

Reversed-phase high-performance liquid chromatographic separation of some trace impurities in oxygen-free electronic copper by post-column chelation with 4-(2-pyridylazo)resorcinol and Arsenazo-III

Rajananda Saraswati and T. H. Rao

Defence Metallurgical Research Laboratory, Kanchanbagh P.O., Hyderabad 500 258 (India)

(First received October 9th, 1991; revised manuscript received March 4th, 1992)

ABSTRACT

Trace amounts of impurities such as Al, Cr, Mn, Fe, Co, Ni, Zn, Bi and Pb in oxygen-free electronic copper were separated and determined by reversed-phase high-performance liquid chromatography (HPLC) with spectrophotometric detection using post-column reaction methods. 4-(2-Pyridylazo)resorcinol (PAR) and 2,2'-(1,8-dihydroxy-3,6-disulphonaphthylene-2,7-bisazo)bisbenzenearsonic acid (Arsenazo-III) were used as post-column chelating agents. The requirements for sample preparation, characterization of the post-column reaction and the optimum conditions for the sensitive detection of these trace amounts of metal ions after ion chromatographic separation are discussed. The concentration of PAR, Arsenazo-III and the composition of the eluent were investigated. A baseline separation of these impurities is achieved after 15 min using PAR and at 40 min using Arsenazo-III. The speed of separation was increased by a concentration gradient technique. The detection limits achieved were 1.0, 0.2, 0.1, 2.0, 0.2, 0.6, 2.4, 0.6 and 1.0 ng for Al, Cr, Mn, Fe, Co, Ni, Zn, Bi and Pb, respectively. The results obtained by HPLC methods compare well with those of graphite furnace atomic absorption spectrometry and certified values of MBH.

INTRODUCTION

Studies of the influence of various impurities on the annealing properties and electrical conductivity of oxygen-free electronic copper (OFEC) have shown that the higher the concentrations of impurities the higher the softening temperature and the lower the electrical conductivity [1–6]. For example, every 5 ppm of lead in the range 0–25 ppm reduces the electrical conductivity of copper by about 0.1% IACS (International Annealed Copper Society). Similarly, every 5 ppm increase in the concentration of antimony in the range 0–25 ppm lowers the conductivity by 0.15% IACS. The presence of the order

of 0.001% Fe, however, would lead to embrittlement and loss of ductility [1]. The presence of Bi at 0.001% (at a Cu purity of 99.999%) will result in intergranular fractures due to microcracks and micropores as Bi segregates to the grain boundary causing the embrittlement of Cu even at low stress levels. Therefore the accurate determination of trace amounts of impurities in Cu has become increasingly important. Several schemes for systematic analysis have been described previously [7–10]. None of the schemes includes the determination of all impurities in a single sample, although several independent procedures have been proposed. With the advent of atomic absorption spectroscopy (AAS), many procedures for the determination of trace amounts of impurities in copper have been developed. However, the detection limits of AAS procedures have been severely influenced by matrix

Correspondence to: Dr. R. Saraswati, Defence Metallurgical Research Laboratory, Kanchanbagh P.O., Hyderabad 500 258, India.

effects. In this context, the high-performance ion chromatographic separation and detection technique seems to be one of the most promising tools.

High-performance liquid chromatography (HPLC) is extensively used for the separation of organic compounds. In recent years, this technique has also become an attractive method for the determination of trace amounts of metals [11–13]. In fact, the advances that have taken place in column and detection techniques [14–20] have allowed HPCL to be used to characterize a wider range of anions and cations as individual metals and metal compounds form distinct ions with differing retention times, it is possible to determine several ions in a single run. The separation and simultaneous determination of mixtures of metal ions as their chelates with organic reagents by HPLC has received increasing attention. A wide variety of organic reagents has been used to complex with metal ions before separation [21] and some reagents such as 4-(2-pyridylazo)resorcinol (PAR) and 2,2'-(1,8-dihydroxy-3,6-disulphonaphthylene-2,7-bisazo)bisbenzenearsonic acid (Arsenazo-III) also act as very good post-column reagents.

PAR and Arsenazo-III are azo dyes that have been widely used for compleximetric titrations and spectrophotometric determination of over 40 different metals [22–24]. These reagents can form ionic compounds with metal ions which are water-soluble with unique absorption characteristics. Hence the spectrophotometric determination is usually performed in an aqueous solution. This is one of the features that makes them useful and effective chelating agents for the determination of metals using HPLC with either pre-column or post-column techniques [25].

In previous papers [26,27] we have discussed the separation of transition and rare earth metals which are present in trace amounts in low-alloy steels and transition metals in stainless steels. This paper describes the determination of the optimum chromatographic conditions for the separation and determination of some of the trace amounts of impurities in OFEC after post-column reaction with PAR and Arsenazo-III.

EXPERIMENTAL

The Waters gradient-control ion chromatograph-

ic (IC) system used consists of Model 501 pumps with a Waters U6K injector. A Spherisorb S-5 ODS I separation column was used. A Waters 486 tunable absorbance UV-visible spectrometric detector with a 12- μ l flow cell was used to monitor the effluent from the column. A Waters post-column reagent mixture module was used together with a Waters maxima 820 chromatography workstation with a printer.

The laboratory equipment was used after conditioning in an ultrasonic cleaner and equilibrating in reagent-grade water (18 Ω resistance) from a Millipore Milli Q water system with 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 in a laminar flow fume hood of class 100 condition with the total laboratory facility maintained at class 10 000 level to overcome dust and particulate contamination. Pure metals from Johnson Matthey (JMC) and certified reference materials from MBH were used for the preparation of standards and eluents.

Chromatograms were recorded by injecting 20 μ l of standards solutions of ions which were prepared by dissolving known amounts of pure metals and further diluting to the required levels, 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 mixtures and recording the peak heights of the respective ions.

Sample preparation and matrix separation

A 10-g amount of sample (which had previously been washed with methanol and dried with an infrared lamp) was dissolved in a requisite amount (\approx 40 ml) of nitric acid (1 + 1), covering the beaker and heating to below the boiling point. After the sample had been dissolved, the solution was boiled to remove nitrogen oxides. The solution was cooled and the surface of the dish and the inner walls of the beaker were blow-washed with water. The solution was then diluted to approximately 100 ml.

The sample solution obtained contains lot of copper matrix. This may have detrimental effects on the chromatographic column and the separation of impurities. Therefore the separation of copper is a pre-

requisite for achieving reliable trace element determinations when IC procedures are used with post-column reaction detection. This matrix separation is achieved by subjecting the sample solution to electrolysis at 0.6 A using platinum gauge electrodes and a magnetic stirrer. The solution was covered and heated on an electrothermal plate to concentrate it, and then the solution was diluted to 25 ml in a standard flask and further diluted as required. Aliquots (20 μ l) of the solution were used for injection after filtering solution through a 0.45- μ m filter.

The concentration gradient technique for elution was used for better resolution and separation. The concentration of the eluent (sodium octane-1-sulphonate–tartaric acid) was varied from 10 to 50% during analysis.

Post-column reaction detection

Good sensitivity for the detection of the individual transition elements Mn, Fe, Co, Ni, Zn, Bi and Pb was obtained with a solution of $2 \cdot 10^{-4}$ M PAR and $2.308 \cdot 10^{-2}$ M tartrate. The Arsenazo-III ($1 \cdot 10^{-3}$ M) solution containing 3 ml l^{-1} ammonia solution was preferred for the detection of Al, Cr, Zn and Pb.

The colour-forming reagents PAR and Arsenazo-III were delivered by the reagent delivery module and mixed with the eluent after passing through the column. The resulting derivative was detected at 533 and 600 nm using the UV–visible spectrophotometric detector.

Instrumental methods

A GBC Model 902 atomic absorption spectrometer 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 a light source. Solutions were injected by a GBC PAL-2000 autosampler. All absorbances were measured as peak heights and were recorded with an Epson Lx-800 printer. The system was operated by a Philips Model P-3105 data station connected on-line.

A 1-g amount of sample was dissolved in 5 ml of dilute nitric acid (1+1) and solution was made up to 100 ml with water and further diluted as required.

RESULTS AND DISCUSSION

The results for four sample materials are presented in Table I. For comparison, the values (% w/w) obtained by AAS and the certified values from the MBH samples 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 octane-1-sulphonate combined with water were investigated as binary and ternary mobile phases. The sodium octane-1-sulphonate (10^{-3} M) and the tartaric acid (0.1 M)–water system were found to be satisfactory for the separation of Mn, Fe, Co, Ni, Cu, Zn, Bi, Pb, Al and Cr metal chelates. PAR and Arsenazo-III were found to be good colour-forming post-column reagents. The metal ions Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Bi^{3+} and Pb^{2+} gave stable colours with PAR, whereas Al^{3+} , Cr^{3+} , Zn^{2+} and Pb^{2+} gave good colours with Arsenazo-III. The important factors that influence the sensitivity and resolution of metal ions are the rate of reaction between the reagent and the metal ions, the background absorbance, noise and the efficiency of the mixing cell.

PAR is a tridentate ligand [25] 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 Al–PAR, Cr–PAR, Mn–PAR, Fe–PAR, Co–PAR, Ni–PAR, Cu–PAR, Zn–PAR, Bi–PAR and Pb–PAR chelates was at a maximum in the pH range 5–6. Below this pH there is a marked decrease in the absorbance of some of the chelates which may be due to protonation equilibria, as was found for the Cr–PAR chelate [28].

The effect of various buffers such as tartrate, oxalate and citrate on the absorbance of these chelates was studied. The maximum absorption was obtained in tartrate buffer. It was also found that the absorption of the metal–PAR chelates was influenced by the concentration of tartrate added. The maximum absorption of M–PAR chelates was obtained when the concentration of tartrate was about $2.308 \cdot 10^{-2}$ mol dm^{-3} . A possible explanation is

TABLE I

COMPARISON OF RESULTS (% w/w) OBTAINED BY HPLC AND GRAPHITE FURNACE AAS WITH THE CERTIFIED VALUES OF MBH SAMPLES

Values in square brackets were obtained by graphite furnace AAS and values in parentheses are for MBH samples. Results given as mean \pm relative standard deviation (%). $n = 5$.

	17867B	17868B	17869B	17870B
Mn	0.008 \pm 2.1 [0.008 \pm 4.2] (0.009)	0.0215 \pm 2.6 [0.0215 \pm 6.2] (0.0216)	0.0286 \pm 2.0 [0.0288 \pm 4.9] (0.030)	0.040 \pm 3.8 [0.040 \pm 7.8] (0.0405)
Fe	0.0120 \pm 4.2 [0.0125 \pm 6.1] (0.0125)	0.028 \pm 0.8 [0.026 \pm 1.2] (0.029)	0.037 \pm 1.9 [0.037 \pm 7.2] (0.038)	0.053 \pm 2.5 [0.055 \pm 6.8] (0.055)
Co	0.035 \pm 4.5 [0.032 \pm 3.8] (0.037)	0.030 \pm 1.2 [0.030 \pm 5.2] (0.030)	0.016 \pm 1.8 [0.018 \pm 7.6] (0.016)	0.001 \pm 2.5 [0.001 \pm 6.6] (0.001)
Ni	0.039 \pm 6.1 [0.035 \pm 9.8] (0.040)	0.0336 \pm 2.9 [0.0333 \pm 8.6] (0.0340)	0.020 \pm 1.3 [0.021 \pm 3.2] (0.020)	0.0048 \pm 2.1 [0.005 \pm 6.1] (0.005)
Zn	0.030 \pm 5.2 [0.035 \pm 9.2] (0.030)	0.0241 \pm 5.7 [0.0245 \pm 10.6] (0.0245)	0.0130 \pm 5.0 [0.0130 \pm 5.5] (0.0135)	0.0020 \pm 1.6 [0.002 \pm 12.8] (0.0022)
Bi	0.011 \pm 1.1 [0.011 \pm 9.6] (0.011)	0.0290 \pm 1.8 [0.0290 \pm 4.4] (0.0295)	0.035 \pm 5.0 [0.038 \pm 5.3] (0.0385)	0.054 \pm 3.6 [0.055 \pm 4.5] (0.055)
Pb	0.012 \pm 4.2 [0.015 \pm 8.1] (0.013)	0.024 \pm 4.0 [0.025 \pm 7.6] (0.025)	0.0380 \pm 6.9 [0.0389 \pm 5.8] (0.0385)	0.046 \pm 7.2 [0.049 \pm 4.1] (0.048)
Al	0.008 \pm 4.2 [0.008 \pm 4.6] (0.009)	0.020 \pm 1.5 [0.022 \pm 3.6] (0.020)	0.031 \pm 6.8 [0.035 \pm 4.6] (0.034)	0.044 \pm 1.2 [0.046 \pm 1.4] (0.045)
Cr	0.0045 \pm 8.1 [0.0040 \pm 2.9] (0.0046)	0.003 \pm 7.5 [0.0033 \pm 0.6] (0.0034)	0.002 \pm 6.9 [0.003 \pm 7.8] (0.003)	0.0005 \pm 1.8 [0.0006 \pm 6.5] (0.0006)

that, in a weakly acidic medium, the concentration of hydroxy groups is low and hence the hydroxy groups coordinated to metal ions could be replaced by tartrate. As a result, coloured ternary M-tartrate-PAR complexes would be formed. Therefore the absorbance increases 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.

The chromatograms obtained for some of the trace amounts of impurities are illustrated in Fig. 1. The chromatograms were recorded at 533 nm as all

the chelates showed significant absorption at this wavelength. Based on the spectrophotometric studies described earlier, the chromatographic separation was performed in tartrate buffer. When the separation of these elements was performed without a solvent programme, 15 min were required to complete the separation (Fig. 1a). Pb was separated at about 3 min 30 s, followed by Fe (4 min 10 s), Bi (4 min 46 s), Cu (5 min 15 s), Ni (5 min 50 s), Zn (6 min 30 s), Co (9 min 40 s) and Mn (15 min 5 s). However, the speed of separation was increased by using a concentration gradient for elution, the concentration of the eluent being increased five-fold (Fig. 1b).

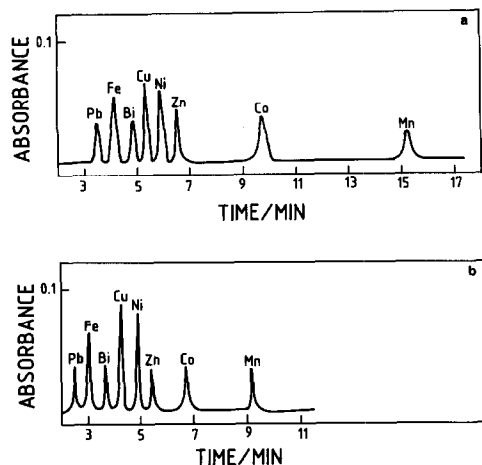


Fig. 1. Separation of some trace amounts of metals in OFEC sample (CRM 17867B) by HPLC using PAR as the post-column reagent. (a) Without solvent programme and (b) with gradient elution using octane-1-sulphonate ($1 \cdot 10^{-3} M$)-tartaric acid ($0.123 M$) as the mobile phase; pH 5.5. Flow-rate 1 ml min^{-1} ; PAR ($2.5 \cdot 10^{-4} \text{ mol dm}^{-3}$); column length, $300 \times 3.9 \text{ mm I.D.}$; detection wavelength, 533 nm .

Al and Cr were not detected using PAR as the post-column reagent, but Arsenazo-III was found to be the preferred reagent for the detection of Al and Cr together with Zn and Pb (Fig. 2).

Arsenazo-III is a weak octabasic acid and is one of the most often used azo dyes, forming metal chelates which absorb in the visible region. It was found that Arsenazo-III ($1 \cdot 10^{-3} M$) solution containing $3 \text{ ml l}^{-1} \text{ NH}_3$ gives good detection of Al, Cr, Zn and Pb in the pH range 3.5–4 at 600 nm . Pb was detected at about $4 \text{ min } 8 \text{ s}$ followed by Cu ($5 \text{ min } 35 \text{ s}$), Zn ($7 \text{ min } 10 \text{ s}$), Al ($12 \text{ min } 22 \text{ s}$) and Cr ($40 \text{ min } 15 \text{ s}$). The speed of separation of Cr was increased by a concentration gradient, the concentration of the eluent being increased ten-fold (Fig. 2b).

The composition of the eluent was also studied. As mentioned earlier, the absorption characteristics of the chelates are influenced by the concentration of tartrate and PAR. Therefore the effect of tartrate and PAR on the separation and detection of the chelates was studied by monitoring chromatograms as a function of the reagent concentration in the mobile phase. It was found that the effect of the tartrate concentration in the range $1.2 \cdot 10^{-2}$ to $2.33 \cdot 10^{-2} \text{ mol dm}^{-3}$ and the PAR concentration in the

range $2.0 \cdot 10^{-4}$ to $5.0 \cdot 10^{-5} \text{ mol dm}^{-3}$ on retention times and the detection of the metal ions Pb^{2+} , Fe^{3+} , Bi^{3+} , Ni^{2+} , Zn^{2+} , Co^{2+} and Mn^{2+} was very slight. The best separation and detection was obtained at tartrate and PAR concentrations of $2.308 \cdot 10^{-2}$ and $2.5 \cdot 10^{-4} \text{ mol dm}^{-3}$, respectively.

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 occurs in the pH range 3.5–7.0, the effect of varying the pH of the eluent was carefully studied within this range. It was observed that the retention time increases with decreasing pH. This is because a decreased pH decreases the ionization of tartrate, which in turn decreases the degree of metal complexation, thereby increasing retention times. It was found that a pH of 5.5 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 carried out by plotting calibration graphs for individual elements, taking the peak

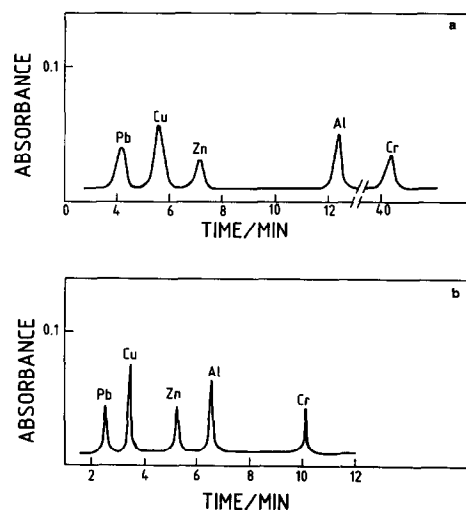


Fig. 2. Separation of some trace amounts of elements in OFEC sample (CRM 1786B) by HPLC using Arsenazo-III as the post-column reagent. (a) Without solvent programme and (b) with gradient elution using octanesulphonate ($1 \cdot 10^{-3} M$)-tartaric acid ($0.023 M$) as the mobile phase; pH 6.0. Flow-rate 1 ml min^{-1} ; Arsenazo-III ($10^{-3} M$) containing $3 \text{ ml l}^{-1} \text{ NH}_3$; column length, $300 \times 3.9 \text{ mm I.D.}$; detection wavelength, 600 nm .

heights at different concentrations and comparing the results with those for samples. The absolute detection limits, calculated as the amount injected that gave a signal that was three times the background noise (*i.e.* a signal-to-noise ratio of 3:1), were 1.0, 0.2, 0.1, 2.0, 0.2, 0.6, 2.4, 0.6 and 1.0 ng for Al, Cr, Mn, Fe, Co, Ni, Zn, Bi and Pb, respectively.

The other trace elements that are normally present in OFEC are Se, Te, Mg, As and Sn. Neither PAR nor Arsenazo-III give any detectable colour with these impurities.

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

CONCLUSIONS

By using PAR and Arsenazo-III as post-column chelating agents some of the trace impurities in OFEC have been successfully separated and determined by reversed-phase HPLC on a C₁₈ column. This chromatographic method is fairly selective and sensitive and can be used for the simultaneous determination of trace impurities of Al, Cr, Mn, Fe, Co, Ni, Zn, Bi and Pb in OFEC at sub-ppm levels.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. P. Rama Rao, previous Director, DMRL and Shri S.L.N. Acharyulu, Director, for permission to publish this paper.

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