Technical note

Method for the examination of the deposition of dynamically formed zirconium membranes

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Abstract

An improved method for the preparation of samples before the spectrophotometric determination of micro-amounts of Zr(IV) using sodium alizarin sulphonate as the colour reagent is described. The concentration range applied is 0,91 to 91 mg of Zr(IV)/ℓ and the relative standard deviation is 0,8%. A comparative study of the aging of Zr(IV) solutions shows that hydrolysis can be prevented if sample preparation includes acidification to pH 0,5 and equilibration of the zirconium species for 24 h prior to analysis. All reagents are also acidified to pH 0,5. At this pH the colour complex exhibits an absorption maximum and, in addition, low results due to hydrolysis of Zr(IV) are avoided. The method of analysis was employed for post-examination of the formation of zirconium based polymeric ultrafitration membranes (dynamic membranes) laid down from Zr(IV) solutions. An alternative method for monitoring the progress of membrane deposition involves colour development at pH 0,5 and at 85°C to accelerate equilibration to the stable form.

Introduction

In recent years various zirconium based dynamic ultrafiltration plants have been installed in South Africa to treat a range of industrial effluents (Groves *et al.*, 1983 (a), (b) and (c) and 1984). The zirconium membranes are laid down *in situ* onto porous supports from zirconium (IV) solutions. In order to permit monitoring or post-examination of this deposition process, a reliable and reasonably rapid method for the quantitative determination of the zirconium levels in the feed, reject and permeate streams is required.

Spectrophotometric procedures using alizarin sulphonate as the complex former are established methods for the quantitative determination of Zr(IV) ions in solution (Green, 1948; Hok, 1949; Mayer and Bradshaw, 1952 and Kolthoff and Elving, 1961). The zirconium alizarin sulphonate "lake" has excellent sensitivity, is accurate and is stable at high acidities, hence its specificity (Green, 1948). In addition, the zirconium alizarin sulphonate "lake" follows Beer's Law up to higher concentrations than do most other coloured Zr(IV) complexes.

The published methods for the spectrophotometric determination of aqueous Zr(IV) (Green, 1948; Hok, 1949; Mayer and Bradshaw, 1952 and Kolthoff and Elving, 1961) and for the spectrophotometric determination of zirconium in geological deposits (Schutte, 1965) using alizarin sulphonate specify a range of conditions of pH, temperature and time for the development of the colour complex.

Complex formation is proposed in either 0,1M (Green, 1948) or 0,2M (Hok, 1949) hydrochloric acid i.e. pH 1 and pH 0,7 respectively. Colour development periods of 20 min (Green, 1948) to 1 h (Hok, 1949) are recommended. It is suggested that colour development is complete 1 h after the addition of the dye and that the colour is stable for at least 3 h thereafter (Kolthoff and Elving, 1961).

It is reported that the procedures proposed earlier (Green, 1948 and Hok, 1949) gave low results due to hydrolysis, olation and polymerisation of Zr(IV) solutions (Mayer and Bradshaw, 1952). Mayer and Bradshaw also suggested that hydrolysis is reversed by development of the colour at 85°C in 1,5M (pH 0,2) hydrochloric acid for 2 min.

Dynamic membranes are laid down from solutions containing approximately 10^{-4}M Zr(IV) at pH 3,5 to 4,0. The state of the species in solution at any time is dependent on the pH, time and temperature history of that particular solution. Initial studies revealed that even minimal time delay between the sampling of the various streams during membrane formation and their analysis, resulted in hydrolysis of the Zr(IV) solution. This was a significant limitation to the accuracy of the quantitative determination of Zr(IV) using the selected spectrophotometric method (Hok, 1949). The need existed, therefore, for the hydrolysis reaction to be halted (and reversed) in order to enable the concentration of the monomeric Zr(IV) species to be determined.

Modifications to this selected procedure were required, particularly with regard to sample preparation and to the prevention of further hydrolysis of solutions before analysis. The sample preparation procedure, the analytical method and the details of the investigations which resulted in the determination of the optimum sample preparation requirements are described in this communication.

Experimental

The analytical method, including appropriate sample preparation procedure, is described below.

Apparatus

A PYE UNICAM SP-177 spectrophotometer was employed for measuring absorbance.

Reagents

All reagents used were of analytical grade. The working standards were prepared from a stock solution of zirconium oxychloride containing 1 000 mg/ℓ Zr(IV). The pH of this solution was below 0,5. (Supplied by Echalaz and Osborne (Pty) Ltd., Durban, RSA).

A solution of HCl (10M) was employed for pH adjustment of all samples, standards and reagents.

The colour reagent was prepared by dissolving sodium alizarin sulphonate (supplied by SAARCHEM Chemicals, Durban, RSA) (0,034% w/v) in distilled water and HCl so that the final pH was 0,5.

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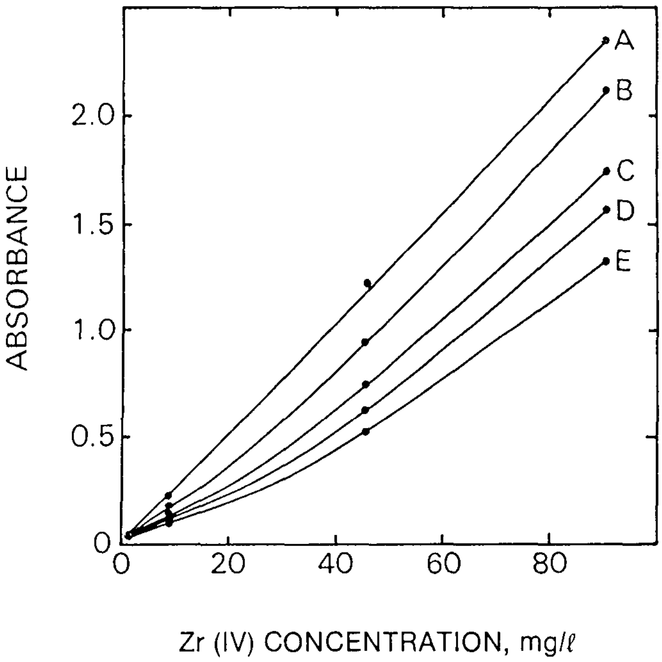

Figure 1
Aging effect of Zr(IV) solutions (stored at pH 3 to 4) on absorbance of colour complex A, day 1; B, day 2; C, day 5; D, day 8; E, day 16.

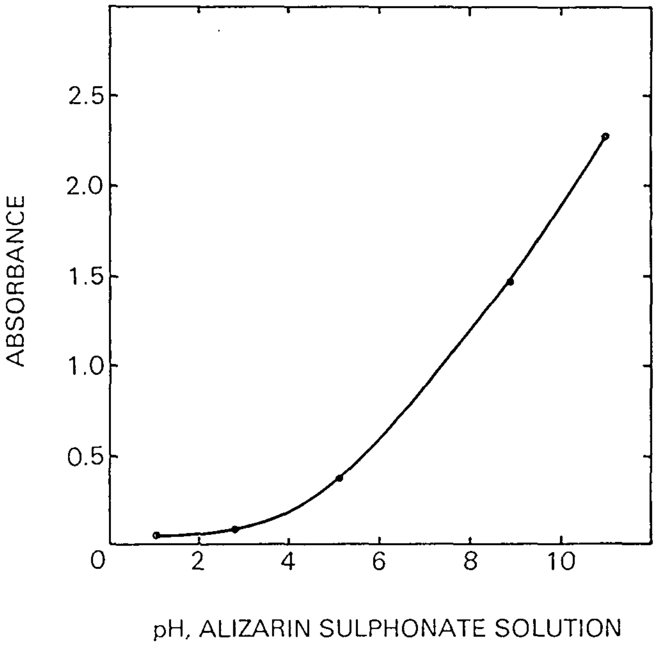

Figure 2
Absorbance of alizarin sulphonate solution over pH range 1 to 11. [NaA] = 342 mg/ℓ.

Preparation of standards

A set of standards containing 1, 5, 10, 30 and 50 mg/ℓ Zr(IV) was prepared by diluting 1, 5, 10, 30 and 50 mℓ of stock solution to 1 000 mℓ with distilled water and hydrochloric acid so that the final pH was 0,5. The standards were left to equilibrate for 24 h before being employed; thereafter they were stable indefinitely.

Preparation of sample

The sample for analysis was acidified to pH 0,5 with HCl and allowed to equilibrate for 24 h before analysis.

Procedure

A 10 mℓ aliquot sample of solution containing 10 to 500 µg Zr(IV) was added to 10 mℓ of the freshly prepared colour reagent. The colour was allowed to develop for 1 to 4 h. The absorbance of the solution was measured against a reference solution containing no zirconium (10 mℓ HCl at pH 0,5 and 10 mℓ colour reagent) at 530 nm. Sample absorbances were compared with the standard absorbance curve to give the concentration of Zr(IV) in solution.

Results and discussion

In this section the results of the investigations which were conducted to evaluate the originally selected spectrophotometric procedure are discussed and the appropriate sample preparation procedure prior to analysis is determined.

Limitations of original procedure

In the selected analytical procedure (Hok, 1949) colour development was carried out in 0,2M HCl (pH 0,7). No allowance was made in this procedure for the effects of aging (hydrolysis) on the standards or samples prior to analysis. The aging effect of a Zr(IV) solution (pH 3 to 4) is shown in Fig. 1. The absorbance by the colour complex formed from standard samples was found to decrease with the age of the sample. This is due to hydrolysis and polymerisation reactions which result in the formation of hydrous Zr(IV) oxides (Mayer and Bradshaw, 1952; Gubeli and Jacob, 1956 and Clearfield, 1964). These gelatinous oxides are resistant to chemical degradation and are not detected by spectrophotometric methods of analysis. The rate of hydrolysis reaches appreciable rates in solutions above pH 2,8 and at even lower pH values when solutions are stored over a period of time. Polymerisation is more pronounced in concentrated Zr(IV) solutions.

Establishment of the optimum pH for sample preparation and analysis

Because the acidity of the solution is the major determining factor in the chemical nature of the Zr species in solution, the pH at which the sample is prepared and analysed is very important in determining the optimum pH for sample preparation and analysis, and various pH effects must be considered:

- The effect of pH on the absorbance of the uncomplexed colour reagent at 530 nm is shown in Fig. 2. To minimise interferences from uncomplexed alizarin sulphonate in the spectrophotometric determination of Zr(IV) the pH during analysis must be maintained below 2,0.

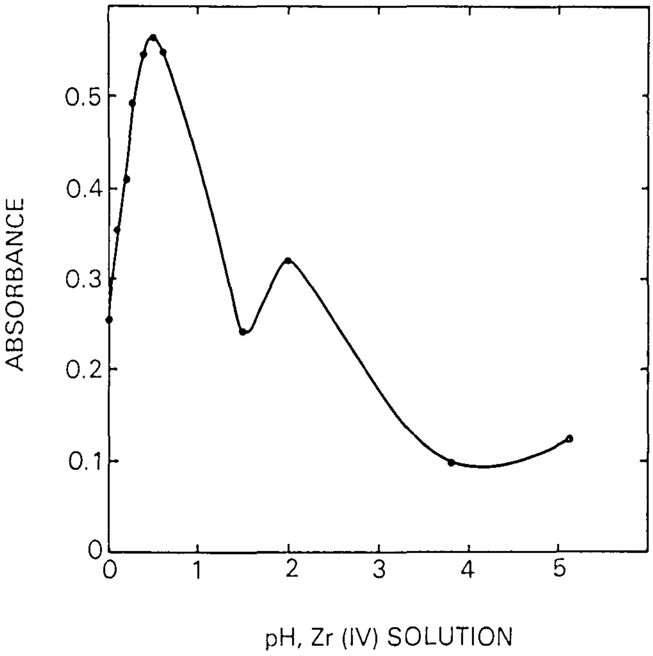

Figure 3
Effect of pH of Zr(IV) solution on absorbance of colour complex. [*Zr(IV)*] *= 20 mg/ℓ.*

- Fig. 3 shows the effect that the pH of the zirconium (IV) solution has on the absorbance by the colour complex at 530 nm when the pH of the colour reagent is also 0,5. Maximum absorbance is obtained when the pH of the sample before analysis is 0,5. At higher pH values hydrolysis of Zr(IV) may occur and uncomplexed colour reagent may interfere with the absorbance. At lower pH values the large excess of acid would depress the dissociation of the colour reagent:

$$HA \rightleftharpoons H^+ + A^-$$

thus preventing the formation of the Zr(IV) A^- complex.

Consideration of these pH effects and comparison of data in Table 1 with the curves in Fig. 1 indicated that the preparation of Zr(IV) solutions by acidification to pH 0,5 would be effective in preventing aging of the solution over an indefinite period. Although Johnson and Kraus (1956) propose that polymerisation occurs at pH values above 0,2, the degree of polymerisation at pH 0,5 appears to be so small that it does not effect the analysis. In addition, analysis at pH 0,5 would result in minimal interference by uncomplexed colour reagent, while at the same time ensuring that the required amount of dissociation of the colour reagent existed.

Establishment of the time requirements for the attainment of equilibrium after sample acidification

Apart from the number of different species of Zr(IV) co-existing in solution, there is an added complication in that there is a slow adjustment to equilibrium within the solution (Lister and McDonald, 1952; and Johnson and Kraus, 1956).

Fig. 4 shows the establishment of equilibria of a 10 mg/ℓ Zr(IV) solution, made up in acid solution to pH 0,5, over a period of 48 h. For the purpose of the analysis, it is assumed that equilibrium is reached, and that the maximum (and constant) absorbances are obtained, if Zr(IV) solutions are allowed to equilibrate for at least 24 h after preparation of the sample acidification to pH 0,5.

Application of method

This method is applicable to solutions containing Zr(IV) which have not been stored for long periods of time (i.e. for less than one day) at pH levels above 0,5 and which have been acidified immediately after sample collection. Preparation of standards by acidification prior to storage ensures minimal hydrolysis of Zr(IV) over an indefinite period. However, if solutions of Zr(IV) undergo hydrolysis before analysis then low results may be prevented by developing the colour complex at 85 °C for 2 min at pH 0,5. The absorbances of these solutions may be compared with absorbances by standards prepared using the modified procedure. This was verified as described below.

Three sets of standards at neutral pH were prepared. One set was acidified to pH 0,5 immediately to prevent hydrolysis. Another set was allowed to hydrolyse for one week. The third set was allowed to hydrolyse for one week with no polymerisation reversal before analysis. During colour development the second set was heated to 85 °C for 2 min at pH 0,5. Table 2 shows that the absorbances by the colour complex in the first two sets of standards compared favourably. The third set of standards gave much lower results.

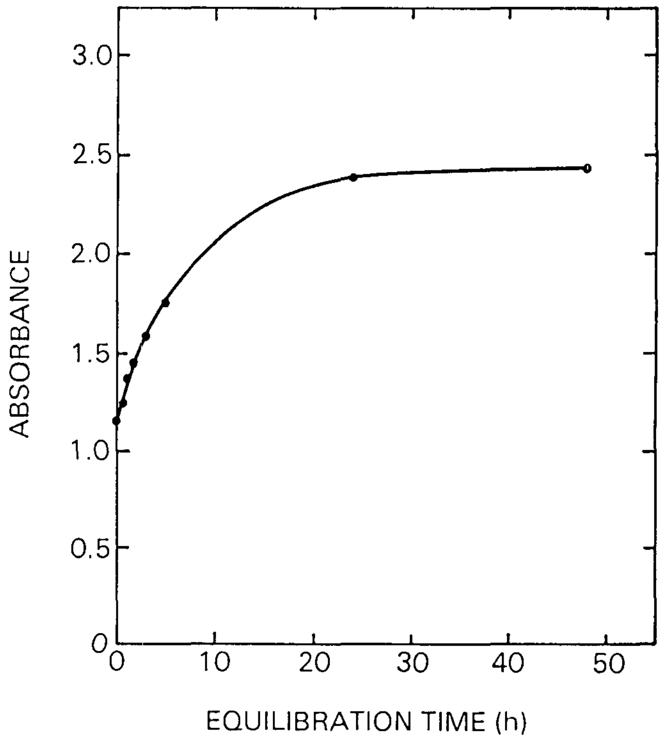

Figure 4
Effect of equilibrium time allowed after acidification to pH 0,5 of Zr(IV) solution on absorbance of colour complex. [*Zr(IV)*] *= 10 mg/ℓ.*

TABLE 1
ABSORBANCES OF THE COLOUR COMPLEX FORMED FROM ACIDIFIED Zr(IV) SOLUTIONS STORED INDEFINITELY

Storage time in days	Absorbance[a] of colour complex for Zr(IV) solutions[b] of concentration in mg/ℓ				
	1	5	10	30	50
1	0,064	0,185	0,346	1,052	1,713
7	0,059	0,177	0,337	1,030	1,662
8	0,063	0,185	0,346	1,060	1,708
15	0,056	0,173	0,333	1,038	1,676
16	0,068	0,190	0,359	1,046	1,740
21	0,070	0,210	0,373	1,066	1,742
41	0,065	0,188	0,356	1,062	1,714
74	0,065	0,184	0,348	1,048	1,698
145	0,056	0,181	0,340	1,056	1,706

[a] Absorbances at 530 mm
[b] Zr(IV) solutions and colour reagent at pH 0,5

TABLE 2
COMPARISON OF METHODS FOR PREVENTION OF LOW RESULTS DUE TO HYDROLYSIS OF Zr(IV)

Zr(IV) in mg/ℓ	Absorbance of colour complex for Zr(IV) solutions in		
	set 1[a]	set 2[b]	set 3[c]
1	0,063	0,064	0,060
5	0,197	0,187	—
10	0,299	0,349	0,120
30	1,022	1,050	0,360
50	1,880	1,708	0,750

[a] Hydrolysis prevented by immediate acidification of Zr(IV) solution.
[b] Hydrolysis which occurred during storage of Zr(IV) solution for one week at neutral pH reversed by colour development at 85 °C for 2 min at pH 0,5.
[c] Hydrolysis which occurred during storage of Zr(IV) solution for one week at neutral pH was not reversed prior to analysis.

Interferences

It is reported (Green, 1948; and Kolthoff and Elving, 1961) that interfering substances include oxidising ions which destroy the colour reagent and anions which may complex with Zr(IV) e.g. sulphates and phosphates. Some multivalent cations (oxidation state + 3 or more) interfere with colour formation.

Optimum concentration range; precision

Beer's law is obeyed over the concentration range under investigation (0,91 to 91 mg Zr(IV)/ℓ). The relative standard deviation of the method was found to be 0,8%.

Conclusion

A reliable method which is useful for the determination of zirconium concentrations in the feed during the deposition of dynamic ultrafiltration membranes has been developed. For monitoring purposes, colour development in hydrolysed zirconium solutions must be carried out at 85 °C for 2 min at pH 0,5. Reported spectrophotometric procedures for the determination of Zr(IV) give low results due to hydrolysis. Acidification of samples of the membrane formation streams to pH 0,5 prevents hydrolysis indefinitely. Samples are acidified on collection and allowed to equilibrate for 24 h prior to analysis. At this pH, the colour complex exhibits an absorption maximum. Relative standard deviation is 0,8%.

Acknowledgements

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References

CLEARFIELD, A (1964) *Rev. Pure and App. Chem.* **14** 91.

GREEN, D (1948) *Anal. Chem.* **20** 370.

GROVES, GR, BUCKLEY, CA, COX, JM, KIRK, A, MACMILLAN, CD and SIMPSON, MJ (1983) (a) Dynamic membrane ultrafiltration and hyperfiltration for the treatment of industrial effluents for water reuse. *Desalination* **47** 305.

GROVES, GR, BUCKLEY, CA, CASTLEDON, A, MERCER, HG, KLUK, G and HART, OO (1983) (b) Application of membrane technology to industrial effluent treatment and water recycling. NIWR/IWPC Symposium on Desalination: New Developments and Industrial Applications. Pretoria, South Africa.

GROVES, GR, SIMPSON, M, COX, JM and KIRK, ARM (1983) (c) The treatment of industrial effluents by dynamic membrane technology. Institute of Water Pollution Control Biennial Conference. East London, South Africa.

GROVES, GR, BUCKLEY, CA, COX, JM, KIRK, A and SIMPSON, MPJ (March 1984) The treatment of industrial effluents by dynamic membrane technology. 4th Nat. Meeting of SAIChe, Potch. Univ. for CHE. Potchefstroom, South Africa.

GUBELI, O and JACOB A (1956) *Helv. Chim. Acta* **38** 1026.

HOK, B (1949) M.Sc. Thesis, Univ. of Minnesota.

JOHNSON, JS and KRAUS, KA (1956) *J. Am. Chem. Soc.* **78** 3937.

KOLTHOFF, IM and ELVING, PJ (1961) *Treatise on analytical Chemistry, Part II: Analytical chemistry of inorganic and organic compounds.* Vol. 7, Wiley-Interscience, New York.

LISTER, BAJ and MCDONALD, LA (1952) *J. Chem. Soc.* (London) 4315.

MAYER, A and BRADSHAW, G (1952) *Analyst* 77 476.

SCHUTTE, CEG (1965) *J. South African Chem. Inst.* **18** 13.

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