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Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

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To cite this Article Butt, S. Bilal , Riaz, M. , Waqar, F. , Jan, S. and E-ul-Haq(1998) 'Trace Level Determination of Iron in High Purity Copper by Ion Pair Liquid Chromatography', *Journal of Liquid Chromatography & Related Technologies*, 21: 6, 843 – 853

To link to this Article: DOI: 10.1080/10826079808000513

URL: <http://dx.doi.org/10.1080/10826079808000513>

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TRACE LEVEL DETERMINATION OF IRON IN HIGH PURITY COPPER BY ION PAIR LIQUID CHROMATOGRAPHY

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ABSTRACT

Iron has been determined in commercial and high purity copper cables using high performance ion-pair liquid chromatography (IPC). The proposed method avoids pre separation/ preconcentration of trace impurities from bulk copper saving considerable sample preparation time. Tetrabutyl ammonium ion (TBA)⁺ was mainly used as an ion pairing reagent. The UV detector response for iron and copper at various wavelengths has been optimized. The accuracy of the developed method is tested by comparing its results with inductively coupled plasma atomic emission spectrometry for the assay of iron in spiked solutions, standard reference material (SRM), and in locally available copper based electrical cables. The relative standard deviation for sample 7 (n = 5) is 1.23%.

INTRODUCTION

High purity copper is being used in the electrical/electronic industry for the recording of high and low pitch sound, electrical transmission, and image recording.¹ Strict quality criteria on purity of copper is practiced. High purity copper, produced by electrolytic refining, contains impurities ranging from 1-20 $\mu\text{g g}^{-1}$.² These impurities lower the electrical conductance and enhance softening temperature if their concentration is more than the permissible level.^{3,4} In this reference, impurities of iron, arsenic, and phosphorous are of vital importance. Particularly, the presence of 0.4 % iron reduces the electrical conductance of copper to 64 %.⁵ Also, in the ASTM specification of chemical composition of oxygen free electrolytic copper, iron is one of the elements to be analysed.⁶

Various analytical techniques such as atomic absorption spectroscopy (AAS)⁷⁻⁸ and secondary ion mass spectroscopy (SIMS)⁹ have been described for the determination of iron in high purity copper. The direct determination of impurities in copper by electrothermal AAS strongly contaminates the graphite furnace due to copper adsorption. It makes trace level copper analysis in other sample difficult because of the high back ground noise. In certain cases the graphite tube has to be replaced. The other associated drawbacks with these techniques may be, recovery problems and prolonged analysis time. Therefore, most of these analytical techniques employ pre-sampling such as precipitation, solvent extraction, and selective ion exchange.⁷

In the present communication, an ion pair high performance liquid chromatographic procedure has been optimized for the assay of trace levels of iron without incorporating any pre-sampling procedure. The developed method is highly sensitive and selective for iron detection. Therefore, small amounts of copper samples are required for sampling. The reliability of the reported method has been counter checked by an optimized inductively coupled plasma-atomic emission spectroscopic (ICP-AES) procedure.

EXPERIMENTAL

Reagents

Tetramethylammonium bromide (TMAB), Tetrabutylammonium perchlorate (TBAP), and Tetrahexylammonium bromide (THAB) were from Fluka, Switzerland. Copper sulphate, ferric sulphate, sodium dihydrogen phosphate, and phosphoric acid, all of analytical grade and acetonitrile (ACN)

Lichrosolve grade, were from E-Merck, Germany. High purity copper oxide was from Johnson and Mathey, UK. Standard solutions each of 1000 mg L⁻¹ of copper and Fe (III) were prepared in 0.5 M HNO₃. Copper cable (0.5-1 gm) was dissolved in 5 ml of concentrated HNO₃.

The solution was heated to expel oxides of nitrogen and diluted to 25 mL with double deionized water. Deionized water was obtained using a Sybron deionizer.

INSTRUMENTATION

High Performance Liquid Chromatography

A Perkin Elmer USA Series 10 solvent delivery system was fitted with a 6 μ L loop and Rheodyne 7120 sample injector. A UV detector Du Pont, USA and data processor D-2500 from Hitachi, Japan were used. The analytical column was ET 250/ 8/ 4 Nucleosil C₈ (250 x 4.6 mm) particle size 5 μ m Macherey Nagel, Germany.

The Pope 1501 pH meter, USA was calibrated with two standard buffers and the mobile phase pH was adjusted with 10 % phosphoric acid. All the measurements were carried out at room temperature 25 \pm 2°C.

Inductively Coupled Plasma-Atomic Emission Spectroscopy

An Applied Research Laboratories ICP model 3580 with two spectrometers, fully controlled by PDP 11/23+ computer was used. The technical data for ICP spectrometer are as follows:

Spectrometer	1 m, sequential, paschen runge 1 m, simultaneous paschen runge
Grating	1035 grooves mm ⁻¹
Torch	Fassel type
Nebulizer	Mainhard type
Gas flow	
Outer	12 L min ⁻¹
Intermediate	0.8 L min ⁻¹
Aerosole carrier	1 L min ⁻¹
Incident power	1.5 kW
Observation height	16 mm above coil

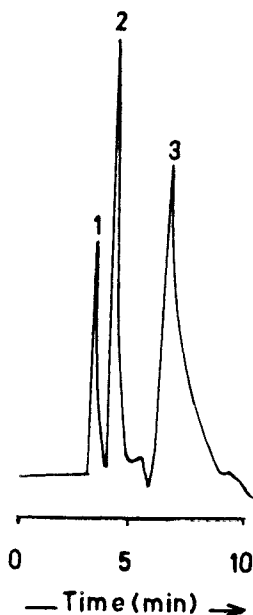


Figure 1. Ion-pair chromatographic separation of standard metal ions solution. Column: Nucleosil C₈; Detector: UV: 270 nm, Eluent: ACN: 3% in water; TBAP 5 mM L⁻¹, NaH₂PO₄: 30 mM L⁻¹; pH: 2; Flow rate: 0.5 mL min⁻¹. Peak identification: 1= Cu (II) 500 mg L⁻¹; 2= Fe(III) 6 mg L⁻¹; 3= NO₃⁻¹.

Iron was determined at its most sensitive line 259.94 nm on simultaneous spectrometer. The scan profiles of sample solution and the matrix matched blank did not indicate any spectral interference. The recoveries of iron spiked in copper were 101 %. The bulk copper has no suppressing or enhancing effect on 0.1 mg L⁻¹ spiked iron. However, below 0.1 mg L⁻¹ of iron the presence of bulk copper did interfere.

RESULTS AND DISCUSSION

The complexation of Fe (III) with ligand H₂PO₄⁻ has been reported.¹⁰ The concentration of proposed complex [Fe(H₂PO₄)₄]⁻ varies with the concentration of H₂PO₄⁻, Fe (III) and H⁺, respectively. The detailed anionic complexation of Fe (III) in phosphate media has been given elsewhere.¹¹ The Cu (II) neutral complex with H₂PO₄⁻ has also been reported.¹²

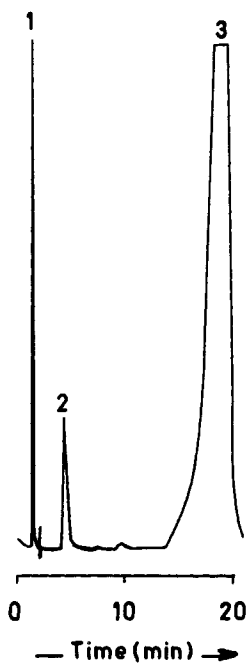
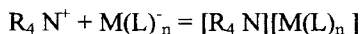


Figure 2. Ion-pair chromatographic separation of standard metal ions solution. Conditions as per Figure 1 except ACN: 10 % in water; THAB 2.5 mM L⁻¹.

Optimization of Chromatographic Conditions

Cations of Tetraalkylammonium salts (TAAS, R₄N⁺) are used as ion pairing agent for anionic metal complex to form a neutral species as follows:



Where R₄N⁺, and [M(L)_n]⁻ and [R₄NM(L)_n] are tetraalkylammonium cation, metal anionic complex and neutral complex, respectively. The TAAS are known to be retained dynamically onto the alkyl bounded silica support. The adsorption of R₄N⁺ is according to ion-exchange and hydrophobic interaction mechanism. The hydrophobicity of TAAS increases as carbon chain length increases from TMA < TBA < THA. The presence of TAAS in the mobile phase prevents the strong retention of metal chelates on the column. However, the retention of anionic metal complexes can be controlled by varying the alkyl chain length and its concentration.^{13,14} Therefore, a systematic study

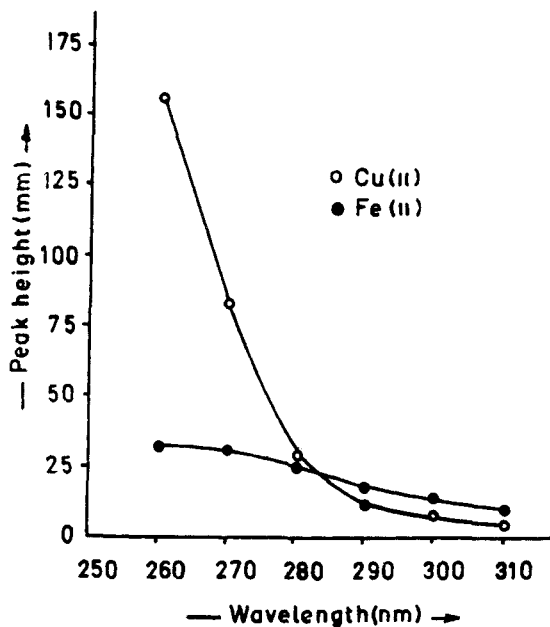


Figure 3. The response of metal ions at varied detector's wavelength.

of the type of ion-pair reagent for the desired separation of copper and iron was carried out. The experimental conditions were also optimized regarding the concentration of ion-developer, organic modifier, pH and detector's wavelength. The ion-pair used were TMAB, TBAP and THAB. The initial mobile phase concentration of TMAB and TBAP was 5 mM L^{-1} with 3% ACN-water, 5 mM L^{-1} NaH_2PO_4 and pH 3 adjusted with 10% H_3PO_4 . The presence of TMAB partially resolved copper and iron when used up to 60 mM L^{-1} even in the absence of organic modifier. The incorporation of TBAP completely resolved copper iron and nitrate in almost 10 minutes in the same order as shown in Figure 1.

The column resolution (R_s) for the two metal ions was 1.02. Moreover, TBAP did not pose any solubility problem and column equilibration was also faster. The use of 2.5 mM L^{-1} THAB in 10 % ACN-water excellently resolved copper and iron with R_s of 4.34, however, NO_3^{-1} was strongly retained and it was eluted after 20 minutes as shown in Figure 2. The equilibrium of THAB with column is extremely slow. It requires almost 2-4 hours for reproducible elution. Considering the above mentioned advantage of TBAP its

Table 1

**Order of Elution, Retention Times, Detection Limits,
and Linear Ranges in (mg L^{-1}) of Metal Ions**

Sr. No.	Metal Ions	Retention Time (Min)	Detection Limits	Linear Range
1	Cu(II)	3.01	2	2-75
2	(FeIII)	4.20	0.5	1-10

Table 2

Linear Regression Analysis of Chromatographic Data

Metal	Slope	Intercept	Correlation Factor
Cu(II)	1.3 ± 0.04	0.8 ± 2.6	0.9956
Fe(III)	10.2 ± 0.4	-0.4 ± 1.8	0.9952

concentration was optimized for further investigations. The concentration of TBAP was varied in steps from 2-10 mM L^{-1} . The optimum concentration was 5 mM L^{-1} . A variation of 5-30 mM L^{-1} of NaH_2PO_4 enhances the sensitivity for each metal ion due to an increase in the quantity of phosphato complex formed for the fixed quantity of each metal ion injected. Above 30 mM L^{-1} NaH_2PO_4 , resolution of metal ions started to decrease. Therefore, 30 mM L^{-1} NaH_2PO_4 was opted for further studies. The pH of eluent was lowered in steps from 3 to 2. At pH 2 sensitivity for copper and iron was increased five and two times, respectively. Moreover, pH peak which interferes with iron at pH 3 is merged into base line at pH 2. A change in detector wavelength from 310-260 nm enhanced the sensitivity for Cu (II) manifold, but for Fe (III) it increases gradually as shown in Figure 3. By opting the appropriate wavelength the intensity of the copper signal can be controlled as per requirement without effecting the intensity of iron signal. The optimum selected wavelength is 270 nm. The order of elution, retention time, linear range, and lowest detection limit of investigated metal ions are given in Table 1. The linear range for iron can be extended by selecting the proper plotter full scale. It indicates that the detection limit of Fe (III) is quite low and is significantly important for its trace level analysis in various matrices of interest, e.g. in high purity copper metal. Linear regression analysis¹⁵ of the analytical data was performed using peak height (mm) against concentration (mg L^{-1}) and its details are given in Table 2.

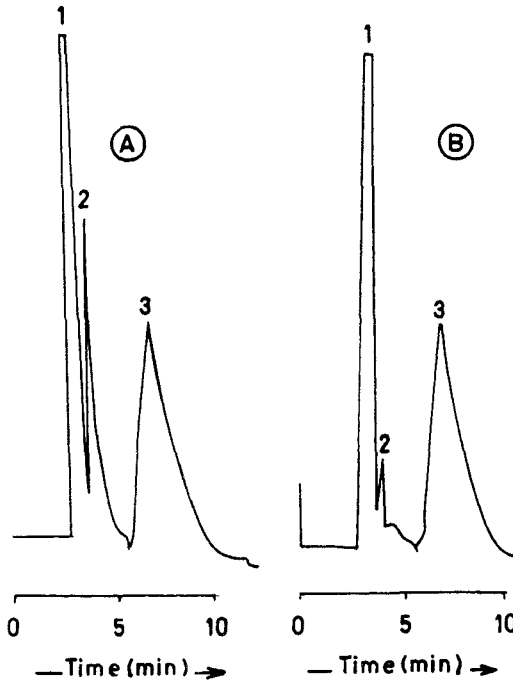


Figure 4. (a) Iron determination in commercial copper cable. Chromatographic conditions as per Figure 1. Peak identification 1= Cu (II); 2= Fe (III); 3= NO_3^- . (b) Chromatographic analysis of iron in spiked copper oxide 1= Cu (II); 2= Fe (III) 1 mg L^{-1} spiked, 3= NO_3^- .

Table 3

Investigated Tolerance Limits of Various Ions as Expected Interferents

Elements	Concentration (mg L^{-1})
Na, K, Mg, Ca, Sr, Ba	250
Al, Mn, Ni, Mo, Ce, Cr, Zn	50
Fluoride, Sulphate, Chloride	50
EDTA	300

Table 4

Chromatographic and ICP-AES Iron Analysis of Standard Reference Material, Spiked Solutions and Copper Cables. Results are Reported in $\mu\text{g g}^{-1}$ as Mean of Triplicate Measurements

Sample Code	Certified Value/ Known Conc.	IPC Results	ICP-AES Results
S ₁	118	114 ± 3	116 ± 2
S ₂	<1	N.D.	N.D.
S ₃	1	0.9 ± 0.2	1.01 ± 0.1
S ₄	2.0	1.9 ± 0.3	2.01 ± 0.1
S ₅	10	9.8 ± 0.5	10.1 ± 0.3
S ₆	---	N.D.	5.4 ± 0.2
S ₇	---	165 ± 2	149 ± 1
S ₈	---	215 ± 2	196 ± 2
S ₉	---	315 ± 3	290 ± 2
S ₁₀	---	440 ± 4	422 ± 3
S ₁₁	---	890 ± 15	858 ± 12

S₁ = Kale, SRM NIST. S₂ = Specpure copper oxide. S₃-S₅ = S₂ spiked with iron. S₆-S₁₁ = Commercial Copper based electrical cables, values corrected against blank. N.D. = Not detected, being below the detection limits.

Diverse Ions Effect and Analysis of Samples

Interference of various cations expected to be present in high purity copper and some additional cations as given in Table 3 was investigated. The concentration of selected cations is almost the same as could be found in real samples. Each cation and anion was injected individually. Only cerium (III) and chromium (VI) interfered with copper. Among the investigated anions only EDTA reduced the intensity of iron signal. All the samples (prepared in the experimental section) were diluted to 5 times in double deionized water to minimize overloading of Cu (II) and acidity effect on column performance. The concentration of iron was measured by external calibration method and its presence in the analyzed samples was confirmed by standard addition method. However, iron could not be detected in specpure copper oxide (S₂) being below the detection limit. The spiked copper oxide with variable Fe (III) was analyzed for recoveries of iron. The iron contents in various cables are price dependent. The S₆ cable is of highest price whereas S₁₁ is four times less in

price as compared to S_6 . The chromatographic detection of iron in sample S_{10} and in iron spiked copper oxide is depicted in Figure 4. All the samples and SRM's were also analyzed by ICP-AES without any prior dilution. The results of IPC and ICP-AES techniques are given in Table 4. These are almost in agreement with each other except that the standard deviations and detection limits of ICP-AES are relatively better than IPC. The comparison with ICP-AES has enhanced the reliability of the reported IPC procedure.

CONCLUSION

The present method is capable of analysing trace level of Fe (III) in high purity copper. It is simple, sensitive, and free from interference from most of the ions investigated. The detection limit is well below the permissible limit of 50 mgL^{-1} of iron in high purity copper.⁴ The present method could be used as an additional technique for the trace level analysis of iron in high purity copper for its quality control.

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Received January 30, 1997

Accepted March 4, 1997

Manuscript 4382