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Simultaneous determination of NaOH, Na_2CO_3 and Al_2O_3 in sodium aluminate solutions by flow injection titration①

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[Abstract] A flow injection titration method for simultaneous determination of hydroxide, carbonate and alumina in sodium aluminate solutions was proposed. 150 μL sample was injected and firstly reacted with a mixture of methyl orange, phenolphthalein and sulfosalicylic acid, and secondly, a mixture of chlorhydric acid, ammonium fluoride and phenolphthalein. Methyl orange and phenolphthalein in the first are the corresponding indicators for the determination of hydroxide and carbonate; sulfosalicylic acid is both the titrant and masking agent for aluminum. Ammonium fluoride in the second is complexing agent for alumina and makes it release corresponding amounts of hydroxide ion to aluminum; phenolphthalein is the corresponding indicator for the determination of hydroxide, carbonate and alumina. Chlorhydric acid is the titrant agent for the three. The proposed method can be employed to analyze aluminate solutions containing hydroxide 3.1~15.5 g/L^{-1}, carbonate 3.1~15.5 g/L^{-1} and alumina 0.51~1.02 g/L^{-1} with a sampling frequency of 30 samples per hour. 0.54% and 0.89% are the RSD of sodium oxide and of alumina respectively (n= 11).

[Key words] hydroxide; carbonate; alumina; aluminate; FIA titration

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1 INTRODUCTION

The hydroxide, carbonate and aluminum contents of sodium aluminate solutions are the most important chemical information required for process control in the industrial production of aluminum oxide — the key raw material for the production of aluminum by molten electrolysis. With the development of process automation of aluminum production, automatic determination of sodium aluminate solutions becomes more and more important for industrial production analysis[1]. There is need for fast, selective and automated method for its determination, particularly in routine analysis. Several analytical techniques have been proposed, i. e. traditional chemical analysis methods, thermometric titration, potentiometric titration electric conductance determination and photometric titration techniques. However, aluminate solutions are highly concentrated, industrial samples are often viscous, what's more, their viscosity may vary with different contents of aluminate. There are still many drawbacks in the above methods, so traditional chemical analysis methods are still the most commonly used in our country.

Flow injection analysis (FIA) is a microchemistry technique and automatic solution handling technique[2, 3]. It is a non-chromatography flow analytical method in which quantitative information of eka-determined sample under non-thermodynamic equilibrium conditions[4]. In recent years, much attention has been given to FIA for its advantages including low reagent and sample consumption, simplicity in instrumentation, good repeatability, fast operating and easy automatization[5]. FIA is used in the field of automatic analysis of hydroxide, carbonate and alumina in sodium aluminate solutions and has got some improvements[6~10]. Among them there is an automatic micro-titration method[10], which uses an FI apparatus to collect a micro sample and to deliever titrants, but its principle is the same as the chemical analysis methods[11].

This paper reports a fast, simultaneous and automatic determination of hydroxide, carbonate and alumina in sodium aluminate solutions by flow injection titration with two indicators and single sampling. The repeatability, accuracy and precision of this method and range of determination are studied.

2 EXPERIMENTAL

2.1 Reagents and solutions

The reagents and solution were: sulfosalicylic acid solution (SAL), 0.5 mol/L; phenolphthalein solution, 1 g/L; methyl orange solution, 1 g/L; sodium hydroxide solution, 0.2 mol/L; sodium carbonate solution, 0.1 mol/L; sodium aluminate solution, 0.5 mol/L; chlorhydric acid solution (HCl), 0.5 mol/L; ammonium fluoride solution (NH_4F), 0.5 mol/L. All the reagents are of analytical grade, except where otherwise stated. Distilled water was also used.

2.2 Apparatus

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The self-constructed flow injection spectrophotometry system depicted in Fig. 1 is constructed from the following components: lz-1010 peristaltic pump and 16-port rotary valve; 486 microcomputer system which is used to control the state of valve, magnify photometric signal and transform it to digital signal, plot response curve and calculate peak width (Δt); spectrophotometer of type 721.

C: carrier solution (water); P: pump; R_1: the mixture of HCl, NH_4F and phenolphthalein solution, 150 μL; R_2: the mixture of SAL, phenolphthalein solution and methyl orange, 150 μL; S: sample, 300 μL; R C: reaction coil; D: photometric detector equipped with flow cell; W: waste; PC: microcomputer system.

2.3 Procedure

Turn on the microcomputer and spectrophotometer and preheat them for about 20 min. Enter the automatic analysis system and the integrated software, then correct mechanical zero of spectrophotometer, turn on the peristaltic pump, pump distilled water and move the valve from the state of sampling to the state of injection for several times until there was no gas bubble in the pipeline and the value of absorbance should be zero (w = 540 nm). Load standard solutions and plot the typical curve of logarithm of concentration versus peak width 300 μL sample was loaded, the reagent syringe was filled, the loaded sample was injected and propelled by the carrier solution. Measure the absorbance at 540 nm.

2.4 Absorbance and pH change during a typical titration

As shown in Fig. 2, there are several distinguishable segments in curve (1) and curve (2). Curve (1) indicates the change of pH. Water is carrier, so it is the first material which flows into the system, at pH = 7. From a to b, with the mixing of carrier (water) and R_1 (HCl + NH_4F + phenolphthalein), pH declines; from b to c, with the mixing of R_1 and sample, pH rises; from c to d, with the mixing of sample and R_2(SAL + methyl orange + phenolphthalein), pH declines; from d to e, with the mixing of R_2 and carrier, pH rises. But at last, carrier (water) is left in the system, so at that time, pH returns to 7 and is not changeable.

Curve (2) indicates the change of absorbance. Before point A, water is colorless, so absorbance is not changeable. From A to B, pH < 8, phenolphthalein is colorless; from B to C, absorbance rises owing to the red color of phenolphthalein in the basic medium; from C to D, the recorded absorbance declines owing to the decrease of pH, in this segment, phenolphthalein is red, methyl orange is yellow; from D to E, the absorbance rises owing to the red color of methyl orange in acid medium, at the same time, phenolphthalein is colorless; from E to G, the recorded absorbance declines, in this segment, phenolphthalein is colorless and methyl orange is yellow; from G to H, because water is still pumped into the system, the absorbance is not changeable.

At the same distraction degree of the solutions, the distance from the color changing points of different indicators to the first peak (point C) is the corresponding peak width (Δl). In Fig. 1, the distance from the color changing point of phenolphthalein (J) to C is peak width Δl_1, at this time, sodium hydroxide is titrated completely by SAL but sodium carbonate is only titrated to sodium hydrocarbonate. The distance from the color changing point of methyl orange (I) to C is peak width Δl_2, and both sodium hydroxide and sodium carbonate are titrated completely by SAL. The distance from the color changing point of phenolphthalein (F) to C is peak width Δl_3, at this time, sodium hydroxide, sodium carbonate and aluminium oxide are totally titrated.

3 RESULTS AND DISCUSSION

3.1 Typical curve of absorbance versus wavelength

Because a model 721 spectrophotometer can only design one wavelength for determination at one time, detected wavelength should be chosen the one at which two indicators have high absorbance. In this experiment, the higher absorption wavelength of both the color of phenolphthalein in the basic medium and the color of methyl orange in the acid medium was found to be at 540 nm, while the absorbance of phenolphthalein in the acid medium and methyl orange in

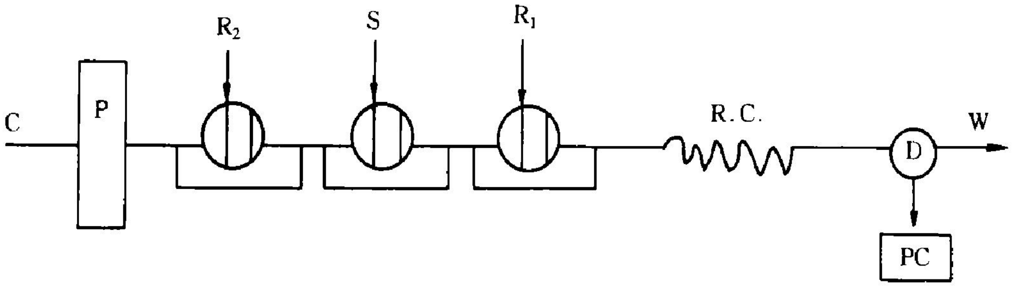

Fig. 1 Manifold configuration

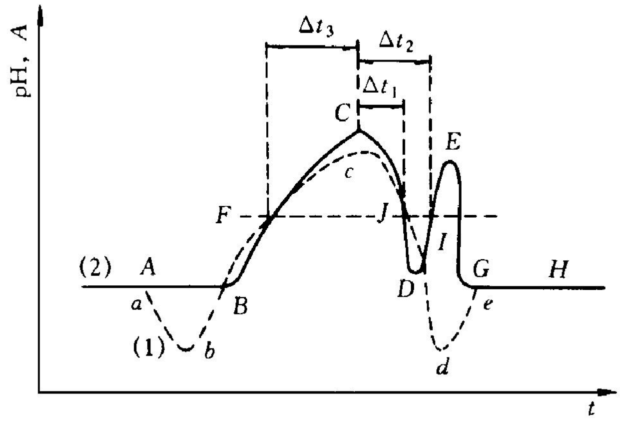

Fig. 2 Absorbance and pH change during typical titration

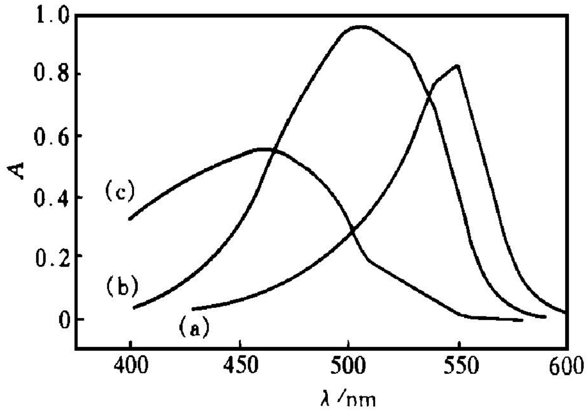

Fig. 3 Absorbance changes in different wavelengths
(a) —Curve of phenolphthalein in basic medium;
(b) —Curve of methyl orange in acid medium;
(c) —Curve of methyl orange in basic medium

the basic medium is low (see Fig. 3). So 540 nm is chosen as the detected wavelength.

3. 2 Optimization of FIA system

Flow injection and chemical variables were optimized for the proposed FI method. This study is carried out by altering each variable in turn while keeping the others constant.

3. 2. 1 Choice of composition concentration of carrier and sampling volume

If the volume of sample was less than the volume of reagents, reagents R_1 and R_2 will be mixed, owing to the impact of carrier, and influence determination. In this experiment, 300 μL sample, 150 μL R_1 and 150 μL R_2 were used. The shape of absorbance curve is good. 0.6 mL Phenolphthalein solution and 0.6 mL of methyl orange solution were used.

3. 2. 2 Choice of inside diameter, length of reaction tube, sampling rate and flow-rate

Experiments indicate that the decrease in absorbance obviously depends on the residence time of the sample zone in the flow system, i.e. on the total flow rate and the coil length. The lower flow rates and longer coil give higher absorbance, but the reproducibility is poor and the peaks are so broad that the sample throughput is very slow. A tube inside diameter of 0.5 mm, a reaction coil of 100 cm, a water flow rate of 1.5 mL/min, were chosen as a compromise between sensitivity and sampling rate. The sampling rate is about 30 samples per hour.

3. 3 Calibration graph

The optimum conditions for determination can be represented as: SAL 2.50 mol/L, mixture of phenolphthalein solution 0.016 g/L and methyl orange solution 0.016 g/L, HCl 2.50 mol/L, phenolphthalein solution 0.016 g/L, the tube length of 100 cm, the reagent flow-rate of 4.0 mL/min. Sample volume was 300 μL, reagent loop volume was 150 μL, a flow-through cell was 1 cm. All measurements were carried out at 540 nm.

The volume of sodium carbonate solution is changed and three regression equations, Eqns. (1), (2) and (3) are obtained.

$$\lg(\rho_k + 1/2\rho_c) = 0.0869\Delta l_1 - 0.01838$$

$$r = 0.9997 \qquad (1)$$

$$\lg(\rho_t) = 0.1045\Delta l_2 - 0.18956$$

$$r = 0.9991 \qquad (2)$$

$$\lg(\rho_k + 1/2\rho_c + \rho) = 0.0623\Delta l_3 + 0.00382$$

$$r = 0.9998 \qquad (3)$$

The volume of sodium hydroxide solution is changed and three regression equations, Eqns. (4), (5) and (6) are obtained.

$$\lg(\rho_k + 1/2\rho_c) = 0.07743\Delta l_1 + 0.0176$$

$$r = 0.9992 \qquad (4)$$

$$\lg\rho_t = 0.09964\Delta l_2 + 0.00694$$

$$r = 0.9996 \qquad (5)$$

$$\lg(\rho_k + 1/2\rho_c + \rho) = 0.0618\Delta l_3 + 0.00562$$

$$r = 0.9990 \qquad (6)$$

The volume of aluminium oxide solution is changed and a regression equation, Eqn. (7) is obtained.

$$\lg(\rho_k + 1/2\rho_c + \rho) = 0.05889\Delta l_3 + 0.00662$$

$$r = 0.9994 \qquad (7)$$

where ρ_k and ρ_c are the concentrations of hydroxide and carbonate expressed as g/L of Na_2O_k and Na_2O_c, respectively. ρ_t is the concentration of total alkali expressed as g/L of Na_2O. ρ is concentration of Al_2O_3. Δl_1, Δl_2, and Δl_3 are the peak width. r is the correlation coefficient.

Experiments indicate that the variation of aluminium oxide concentration between 0.5 g/L and 1.02 g/L doesn' t influence on the contents of hydroxide and carbonate.

3.4 Accuracy and precision

Several samples are analyzed both by the method mentioned above and by the traditional titration method. The results are listed in Table 1. The results obtained by the two different methods match well. The repeatability of this method is good.

Table 1 Results of sample analysis

Component	This method		The classical method	
	Average value /(g·L^{-1})	RSD /%	Average value /(g·L^{-1})	RSD /%
Na_2O_k	4.452	0.47	4.409	0.52
Na_2O	15.44	0.47	15.44	0.44
Al_2O_3	0.576	0.45	0.579	0.47
Na_2O_k	7.223	0.94	7.220	0.92
Na_2O	27.50	0.57	27.49	0.57
Al_2O_3	0.732	0.46	0.738	0.48
Na_2O_k	12.74	0.47	12.75	0.45
Na_2O	33.08	1.00	33.08	0.97
Al_2O_3	0.902	0.51	0.900	0.53

4 CONCLUSIONS

The proposed method is a simple, selective, rapid, automatic and inexpensive technique for the simultaneous determination of hydroxide (3.1~15.5 g/L of Na_2O_k), carbonate (3.1~15.5 g/L of Na_2O_c) and alumina (0.51~1.02 g/L of Al_2O_3) in sodium aluminate solution. To make a compromise between precision and sampling rate, the sampling rate is about 30 samples per hour.

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