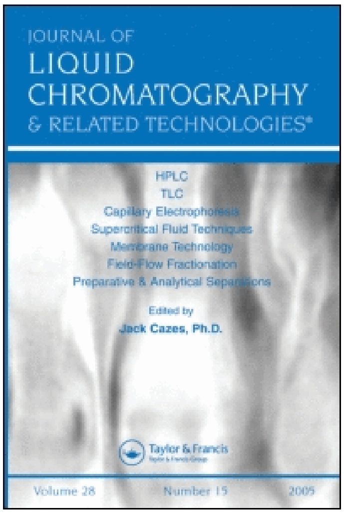

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ION-CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF SOME METAL IONS IN STAINLESS STEELS BY PRE-COLUMN CHELATION WITH 4-(2-THIAZOLYLAZO)RESORCINOL

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ABSTRACT

The separation and determination of components of stainless steels by ion Chromatograph (IC) with spectrophotometric detection using pre-column reaction methods are described. 4-(2-Thiazolylazo)resorcinol (TAR) was used as pre-column chelating agent. The requirements for sample preparation, and the conditions for pre-column chelation reaction are discussed. The optimum conditions for the sensitive detection of these metal ions V, Zr, Cu, Ni, Mn, Co, Pb, Nb and Ta after ion-chromatographic (IC) separation are set. The pH of the chelating medium and the eluent, the concentration of TAR and the composition of the eluent were investigated. The detection limits achieved were 3.2, 2.5, 0.6, 0.8, 1.2, 2.9, 3.0, 4.2, and 4.0 ng for V, Zr, Cu, Ni, Mn, Co, Pb, Nb and Ta respectively. The results obtained by IC methods compare well with those of Graphite Furnace Atomic Absorption Spectrometry (GFAAS) methods and the certified values of SRM (Nos. C1151, C1152, C1153 and C1154), NIST, USA.

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INTRODUCTION

In recent years, ion chromatography has become an attractive method for trace metal determination [1-3]. In fact the advances that took place in column and detection techniques [4-10] have explained the capability of IC to characterize a wider range of anions and cations. Since individual metals and metal compounds form distinct ions with differing retention times, it is possible to analyze several of them in a single run.

The separation and simultaneous determination of metal ions as their chelates with organic reagents by IC has received much attention. A wide variety of organic reagents have been used to complex with metal ions prior to separation [11-15]. The most popular complexing agents such as dithiocarbamates [16], 8-hydroxy-quinoline [17], 4-(2-pyridylazo)resorcinol (PAR) [12], and other high sensitive azo dyes [18] have been investigated. These reagents form either neutral or ionic chelates with a large number of metal ions, and the chelates in the elute can be detected spectrophotometrically.

4-(2-Thiazolylazo)resorcinol (TAR) is one of such reagents which has been used extensively for the spectro-photometric determination of numerous ions [19]. TAR and its chelates with metal ions are insoluble in water. However, they are readily soluble in some solvents that are miscible with water and they can be extracted into solvents that are immiscible with water. Therefore, most metal chelates with TAR can be separated by IC and can be detected spectrophoto-metrically. Though several ion chromatographic (IC) methods are available for the separation of transition metals, no reports on the separation and determination of transition metal ions in stainless steel samples as chelates with TAR using IC have been reported.

In previous communications, [20,21] separating transition and rare earth metals present in low-alloy and stainless steel samples using PAR and Arsenazo-III as post-column chelating agents are discussed. Our current research efforts, as described here, are focused on separation and determination of trace and major transition metals which are present in SRM C1151, C1152, C1153 and C1154 stainless steels by ion chromatograph using TAR as pre-column chelating agent.

EXPERIMENTAL

Apparatus

The Waters Ion Chromatography system consists of Model 501 pumps with Waters U6K injector. A Sperisorb S-5 ODS I separation column was employed. A Waters 486 tunable absorbance uv-visible spectrometric detector with a 12 µl flow cell was used to monitor the effluent from the column. A Waters maxima 820 chromatography workstation along with a printer was employed.

The lab-ware was used after conditioning in an ultrasonic cleaner and equilibrating in reagent grade water (18Ωresistance) from a Millipore Milli Q water system having the total metallic impurities less than 1 ppb.

Reagents and solutions

High-purity 'Suprapure' grade chemicals from E.Merck were used. Solvents were further purified using isothermal sub-boiling distillation in a laminar flow fume hood having class 100 condition with a total lab facility maintained at class 10000 level to overcome dust and particulate contamination. Pure metals from Johnson Matthey (JMC) and Standard Reference Materials from NIST were used for the preparation of standard solutions and eluents.

4-(2-Thiazolylazo)resorcinol (purity, 97%) from Aldrich was dissolved in methanol to get a concentration of 5 x 10^{-3} mol dm^{-3}.

Standard solutions of ions were prepared by dissolving known amounts of pure metals and further diluted to required levels. Elution was performed with 10^{-3} mol dm^{-3} sodium oct-ane-1-sulphonate (54 mg in 250 ml) solution - 0.023 mol dm^{-3} tartaric acid at a flow rate of 1 ml min^{-1}. Calibration graphs were obtained with the chosen parameters by injecting standards separately and in mixtures and recording the peak heights of the respective ions.

Sample Preparation and Matrix Separation

A 1-g amount of stainless steel sample (which was previously washed with methanol and dried with IR lamp) was dissolved in 15 ml of concentrated HCl and 5 ml of concentrated HNO_3 on a hot plate, evaporating to near dryness and then diluting with water. The resulting solution was made up to 100 ml with water and was further diluted as required. The sample solution obtained contains lot of iron matrix. This may have detrimental effect on the chromatographic column and the separation. Therefore, separation of iron matrix is a prerequisite for achieving reliable trace element determinations when IC procedures are used. The matrix separation can be achieved by several techniques. Classical precipitation by adjustment of the pH to 3.5 followed by clarification in a centrifuse is satisfactory. Ion chromatographic techniques as described earlier [21] are also useful. A 20 ml portion of the solution was used for injection after filtering this solution through a 0.45 µm filter.

Preparation of Metal Chelates

10.0 ml of 1.0 mol dm^{-3} tartrate buffer (pH 6.0) and 4.0 ml of TAR (5 x 10^{-3} mol dm^{-3}) solution were mixed with a known volume of the above sample solution. The mixture was diluted upto 25.00 µl with water and heated in boiling water for 1 hour, then cooled to room temperature before injecting.

Separation of the Chelates and Reagent

The ODS column was equilibriated with sodium octanesulphonate (1 x 10^{-3} mol dm^{-3}) - water (50:50 v\v containing 0.023 mol dm^{-3} tartrate buffer, pH 6.0). A 20 µl aliquot of the prepared test solution was injected into the ODS column and the complexes were eluted at a flow rate of 1.0 ml min^{-1}. The detection wavelength was set at 580 nm.

Instrumental methods

A GBC Model 902 atomic absorption spectrophotometer was used, equipped with a GBC Model GF 2000 graphite furnace. A deuterium lamp was used for background correction. Visimax II hollow cathode lamps were used as light source. Solutions were injected by a GBC PAL-2000 auto-sampling system. All absorbances were measured as peak heights and was recorded with an Epson Lx-

800 printer. The system was operated by a Phillips Model P-3105 data station connected on line.

A 1-g amount of sample was dissolved in 15 ml of concentrated HCl and 5 ml concentrated HNO_3, and solution was made upto 100 ml with water, and further diluted as required.

RESULTS AND DISCUSSION

The results for four SRM stainless steel sample materials are presented in Table 1. For comparison, the values (wt%) obtained by graphite furnace atomic absorption spectrometry (GFAAS), and the certified values from SRM are also given. The agreement between the results is excellent as are the relative standard deviations. Several organic solvents such as, methanol, ethanol, acetonitrile, tetrahydrofuran, isopropylalcohol and sodium ocatanesulphonate combined with water, were investigated as binary and ternary mobile phases. A simple methanol-water, ethanol-water or acetonitrile-water binary system mobile phase gave tailing peaks and low sensitivities, and the unreacted reagent appeared as two peaks which overlap with the peaks of Ni-, Cu- and Fe-TAR chelates. However, the sodium octanesulphonate-tartaric acid system gave excellent peak shapes and high sensitivities for the separation of V, Mn, Fe, Co, Ni, Cu, Zr, Ta, Nb and Pb metal chelates with TAR which was found to be good colour forming pre-column reagent. The effect of the concentration of sodium octanesulphonate in the mobile phase on the retention of the chelates is shown in Figure 1. The chromatograms were recorded at 580 nm as all chelates showed significant ab-sorption at this wavelength. However, below this

TABLE 1 COMPARISON OF RESULTS (% W/W) OBTAINED BY IC AND GRAPHITE FURNACE AAS WITH THE CERTIFIED VALUES OF NIST SAMPLES
Values in square brackets were obtained by graphite furnace AAS and values in parentheses are for NIST samples. Results given as mean ± relative standard deviation (%) n=5

	C 1151	C 1152	C 1153	C 1154
Mn	2.45±2.7 [2.44±4.2] (2.50)	0.90±2.5 [0.95±6.4] (0.96)	0.46±2.2 [0.48±4.3] (0.50)	1.40±3.0 [1.40±7.1] (1.42)
Cu	0.40±3.7 [0.42±6.8] (0.418)	0.100±2.8 [0.110±1.2] (0.102)	0.22±4.9 [0.24±7.5] (0.23)	0.40±3.5 [0.41±6.8] (0.40)
Ni	7.25±4.5 [7.23±3.8] (7.29)	10.60±1.2 [10.54±5.2] (10.88)	8.71±3.8 [8.67±4.6] (8.77)	12.44±4.5 [12.78±6.6] (12.92)
V	0.035±6.4 [0.035±9.8] (0.037)	0.030±4.9 [0.032±8.6] (0.030)	0.16±6.3 [0.18±3.2] (0.18)	0.134±2.1 [0.133±6.1] (0.135)
Mo	- [0.77±9.2] (0.80)	- [0.45±10.6] (0.43)	- [0.24±5.5] (0.24)	- [0.066±8.8] (0.07)
Co	0.03±1.9 [0.029±5.6] (0.032)	0.021±2.8 [0.020±4.4] (0.022)	0.124±5.0 [0.127±5.3] (0.127)	0.36±4.2 [0.36±4.5] (0.38)
Nb	0.014±6.2 [0.015±8.1] (0.014)	0.166±4.8 [0.158±7.6] (0.160)	0.049±6.0 [0.047±5.8] (0.050)	0.25±3.3 [0.25±4.1] (0.23)
Ta	0.005±3.9 [0.005±5.6] (0.006)	0.001±2.8 [0.001±4.4] (0.001)	0.035±5.7 [0.034±5.3] (0.032)	0.070±2.2 [0.072±4.5] (0.075)
Pb	0.0036±5.2 [0.004±8.1] (0.0039)	0.0045±4.0 [0.0045±7.6] (0.0047)	0.0055±6.1 [0.0054±5.8] (0.0054)	0.0176±4.3 [0.0175±4.1] (0.0178)
Zr	0.0048±3.8 [0.0046±8.1] (0.005)	0.004±4.7 [0.004±4.9] (0.004)	0.0026±6.6 [0.0028±5.1] (0.003)	0.0037±5.9 [0.0033±2.6] (0.004)

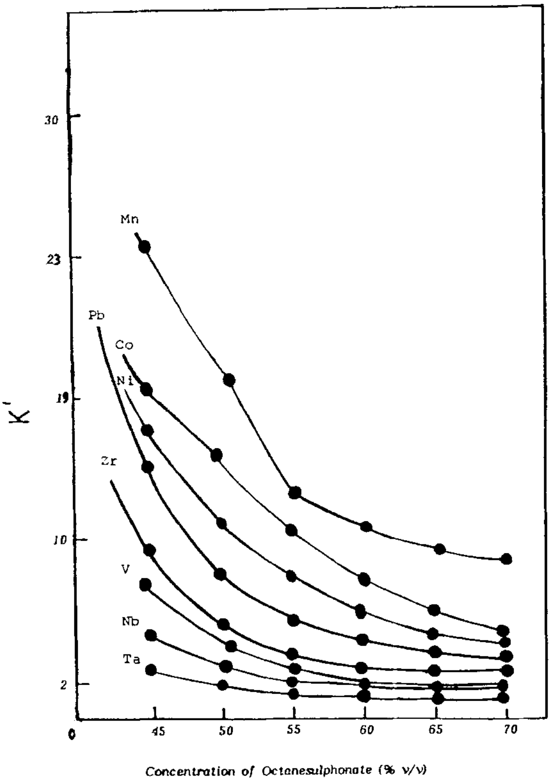

Fig. 1. Effect of sodium octane-1-sulphonate concentration on the retention times of the TAR chelates; Buffer, tartrate (2.308 x 10^{-2} mol dm^{-3}); pH 6.0; Flow rate 1 ml min^{-1}; column length, 300 x 3.9 mm ID (Sperisorb S-5 ODS-I); Detection wavelength 580 nm.

wavelength there was an indication of overlap of the peaks of the unreacted reagent and the Ni-TAR chelate peak.

As the pH of the mobile phase shows, the absorption spectra were recorded under mild acidic conditions and it was observed that the absorption of these metal-TAR red chelates was influenced by the hydrogen ion concentration. The absorption of

Table 2 Absorption characteristics of the metal-TAR chelates in various buffers

Chelate	Tartrate	Oxalate	Acetate
	(Molar absorptivity/10^4 dm^3 mol^{-1} cm^{-1})		
V-TAR	3.7	2.2	1.6
Pb-TAR	3.3	2.3	2.5
Nb-TAR	3.7	2.2	1.8
Ta-TAR	3.9	2.4	2.1
Cu-TAR	4.6	3.0	2.6
Ni-TAR	4.3	2.1	1.7
Zr-TAR	4.1	2.3	2.2
Mn-TAR	3.6	2.1	1.5
Co-TAR	4.0	2.8	2.4

Buffer concentration, 2.308 x 10^{-2} mol dm^{-3}; pH 6.0; Flow rate 1 ml min^{-1}; column length, 300 x 3.9 mm ID (Sperisorb S-5 ODS-I); Detection wavelength 580 nm.

these chelates was found to be maximum around the pH of 6.0. Below this pH there is marked decrease in the absorption which may be due to protonation equilibria as was found in case of the Cr-PAR chelates [22].

Various buffers like tartrate, oxalate, citrate, KH_2PO_4 - Na_2HPO_4, and Tris-(hydroxymethyl)aminomethane (Tris), were used to determine the optimum pH range of the mobile phase. Tartrate was found to improve the peak shapes and produce higher peak heights for the TAR chelates of Fe, Co, Ni, Mn and Cu. Tris and KH_2PO_4 - Na_2HPO_4 had no beneficial effect on the separation, and the retention of these metal-TAR chelates changed very little, but that of Fe- and Co-TAR chelates increased markedly in the pH range of 6.0-7.0. The effect of buffers like tartrate, oxalate, and citrate on the absorbance of these chelates is given in table 2. As can be seen the maximum absorption was obtained in tartrate buffer. It was also found that the absorption of the metal-TAR chelates was influenced by the concentration of tartrate added. With the increase in concentration of tartrate, the absorption increases progressively and then decreases. A possible explanation is, in a weakly acidic medium, the concentration of hydroxy groups would be low; hence the hydroxy groups coordinated to metal ions could be replaced by tartrate. As a result, coloured ternary (M-tartrate-TAR) complexes would be formed. Therefore, the absorbance increases as the tartrate concentration increases. However, at high concentrations of tartrate, the coordinated TAR would be replaced by tartrate which would lead to a decrease in the absorbance. The optimum concentration for the maximum absorption of M-TAR chelates was obtained when the concentration of tartrate was about 2.308×10^{-2} mol dm^{-3}.

The chromatograms obtained for some of the transition metal ions are illustrated in Figure 2 and 3. Based on the spectrophotometric studies described above, the complete separation of these elements require about 14 minutes.

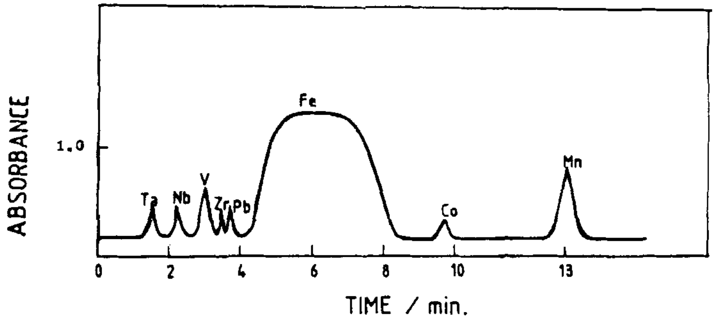

Fig. 2. Separation of major and minor components in stainless steel sample (SRM C 1151) without removal of iron matrix by IC using TAR as pre-column chelating agent.
using octanesulphonate (10^{-3} mol dm^{-3}) with tartrate buffer (2.308×10^{-2} mol dm^{-3}) as mobile phase; pH 6.0; Flow rate, 1 ml min^{-1}; column length, 300 x 3.9 mm ID (Sperisorb S-5 ODS-I); Detection wavelength 580 nm.

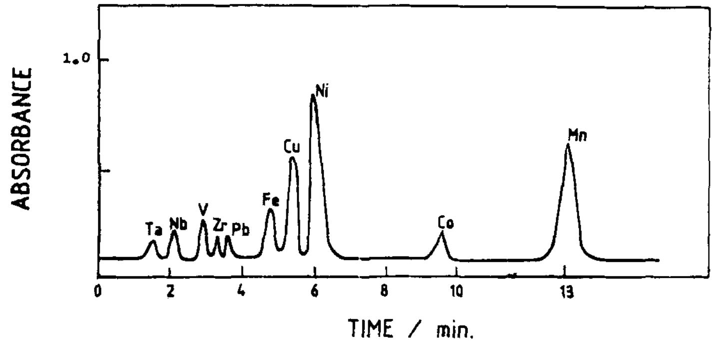

Fig. 3. Separation of Ta, Nb, V, Zr, Pb, Fe, Cu, Ni, Co and Mn-TAR complexes by IC in stainless steel sample (SRM C 1151) after removing the iron matrix. TAR (5×10^{-3} mol dm^{-3}) was used as pre-column chelating agent.
Mobile phase, octanesulphonate (10^{-3} mol dm^{-3}) with tartrate buffer (2.308×10^{-2} mol dm^{-3}); pH 6.0; Flow rate, 1 ml min^{-1}; column length, 300 x 3.9 mm ID (Sperisorb S-5 ODS-I); Detection wavelength 580 nm.

As the optimum performance of silica based bonded columns occurs in the pH range 3.5 - 7.0, the effect of variation of the pH of the eluent was carefully studied within this range. It was observed that the retention time increases with the decrease in pH. This may be because of decreased pH decreases the ionization of tartrate, which in turn decreases the degree of metal complexation, thereby increasing retention times [23]. It was found that a pH of 6.0 gave the best separation and detection.

The peaks that appeared in the chromatograms were identified by spiking with authentic (i.e., known) metal ion solutions. Quantitative measurements were done by plotting calibration graphs for individual elements taking peak heights at different concentrations and comparing the result for samples. The absolute detection limits, calculated as the amount injected that gave a signal that was three times the background noise (i.e., signal to noise ratio of 3:1) were 3.2, 2.5, 0.6, 0.8, 1.2, 2.9, 3.0, 4.2,and 4.0 ng for V, Zr, Cu, Ni, Mn, Co, Pb, Nb and Ta respectively.

The other trace elements such as Al, Cr and Mo which are present in stainless steels were not detectable using TAR as chelating agent.

No significant change in peak width was observed during the separation of ions using same volume of the sample solution indicating an excellent column performance throughout the analysis.

CONCLUSIONS

By using TAR as pre-column chelating agent, it is possible to separate and determine the metal ions in stainless steel samples by ion chromatograph on a C_{18} column. This chromatographic method is fairly selective and sensitive and can be applied to other metallurgical samples.

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REFERENCES

1. B.R.Willford and H.Veening, J.Chromatogr., 251 (1982) 61.
2. G.Nickless, J.Chromatogr., 313 (1985) 129.
3. B.Steinbrech, J.Chromatogr., 410 (1987) 1.
4. F.Vlacil, L.Vins and J.Coupek, J.Chromatogr., 391 (1987) 113.
5. F.Vlacil, L.Vins and J.Coupek, J.Chromatogr., 391 (1987) 119.
6. Yu.E.Pazukhina, O.A.Shpigun, I.N.Voloschits and M.I.Lithvina, Zh. Anal. Khim., 43 (1988) 117.
7. J.S.Fritz, D.J.Gjerde and R.M.Becker, Anal.Chem., 52 (1980) 1519.
8. J.S.Fritz and G.j.Sevenich, Anal. Chem., 55 (1983) 12.
9. J.F.Jen, K.E.Daugherty and J.G.Tarter, J.Chromatogr., 436 (1988) 86.

10. Z.Hu and Y.Tans, Analyst, 113 (1988) 179.

11. Chang-shan Lin, Xiao-song Zhang and Xue-zhu Liu, Analyst, 116 (1991) 277.

12. D.A.Roston, Anal. Chem., 56 (1984) 241.

13. A.R.Timerbaev and O.M.Petrukhin, Talanta, 38 (1991) 467

14. Liu Qiping, Zhang Huashan and Cheng Jieke, Talanta, 38 (1991) 669.

15. S.J.Tsai and Y.Lee, Analyst, 116 (1991) 615.

16. J.N.King and J.S.Fritz, Anal. Chem., 59 (1987) 703.

17. A.M.Bond and Y.Nagaosa, Anal. Chem. Acta., 178 (1985) 197

18. Y.Shijo and K.Sakai, J. Chromatogr., 333 (1985) 133.

19. CRC Handbook of Organic Analytical Reagents, Eds. K.L.Cheng, K.Ueno and T.Imamura, CRC Press, Boca Raton, FL, (1982) pp 203-218.

20. R.Saraswati, N.R.Desikan, S.V.Athavale and T.H.Rao, Anal. Chim. Acta., 237 (1990) 325.

21. R.Saraswati and T.H.Rao, Analyst, 117 (1992) 735.

22. H.Hoshino and T.Yotsuyanagi, Anal. Chem., 57 (1985) 625.

23. P.R.Haddad and P.E.Jackson, "Ion Chromatography: Principles and Application", p. 103 and 186, Elsevier, Amsterdam, 1990.

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