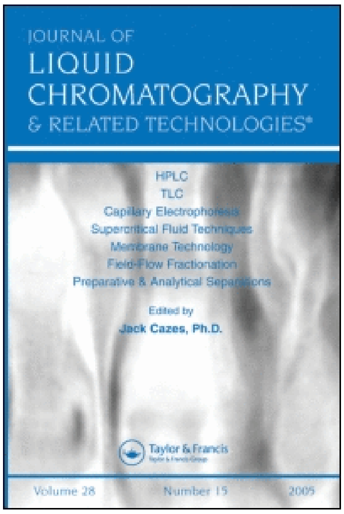

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

A Fast Cation Exchange Separation of Iron(II) and Iron(III) on Zirconium(IV) Arsenophosphate Columns Using Potassium Thiocyanate as a Complexing Agent

K. G. Varshney[a]; Sanjay Agrawal[a]; Kanak Varshney[a]
[a] Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh, India

To cite this Article Varshney, K. G. , Agrawal, Sanjay and Varshney, Kanak(1984) 'A Fast Cation Exchange Separation of Iron(II) and Iron(III) on Zirconium(IV) Arsenophosphate Columns Using Potassium Thiocyanate as a Complexing Agent', Journal of Liquid Chromatography & Related Technologies, 7: 1, 201 — 206

To link to this Article: DOI: 10.1080/01483918408073960

URL: http://dx.doi.org/10.1080/01483918408073960

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(1), 201-206 (1984)

A FAST CATION EXCHANGE SEPARATION OF IRON(II) AND IRON(III) ON ZIRCONIUM(IV) ARSENOPHOSPHATE COLUMNS USING POTASSIUM THIOCYANATE AS A COMPLEXING AGENT

K.G.Varshney, Sanjay Agrawal and Kanak Varshney

Analytical Laboratories,
Chemistry Section,
Faculty of Engineering & Technology,
Aligarh Muslim University,
Aligarh-202001, India.

ABSTRACT

A new quantitative method has been developed for the separation of ferrous and ferric iron on zirconium(IV) arsenophosphate columns using the cation exchange properties of this material and the complex forming ability of potassium thiocyanate. The method is rapid and requires simply water as the eluant, the results obtained being precise and accurate within the experimental error range (±3%).

INTRODUCTION

Separation of the different valence states of iron has been the subject of several investigations during the past many years using various analytical techniques such as paper chromatography (1-3), electrophoresis (4), solvent extraction (5) and thin layer

0148-3919/84/0701-0201$3.50/0

chromatography (6). Ion-exchange chromatography is a convenient and versatile analytical technique for such difficult separations and a survey of literature reveals that mostly anion exchangers have been used for the separation of ferrous and ferric iron (7-10). Only rarely a cation exchanger has been used for this separation (11). Moreover, as far as we are aware, inorganic ion-exchangers have not been used so far for the separation of different valence states of the same metal. The present article summarizes our efforts in this direction which have resulted a rapid and quantitative separation of Fe(II) and Fe(III). Zirconium(IV) arsenophosphate (ZAP) has been selected because it has earlier (12) shown excellent stability and ion-exchange behaviour.

EXPERIMENTAL

Reagents and Chemicals

Zirconyl chloride, tri-sodium orthophosphate, di-sodium arsenate, potassium thiocyanate, ferrous ammonium sulphate and ferric nitrate used in these studies were of AnalaR grade (98-99%) obtained either from the B.D.H.Poole (England) or E.Merck (Darmstadt).

Apparatus

A Pye unicam model SP 2900 atomic absorption spectrophotometer was used for all the determinations.

Synthesis and Ion-Exchange Behaviour of ZAP

ZAP was synthesized by the method reported earlier (12). It was subjected to heating at 200°C for 1 h in a muffle furnace to obtain α-ZAP as a modified phase (13) showing the Na^+-exchange capacity as 1.03 meq/dry g. This phase has an unusually high selectivity for iron and shows an excellent reproducibility in its ion-exchange behaviour with a high regeneration power in addition to its improved chemical stability (14). It was boiled with 4M HNO_3 to remove any metallic or non-metallic impurities, washed with demineralized water (DMW) and dried as usual before use.

Separation Procedure

The sample solution (1 ml) containing Fe(II) and Fe(III) ions was treated with an excess of potassium thiocyanate (1M) solution and the red solution, thus obtained, was loaded on a column of the ion-exchange material (2 g) in a glass tube (internal diameter ~ 0.6 cm). The elution was performed with 15 ml DMW to remove ferric ions while ferrous ions were eluted out with ~ 25 ml of 2M HNO_3 at a flow rate of 3.5 ml per minute. The effluents were analyzed for their iron contents by atomic absorption spectrophotometry, the results being summarized in Table 1.

RESULTS AND DISCUSSION

The main feature of this study has been to devise a fast analytical procedure for the quantitative separation of Fe(II) and Fe(III). Depending upon its concentration thiocyanate gives a series of intensely red-coloured soluble complexes (15) with Fe(III), formulated as $[Fe(SCN)_n]^{3-n}$ where n = 1 .... 6. At a very high thiocyanate concentration, the complex formed is $[Fe(SCN)_6]^{3-}$. Thus, when to a mixture

TABLE 1

Quantitative Separation of Fe(II) and Fe(III) on α-ZAP Columns

Sl. No.	Amount of iron loaded (μg)		Amount of iron determined* after separation (μg)		Error, %		Standard deviation, %	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
1.	112	112	110.32	115.00	-1.50	+2.68	0.14	0.08
2.	168	168	165.20	171.36	-1.70	+2.00	0.03	0.07
3.	224	224	221.41	229.16	-1.16	+2.30	1.01	0.94
4.	280	280	273.10	286.70	-2.46	+2.39	0.67	0.38
5.	560	560	545.96	576.80	-2.51	+3.00	0.19	0.43
6.	56.0	280	53.410	283.10	-1.05	+1.11	0.29	1.81
7.	280	56.0	275.20	59.910	-1.71	+6.98	0.44	1.36

*Mean value of five replicates.

containing Fe(II) and Fe(III) ions, an excess of concentrated potassium thiocyanate solution is added, ferric iron is complexed to give negatively charged species. On passing this red colored solution through a column of α-ZAP in H^+-form, ferric iron is removed simply by washing with DMW. Ferrous is then eluted out with 2M HNO_3. The method is quite fast and specific for this separation. It requires only 10-15 minutes for the complete process.

As Table 1 indicates the method gives reproducible and accurate results. However, the assays tend to be slightly higher for iron(III) and lower for iron(II). Also, a higher Fe(II)/Fe(III) ratio in the sample solution results in a higher error range for Fe(III). It may be due to some auto-oxidation of Fe(II) by the residual air in the solvent, as observed earlier by other workers (4,5) for this separation.

ACKNOWLEDGEMENTS

The authors thank Prof. Mohsin Qureshi for research facilities and to the C.S.I.R. India for the financial support.

REFERENCES

1. Stevans,H.M., Anal.Chim.Acta, 15, 538, 1956.

2. Pollard,F.H., McOmie,J.F.W., Banister,A.J. and Nickless,G., Analyst, 82, 780, 1957.

3. Qureshi,M., Akhtar,I. and Varshney,K.G., Anal. Chem., 38, 1415, 1966.

4. Lingren,W.E., Reeck,G.R. and Marson,R.J., Anal. Chem., 40, 1585, 1968.

5. Lieser,K.H. and Schroeder,H., Z.Anal.Chem., 174, 1960.

6. Johri,K.N. and Mehra,H.C., Chromatographia, 4, 80, 1971.

7. Kraus,K.A. and Moore,G.E., J.Am.Chem.Soc., 75, 1460, 1953.

8. Pollard,F.H., McOmie,J.F.W., Nickless,G. and Hanson,P., J.Chromatogr., 4, 108, 1960.

9. Pollard,F.H. and Nickless,G., J.Chromatogr., 4, 196, 1960.

10. Sagortschew,B., Chem.Anal. (Warsaw), 17, 973, 1972.

11. Popa,G., Vladescu,L. and Preda,E., Rev.Chim., 28, 582, 1977.

12. Varshney,K.G. and Premadas,A., Sepn.Sci. & Technol., 16, 793, 1981.

13. Varshney,K.G., Varshney,K. and Agrawal,S., Sepn.Sci. & Technol., (in press).

14. Varshney,K.G., Agrawal,S. and Varshney,K., J.Liquid Chromatogr., (in press).

15. Vogel,A.I., A Textbook of Quantitative Inorganic Analysis, Longman Inc., New York, 1978, p. 741.