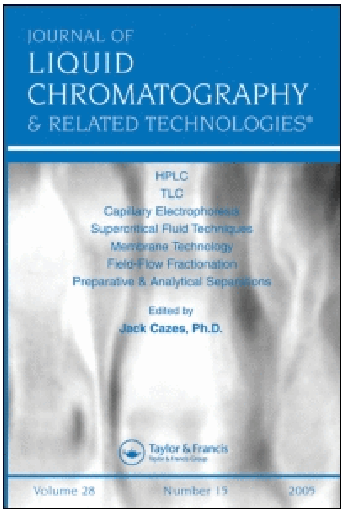

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SIMULTANEOUS DETERMINATION OF TRANSITION AND RARE EARTH METAL IONS IN Nd-Fe-B MATERIAL BY HIGH PERFORMANCE ION CHROMATOGRAPHY USING POST-COLUMN CHELATION TECHNIQUE

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ABSTRACT

The transition and lanthanide metal ions of Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in Neodymium-iron-boron (Nd-Fe-B) magnetic material are separated and determined by high performance ion chromatography (HPIC) with spectrophotometric detection using post-column reaction methods. 4-(2-pyridylazo)resorcinol (PAR) and 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)benzenearsonic acid (Arsenazo-III) are used as post-column chelating agents. The requirements for sample preparation, and characterization of the post-column reaction and the optimum conditions for the sensitive detection of these metal ions after ion chromatographic separation are discussed. The concentration of pH of the chelating medium and the composition of the eluent and the detection limits are investigated.

INTRODUCTION

Samarium-cobalt and Neodymium-iron-boron rare earth magnetic materials are used as substitutes for Alnico and Ferrite magnetic

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materials [1]. In fact Nd-Fe-B magnetic materials are the highest strength magnets currently in use. The Nd-Fe-B magnetic materials withstand high demagnetizing field because of its high coercivity of 11 kOe (3 kOe for ferrite and 2 kOe for Alnico magnets). The coercivity can be altered by the addition of small (trace) amounts of some of the heavy rare earth metals such as terbium, dysprosium, holmium, erbium or ytterbium and some transition metals such as titanium, molybdenum, zirconium, niobium or hafnium. Therefore it has become essential to determine the trace components in these materials. Although several schemes for the systematic analysis of individual metal ions are available, the high matrix interference makes it difficult to analyze many of these trace components in a single sample. The high performance ion chromatographic technique has become an attractive method for trace metal determination because of the advances that took place in column and detection techniques [2-10]. The use of HPIC rather than other instrumental techniques e.g. Atomic Absorption Spectrometry or Inductively Coupled Plasma Spectrometry, is favored in some circumstances because this technique is capable of multielement determination as individual metals and metal complexes form distinct ions with differing retention times which makes it possible to analyze several of them in a single run.

The separation and simultaneous determination of mixtures 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 or as post-column reagents[11-14]. PAR and Arsenazo-III are azo dyes that have been widely employed for the complexometric titrations and spectrophotometric determination of various metals [15-17]. These reagents can form ionic compounds with metal ions which are water soluble with unique absorption characteristics. This is one of the features that makes them useful and effective chelating agents for the determination of metals using IC with either precolumn or post-column techniques.

The lanthanide metals can be separated by cation or anion exchange, but a number of transition metals co-elute with the lanthanides under the same conditions. The separation of transition and lanthanide elements can be achieved by changing the concentration of the eluent[18]. After the transition metals have been separated and completely eluted from the column, the lanthanide metals are separated by increasing the concentration of the eluent [19]. Our current efforts as described here, are focused on separating transition and rare earth metals in Nd-Fe-B matrix using PAR and Arsenazo-III as post-column reagents.

EXPERIMENTAL

The Waters ion chromatography system consists of Model 501 pumps with Waters U6K injector. A Spherisorb S-5 ODS 1 separation column was employed. A Waters 486 tuneable absorbance uv-visible spectrometric detector with a 12 µl cell was used to monitor the effluent from the column. A Waters post-column reagent mixture module was employed along with a Waters maxima 820 chromatography workstation with a printer.

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

High-purity "Suprapure" grade chemicals from E.Merck were used. Solvents were further purified using isothermal sub-boiling distillation. Pure metals from Johnson-Mathey (JMC) were used for the preparation of standards and eluents.

The Nd-Fe-B material from DMRL, India was used as sample.

Chromatograms were recorded by injecting 20 μl (after filtering through a 0.45 μm filter) of standard solutions of ions and elution with 10^{-3}M sodium octane-1-sulphonate (54 mg in 250 ml) solution - 0.023 M tartaric acid at a flow rate of 1 ml min^{-1}. Standard calibration graphs were obtained with the chosen parameters by injecting standards separately and in mixture and recording the peak heights of the respective ions.

Good sensitivity for the detection of individual transition and lanthanide elements was obtained with a solution of 2×10^{-4} M PAR, and 2.308×10^{-2} tartrate solution. The Arsenazo-III (1×10^{-3}) solution containing 3 ml l^{-1} ammonia solution was used for the detection of Cu, Zn, Zr, Cr and lanthanide metal ions.

Sample Preparation

A 1 g amount of sample was dissolved in 15 ml of concentrated HCl + 5 ml of concentrated HNO_3 and was diluted up to 100 ml with water. The solution was further diluted with water as required. In this solution the concentration of matrix elements, particularly iron and neodymium are very high. Because of the excess of Fe and Nd, the chromatographic column can be overloaded locally which may have detrimental effects on the separation. Therefore separation of matrix is a prerequisite for achieving reliable trace element determinations when IC procedures are used with post-column reaction detection. The separation of iron and neodymium matrix was achieved by procedure discussed earlier [20].

The color forming reagents PAR and Arsenazo-III were delivered by the reagent delivery module and mixed with the elute after the column. The resulting derivative was detected at 533 nm (with PAR) and 600 nm (with Arsenazo-III) using the uv-visible spectrometric detector.

RESULTS AND DISCUSSION

PAR, Arsenazo-III were used as color forming post-column reagents. The metal ions Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Zr^{4+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+} gave stable colors with PAR. Whereas the ions of Cr, Cu, Zr and lanthanide metals gave good colors with Arsenazo-III. Sodium octanesulphonate -tartaric acid solution was very good mobile phase for the separation of these metal ions. the important factors that influence the sensitivity and resolution of metal ions are the rate if reaction between the reagent and the metal ions, background absorbance, noise and the efficiency of the mixing cell.

4-(2-Pyridylazo)resorcinol is a tridentate ligand that forms metal chelates which absorb in the visible region. The absorption of these red chelates of metal ions with PAR is influenced by the hydrogen ion concentration. The absorption spectra were recorded under acidic conditions as chromatographic studies were to be performed on silica-bonded phase columns. The absorption due to

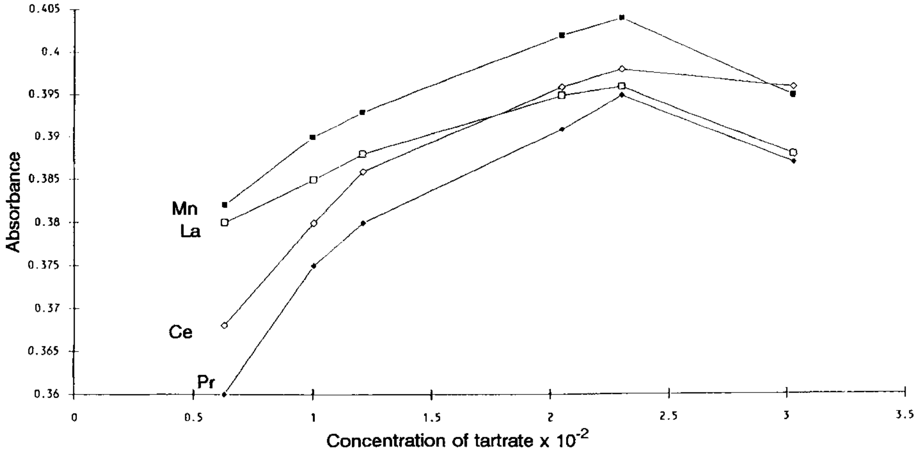

Fig.1 Effect of tartrate concentration on absorbance of metal-PAR chelates

metal-PAR chelates found to be maximum in the pH range of 5-6. Below this pH range, there is marked decrease in the absorbance of some of the chelates which may be due to protonation equilibria as was found in case of the Cr-PAR chelate [21].

The effect of various complexing agents like tartrate, oxalate, and citrate on the absorbance of these chelates was studied. It was observed that the metal-PAR chelates gave maximum absorption in presence of tartrate. It was also found that the absorption of the metal-PAR chelates was influenced by the concentration of tartrate added. Maximum absorption for most of the metal-PAR chelates was obtained when the concentration of tartrate was about 2.308 x 10^{-2} mol dm^{-3} (Fig.1). 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

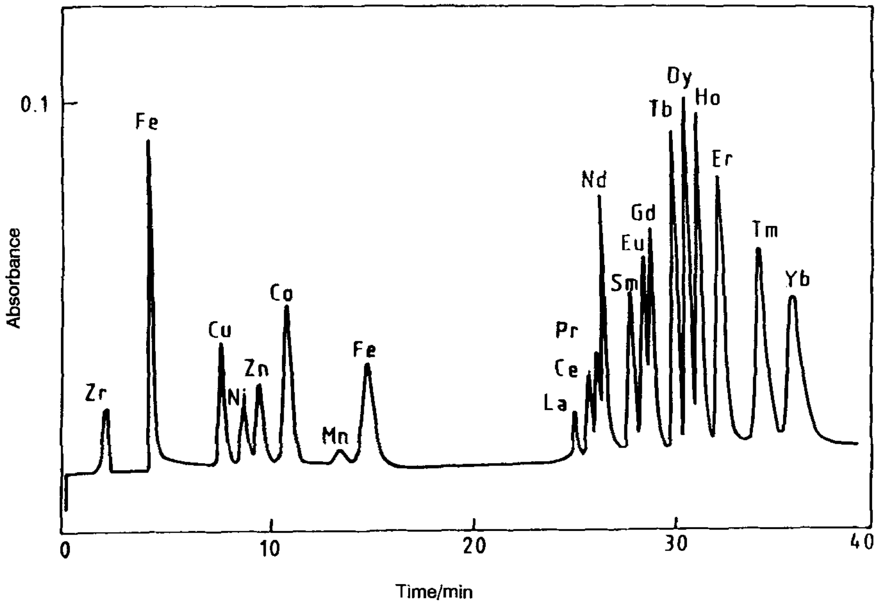

Fig.2 Separation of transition and rere earth metal ions using PAR as post-column chelating agent. Octanesulphonate solution-tartaric acid as mobile phase; pH 5.5; Flow rate 1 ml/min; column length 300 x 3.9 mm ID; detection wavelength 533 nm.

could be replaced by tartrate. As a result, colored ternary (M-tartrate-PAR) complexes would be formed. Therefore, the absorbance increase as the tartrate concentration increases. However, at high concentrations of tartrate, the coordinated PAR would be replaced by tartrate which would lead to a decrease in the absorbance. It was also observed that the maximum absorption of the chelates was obtained when the concentration of PAR was kept at 2.5 x 10^{-4} mol dm^{-3}.

The chromatograms obtained are illustrated in Figures 2 and 3. The chromatograms were recorded at 533 nm (with PAR) and at 600

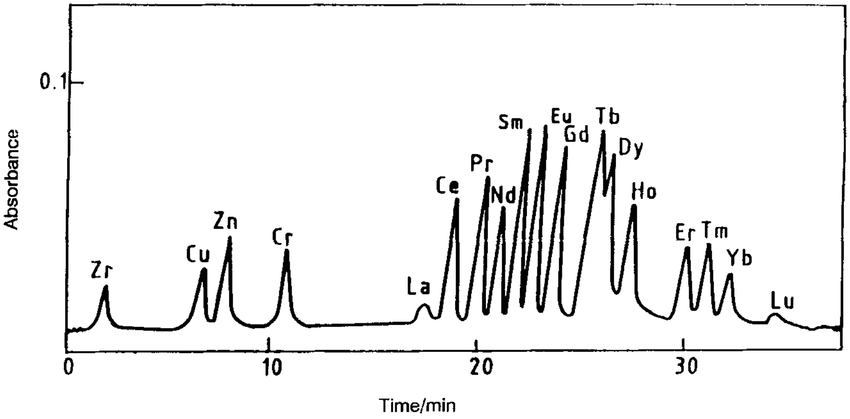

Fig.3 Separation of transition and rere earth metal ions using Arsenazo-III as post-column chelating agent. Octanesulphonate solution-tartaric acid as mobile phase; pH 4.5; Flow rate 1 ml/min; column length 300 x 3.9 mm ID; detection wavelength 600 nm.

(with Arsenazo-III) as all chelates showed significant absorption at these wavelengths. Around 35 minutes were taken for complete separation of transition and lanthanide metal ions using PAR as post-column reagent. Zirconium was separated at about 2.5 minutes followed by other metal ions as shown in Table 1. It was found that Arsenazo-III solution containing 3 ml l^{-1} NH_3 gives good detection of Zr, Cu, Cr and lanthanide metal ions. The eluting times are given in Table 1.

The results of the spectrophotometric studies indicated that the pH of the chelating medium has a significant effect on the absorption of the metal PAR complex. The reversed-phase separation was performed on silica based bonded columns. As the optimum performance of these columns occur in the pH range 3.5 - 7.0, the effect of variation of the pH of the eluent was carefully studied

Table 1 Eluting times (in minutes) of various metal chelates using PAR and Arsenazo-III as chelating agents with octanesulphonate-tartaric acid as mobile phase

Metal-chelate	PAR	Arsenazo-III
Zr	2.50	2.03
Fe	4.87	---
Cu	7.50	6.87
Ni	8.60	---
Zn	9.40	7.08
Co	10.58	---
Cr	---	11.25
Mn	13.27	---
La	24.70	17.80
Ce	25.33	18.92
Pr	25.67	20.30
Nd	26.07	21.08
Sm	27.30	22.20
Eu	27.93	23.07
Gd	28.33	24.03
Tb	29.33	25.47
Dy	30.03	26.40
Ho	30.50	27.50
Er	31.60	30.42
Tm	33.53	31.33
Yb	35.17	32.58
Lu	---	34.92

Table 2 Detection limits for various metals using ion chromatographic methods with PAR and Arsenazo-III as post-column chelating reagents.

Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	La	Ce	Pr
0.8	0.5	0.6	0.9	0.2	0.6	0.7	1.4	1.2	1.7	1.3
Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1.1	1.8	2.9	2.8	3.4	2.7	4.2	2.6	3.3	1.1	2.5

within this range. It was observed that the retention time increases with the decrease in pH. This may be attributed to a decrease in the ionization of tartrate at decreased pH. This in turn decreases the degree of metal complexation, thereby increasing retention times [22]. It was found that a pH of 5.5 (4.5 with Arsenazo-III) gave the best separation and detection.

The peaks that appeared in the chromatograms were identified by authentic (i.e. known) metal ion solution. Quantitative measurements were done by plotting calibration graphs for individual elements taking peak heights at different concentrations and comparing the results for samples. The absolute detection limits were 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) (Table 2). No significant change in peak width was observed during the separation of ions using same volume of sample solution.

CONCLUSION

By using PAR and Arsenazo-III as post-column chelating agent it is possible to separate and determine the transition and rare earth metal ions in Nd-Fe-B magnetic material by HPIC on a C_{18} column. This chromatographic method is fairly selective and sensitive and can be used for the simultaneous determination of trace (minor) components of transition and rare earth metals in Nd-Fe-B magnetic material.

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