



## SPECTROPHOTOMETRIC AND DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH HYDROXYNAPHTHOL BLUE

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**Summary**—The reaction of aluminium(III) with Hydroxynaphthol Blue (HNB) in aqueous media at apparent pH 5.5 results in a red complex that is stable for at least 4 hr. Beer's Law is obeyed up to 1.6  $\mu\text{g/ml}$  of aluminium(III) with an apparent molar absorptivity of  $1.66 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 569 nm. This paper proposes procedures for aluminium(III) determination by ordinary and first-derivative spectrophotometry. The results demonstrated that the linear dynamic range is 0.03–1.60  $\mu\text{g/ml}$  for ordinary spectrophotometry and 11.8–320.0 ng/ml for first derivative spectrophotometry. The HNB is not selective for aluminium, but the addition of EDTA allows the aluminium determination in the presence of accepted amounts of Ca(II), Mg(II), Mn(II), Ba(II), Sr(II), Cd(II), Pb(II), La(III), In(III), Bi(III) and Zn(II). The interference of Cu(II) and Hg(II) can be masked by thiosulphate. Ions such as  $\text{UO}_2(\text{II})$ , Mo(VI), Co(II), Ti(IV) and  $\text{PO}_4(\text{III})$  do interfere seriously. This method was applied for aluminium determination in copper-base alloy, zinc-base alloy, magnesium-base alloy, iron ore, manganese ore, cement, dolomite, feldspar and limestone. The results indicated high accuracy and precision.

Numerous spectrophotometric methods for aluminium determination have been published, normally these methods are not simple and usually they have low confiability. The most frequently reagents used are 8-hydroxyquinoline, aluminon, eriochrome cyanine R, chrome azurol S and stilbazo.<sup>1</sup>

8-Hydroxyquinoline<sup>2</sup> is not very sensitive, but with the use of appropriate masking agents it is highly selective. This method is widely used, but requires extensive and laborious extraction steps. Eriochrome cyanine R<sup>2</sup> is one of the most sensitive spectrophotometric reagents for aluminium determination, but the complex formation is greatly influenced by pH; the stoichiometry is even observed to change with variation in pH. Chrome azurol S<sup>2</sup> has been widely applied, but the aluminium complex solution does not obey Beer's Law and the absorbance signal is very influenced by the reagent concentration. Aluminon<sup>1</sup> is also an important reagent, it reacts with aluminium(III) cation forming a lake and, protective colloids such as gelatin, acacia gum, arabic gum or surfactants must be used to stabilize the formed lake. The rate of lake formation is very slow and

in many cases, require heating of the reagents at 100°C. Stilbazo<sup>1</sup> reacts with aluminium(III) ions forming a lake. The color develops in 10 min and is stable for 45 min. This reagent cannot be used in the presence of high concentrations of electrolytes because of salting out. Many procedures with it have been proposed.

In aqueous weakly acid media, the instantaneous reaction of the aluminium(III) cation with the Hydroxynaphthol Blue (HNB) reagent provides a new spectrophotometric method for aluminium determination. The use of EDTA as masking agent increase the selectivity of the proposed procedure. A derivative spectrophotometric method is also proposed and have higher sensitivity than the ordinary method.

HNB was proposed as spectrophotometric reagent by Brittain.<sup>4</sup> In his study, HNB was used for determination of alkaline earth and lanthanide elements. In another paper, he indicated the use of HNB for spectrophotometric and fluorimetric determination of uranium.<sup>4</sup> Recently Farias and co-workers<sup>5</sup> proposed the use of HNB for nickel determination by cathodic adsorptive stripping voltammetry.

## EXPERIMENTAL

*Reagents*

All reagents were of analytical reagent grade unless otherwise stated.

*Aluminium(III) solution* (1000  $\mu\text{g/ml}$ ). Prepared by dissolving pure aluminium (99.99%) in diluted hydrochloric acid and dissolution up to 1 l with demineralized water

*HNB solution* (0.25%). Prepared by dissolving 0.25 g (Merck) in 100 ml of demineralized water. This solution should be prepared weekly.

*Buffer solution* (pH 5.5). Prepared by mixing 74.6 g of anhydrous sodium acetate and 5.3 ml of glacial acetic acid in 1 l. of demineralized water.

*EDTA solution* (0.20%). Prepared by dissolving 0.20 g of EDTA disodium salt (Merck) in 100 ml of demineralized water.

*Sodium thiosulfate solution* (10%). Prepared by dissolving sodium thiosulfate pentahydrate in demineralized water.

*Apparatus*

Absorption spectra, first-derivative spectra and absorbances were recorded and measured with a Varian DMS-80 spectrophotometer and a Intralab recorder using 1.0-cm cells. A 300 Analyser pH meter was used to measure the pH values

*General procedure*

*Spectrophotometric determination of aluminium (procedure A)*. A portion of solution containing 10.00  $\mu\text{g}$  of aluminium(III) was transferred to a 25 ml standard flask, 5.0 ml

HNB 0.25% and 5.0 ml acetate buffer (pH 5.5) added, mixed and after 10 min 2.0 ml EDTA solution 0.20% added and diluted to the mark with water. The absorbance at 569 nm was measured in a 1-cm cell, using an appropriate blank. A calibration curve covering the range from 4.0 to 40.0  $\mu\text{g}$  of aluminium(III) per 25 ml was prepared.

*First-derivative spectrophotometry (procedure B)*. A portion of solution containing 4.00  $\mu\text{g}$  of aluminium(III) was transferred to a 25 ml standard flask. Then 5.0 ml of HNB 0.25%, 5.0 ml acetate buffer (pH 5.5) were added and mixed. After 10 min 500  $\mu\text{l}$  of EDTA solution (0.20%) was added, diluted to the mark with water, mixed and the first-derivative spectrum from 800 to 500 nm recorded against an appropriate blank, at a scan speed of 100 nm/min and slit of 4 nm.

The first-derivative signal amplitude ( $H$ ) was measured with the recorder voltage 10 or 5 mV.

A calibration curve covering the range from 0.5 to 8.0  $\mu\text{g}$  of aluminium(III) per 25 ml was prepared

## RESULTS AND DISCUSSION

*Characteristics of the reagent and the complex*

The 1-(2-naphthalazo-3,6-disulfonic acid)-2-naphthol-4-sulfonic acid, Hydroxynaphthol Blue (HNB), is an *o,o'*-dihydroxyarylo compound, whose trisodium salt has high solubility in water. The aluminium(III) cation reacts with it forming a red complex with absorption maximum at 569 nm. The complex is formed immediately and is stable for at least 4 hr. The

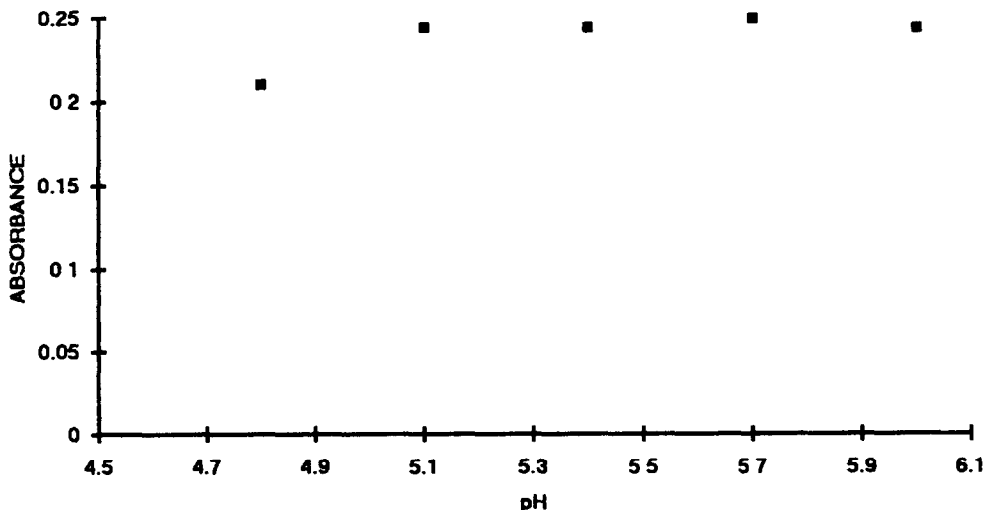


Fig 1 Effect of the pH on the Al(III)-HNB system  $[\text{Al}^{3+}] = 10.00 \mu\text{g}/25 \text{ ml}$ ,  $[\text{EDTA}] = 5.37 \times 10^{-4} \text{ M}$ ,  $[\text{HNB}] = 0.05\%$

Table 1 Effect of the order of addition

Order of addition	Absorbance at 569 nm
Al(III) + HNB + buffer	0.254
Al(III) + buffer + HNB	0.252
Al(III) + HNB + buffer + EDTA	0.242
Al(III) + buffer + HNB + EDTA	0.247
Al(III) + HNB + EDTA + buffer	0.048
Al(III) + buffer + EDTA + HNB	0.002
Al(III) + EDTA + HNB + buffer	0.002
Al(III) + EDTA + buffer + HNB	0.001

HNB reagent has a absorption maximum at 529 nm (at pH 5.5).

#### Effect of pH

The effect of the pH on the aluminium(III)-HNB system was studied and the results demonstrated that the absorbance signal is maximum and constant in a pH range of 5.1-6.0 (Fig. 1). The general procedure was developed with an acetate buffer at pH 5.5, because at this pH, the buffer-index of the acetate buffer is higher than at pH 6.

#### Effect of the amount of acetate buffer solution

The effect of the buffer concentration on the aluminium(III)-HNB complex was studied and the results demonstrated that it does not affect the absorbance signal of the system when the buffer is in the concentration range of 0.1-0.4M in acetate.

#### Effect of the order of addition of reagents on the complex formation

The addition order of the reagents was studied and the results demonstrated that the com-

plex formation was affected by it. The EDTA must be added after the complex formation of the aluminium(III)-HNB, that is only formed after the reaction between aluminium(III) ions with HNB and pH adjustment with addition of the buffer solution (Table 1). The EDTA must be added after 10 min of the complex formation of the chromogenic complex, simply to guarantee the stabilization.

#### Effect of the EDTA amount on the aluminium(III)-HNB complex

HNB is not a selective reagent for aluminium determination. However, the use of EDTA as masking agent solves this inconvenience. The effect of the amount of EDTA on the aluminium(III)-HNB system was studied and the results (Fig. 2) showed that it can be used as a masking agent when present with a concentration for up to of  $1.30 \times 10^{-3}M$ . The presence of EDTA does not affect the stability of the system for at least 4 hr, as can be seen in Fig. 3.

#### Amount of HNB for complex formation

A maximal and constant absorbance signal was obtained for 10.00  $\mu g$  of aluminium(III) with 1.0 ml of 0.25% HNB solution per 25 ml. Thus, 5.0 ml of HNB solution was selected as optimal for the general procedure.

#### Conditions for the measurement of first-derivative value

The absorption spectra and first-derivative spectrum of the aluminium(III)-HNB complex is shown in Fig. 4. Effects of the scan speed and

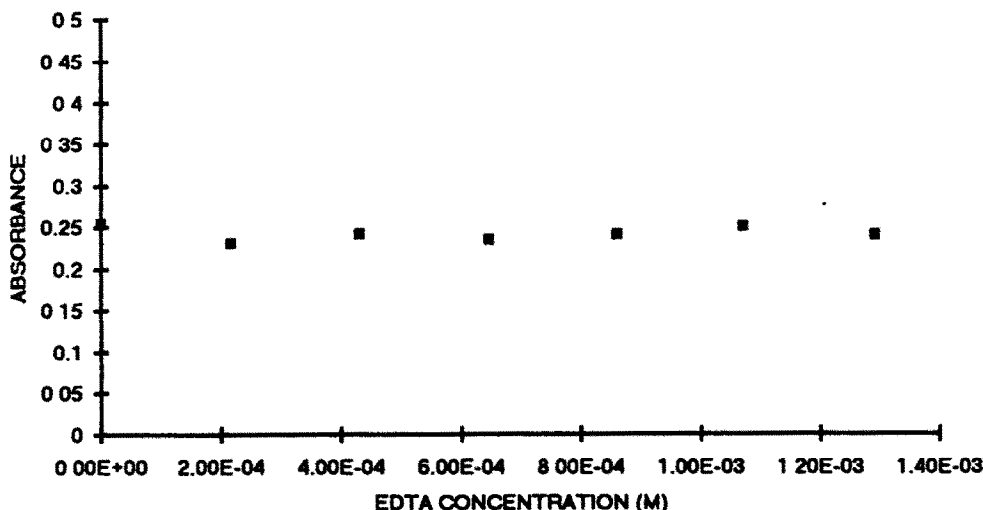


Fig. 2 Effect of EDTA amount on the Al(III)-HNB system  $[Al^{3+}] = 10.00 \mu g/25 ml$ ,  $[HNB] = 0.05\%$ , pH 5.50

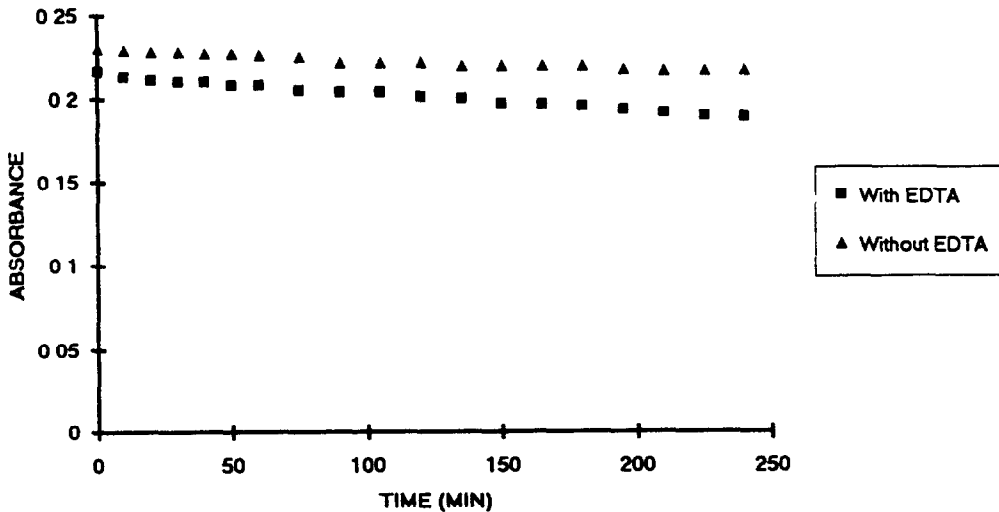


Fig 3 Effect of EDTA on the stability of the Al(III)-HNB system  $[Al^{3+}] = 10.00 \mu\text{g}/25 \text{ ml}$ ,  $[EDTA] = 1.30 \times 10^{-3} M$ , pH 5.50

of the slit width ( $\Delta l$ ) were examined on the measurement of the first-derivative signal. The results showed that scan speed did not affect the value. In this way, the scan speed of 100 nm/min was chosen. It was also found that there was no significant difference in sensitivity among various  $\Delta l$ 's, but the increase of slit width decreased the noise, hence a slit of 4 nm was selected in the measurements. The decrease of recorder voltage obviously does increase the first-derivative signal but also increase the noise.

The method used for the quantitative evaluation of derivative spectra signal is classified as the 'Peak-zero method'.<sup>6</sup>

#### Effect of interfering ions

Solutions containing 10.00  $\mu\text{g}$  of aluminium (III) and various proportions of several cations and anions were prepared and procedure A was followed. The interference limit of an ion was defined as the proportion in which a change of  $\pm 2\%$  in absorbances of the chelates were observed. The results are listed in Table 2.

The interference of mercury(II) and copper (II) can be masked with thiosulfate or thiourea. The addition of 200 mg of sodium thiosulphate is enough to mask 1000  $\mu\text{g}$  of copper(II) cation. Fluoride does interfere seriously but its interfer-

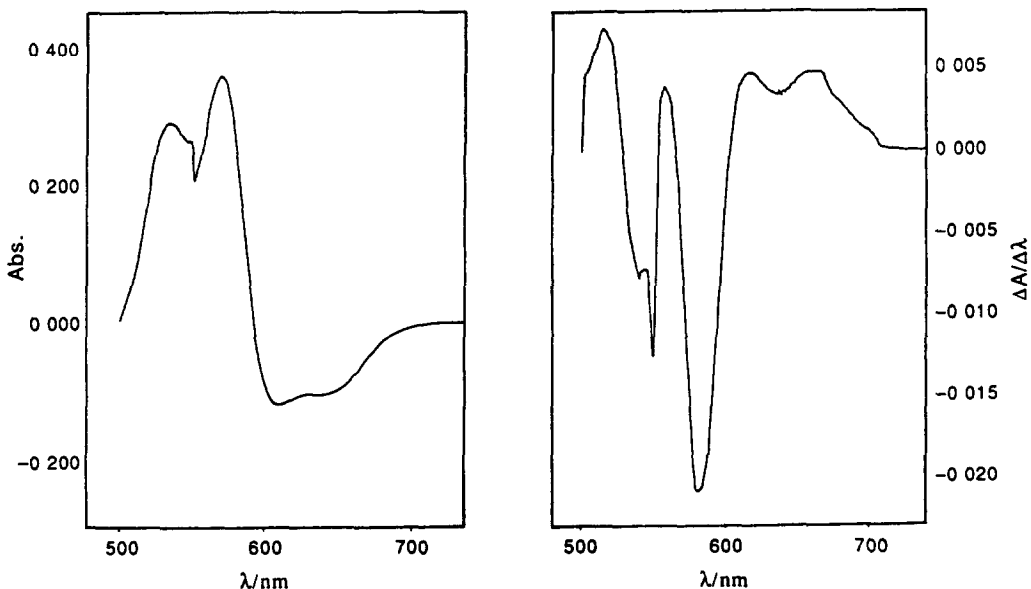


Fig 4 The absorption spectra and derivative spectrum of the Al(III)-HNB complex  $[Al^{3+}] = 10.00 \mu\text{g}/25 \text{ ml}$ ,  $[EDTA] = 5.37 \times 10^{-4} M$ ,  $[HNB] = 0.05\%$ , pH 5.50

Table 2 Aluminium determination in the presence of various ions

Ion	100 × 1	10 × 1	1 × 1	Allowed	
				proportion	Reagent used
Pb(II)	N	N	N	—	Pb(NO <sub>3</sub> ) <sub>2</sub>
Mn(II)	N	N	N	—	MnSO <sub>4</sub> 6H <sub>2</sub> O
Sr(II)	N	N	N	—	Sr(NO <sub>3</sub> ) <sub>2</sub>
Ba(II)	N	N	N	—	BaCl <sub>2</sub> 2H <sub>2</sub> O
Ca(II)	N	N	N	—	CaCO <sub>3</sub> /HCl
Mg(II)	N	N	N	—	MgCl <sub>2</sub> 6H <sub>2</sub> O
La(III)	I	N	N	80 ×	LaCl <sub>3</sub> 7H <sub>2</sub> O
In(III)	I	N	N	50 ×	In <sub>2</sub> O <sub>3</sub> /HCl
Zn(II)	I	N	N	40 ×	ZnSO <sub>4</sub> 7H <sub>2</sub> O
Cu(II)*	I	N	N	50 ×	CuSO <sub>4</sub> 5H <sub>2</sub> O
Fe(III)	I	I	N	10 ×	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> /HCl
Ni(II)	I	I	N	5 ×	NiSO <sub>4</sub> 7H <sub>2</sub> O
Ti(IV)	I	I	N	2 ×	TiO <sub>2</sub> /H <sub>2</sub> SO <sub>4</sub>
Hg(II)*	I	I	N	—	HgO/HNO <sub>3</sub>
Co(II)	I	I	N	—	CoSO <sub>4</sub> 7H <sub>2</sub> O
Fe(II)**	I	I	I	—	Fe(III)/NH <sub>2</sub> OH HCl
F(I)‡	I	I	N	—	NaF
PO <sub>3</sub> (III)	I	I	N	—	NaPO <sub>3</sub>

\*High concentrations can be masked with thiosulphate

†Easily masked by oxidation with nitric acid

‡Interference eliminated by heating with sulphuric acid

Table 3 Analytical characteristics of the procedures

	Ordinary spectrophotometric	First-derivative spectrophotometric
Calibration sensitivity	0.617 ml/μg	47.3 ml/μg
Analytical sensitivity	238.22 ml/μg	635.75 cm/ml/μg
Limit of detection	10.21 ng/ml	3.56 ng/ml
Limit of quantification	34.04 ng/ml	11.8 ng/ml
Linear dynamic range	0.03–1.60 μg/ml	11.8–320 ng/ml
Coefficient of variation	0.46%	0.79%

ence can be easily eliminated by the heating solution in the presence of sulphuric acid or perchloric acid. The effect of ionic strength on the aluminium(III)–HNB system is negligible for 0.1M concentrations of sodium chloride and potassium nitrate.

#### Analytical characteristics of the method

The calibration curves were determined as described in the procedure A (for ordinary spectrophotometric method) and procedure B for first-derivative method. The calibration sensitivity,<sup>7</sup> limit of detection  $C_L$ <sup>8</sup> as well as other analytical characteristics of the method are summarized in the Table 3. Obviously, the derivative method is more sensitive than the ordinary spectrophotometric method.

#### Application

The proposed method (procedure A) was applied for aluminium determination in copper-base alloy, zinc-base alloy, magnesium-base alloy, iron ore, manganese ore, cement, dolomite, feldspar and limestone. Results are described in Tables 4 and 5.

The results of the Table 4 demonstrate that there is no significant difference between the certified value and the found value with HNB at the 95% confidence level. The paired *t* test<sup>9</sup> was applied to the results of Table 5 and it revealed that there is no significant difference between the ICP method and the HNB method in aluminium determination to these matrices at the 95% confidence level.

Table 4 Aluminium determination in standards

Standards	Aluminium certified	Aluminium found	(N)
Zinc-base alloy			
NIST 94c	4.13%	4.13 ± 0.06%	(4)
Copper-base alloy			
NIST 164	6.21%	6.24 ± 0.04%	(5)
Iron ore IPT 23	0.59%	0.59 ± 0.01%	(5)

Table 5 Aluminium determination in samples

Samples	ICP method	HNB method
Cu-base alloy	1.38%	1.49 ± 0.01% (3)
Mg-base alloy	2.78%	2.64 ± 0.04% (5)
Feldspar	10.49%	10.36 ± 0.25% (3)
Limestone	0.80%	0.83 ± 0.04% (3)
Manganese ore	4.58%	4.64 ± 0.08% (3)
Dolomite	0.34%	0.33 ± 0.02% (3)
Cement	0.11%	0.10 ± 0.01% (3)

Sample preparation of geological matrices<sup>10</sup> were made using hydrochloric acid, sulphuric acid and hydrofluoric acid, copper-base alloy and zinc-base alloy with nitric acid and magnesium-base alloy with hydrochloric acid. In copper-base alloy, the copper was masked with thiosulphate<sup>11</sup> and in iron ore, the iron(III) cation was extracted<sup>12</sup> as chloride complex using the ethyl acetate as extractor solvent.

Procedure B was applied for aluminium determination in synthetic aqueous solutions containing iron(III), magnesium(II) and calcium (II). The results demonstrated that this method can be used for aluminium determination in fresh water

### CONCLUSIONS

The proposed method can be applied for spectrophotometric determination of aluminium in matrices that do not contain significant amounts of interferents such as titanium(IV), iron(II), molybdenum(VI), cobalt(II), uranyl(II) and phosphate. Titanium(IV) cation is one of the main interferent in aluminium determination with HNB. However, the aluminium amounts in several geological matrices is much higher than the titanium amounts.

EDTA can be used as masking agent because its reaction with aluminium(III) cation is very slow, when carried out at ordinary temperature and in weakly acid medium, on the other hand

the aluminium(III) cation reaction with HNB is instantaneous

The application of the proposed method indicated that it has very good accuracy and precision. As a result, the proposed method is useful for routine analysis owing to its simplicity comparable with another methods described in the Introduction section.

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