Method for the determination of Zr in sub-microgram levels with sodium lauryl sulphate

Enhancing the spectrophotometric sensitivity for rare metal analysis in the visible region using coloured metal chelate systems sensitized by the presence of a third component, has been a new area of study. The use of the binary metal ion complexes or organic dye stuffs such as catechol violet[1] or bromopyrogallol red[2], sensitized by the addition of long-chain cationic surfactants such as cetyl trimethyl ammonium bromide has been reported. Efforts to improve the absorption characteristics of metal dye complexes in the presence of surfactants and to develop methods for determination of metal ions have been made by several workers[3,4]. Zirconium is an important

ingredient in the local beach sand. Attempt has been made to improve the existing spectrophotometric method by using sodium lauryl sulphate (SLS). This correspondence reports the results on the estimation of zirconium with 2,7-*bis*(2-arsonophenylazo)-1,8-dihydroxy naphthalene-3,6-disulphonic acid (arsenazo-III) in the presence of SLS.

Zirconium standard solution containing 1000 mg/l Zr (zirconium oxy chloride in hydrochloric acid; E. Merck, Germany) was used as the stock solution. (One ml of this solution is equivalent to 1 mg of Zr). Ten millilitres of this solution is diluted to 100 ml in a volumetric flask containing 5 ml hydrochloric acid.

(One millilitre of the solution is equivalent to 0.1 mg of Zr).

Next, 0.2 g of arsenazo-III (2,7-*bis*(2-arsonophenylazo)-1,8-dihydroxy naphthalene-3,6-disulphonic acid disodium salt (E. Merck) was dissolved in 100 ml distilled water with constant stirring. The solution was filtered using Whatman No. 42 filter paper to an amber-coloured bottle. (One ml of the above solution is equivalent to 2.25×10^{-5} M of arsenazo-III.) Then 14.42 g of SLS (E. Merck) was dissolved in 500 ml of distilled water (0.1 M). Appropriate volume of the solution was diluted for measurements. All reagents used were of analytical grade.

A Perkin–Elmer spectrophotometer model Lambda-14 with 1 cm matched quartz cuvettes was used to measure the optical densities of the solutions.

Standard zirconium solutions (0.02, 0.03, 0.05 and 0.07 mg) were transferred by a pipette to a series of 100 ml standard volumetric flasks. To each of the above solutions, 50 ml of 1:1 hydrochloric acid followed by 10 ml of 0.1 M SLS solution was added. Two millilitres of 0.2% (w/v) arsenazo-III solution was added to the above solutions. After 10 min, the absorbances were measured in 1 cm cuvette against reagent blank at 680 nm. A plot of absorbance against zirconium concentration was a straight line that passes through the origin. This serves as a calibration graph.

Absorption spectra of arsenazo-III obtained in the absence and presence of SLS are given in Figure 1. The peak at 530 nm in the absence of SLS disappears in its presence, and a small peak appears at 680 nm. It may be noted that the effect is a pronounced one and absorbance by the reagent is minimal at the wavelength of the maximum absorption of the sensitized zirconium complex (680 nm), thus presenting conditions that are nearly ideal for analytical measurement.

Variation of arsenazo-III concentration showed that the use of 4.5×10^{-7} M concentration of the indicator in hydrochloric acid medium was ideal for developing the colour in the presence and absence of SLS for zirconium concentrations above 0.02 ppm. Absorbance measurement in the presence of different hydrochloric
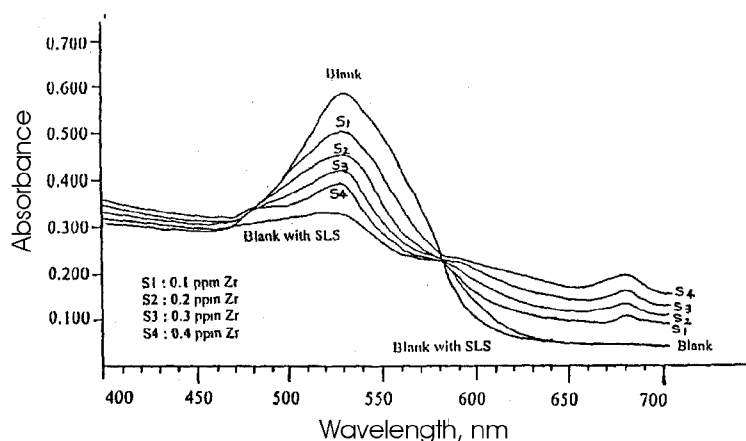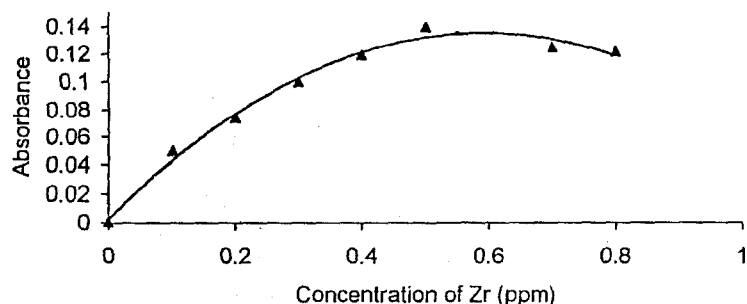

Figure 1. Absorption spectra of arsenazo-III in the absence and presence of SLS.

Table 1. Effect of hydrochloric acid concentration (normality) with zirconium concentration range: 0.02 to 0.07 ppm

Acid concentration (N)	Surfactant concentration (M)	Arsenazo-III concentration (molar)	Mean extinction coefficient (E) $mol^{-1} cm^{-1}$	Correlation coefficient of concentration vs absorbance
1.5	0.01	4.5×10^{-7}	0.06	0.994
1.5	0	4.5×10^{-7}	– 0.89	0.679
1.5	0.005	4.5×10^{-7}	0.09	0.994
1.5	0	4.5×10^{-7}	– 0.76	– 0.219
3	0.01	4.5×10^{-7}	0.15	0.999
3	0	4.5×10^{-7}	0.18	0.992
3	0.005	4.5×10^{-7}	0.24	0.999
3	0	4.5×10^{-7}	0.01	0.746
6	0.01	4.5×10^{-7}	– 0.9	0.712
6	0	4.5×10^{-7}	– 0.05	0.982
6	0.005	4.5×10^{-7}	0.21	0.999
6	0	4.5×10^{-7}	0.02	0.921

Table 2. Effect of hydrochloric acid concentration (normality) with zirconium concentration range: 0.2 to 0.7 ppm

Acid concentration (N)	Surfactant concentration (M)	Arsenazo-III concentration (molar)	Mean extinction coefficient (E) $mol^{-1} cm^{-1}$	Correlation coefficient of concentration vs absorbance
1.5	0.01	4.5×10^{-7}	0.12	0.998
1.5	0	4.5×10^{-7}	0.09	0.096
1.5	0.005	4.5×10^{-7}	0.16	1.000
1.5	0	4.5×10^{-7}	0.13	0.998
3	0.01	4.5×10^{-7}	0.19	0.996
3	0	4.5×10^{-7}	0.25	0.999
3	0.005	4.5×10^{-7}	0.18	0.998
3	0	4.5×10^{-7}	0.10	0.952
6	0.01	4.5×10^{-7}	0.29	0.990
6	0	4.5×10^{-7}	0.52	0.990
6	0.005	4.5×10^{-7}	0.09	0.997
6	0	4.5×10^{-7}	0.08	0.980

Figure 2. Chart showing zirconium–arsenazo-III complex structure.

acid concentrations was carried out in order to fix the optimum HCl concentration needed for obedience of absorbance values of Beer–Lambert's law (Tables 1 and 2). It is seen that zirconium concentration in the range of 0.02 to 0.07 ppm (Table 1) and 0.2 to 0.7 ppm (Table 2), containing an optimum HCl concentration of 1.5 N in presence as well as absence of SLS obeyed the Beer–Lambert's law. When HCl concentration is increased to 3 N, absorbance in the absence as well as presence of SLS remains constant. With higher HCl concentration (6 N), absorbance decreases in the pres-

ence of SLS, making the method unsuitable. Use of sulphuric acid at a concentration of 4.5 N resulted in agreement with the Beer–Lambert's law, for zirconium concentration in the range 0.2 to 0.7 ppm. However perchloric acid was found unsuitable. Order of mixing the reagent has no effect on the determination of zirconium. The colour formation was complete at room temperature within 30 min. Increase in the temperature of the mixture leads to decrease in extinction coefficient and is therefore not suitable. Ageing time is found to be 30 min. Standing of the mixture for longer dura-

tion has an adverse effect on the extinction coefficient and the Beer–Lambert's law is not obeyed.

Optimum SLS concentration is found to be 0.005 M (Table 1), where maximum extinction coefficient for the zirconium–arsenazo-III complex is observed in the zirconium concentration range 0.02 to 0.07 ppm.

Spectrophotometric titration of arsenazo-III against zirconium ion (Job's method) showed a plateau corresponding to formation of 1 : 1 zirconium–arsenazo-III complex (Figure 2).

In the absence of SLS the extinction coefficient was found to be negative for the detection of low concentration of zirconium (0.02 to 0.07 ppm); but in presence of SLS, it was found to be positive (Table 1). Hence, the present work provides the basis of a sensitive method for the determination of traces of zirconium up to 0.02 ppm (0.000002%).

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