Derivative Spectrophotometric Determination of Aluminium in Presence of Titanium with Alizarine Red-S in Basic and Ultra Basic Rocks

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Abstract

A derivative spectrophotometric method has been developed to overcome the interference of Ti (IV) in aluminium determination with alizarin red S (ARS) without cumbersome, time consuming additional chemical separation steps (which may involve loss of analyte) in Shapiro and Brannock method devised for schematic whole silicate rock analysis. The method is mostly followed for other rock types also due to the relative simplicity. Determination of aluminium one of the major constituent of rocks with alizarin red -s (ARS), essential in their characterization, inevitably needs correction for titanium using different factors at different aluminium concentrations besides use of complexants ferro-ferricyanide, thioglycolic acid etc. to avoid interference of iron.

The derivative approach has been utilized to remove the interference of titanium in aluminium determination using alizarine red-s (ARS). The conventional spectrum of aluminium complex with ARS is resolved from that of titanium in second order derivative at the zero-crossing point of the titanium complex, at 504.0 nm. Furthermore, the ferro-ferricyanide complex also shows a zero point at the wavelength in second derivative and avoids the need of thioglycolic acid, an additional complexant at iron concentrations higher than 50 µg in final solution. The zero-point wavelength for Ti-ARS and ferro-ferricyanide complexes do not shift in their mixtures containing up to 30 µg and 300 µg of titanium and iron respectively in the final solution and avoids the need to apply correction for titanium using different factors at different aluminium concentration in rocks using Shapiro and Brannook method. Validity of the method is tested to international geochemical reference samples (BCR-1, MRG-1, ASK-2, BHVO-1, BE-N and BR)

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and the results obtained is compared with published data which are found to be in close agreement with the reported values. The determination of Al (III) using the method in percentage range was found to be with RSD ±2.7%.

Key Words: **Alizarine red-s, aluminium in presence of titanium, basic and ultrabasic rocks, second derivative spectrometry, geo-standards, Shapiro and Brannock.**

1. Introduction

Aluminium determination has gained importance in nuclear industry due to iron-chrome-aluminium (FeCrAl) alloy cladding being proposed as an alternative owing to its several orders of magnitude higher resistance than UO_2-zirconium alloys cladding. Besides its applications in nuclear and other industries, aluminium determination is significant in different types of rocks due to aluminium being a major constituent of rocks.

Shapiro and Brannock[1] utilized the formation of Al (III) complex with alizarine red-s (ARS) at pH 4.55 in presence of calcium and measuring the absorbance of the of the complex at 475 nm for the spectrophotometric determination of Al (III) in their schematic method devised for the whole rock analysis of silicate rocks. The method is mostly employed for determination of Al (III) in other rock analysis also, because of its relative ease of operation in comparison to more sensitive reagents. Furthermore, relatively low sensitivity of ARS avoids higher dilutions for the determination of aluminium a major element, in rocks. However, Fe (III) and Ti (IV) also form complex with the ligand with overlapping absorption spectra with that of Al (III) causing interference in the estimation of aluminium at the wavelength (475 nm). The interference due to Fe (III) (up to 50 µg in final solution) is eliminated by converting it into Ferro-ferricyanide complex prior to addition of the ligand (ARS) but no simple mean is available for the selective masking or separation of titanium from aluminium. This makes correction for titanium as well as iron (> 50 µg in final solution) inevitable in the determination of AI (III) by the conventional spectrophotometric method. However, the correction does not give aluminium values of high accuracy specially in case of basic and ultrabasic rocks containing relatively low aluminium but high titanium and iron. Different factors are used for titanium correction in different concentration range of aluminium[2] (however, iron needs separation). Furthermore, some authors

recommend a factor of 0.5 for titanium correction in silicate rocks, therefore, it was thought of interest to use derivative spectrophotometry (DS) to resolve the overlying absorption spectra of aluminium from titanium and iron to avoid their interference.

DS is used to eliminate background interference as well as to resolve overlapping absorption band[3] with higher sensitivity for the analyte in general. DS has been widely used in pharmaceutical analysis[4-5], clinical chemistry[6], environmental analysis etc but less often in inorganic analysis[7-17]. The derivative method has found application not only in ultraviolet-visible region spectrophotometry, but also in infrared[18], atomic absorption and flame emission spectrometry[19] and in fluorimetry[20] (normal[21] and synchronous scanning[22-23]).

The present method describes the use of derivatives spectrophotometry (DS) to achieve spectral selectivity to eliminate the interference of titanium (IV) and Iron (III) in the determination of aluminium with ARS in basic and ultrabasic rocks.

2.Experimental

2.1Apparatus:

A Hitachi U-2000 Double beam spectrophotometer was used with 10 mm matched quartz cuvettes for recording normal and derivatives absorption spectra.

2.2 Reagents:

All reagents used were of analytical reagent grade. Stock solutions (100 µg/ mL) of aluminium, titanium and iron were prepared from their respective salts. Further dilutions were made to prepare lower standards (10 µg/ mL and 1 µg/ mL) as per need and used to prepare 5 to 70 µg aluminium standards in 100 mL volume.

2.3 Sample Preparation:

0.05 g sample (Al concentration in the range 1.0 %-12.0 %) (-100 mesh) was fused with NaOH in a nickel crucible, the melt was cooled and 50 mL water was added to the crucible, covered and allowed to stand overnight. The contents were then, transferred to 1 L volumetric flask containing 20 mL of HCl (6M) and the volume was made up. 10 mL aliquot was taken in 100 mL volumetric flask for further procedure.

2.4 Procedure:

Colour development: Suitable individual aliquots of AI (III), Ti (IV) and Fe (III), their binary and ternary mixtures were taken in 100 mL standard flask. To the aliquots, 1 mL of Ca (1.0 % w/v), 1mL of hydroxylamine hydrochloride (10% w/v), 1mL of $K_3Fe(CN)_6$ (1% w/v) were

mixed respectively, and after five minutes 10 mL of acetic acid – sodium acetate buffer (pH 4.55) was mixed and allowed to stand for 10 minutes. To the mixture, 5mL of ARS (0.1% w/v) was added and volume was made up with water and measurements were made after 1 hour.

Spectral measurements: A reagent blank (prepared as described above) was placed in sample and reference cells and scan was obtained from 1000-400 nm to set up the base line. The blank solution in the sample cell was replaced with the sample solution and spectral scan was repeated at a scan speed of 100 nm per minutes, over the range 600-400 nm and the spectrum recorded was stored in a save scan file. The second derivative spectra were recorded and the derivative amplitudes were read at 504.0 nm. The calibration curve was prepared by recording the second derivative amplitude at the wavelength and plotting the amplitude Vs metal ion concentration in the 5-70 µg range.

3.Results and Discussion

3.1 Interference of titanium and its removal using derivative spectrometry:

The ordinary absorption spectra (Figure 1) of Al (III), Ti (IV) and Fe (III) complex with ARS were found to be overlapping to allow determination of Al (III) in their presence at 495 nm, λ_{max} of the Al (III)- ARS complex and 475 nm, the wavelength used normally. The absorption measurements at 475 nm show slightly reduced degree of interference from Ti (IV) and Fe (III).

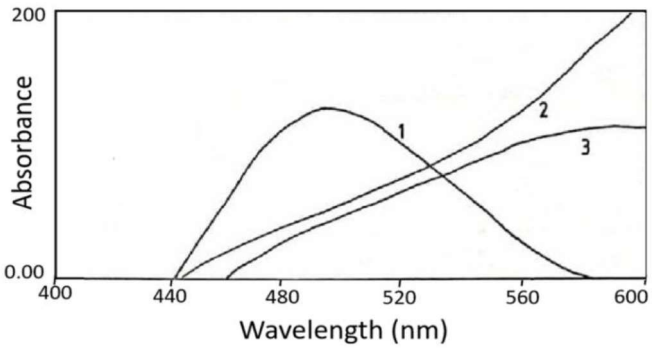


Fig. 1. Absorption spectra of Alizarin red-S with (1) Al (III) 20µg (2) Fe (III) 20µg (3) Ti (IV) 20 µg against reagent blank

Fe (III) after reduction and complexation with $K_3Fe(CN)_6$ does not form complex with ARS and the colour of ferro-ferricyanide complex of iron up to 50 µg concentration in final solution does not show measurable absorbance at 475 nm but simple method for separation of titanium from

aluminium or preferential masking of titanium and iron (>50 µg concentration in final solution) to prevent formation of titanium and iron (>tolerance level) -ARS complex is not available. To avoid interference of Ti (IV), the derivative spectra (DS) in first, second, third and fourth order were studied. The DS showed that the spectra of iron, aluminium and titanium were resolved in the second derivative. The wavelength at which the interferent spectra were resolved was determined by the zero-point wavelength (ZPW) method[24]. The method involves the measurement of derivatives amplitude (DA) at a wavelength corresponding to zero crossing point of the DS of the interferent. The ZPW was confirmed by the point of intersection (PI method) referred to as the zero-crossing method elsewhere[15], which involved the measurement of the wavelength at which DS of Al complex and the binary mixture of the interferent with Al intersect. At this point DA of the binary mixtures are equal to the DA of the Al i.e. at this wavelength the amplitude of the derivative signal of the interferent passes through zero; measurement of the value of derivative spectrum of the mixture (DA) made at the intersection point, therefore, is a function of the concentration of Al alone and not of the interferent. Coincidence of the ZPW with PI confirms the ZPW for the interferent and indicates no shift in ZPW for varying amount of interferant in the concentration range studied. In case of the shift in ZPW for the interferent in a particular derivative, higher order derivatives were explored. Titanium complex shows a ZPW at 504 nm (Figure 2) in the second order DS which coincide with PI of Al and its binary mixture with Ti confirming 504 nm (Figure 3) as a non-interferent wavelength for Ti in second derivative. The increasing concentration of Ti up to 30 µg (in solution) did not shift the ZPW for Ti complex in the second DS.

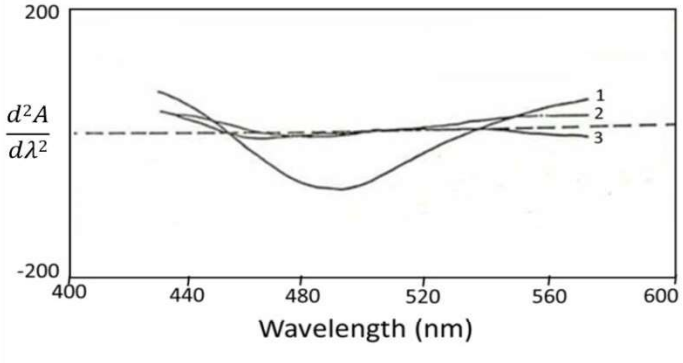


Fig. 2. Second order derivative spectra of Alizarin red -S with (1) Al (III) 20 µg (2) Fe (III) 20 µg (3) Ti (IV) 20 µg

The higher amounts of Ti (IV) [(>30 µg; TiO2 50 µg (10 % in the original sample)] caused turbidity with time (needing dilution to make Ti (IV) in the range) due to hydrolysis at the pH which could not be prevented by using Na-K-tartrate and therefore, the studies were restricted up to 30 µg of Ti in final solution.

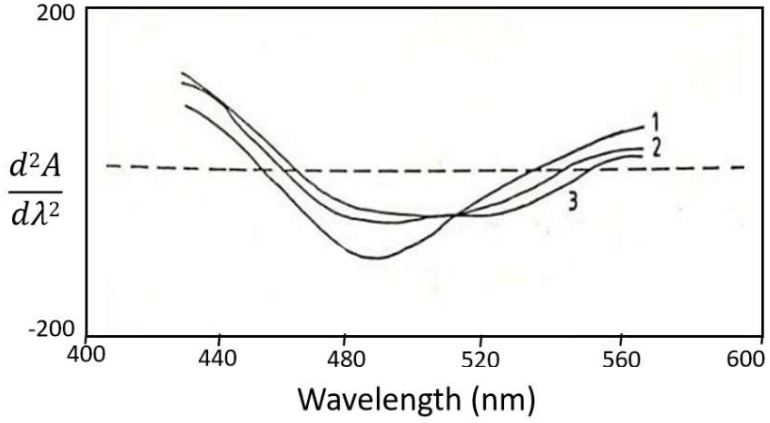
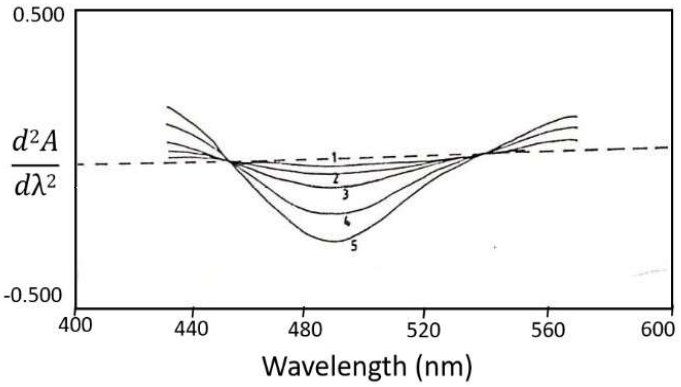


Fig. 3. Second order derivative spectra of Alizarin red -S with (1) Al (III) 20 µg (2) Al (III) 20 µg + Ti (IV) 20 µg (3) Al (III) 20 µg + Ti (IV) 20 µg + Fe (III) 20 µg

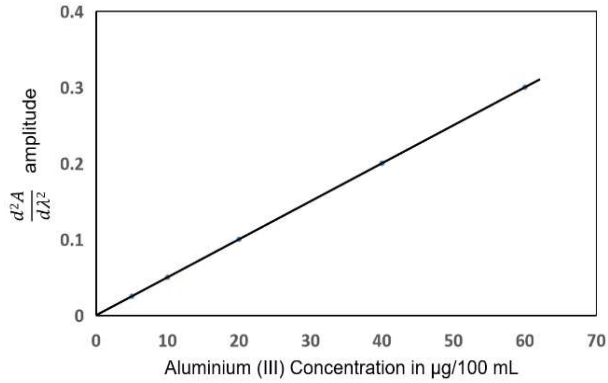
Ferro-Ferricyanide complex of iron at concentration higher than 50 µg shows measurable absorbance at 475 nm due to its colours in zero order and interfere in Al determination. The complex shows the ZPW at 504 nm in second order DS i.e. ZPW of Ti (Figure 2) revealing a ZPW for Fe and Ti both in a ternary mixture (Figure 3) and thus the interference of higher amounts of iron (>50 µg) is eliminated without use of thioglycolic acid, an additional complexant[1]. The concentration of Fe up to 300 µg did not show any shift in zero-point wavelength (504 nm).

As the characteristic of derivatives spectra is dependent on the choice of the instrument parameters, the parameters are optimized with respect to reduction of noise level, stability of zero-point, sensitivity and wavelength range used and other facilities present in the instrument. The best result was obtained at scan speed of 100 nm/min, over the range from 600-400 nm with a wavelength interval of 0.5 nm for the differentiation. The instrument used obtained DS by digital differentiation (convolution method). Calibration curve for the determination of Al (III) was obtained by plotting the second derivative amplitude of absorbance spectra Vs metal ion concentration at the wavelength representing ZPW for Ti (IV) (504 nm). The calibration curve

was found to be linear in the derivative spectra for 5-70 µg of Al (III) in final solution (Figure 4a and 4b).



4a



4b

Fig.4a and 4b. Second order derivative spectra of Al (III) with Alizarin red -S (1) 5 µg (2) 10 µg (3) 20 µg (4) 40 µg (5) 60 µg

The method was applied to the determination of Al (III) in international geostandards (rocks) BCR-1, MRG-1, ASK-2, BHVO-1, BE-N and BR and the values obtained were found to be in good agreement with the values reported in the literature (Table 1).

Table 1: Determination of Aluminium in International Geostandard Reference Samples.

IGS[#]	TiO2%	Al_2O_3%, n=6		%RSD (by proposed method)
		Proposed method	Reported * value	
BCR-1	2.2	13.6	13.5	0.18
MRG-1	3.7	8.4	8.5	0.21
ASK-1	1.0	18.6	18.6	0.13
ASK-2	1.0	18.7	18.8	0.14
BHVO-1	2.8	14.3	14.2	0.17
BE-N	2.5	9.8	9.9	0.28
BR	2.6	10.1	10.1	0.25

[#] International Geostandards

*S.E. Church, Geostandard Newsletter, 1981, 2,133.

Conclusion:

The proposed method removes the interference of titanium and iron in the range studied without their chemical separation for which otherwise also no simple method is available and thus avoids use of varying correction factors dependent upon aluminium concentration, reduced highly analysis time and determines aluminium one of the major rocks forming element accurately in different rock types. Besides, the method is far cost effective relative to ICP devices (OES and MS) with poor nebulising efficiency (1-2%) restricting total dissolved salt concentration (TDS) limiting use of suitable flux for sample attack.

Authors' Contributions:

Authors have contributed equally.

Conflict of Interest

There is no conflict of interest.

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