lação e imobilização, mas no entanto trabalhos anteriores[11] demonstraram que o transporte de ferro da raiz para as folhas envolve o complexo de citrato com ferro (III) e a absorção de ferro na soja envolve a redução de Fe(III) a Fe(II). O Fe(II) tem uma maior mobilidade[12] devido ao envolvimento de complexos de esfera externa com os grupos carboxílicos da pectina.

Tabela I. Constante de equilíbrio empírica (K) para a troca iônica entre pectinato de alumínio e $M(NO_3)$ em solução aquosa a 298 K.

M	pH	K
Ca	4,40	$(2,81 \pm 0,06) \times 10^{-3}$
Mn	5,45	$(4,6 \pm 0,1) \times 10^{-3}$
Zn	4,00	$(5,3 \pm 0,3) \times 10^{-2}$
Cu	4,20	$(1,83 \pm 0,06) \times 10^{-1}$
Fe (III)	4,10 a 3,60	(42 ± 3)

Continuaremos o estudo do equilíbrio de troca iônica com estes metais, variando a porcentagem de esterificação da pectina, para observar o efeito da variação do número de sítios disponíveis na constante de equilíbrio.

Parte Experimental: O pectinato de alumínio sólido foi colocado em soluções de nitrato dos metais citados na tabela 1, sob agitação e num termostato. Após atingido o equilíbrio foram feitas análises do metal e do alumínio na fase sólida e na fase líquida, utilizando-se métodos espectrofotometricos usuais, com as quais se obteve x(M), x(Al), c(M), c(Al).

Agradecemos o auxílio recebido do CNPq.

Referências Bibliográficas

1. M.E. Farago, Coord. Chem. Rev., 36, 155 (1981).
2. E. Epstein, Plant Physiol., 36, 437 (1961).
3. R.F.M. Van Steveninck, Physiol. Plant., 18, 54 (1965).
4. R. Ramamoorthy, J. Theor. Biol., 66, 527 (1977).
5. G.G. Leppart e J.R. Colvin, J. Polymer. Sci. C,36, 321 (1971).
6. R. Goodland, M.G. Ferri, "Ecologia do Cerrado", Editôra da Universidade de São Paulo, São Paulo, 1979.
7. R. Goodland, II Simpósio sobre o cerrado, Editora da Universidade de São Paulo, São Paulo, 1971, p. 44.
8. D.O. Huett, R.C. Menary, Aust. J. Plant Physiol., 6, 643 (1979).
9. D. Reichenberg in "Ion exchange", (J.A. Marinsky Ed.), Marcel Dekker Inc., New York, 1966, p. 227, 274.
10. Y. Marcus, D.G. Howery, "Ions exchange equilibrium constants", Butterworths, Londres, 1975.
11. L.O. Tiffin, Plant Physiol., 45, 280 (1970).
12. G. Micera, S. Deiana, C. Gessa, M. Petrera, Inorg. Chim. Acta, 56, 109 (1981).

DETERMINATION OF SCANDIUM WITH SALICYLALDEHYDE AND 2-AMINOBENZENEARSONIC ACID

Pércio Augusto Mardini Farias, Leopoldo Hainberger and Henrique Antonio de Salles Andrade.
Departamento de Química da PUC/RJ.

Recebido em 19/06/84

ABSTRACT

A new method is described for the spectrophotometric determination of scandium by means of a colored complex formed with salicylaldehyde and 2 - aminobenzenearsonic acid. Lambert-Beer's law is followed in the range of 0,2-2 μg/ml of the final solution. The maximum amounts of 39 ions that may be present without interfering in the method are listed.

RESUMO

É descrito um novo método espectrofotométrico para determinar o escândio por meio do complexo colorido formado com salicilaldeido e ácido 2-aminobenzenoarsônico. A Lei de Lambert-Beer é seguida entre 0,2 e 2 μg/ml na solução final. São dadas as quantidades máximas de 39 ions que podem estar presentes sem interferir.

Kuznetsov (1) stated that an intense yellow color is formed when salicylaldehyde and 2-aminobenzenearsonic acid are added to an acetic solution of scandium. Scandium can be identified in a 1: 2,000,000 dilution. Titanium and thorium also provide a highly colored solution under these conditions. It is known that aromatic o-hydroxyaldehydes form stable chelates in organic solvents by the coordination of the carbonylic oxygen with metals (2) resulting in a configuration similar to that of Figure 1 for the salicylaldehyde, for example.

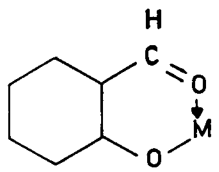

Fig. 1

The fact that titanium reacts with salicylaldehyde in the presence or absence of 2-aminobenzenearsonic acid shows that a complex of this type could be formed. Figure 2 shows the absorbance curves for one of these experiments.

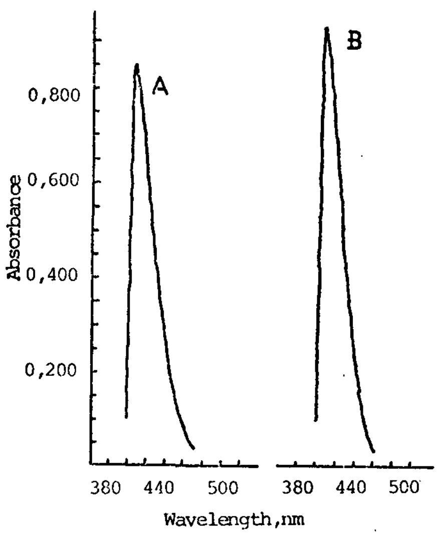

Fig. 2

A. Absorption curve for titanium with salicylaldehyde and 2-aminobenzenearsonic acid.
B. Same curve without 2-aminobenzenearsonic acid.

In both instances (A and B) the final solution contained 10 μg/ml of titanium and all the other conditions were similar except that in Run A, 2-aminobenzenearsonic acid was also present, together with salicylaldehyde. The curves are similar but, in Run B, the sensitivity is a little higher. This does not exclude the possibility - in the case of scandium and thorium - of the formation of a Schiff base that would react through its hydroxyl and arsono groups, to form a new cycle, as stated by Kuznetsov. As these two elements do not form complexes with salicylaldehyde in the absence of 2-aminobenzenearsonic acid, it seems that this probability may be right but it is also possible that the acid only act as an activator.

Reagents

Salicylaldehyde (Riedel prosynth bidistillated)
0,05% aqueous solution of 2-aminobenzenearsonic acid.
95% Ethyl alcohol p.a.
Stock solution of scandium in 0,22N hydrochloric acid.

Apparatus

Spectrophotometers - Hitachi - Perkin Elmer 139 UV-VIS and Shimadzu UV-200

Procedure

One ml of a 0,22N solution of hydrochloric acid, having 2-20 μg of scandium, is transfered to a 10 ml volumetric flask and 1 ml of a 0,05% aqueous solution of 2-aminobenzenearsonic acid, 0,8 ml of salicylaldehyde and 95% ethyl alcohol, to complete the volume of the flask, are also added. The contents are stirred and 30 minutes later the absorbance is read at 440 nm against a reagent blank. The complex is stable for at least 1 1/2 hour, as shown in Figure 3.

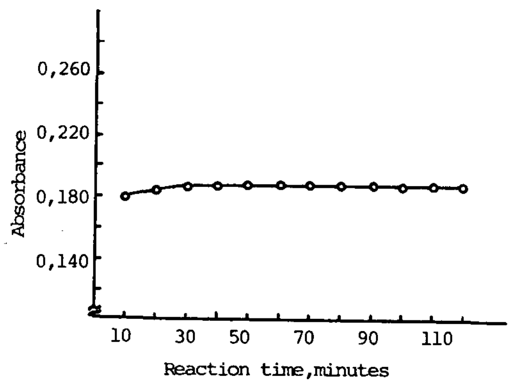

Fig. 3
Stability of the scandium complex

The curve shown in Figure 4 was obtained with 2 μg/ml of scandium in the final solution. Lambert-Beer's law is followed in the range of 0,2 - 2μg/ml of the final solution. The relative error for the lower concentration (0,2 μg/ml in the final solution) was 8,2% and the error diminished rapidly with increasing concentration. The minimum of 0,77% is obtained with 0,8 μg/ml. Thirty-one ions

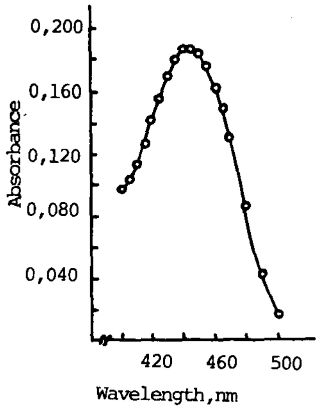

Fig. 4

Absorption Spectrum of the scandium complex

were tested for the study of interfering substances. Table I indicates the maximum amounts that can be present in the final dilution so as to not interfere. The experiments were run in the presence of 1 µg Sc/ml in the final solution.

Table I. Effect of several ions.

Ions tested	Max. Conc. (µg/ml)	Ions tested	Max. Conc. (µg/ml)
$Na^{\%}$	500	Cd^{+2}	2500
K^{+}	2500	Hg^{+2}	1000
Li^{+}	500	Al^{+3}	5
Be^{+2}	25	Sn^{+2}	10
Mg^{+2}	1000	Pb^{+2}	25
Ca^{+2}	2500	La^{+3}	268
Sr^{+2}	2500	Ce^{+3}	5000

Table I (continued)

Ba^{+2}	2500	Th^{+4}	0,5
Y^{+3}	250	U^{+6}	5
Ti^{+4}	0,25	Acetate	10
Zr^{+4}	0,5	SO_4^{-2}	0,5
V^{+5}	0,25	Cl^{-}	5000
Cr^{+3}	25	NO_3^{-}	5000
Mo^{+6}	5	SCN^{-}	500
Mn^{+2}	2500	IO_3^{-}	5
Fe^{+3}	0,25	I^{-}	50
Co^{+2}	250	Citrate	50
Ni^{+2}	250	$H_2PO_4^{-}$	0,5
Cu^{+2}	2,5	Oxalate	1
Zn^{+2}	1000		

The interference of Fe^{+3}, up to 50 µg/ml, may be eliminated by the addition of 0,3 ml of a 1% solution of thioglycolic acid after the introduction of the sample in the volumetric flak . V^{+5}, in a concentration up to 5 µg/ml can also be masked with a 1% aqueous solution of ascorbic acid. Titanium, zirconium and thorium should be absent in concentrations above those indicated in Table I. The present procedure has some advantagens if compared with other methods known in the art. For example, in the determination of scandium with 4-(2-thiazo lylazo) resorcinol, the scandium must almost always be previously separated with ion-exchange resins (3,4). In the method using 8-hydroxyquinoline,the number of interfering substances is very high and benzene is used as a stripping agent and the extract must be filtered (5). In the determination with bromopyrogallol red, there are many interfering substances (6). The same can be said for the method empoying arsenazo and alizarin-S (7).

The scandium content on earth is only 5 x 10^{-4}% but, even though, it is more abundant than gold, silver, mercury, bismuth, etc. Due to its high melting point (1539°C) and low specific gravity (2,992) this metal can be used in astronautics It is relatively abundant in uranium ores where it is a byproduct (8).

Some attempts were performed to also use the reaction between thorium and salicylaldehyde and 2-aminobenzenearsonic acid. The best conditions are similar to those used for scandium. Due to the fact that the limit of determination is high (2 µg/ml) and the number of interfering substances is great, the method is not competitive with others known in the art. The present work showed that other metals react with salicylaldehyde alone besides titanium. These studies will be published later.

Acknowledgements. The authors gratefully acknowledge the financial support from FINEP and CNPq.

References

1. V.I. Kuznetsov, J. Gen. Chem. (USSR), 14, 897 (1944).
2. F. Feigl, "Spot Tests", Elsevier Publishing Company, Amsterdam (1954), p. 268.
3. H.Hamaguchi et al, Anal. Chem., 36, 2304(1964)
4. T.Shimizu, Anal. Chim. Acta, 37, 75 (1967).
5. F. Umland and H. Puchelt, Anal. Chim. Acta, 16, 334 (1957).
6. O.G. Koch and G.A. Koch-Dedic, "Handbuch der Spurenanalyse", Springer-Verlag, Berlin, 1048 (1974).
7. H.Guishi and C.V. Banks, Anal.Chim.Acta,29,249 (1963).
8. O.A. Neumüller,"Römps Chemie-Lexikon",Franksche Verlagshandlung,Stuttgart, 3702 (1975).