1\times10^{-4}$ molL^{-1})

the microwave radiated time / sec	Al_a (%)	Al_b (%)	Al_c (%)
not microwave radiated	46.80	47.60	5.59
microwave radiated 10 s	60.88	35.62	3.50
microwave radiated 30 s	86.03	9.20	4.77
microwave radiated 50 s	91.96	5.36	2.68
microwave radiated 70 s	95.46	1.75	2.79
microwave radiated 120 s	97.83	1.02	1.15
microwave radiated 150 s	98.23	0.65	1.12

The nonheating function of microwave may be decisive effect. Having enforcing microwave, polar molecules will rotate more quickly and neutralize the electric potential of polyaluminum colloid solution. Because Al_b-Ferron timed complex reaction is a process that Al_b molecule gradually depolymerizes and then complexes essentially. Under the radiation of microwave, the reaction kinetics is changed; the activation energy is decreased, and the depolymerization-complexation reaction is accelerated largely. Within the short of 2 mins, polyaluminum molecules have been depolymerized and complexed completely. Although Al_c molecules can hardly be depolymerized under common condition of without microwave, it can be depolymerized quickly under the condition of microwave. In a word, the principle and the test method that microwave radiation can accelerate the slow Al-Ferron chromogenic reaction can be used for improving the traditional test method, to reduce the testing time, and improve the testing accuracy [6].

4. Conclusions

Handling by microwave can obviously shorten the storage time of Ferron mixed chromogenic solution. It can be used straightway after radiation for 30 s, which can overcome the shortcomings that must set 5 days at the traditional method. It can save much testing period and testing cost; Al_b-Ferron timed complex reaction is a process that Al_b molecule gradually depolymerizes and then complexes essentially. That, digesting the mixed chromogenic solution and polyaluminum solution together for 2 mins, can rapidly survey the total aluminum content of polyaluminum solutions, which can reduce many test steps and lots of errors.

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