

Spectrophotometric Determination of Aluminium with Salicylidene-o-aminophenol-4-sulfonic Acid

Michio ZENKI and Kazuko HORI

*Department of Chemistry, Okayama University of Science,
1-1, Ridai-cho, Okayama-shi, 700, Japan*

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Salicylidene-o-aminophenol (SAPH), one of the typical Schiff base, has been studied as a spectrofluorimetric reagent for aluminium¹⁾ and also as a spectrophotometric reagent for copper,^{2,3)} cadmium and zinc.^{2,4)} As be expected from the structure, SAPH and its metal complexes are insoluble in water, then analytical difficulties result from the formation of the precipitates. Therefore, the methods such as precipitation followed by acid dissolution, solvent extraction or solubilization with quaternary ammonium salt are necessary for the determination.²⁻⁴⁾

Salicylidene-o-aminophenol-4-sulfonic acid (SAPS), a SAPH derivative which introduced a sulfonic acid group into a phenyl ring, becomes soluble in water. It is available a simple and rapid determination of certain metals without any treatment. Morishige⁵⁾ had reported the high sensitivity of SAPS on the fluorescence properties compared with 87 Schiff bases. Fluorimetry is more sensitive than spectrophotometry, but requires a instrumental necessity and skillfulness. The authors proposed the use of SAPS for the spectrophotometry in water solution, and determined copper⁶⁾ and vanadium⁷⁾ easily.

This paper presents that SAPS as a spectrophotometric determination for aluminium and application to the determination of aluminium in steels.

Experimental

Apparatus

All absorbances were measured with Hitachi Model 124 and 139 spectrophotometers with 1.00 cm glass cells. pH measurements were made on a Hitachi-Horiba pH meter, model F-7ss.

Reagents

Synthesis of SAPS

An analogous method reported by Capelle,⁸⁾ was used to obtain SAPS. 2-

Aminophenol-4-sulfonic acid (Tokyo Kasei Co.) and salicylaldehyde were allowed to undergo the condensation reaction in aqueous acidic solution (pH 1-2, 60-70 °C, 1 hr.). Yellow precipitates arose from the solution, were filtered by suction and washed three times with ethanol, and once with acetone (yield 87-94 %). The elemental analysis gave the following results: C 49.79 %, H 4.45 % and N 4.49% ; calculated for $C_{13}H_{11}NO_5 \cdot H_2O$: C 50.16 %, H 4.18 % and N 4.50 %.

SAPS solution

0.1 g of SAPS and 2 g of ascorbic acid were dissolved in water and made up to 100 ml (0.1 %). This solution was stable at least for 3 days.

Standard aluminium solution

Dissolve 1.000 g of aluminium (99.9 %) in 10 ml of hydrochloric acid and dilute to 1 liter with water ($1000 \mu\text{g ml}^{-1}$). Dilute this solution as required.

Buffer solution

0.2 M sodium acetate-0.2 M acetic acid (pH 5.2).

All reagents used are of analytical reagent grade.

Recommended procedure

To a sample solution containing up to $40 \mu\text{g}$ of aluminium, add 5 ml of buffer solution (pH 5.2), 3 ml of 0.2 M thiourea solution and 5 ml of SAPS solution. Then dilute the mixture to 25 ml with water. Measure the absorbance of this solution 20-30 min. after dilution at 405 nm against a reagent blank.

Results and Discussion

Absorption spectra

The absorption spectra of aluminium complex and the reagent are shown in Fig. 1. The absorption spectrum of the aluminium complex shows a fairly broad peak with its maximum at 405 nm, while the reagent has no absorption maximum in visible region. The absorbance of the reagent at 405 nm is very small (0.02). This is advantageous because a large excess of reagent can be employed.

Effect of pH

The effect of pH on the absorbance of the complex is indicated in Fig. 2. A constant absorbance was obtained in the pH range between 4.7-6.5.

Effect of standing time

Absorbance readings for this complex reach a stable value about 10 min. after preparation and remain stable until at least 3 hr. Application of heat which pro-

notes a complexation reaction is not necessary⁵⁾.

Effect of reagent concentration

Various amounts of 0.1 % SAPS solution were added to the solution containing 20 μg of aluminium, and the absorbance was measured at pH 5.2. Constant values

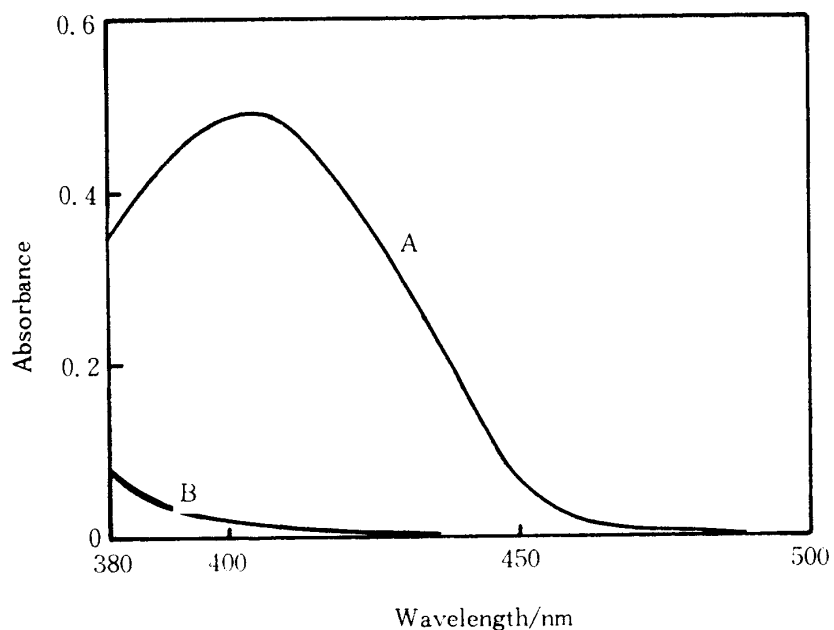


Fig. 1. Absorption spectra: A, Aluminium-SAPS versus reagent blank; B, SAPS versus water.

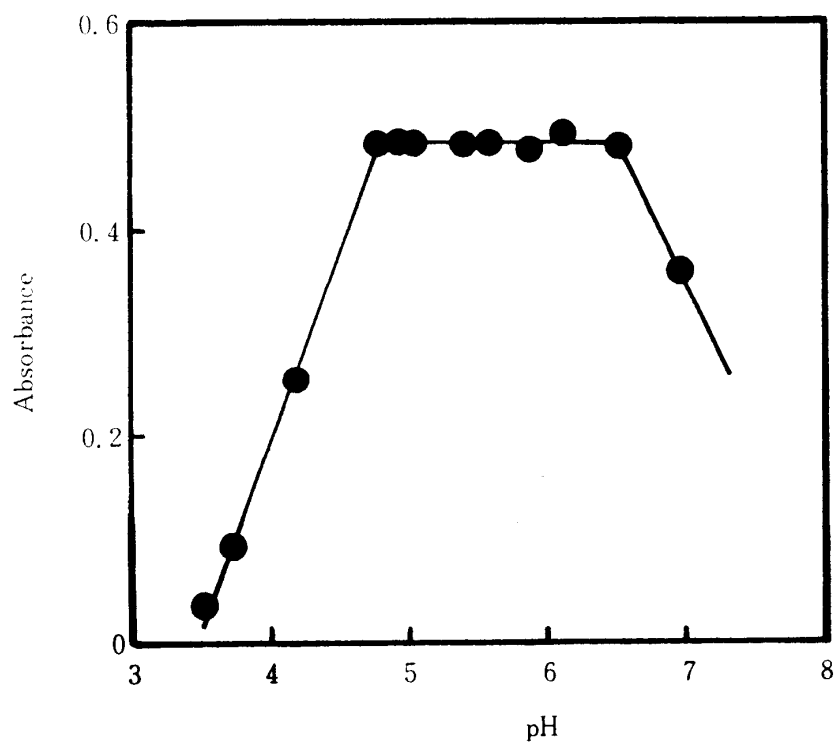


Fig. 2. Effect of pH on absorbance measured at 405 nm.

were obtained more than 3 ml of SAPS solution. In the recommended procedure, 5 ml of 0.1 % reagent used, is corresponding to about 10-fold excess over the upper limit of aluminium used in this investigation.

Calibration curve

The calibration curve was linear in the range of 0–40 μg 25 ml⁻¹ of aluminium. According to Sandell's expression, the sensitivity was 0.0016 μg Al cm⁻² for absorbance of 0.001, and molar absorptivity of the complex at pH 5.2 was 1.7×10^4 l mol⁻¹ cm⁻¹.

It is considered that the sensitivity of SAPS complex is comparable or superior that of alizarin red S, aluminon, arsenazo and 8-hydroxy-quinoline, although inferior to that of catechol violet, eriochrome-cyanine R and stilbazo.⁹⁻¹¹⁾

Repetitive measurements of fifteen samples each containing 20 μg of aluminium, resulted in standard deviation of 0.002 %.

Effect of diverse ions

The interferences of foreign ions in 50 and 5-fold amounts on the determination of aluminium was studied. There was no interference from the following ions: As(III), As(V), Ca(II), Cd(II), Co(II), K(I), Mg(II), Na(I), Si(IV), Sr(II) and Zn(II) (50-fold); Bi(III), Mo(VI) and Ni(II) (5-fold); Cr(III), Cu(II), Fe(III) and V(V) interfere seriously, but they were masked with thiourea except Cr and V. EDTA, fluoride, tartrate, citrate and oxalate also interfered.

Practical applications

The sample solutions were prepared by the method of JIS,¹²⁾ as follows; (0.3–0.7)g of sample was dissolved in aqua regia. The small amount of acidic-insoluble residue was brought into solution by fusion with potassium pyrosulfate, and dissolved melt was combined with the initial solution. The bulk of iron was removed from 6 M hydrochloric acid by extraction with methyl iso-butyl ketone. The aqueous phase was evaporated nearly to dryness in order to remove methyl iso-butyl ketone and residual acid, and diluted with water to 100 ml, and then analyzed by the proposed procedure. National Bureau Standard (NBS) and Japanese Standard Iron and Steel (JSS) samples were used.

The results are shown in Table I.

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Table I. Determination of aluminium in steel

Sample	Sample taken (g)	Aluminium (%)	
		Found*	Certified
SRM 19g	0.4738	0.031 ⁵	0.031
SRM 361	0.7252	0.023 ⁰	0.021
SRM 362	0.3010	0.095 ⁰	0.095
JSS 157	0.6549	0.017 ⁵	0.017
JSS 158	0.5144	0.036 ⁵	0.038
JSS 168	0.5058	0.031 ³	0.032
JSS 169	0.5132	0.043 ⁵	0.045
JSS 171	0.4839	0.040 ³	0.040

*Average of five determinations.

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