

# Capillary gas chromatographic determination of copper and nickel using microwave-induced plasma atomic emission detection

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(First received November 17th, 1992; revised manuscript received January 25th, 1993)

## ABSTRACT

Four tetradentate  $\beta$ -ketoamine reagents were examined for derivatization and the separation of copper and nickel as their chelates, by capillary GC using flame ionization detection. Complete separation between copper and nickel complexes was obtained in each case. The chelates were also evaluated for simultaneous, selective and sensitive spectral detection of copper and nickel at 325 and 301 nm, respectively, using microwave-induced plasma atomic emission detection. The selectivity of copper at 325 nm with respect to nickel was high; some response of copper at the nickel emission line was observed, but it did not interfere with the determination of nickel. The reagent  $H_2(pnAA_2)$  was used for the analysis of copper and nickel in an ore sample. The detection limits for both copper and nickel were 0.8 pg reaching the detector.

## INTRODUCTION

The effective gas chromatography (GC) of metal chelates is dictated by their volatility and thermal stability under instrumental conditions. Complexing reagents used successfully for the GC determination of metals include  $\beta$ -diketones,  $\beta$ -thioketones, bidentate and tetradentate  $\beta$ -ketoamines (ketoenamines), dialkyldithiocarbamates and dialkyldithiophosphates [1]. Tetradentate  $\beta$ -ketoamine ligands are notable because of their selective reaction with a number of divalent metal ions [2], these reactions being generally quantitative at all concentrations. The reagents [4,4'-(1,2-ethanediyl)dinitrilo]bis(2-

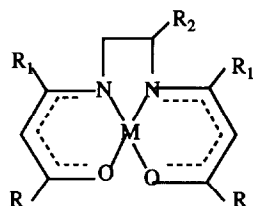
pentanone), or bis(acetylacetonate)-ethylenediimine,  $H_2(enAA_2)$ ], [4,4'-(1-methyl-1,2-ethanediyl)dinitrilo]bis(2-pentanone) [or bis(acetylacetonate)-propylenediimine,  $H_2(pnAA_2)$ ], [4,4'-(1,2-ethanediyl)dinitrilo]bis(5,5'-dimethyl-hexen-2-one), [or bis(acetylacetonate)-ethylenediimine,  $H_2(enAPM_2)$ ] and [4,4'-(1,2-ethanediyl)dinitrilo]bis(6-methyl-hepten-2-one), [or bis(isovalerylactone)-ethylenediimine,  $H_2(enIVA_2)$ ] (Fig. 1), have been used for GC determination of copper and nickel using packed columns and flame ionization detection (FID), but complete separation between copper and nickel complexes has remained a problem [2–7]. These complexes are now examined by capillary column GC with FID or microwave-induced plasma atomic emission detection (MIP-AED) for the quantitative separation and selective determination of these metals.

Interfacing high-resolution chromatography with element-selective detection can simplify complex analyses. GC has been effectively cou-

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Tetradentate  $\beta$ -Ketoamines

M = Cu(II) & Ni(II)

- (1) R = CH<sub>3</sub>, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H  
 (2) R = CH<sub>3</sub>, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = CH<sub>3</sub>  
 (3) R = C(CH<sub>3</sub>)<sub>3</sub>, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H  
 (4) R = CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H

Fig. 1. Structures of reagents and their metal chelates. 1 = Bis(acetylacetonate)-ethylenediamine, H<sub>2</sub>(enAA<sub>2</sub>); 2 = bis(acetylacetonate)-propylenediamine, H<sub>2</sub>(pnAA<sub>2</sub>); 3 = bis(acetylacetylacetonate)-ethylenediamine, H<sub>2</sub>(enAPM<sub>2</sub>); 4 = bis(isovalerylacetonate)-ethylenediamine, H<sub>2</sub>(enIVA<sub>2</sub>).

pled with different atomic spectroscopic systems, atomic absorption spectroscopy (AAS) [8], flame emission spectroscopy (FES) [9] and noble-gas plasma atomic emission spectroscopy (PAES) [10–16]. GC with atomic emission detection (AED) using a helium MIP was described by McCormack *et al.* [17] in 1965. The majority of AED systems for GC are now based on MIP [18].

A GC–AED instrument has been introduced [19,20] which utilizes a water-cooled reentrant cavity to maintain a helium plasma, modified as required by additional reagent gases. The spectrometer, based on a concave holographic grating, is purged with nitrogen and operates from 160 to 800 nm. The detector is a 12.5 mm long 211 pixel silicon photodiode array which can be positioned along the 350 mm length of the focal plane of the spectrometer. The sensitivity and element selectivity of this system are particularly effective for transition metal determinations.

## EXPERIMENTAL

The copper and nickel complexes of the ligands H<sub>2</sub>(enAA<sub>2</sub>), H<sub>2</sub>(pnAA<sub>2</sub>), H<sub>2</sub>(enAPM<sub>2</sub>) and H<sub>2</sub>(enIVA<sub>2</sub>) were prepared as reported previously [3–8].

A Model 3700 gas chromatograph (Varian

Instruments, Palo Alto, CA, USA) was used for FID. A Model HP 5890 II gas chromatograph (Hewlett-Packard, Avondale, PA, USA) was used with a manual and an autoinjector, and a split/splitless capillary injection port operated in the split mode; it was interfaced to a HP 5921 atomic emission detector and HP 330 computer with HP 35920 GC–AED software. High-purity helium was used as carrier and make up gas, and hydrogen and oxygen as reagent gases. The major features of the instrumentation are reported elsewhere [19,20].

Columns used were DB-5 (30 m × 0.25 mm I.D. with 0.25- $\mu$ m layer film thickness and 30 m × 0.32 mm I.D. with 0.25- $\mu$ m layer film thickness) (J&W Scientific, Folsom, CA, USA). Fresh solutions of complexes containing 1 mg/ml were prepared in acetone or cyclohexane and further solutions prepared by appropriate series dilution.

## Solvent extraction procedure

A similar extraction procedure was used as reported earlier [5]. Aliquots (1 ml) of solutions containing 0.1–160 mg of copper and nickel were transferred to screw cap vials, followed by 4 ml of (1%) ketoamine reagent solution in aqueous 2% sodium carbonate. The mixture was warmed at 50–60°C for 10 min and was then allowed to cool at room temperature. Dichloromethane (2 ml) was added and the mixture was shaken for 30 s. The layers were allowed to separate and the organic layer transferred to a glass vial and sealed with a rubber seal and crimp top to prevent evaporation of the solvent. The reagent blank was also run with 1 ml of deionized water.

A matte Ore Sample (No. 1) (Falconbridge Nikkelverk, Kristiansands, Norway) (1.00 g) was dissolved in aqua regia (50 ml) and heated almost to dryness. Two 25-ml portions of concentrated hydrochloric acid were added, the mixture being heated each time gently nearly to dryness. Finally concentrated hydrochloric acid (8 ml) was added and the volume adjusted to 100 ml. The solution was further diluted 50 times and 1 ml was taken for analysis using the described extraction procedure. A sample blank was also prepared using 1 ml of water. Solutions were gas chromatographed in triplicate using the autoinjector, in a sequence from dilute to concentrated

solutions. Column temperature was 240°C and injection port and transfer line temperatures were 260°C. The carrier gas flow-rate was 1.8 ml/min and the split ratio was 1:58.

## RESULTS AND DISCUSSION

The copper and nickel complexes were chromatographed on the 30-m DB-5 column using FID in a column temperature range 220–250°C, with injection port range 230–260°C and helium carrier flow-rate 1.3 ml/min. Complete separation of each of the four metal chelate pairs derived from the ligands  $H_2(enAA_2)$ ,  $H_2(pnAA_2)$ ,  $H_2(enAPM_2)$  and  $H_2(enIVA_2)$  was achieved within 15 min. Fig. 2 shows separations for the first two chelate pairs, the peaks showing only a small amount of tailing. The FID detection limits ( $S/N = 3$ ) for different chelates under the optimum conditions of separation were from 1.47–7.35 ng of a complex, corresponding to 0.23–1.63 ng of copper or nickel. The copper and nickel complexes of the reagent  $H_2(enAPM_2)$  showed maximum FID sensitivity

with lowest detection limits corresponding to 0.25 ng copper and 0.24 ng of nickel, followed in decreasing sequence of detection sensitivity by  $H_2(enIVA_2)$ ,  $H_2(pnAA_2)$  and  $H_2(enAA_2)$ .

To examine the effect of different substituents on the relative retention of metal chelates, separate mixtures of the copper and the nickel complexes of the four ligands were chromatographed under optimal separation conditions. Complete separation was obtained for both copper and nickel series with elution of metal chelates in the sequence  $H_2(pnAA_2)$ ,  $H_2(enAA_2)$ ,  $H_2(enAPM_2)$  and  $H_2(enIVA_2)$  (Fig. 3). A mixture of saturated hydrocarbons between  $C_{22}H_{44}$  and  $C_{30}H_{62}$  was also chromatographed under the conditions used for the separation of copper or nickel complexes in order to calculate Kováts indices for the complexes. The values in Table I indicate that introduction of a methyl group into the parent ligand  $H_2(enAA_2)$  at the bridge position, to form  $H_2(pnAA_2)$ , decreases the Kováts index for their chelates by 85–95 units, but introduction of tertiary butyl or

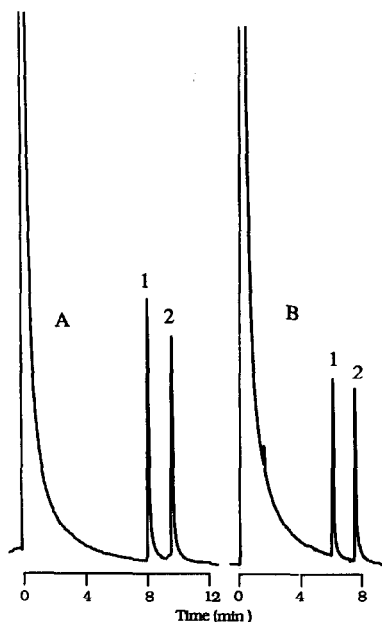


Fig. 2. GC separation of (1) copper(II) and (2) nickel(II) chelates of (A)  $H_2(enAA_2)$  and (B)  $H_2(pnAA_2)$ . Column: DB-5 (30 m  $\times$  0.25 mm); temperatures; column 225°C, injection port and flame ionization detector 250°C. Helium carrier gas flow-rate 1.3 ml/min. Inlet split ratio 1:17.

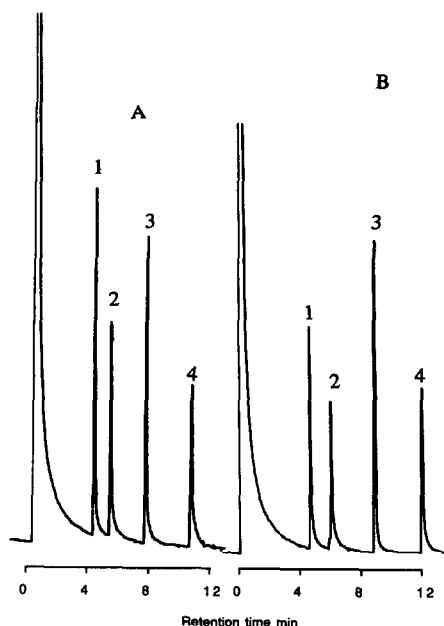


Fig. 3. Comparative GC elution of (A) copper(II) and (B) nickel(II) complexes of (1)  $H_2(pnAA_2)$ , (2)  $H_2(enAA_2)$ , (3)  $H_2(enAPM_2)$  and (4)  $H_2(enIVA_2)$ . Column: DB-5 (30 m  $\times$  0.25 mm); temperatures: column 240°C, injection port and flame ionization detector 260°C. Helium carrier gas flow-rate 1.2 ml/min. Inlet split ratio 1:26.

TABLE I

## KOVATS INDICES FOR COPPER AND NICKEL CHELATES

| Complex                | Kováts index | Complex                 | Kováts index |
|------------------------|--------------|-------------------------|--------------|
| Cu(pnAA <sub>2</sub> ) | 2360         | Cu(enAPM <sub>2</sub> ) | 2575         |
| Ni(pnAA <sub>2</sub> ) | 2410         | Ni(enAPM <sub>2</sub> ) | 2640         |
| Cu(enAA <sub>2</sub> ) | 2445         | Cu(enIVA <sub>2</sub> ) | 2690         |
| Ni(enAA <sub>2</sub> ) | 2505         | Ni(enIVA <sub>2</sub> ) | 2740         |

isobutyl groups adjacent to the carbonyl function in the ligands H<sub>2</sub>(enAPM<sub>2</sub>) and H<sub>2</sub>(enIVA<sub>2</sub>), increases the index for their metal chelates by 130–135 and 235–245 units, respectively, for both copper and nickel complexes.

The copper and nickel complexes were easily separated on the capillary column and showed predicted FID sensitivity, but to examine the selectivity of AED for copper and nickel and its use for their quantitative determination, capillary GC coupled with MIP detection was investigated. The emission wavelengths for copper and nickel at 325 and 301 nm, respectively, were selected for simultaneous monitoring of elemental response. A high flow-rate of helium make up gas (150 ml/min) was preferred along with hydrogen and oxygen as reagent gases at the pre-set flow conditions set by the instrument manufacturer. When a mixture of copper and nickel complexes was injected under the optimized GC conditions, some response of the copper complex at the nickel line was observed. The effects of copper emission on the nickel response and of nickel emission on the copper response were therefore examined. Solutions of copper and nickel complexes of H<sub>2</sub>(enAPM<sub>2</sub>) with chelate ratios of 1:10 and 10:1 were prepared and injected at a column temperature of 250°C and helium carrier flow rate of 1.2 ml/min. No response for nickel at the 325-nm copper line was observed and selectivity of copper against nickel at that wavelength was greater than 10<sup>3</sup>. In contrast, the selectivity of nickel at 301 nm with respect to copper was found to be *ca.* 125; the response of copper at 325 nm was coincidentally *ca.* 125 times greater than at 301 nm. In order to compare the spectral features of copper emission at 325 and 301 nm and of nickel

emission at 301 nm, three-dimensional displays of emission signal output (snapshots) with respect to wavelength and time are shown in Fig. 4. These plots show changes in spectral peak shape with respect to retention time. Nickel and copper show well defined signal peaks at 301 and 325 nm, respectively (Fig. 4A and B), but the

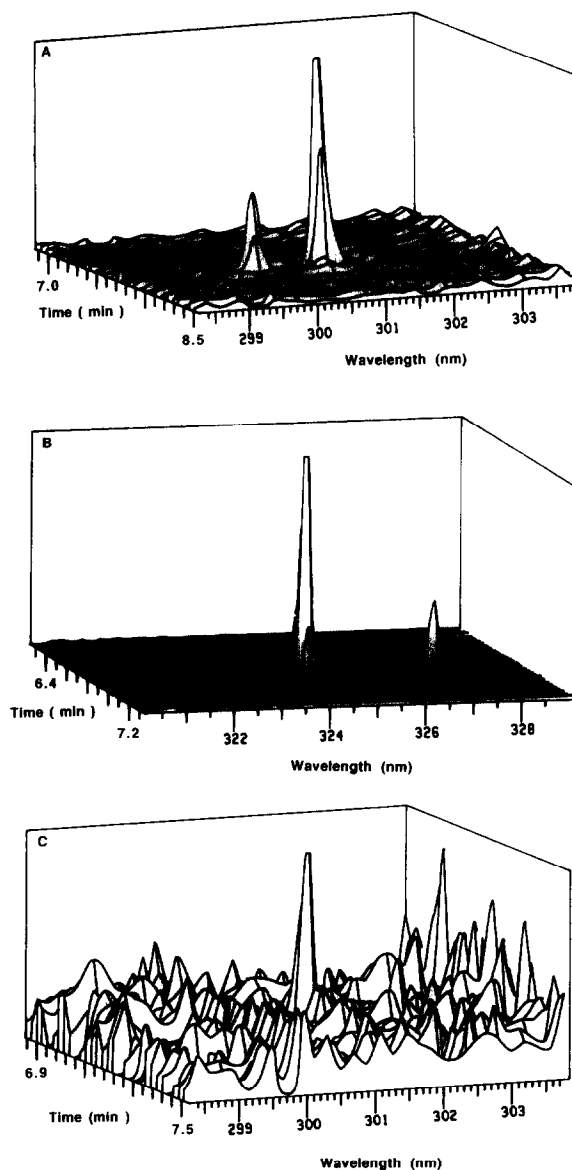


Fig. 4. Three-dimensional spectral-chromatographic detection display (snapshots) of (A) nickel complex at 301 nm, (B) copper complex at 325 nm and (C) copper complex at 301 nm.

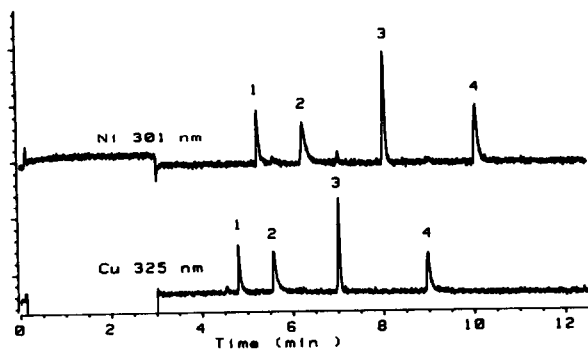


Fig. 5. Element-specific chromatograms for copper at 325 nm and nickel at 301 nm using MIP-AED detection. Copper and nickel chelates of (1)  $H_2(pnAA_2)$ , (2)  $H_2(enAA_2)$ , (3)  $H_2(enAPM_2)$  and (4)  $H_2(enIVA_2)$ . Column: DB-5 (30 m  $\times$  0.25 mm); temperatures: column 250°C, injection port and transfer line 260°C. Helium flow-rate 1.2 ml/min. Inlet split ratio 1:23.

copper response at 301 nm (Fig. 4C) shows low intensity relative to background spectral structure. However since there was complete chromatographic separation of copper and nickel complexes, there was no experimental interference of nickel determination due to copper, and emission signals could be used for the simultaneous determination of copper and nickel. This was confirmed when a mixture of all eight chelates, four copper complexes and four nickel complexes, was chromatographed and their elution monitored at 301 and 325 nm. All peaks were observed independently, without any chromatographic or spectral interference (Fig. 5).

Any of the four reagents could be equally well used for the simultaneous determination of cop-

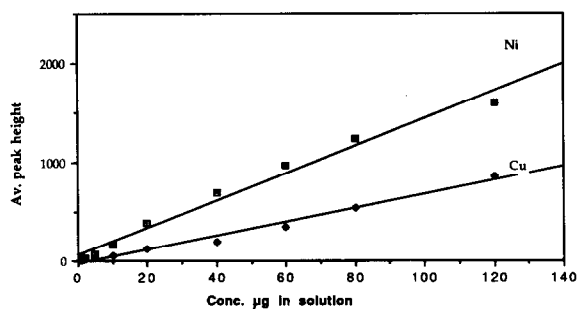


Fig. 6. Calibration graphs of extracted copper(II) and nickel(II) with  $H_2(pnAA_2)$  as complexing agent. Equations: nickel,  $y = 48.944 + 13.920x$ ,  $R^2 = 0.983$ ; copper:  $y = -21.547 + 6.9784x$ ,  $R^2 = 0.989$ .

TABLE II  
ANALYSIS OF MATTE ORE SAMPLE

| Atomic absorption [5]<br>( $\mu\text{g/g}$ ) |     | Packed-column GC-FID [5]<br>( $\mu\text{g/g}$ ) |     | Capillary GC-MIP-AED $\pm$ S.D.<br>( $\mu\text{g/g}$ ) ( $n = 4$ ) |              |
|----------------------------------------------|-----|-------------------------------------------------|-----|--------------------------------------------------------------------|--------------|
| Cu                                           | Ni  | Cu                                              | Ni  | Cu                                                                 | Ni           |
| 215                                          | 469 | 413                                             | 531 | 250 $\pm$ 18                                                       | 425 $\pm$ 22 |

per and nickel using solvent extraction. As an example,  $H_2(pnAA_2)$  was chosen for the GC-MIP-AED analysis of a matte ore sample, to enable comparison with the results reported earlier using atomic absorption and packed-column GC-FID [5]. Calibration curves relating mean peak height to the amount of the copper and nickel injected showed good linearity over the necessary concentration range (Fig. 6). The results of analysis are in good agreement with those obtained from atomic absorption (Table II). The detection limit for copper and nickel in the 1-ml aliquot was *ca.* 100 ng for both copper and nickel. The extraction into 2 ml of dichloromethane, with 1  $\mu\text{l}$  injected at a split ratio of 1:58 on the GC column, corresponds to about 0.8  $\mu\text{g}$  of copper and nickel reaching the detector.

## CONCLUSIONS

The use of capillary GC coupled with FID or MIP-AED for the effective separation and quantitative determinations of copper and nickel as metal chelate compounds has been demonstrated. MIP-AED improves the sensitivity of metal ion detection to  $\mu\text{g}$  levels. Tetradentate  $\beta$ -ketoamine ligands showed adequate thermal stability and volatility for the quantitative GC determination of copper and nickel simultaneously; their reactions are quantitative and the metal chelates are easily extractable into organic solvents.

## ACKNOWLEDGEMENTS

The University of Meshhad, Iran, and the Ministry of Culture and Higher Education, Is-

Islamic Republic of Iran, are acknowledged for the grant of sabbatical leave to one of us (A.S.-Y). M.Y.K. acknowledged the receipt of a Fulbright Research award. We wish to acknowledge support for this work from the Hewlett-Packard Company and the Mobil Research and Development Corporation. Thanks are also due to Bruce Quimby, James Sullivan and Frank DiSanzo for their advice and encouragement.

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