J. Indian Chem. Soc.,
Vol. LIII, October 1976. pp. 1012-1014

Simultaneous Spectrophotometric Determination of Iron(III) and Aluminium(III) with 2-Carboxy-2′-Hydroxy-3′,5′-Dimethylazobenzene-4-Sulphonic Acid.

B. K. DESHMUKH, V. M. PARATE and R. B. KHARAT

Department of Chemistry, Nagpur University, Nagpur 440 010

Manuscript received 21 May 1976 ; accepted 15 July 1976

A spectrohotometric method is developed for the simultaneous determination of Fe(III)and Al(III) in the mixture and in ore, dolomite. 2-Carboxy-2′-hydyroxy-3′, 5′-dimethylazobenzene-4-sulphonic acid (CHDMAS) forms complexes with Fe(III) and Al(III) at *p*H 4.0 which have maximum absorption at 620 nm ($\epsilon = 1275$) and 510 nm ($\epsilon = 2855$) respectively. Fe(III)-CHDMAS complex obeys Beer's law in the concentration range of 0.5—4.0 ppm at 620 nm and 1.0—8.0 ppm at 510nm, whereas Al(III)-CHDMAS complex holds Beer's law in the range of 0.5—2.5 ppm at 620 nm and 0.1—2.0 ppm at 510 nm. The concentration of these elements in an unknown mixture or in the ore, dolomite can be determined from the following equations :

$$[Fe] \times 10^4 = 9.988 \times A_{620} - 3.111 \times A_{510}$$

and $$[Al] \times 10^4 = 4.466 \times A_{510} - 3.179 \times A_{620}$$

The standard deviation of the method is $\pm 0.62\%$ and $\pm 0.82\%$ in the determination of Fe(III) and Al(III) respectively.

RECENTLY, 2-carboxy-2′-hydroxy-3′, 5′-dimethylazobenzene-4-sulphonic acid (CHDMAS) has been described as a new good reagent for spectrophotometric studies of Pd(II), Cu(II), Ni(II)[1,2], Fe(III) and Al(III)[3]. Kharat et al[4]. determined the stepwise stability constants of CHDMAS and its Fe(III) complexes using a potentiometric technique. The studies of azodyes with metals in this laboratory have shown utility of CHDMAS for the spectrophotometric simultaneous determination of Fe(III) and Al(III) in the unknown mixture. The method can be employed in the determination of iron and aluminium in dolomite, directly after the removal of silica.

Davenport[5] determined Al(III) in the presence of Fe(III) in a buffered acetate-acetic acid solution utilizing ferron at *p*H 5.0. These two metals were determined simultaneously by employing 8-quinolinol[6] as extractive spectrophotometric reagent.

The proposed method is simple, selective and applicable at the tracer concentration and affords a quick simultaneous determination of Fe(III) and Al(III) in the synthetic mixture as well as in the ore, dolomite.

Experimental

Apparatus and reagents—Beckman DU2 spectrophotometer with matched 10 mm quartz cells, ELICO *p*H meter with glass and saturated calomel electrodes were used.

2-Carboxy- 2′ -hydroxy-3′, 5′ -dimethylazo- benzene-4-sulphonic acid (CHDMAS) was synthesized as reported earlier[2]. About 0 002 *M* CHDMAS solution was used for the spectrophotometric studies.

$Fe(NO_3)_3 \, 9H_2O$ was dissolved in doubly distilled water and standardized (0.01 *M*) by employing a known method[7]. Standard[7] solution (0.01 *M*) of $Al_2(SO_4)_3 . (NH_4)_2SO_4 . 24H_2O$ was prepared.

General Procedure—An aliquot containing 1.5—4.0 ppm of Fe(III) and 0.7—1.5 ppm of Al (III) and 7.5 ml of the reagent solution in 25 ml was adjusted to *p*H 4.0 by sodium hydroxide and hydrochloric acid The absorbances of the solution were measured at 620 nm and 510 nm against the reagent blank The metals present were computed from the appropriate simultaneous equations.

Analysis of dolomite—After the removal of silica from 0.2 g of dolomite by conventional method, the filtrate was made to 250 ml. 2—3 ml of the filtrate and 7.5 ml of the reagent solution was adjusted to *p*H 4.0 and the above procedure was repeated.

Results and Discussion

Absorption spectra The spectral curve for Fe(III)-CHDMAS complex against reagent blank indicates a maximum at 620 nm. The study of absorption spectra shows that the Al (III)-CHDMAS complex has wavelength of maximum absorption and 510 nm. Hence measurements were made at 620 nm and 510 nm. The spectral data of the complexes are summarized in Table 1. The molar absorptivities of the coloured species were evaluated on the basis of the total metal present.

TABLE 1—SPECTRAL DATA OF THE COMPLEXES

Complex	λ max nm	ϵ_{620}	ϵ_{510}	Validity of Beer's law at 620 nm	*p*H 4.0 at 510 nm
Fe(III)-CHDMAS	620	1275	865	0.5 – 4.0 ppm	1.0 – 8.0 ppm
Al(III)-CHDMAS	510	910	2855	0.05 – 2.5 ppm	0.1 – 2.0 ppm

Effect of pH—The absorption spectra of Fe(III), CHDMAS system at different *p*H values in the *p*H range of 1.0 – 12.0, revealed that the optimum *p*H for the spectrophotometric determination was 4.0. The study of complex formation as a functson of *p*H in case of Al(III) showed that the complex formed at *p*H 4.0 has constant and maximum absorbance. Hence *p*H 4.0 was selected for the entire studies. As the absorbanees are additive, the relation :

$$A_{620} = \epsilon_{620}^{Fe} \cdot [Fe] + \epsilon_{620}^{Al} \cdot [Al]$$

and $$A_{510} = \epsilon_{510}^{Fe} \cdot [Fe] + \epsilon_{510}^{Al} \cdot [Al]$$

(where, A and ϵ indicate absorbance and extinction values, subscript indicates wavelength and supercript the ion) can be used to develop the equations :

$$[Fe] \times 10^4 = 9.988 \times A_{620} - 3.111 \times A_{510}$$

and $$[Al] \times 10^4 = 4.466 \times A_{510} - 3.179 \times A_{620}$$

which can be utilized to get the composition of these elements in the synthetic mixtures as well as in the ore, dolomite. Table 2 summarizes the results of analysis of several synthetic mixtures.

Addition of foreign ions—The ions Ca(II), Mg(II), Mn II), Ti(V) and phosphate had been tried for the interference studies as these are commonly present in the ore, dolomite. The interferences were tested by individual as well as simultaneous addition of these ions. Results with respect to 1.0 ppm of Al(III) and 2.0 ppm of Fe(III) showed that Ca(II). Mg(II) did not interfere at all concentrations. The traces of Mn(II), Ti(IV) and phosphate can be tolerated. Hence, the method may be applied to the ore, dolomite.

Analysis of dolomite—The results showed that the Fe(III) and Al(III) can simultaneously be determined after the separation of silica from the ore. Table 3 shows the results of Al(III) and Fe(III) in the dylomite. The metals were determined in presence of Ca(II) and Mg(II) as well as in the absence of them. The results of this method can be compared well with the classical method.

TABLE 2—ANALYSES OF SYNTHETIC MIXTURES

Mixture No.	Quantity taken in M/litre		Quantity found in M/litre		Relative standard deviation (%)	
	$[Fe] \times 10^5$	$[Al] \times 10^5$	$[Fe] \times 10^5$	$[Al] \times 10^5$	Fe	Al
1	5.00	2.50	5.00	2.42	±0.26	±0.20
2	4.00	3.00	4.10	3.06	±0.23	±0.82
3	3.50	3.50	3.51	3.45	±0.20	±0.11
4	5 00	4.50	5.13	4.43	±0.62	±0.44
5	2.50	5.50	2.49	5.48	±0.25	±0.13

TABLE 3—DETERMINATION OF Fe_2O_3 AND Al_2O_3 IN THE DOLOMITE

Oxides	Quantity found in presence of Ca & Mg	Relative standard deviation (%)	Quantity found in absence of Ca and Mg	Relative standard deviation (%)	Quantity of sequioxide by conventional method
Fe_2O_3	1.82%	±0.50	1.82%	±0.57	3.98%
Al_2O_3	1.80%	±0.55	1.81%	±0.76	

Precision and accuracy—The precision and accuracy of the spectrophotometric method were tested by analysing samples containing the known amounts of Fe(III) and Al(III). With the solutions eontaining 1.0-4.0 ppm of the ions, the standard deviation of the method was $\pm 0.62\%$ for Fe(III) and $\pm 0.82\%$ for Al(III).

Sensitivity—The sensitivity of the method for the simultaneous determination of Fe (III) and Al (III) according to Sandell's[8] definition was 0.0437 $\mu g/cm^2$ and 0.0092 $\mu g/cm^2$ respectively.

Thus, CHDMAS affords a simple method for quick simultaneous determination of Fe(III) and Al(III).

Acknowledgement

Thanks are due to Prof. R. H. Sahasrabudhey, Head, Department of Chemistry, Nagpur University, Nagpur for the requisite facilities.

References

1. O. P. Sharma and R. B. Kharat, *Indian J. Chem.*, 1975, **13**, 848.
2. O. P. Sharma, Thesis submitted for the Ph.D. Degree (Nagpur University, 1975).
3. O. P. Sharma and R. B. Kharat, (Unpublished work).
4. A. Bokare, B. K. Deshmukh and R. B. Kharat, *Indian J. Chem.*, 1976, **14A**, 541.
5. W. H. Davenport, *Anal. Chem.*, 1949, **21**, 718.
6. A. J. Mukhedkar, S. B. Kulkarni and K. P. Chanphalkar, *J. Univ. Poona Sci. Technol.*, 1966, **32**, 47.
7. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", ELBS, 1973.
8. E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience, New York, 1959.