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Reversed-phase high-performance liquid chromatography of several metal–8-quinolinethiol complexes

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ABSTRACT

The reversed-phase high-performance liquid chromatography of 8-quinolinethiol (Hqt) complexes of Fe, Co, Ni, Cu, Zn, Hg and Pb on an octadecyl-bonded silica gel stationary phase was examined. The Pb complex dissociated in the column. The retention and separation of other complexes depended on the composition of the mobile phase. EDTA as an additive displaced the Zn complex and eliminated its peak. All the other metal complexes and also Hqt and its disulphide were separated in 23 min by using methanol–water (82:18, v/v) as the mobile phase. The complexes formed by the reaction of Co(II) and Hqt gave three peaks, which were assigned as *fac*(*S*)-$Co^{III}(qt)_3$, *mer*(*S*)-$Co^{III}(qt)_3$ and $Co^{II}(qt)_2$, respectively. This method is applicable to the simultaneous determination of Fe, Co, Ni, Cu and Hg.

INTRODUCTION

8-Quinolinethiol (Hqt), which preferentially reacts with soft metal ions, has been used as a reagent in spectrophotometry, spectrofluorimetry and solvent extraction [1]. The compositions of the resulting complexes have been studied by various methods, such as solvent extraction, precipitation, mass spectrometry, infrared spectrometry and polarography [2–8], and reported to be $M(qt)_2$ for Ni(II), Cu(II), Zn(II), Hg(II) and Pb(II) and $M(qt)_3$ for Fe(III). For some of them, the crystal structures have also been determined by X-ray crystallography [9]. In the extraction of Co(II) with Hqt into benzene, the complexes formed were diamagnetic and a major species was assigned as *mer*(*S*)-$Co^{III}(qt)_3$ by ^{13}C NMR [2].

König *et al.* [10] studied the thin-layer chromatographic behaviour of seventeen metal complexes with Hqt on silica gel and alumina plates. Using the same reagent, they also examined the separation of Fe, Co and Ni with a silica gel column by high-performance liquid chromatography (HPLC); however, the peaks were not resolved satisfactorily [11].

In this work, we studied the reversed-phase HPLC behaviour of Hqt complexes of Fe, Co, Ni, Cu, Zn, Hg and Pb on an octadecyl-bonded silica gel column. Metal complexes except those of Zn and Pb, excess of Hqt and the oxidation product [diquinolyl disulphide (Ds)] were separated. The elution order of the complexes is discussed in terms of their extractability with chloroform. The chromatographic behaviour of 2-methyl-8-quinolinethiol (Hmqt) complexes was also examined for comparison.

EXPERIMENTAL

Apparatus

The HPLC system (JASCO, Tokyo, Japan) consisted of a Model 880-PU intelligent pump, a Model 860-CO column oven and a MULTI-330 photodiode-array detector (wavelength range 200–800 nm; flow cell 4 μl; 1 mm I.D.; optical path length 5 mm) equipped with an NEC personal computer. An SVI-6U7 sample injector (dead volume 2 μl, sample loop 8 μl) (Sanuki Kogyo, Tokyo, Japan) and a Shim-pack CLC-ODS column (150 mm ×

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6.0 mm I.D.; particle diameter 5 μm) (Shimadzu, Kyoto, Japan) were used.

Reagents

8-Quinolinethiol and its 2-methyl derivative were prepared as described [12] and were stored as their disulphides.

Each disulphide (1 g) was dissolved in a mixture of phosphinic acid (15 ml) and hydrochloric acid (1 ml) and the solution was refluxed under a nitrogen atmosphere for 1 h. After the solution had been neutralized with aqueous ammonia, precipitated Hqt was extracted three times with 20 ml of chloroform. After dilution to 100 ml, the chloroform solution was back-extracted with the same volume of 6 *M* hydrochloric acid. The quinolinethiol hydrochloride solution thus obtained was stored in a refrigerator and used within 1 week.

Copper(II) and zinc(II) solutions were prepared from the analytical reagent-grade metals by dissolution in dilute nitric acid. An iron(III) solution was prepared from ammonium iron(III) sulphate dodecahydrate and other metal ion solutions from the sulphates or the nitrates. These solutions were standardized against an ethylenediamine-N,N,N′,N′-tetraacetate (EDTA) solution.

Chloroform was purified by shaking successively three times with concentrated sulphuric acid, 4 *M* sodium hydroxide solution and distilled water. The chloroform was stored in a refrigerator and used within 1 week.

Preparation of metal–Hqt complex solution

A 5-ml portion of $2.0 \cdot 10^{-5}$–$1.0 \cdot 10^{-3}$ *M* metal ion solution was placed in a 50-ml centrifuge tube with a screw-cap and mixed with 1 ml of $1.0 \cdot 10^{-2}$ *M* Hqt solution in hydrochloric acid. By adding 4 ml of 2.5% aqueous ammonia and 5 ml of 60% sodium acetate solution, the pH of the solution was adjusted to 5.5–6.5 to form precipitates of metal complexes. The suspension was shaken with chloroform (5 ml) for 20 min. The complexes were quantitatively extracted into chloroform.

Chromatographic procedure

An aliquot (10 μl) of the chloroform solution pre-

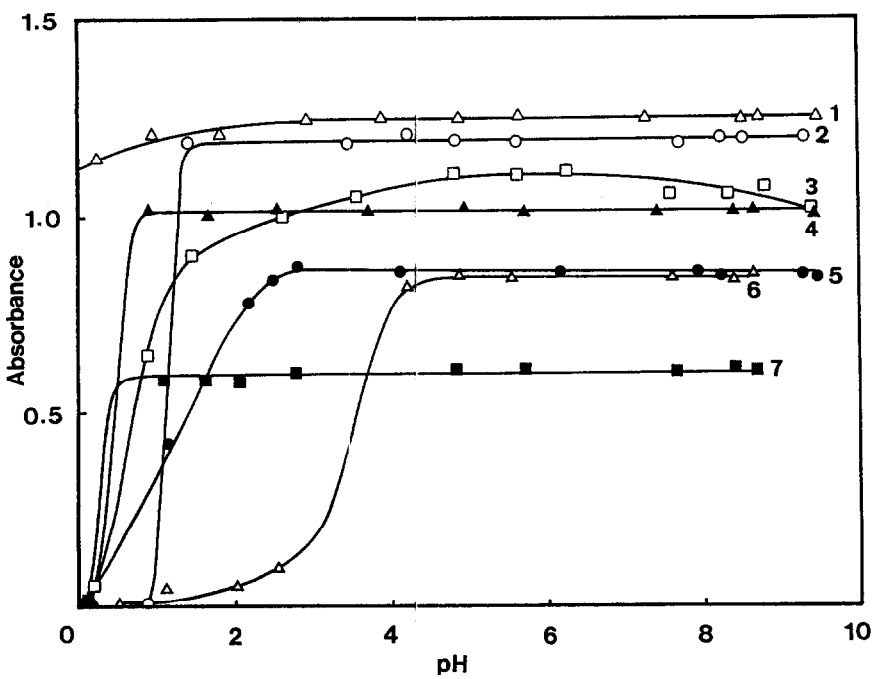


Fig. 1. Effect of pH on the extraction of Hqt complexes. $C_M = 1.0 \cdot 10^{-4}$ *M*, 5 ml; $C_{Hqt} = 1.0 \cdot 10^{-2}$ *M*, 1 ml; buffer, 5 ml; chloroform, 5 ml. Curves: 1 = Hg; 2 = Co; 3 = Fe; 4 = Cu; 5 = Zn; 6 = Pb; 7 = Ni.

pared above was placed on the column via an injection valve. In order to prevent contamination from metal ions from the microsyringe, the sample solution was introduced into the sample loop of the injector by suction. The mobile phase [methanol–water (82:18, v/v)] containing $5 \cdot 10^{-5}$ *M* EDTA was pumped at a flow-rate of 0.8 ml min^{-1}. Elution of metal complexes, excess of Hqt and Ds was monitored at 350–600 nm. The column void volume for calculation of the capacity factors was determined using sodium nitrite.

RESULTS AND DISCUSSION

Extraction conditions

The effect of pH on the extraction of the metal complexes was studied (Fig. 1). The extractability order judged from the half-extraction pH values is Hg >> Cu ≈ Ni > Fe > Co > Zn > Pb. At pH 5–6.5, all the metal ions were quantitatively extracted by shaking for 20 min. Back-extraction of the metals once extracted into chloroform was examined by shaking with a buffer or dilute hydrochloric acid for 20 min. Lead(II) was back-extracted at pH < 4 without EDTA and at pH < 9 with EDTA (10^{-3} *M*), whereas zinc(II) was not back-extracted at pH > 1 without EDTA or at pH > 3 with EDTA. Iron(III), Copper(II), nickel(II) and mercury (II) were not back-extracted with <1 *M* hydrochloric acid. Cobalt complexes were stable even against 5 *M* hydrochloric acid.

Detection wavelength and column temperature

Absorption spectra of Hqt complexes (Fe, Co, Ni, Cu, Hg) obtained using the HPLC system are shown in Fig. 2. The absorption maxima of all the chelates are in the range 350–600 nm, which was employed for detection.

The column temperature was varied from 25 to 45°C. The capacity factors of the complexes decreased by 22–33% with increase in temperature in this range. The temperature of the column oven was kept at 40°C in the subsequent experiments in order to maintain a reasonable flow-rate.

Retention and extractability of Hqt complexes

A solution containing Hqt complexes (Co, Pb, Zn, Fe, Cu, Ni and Hg) was injected into the column and eluted with mobile phase [methanol–water–chloroform (75:20:5, v/v/v)] containing $1 \cdot 10^{-3}$ *M* Hqt. All the peaks were observed for the complexes and excess of Hqt as shown in Fig. 3A.

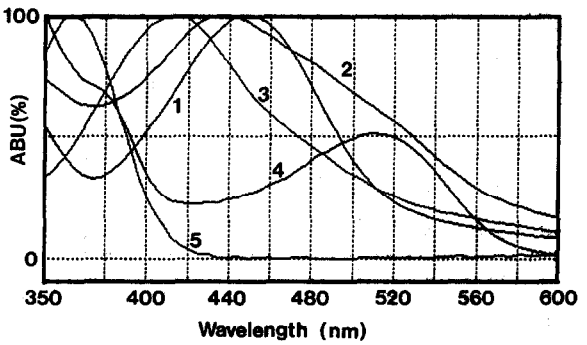


Fig. 2. Absorption spectra of Hqt complexes. (1) *mer*(*S*)-$Co^{III}(qt)_3$; (2) $Fe(qt)_3$; (3) $Cu(qt)_2$; (4) $Ni(qt)_2$; (5) $Hg(qt)_2$. The ordinate (ABU) represents absorbance in arbitrary units.

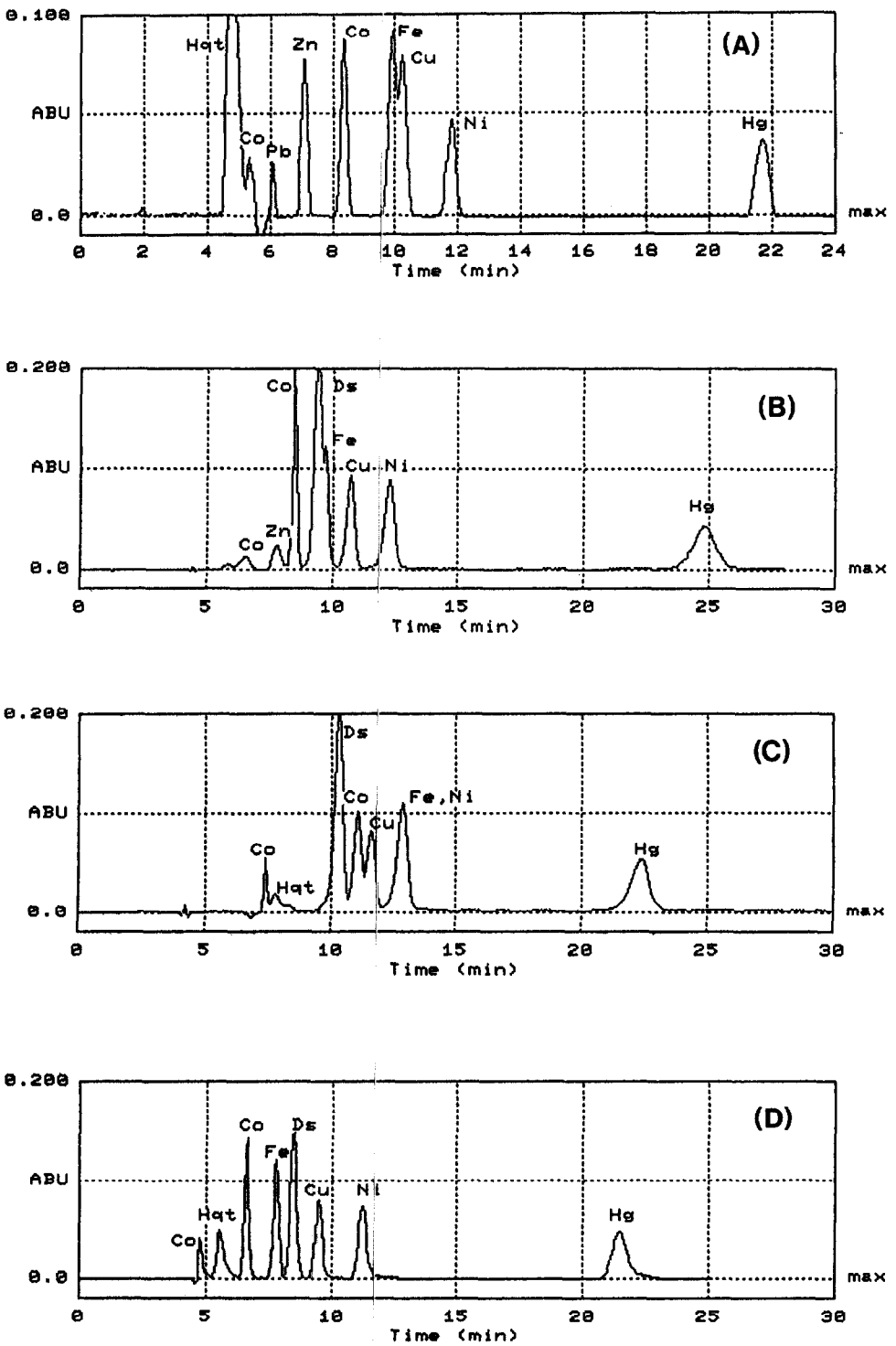
The retention order of the complexes in reversed-phase HPLC, which is the opposite of that in normal-phase TLC or HPLC [10,11], was the same as the order of extractability into chloroform. It is characteristic that square-planar complexes, $Ni(qt)_2$ and $Cu(qt)_2$, are strongly retained in this system.

Effects of mobile phase composition

The peak for Pb was absent without Hqt in the mobile phase and was appreciably lower than those for the others even in the presence of Hqt. Addition of Hqt to the mobile phase led to an unstable background and less reproducible chromatograms, probably owing to the oxidation of excess of Hqt. Thereafter, Hqt was not added to the mobile phase.

When only a chloroform solution of Hqt was injected as a sample, a large peak was obtained for Zn in addition to those for Hqt and Ds. To avoid contamination with Zn from the column and/or stainless-steel tubing, EDTA was added to the mobile phase. In the presence of more than $2 \cdot 10^{-5}$ *M* EDTA, no peaks for Zn and Pb were observed. In subsequent studies, $5 \cdot 10^{-5}$ *M* EDTA was added to the mobile phase. The dissociative nature of Zn and Pb complexes in the chromatographic system corresponds well with the results of back-extraction of these complexes as described above.

Various mixtures of organic solvents such as acetonitrile–water, ethanol–water, ethanol–chloro-


0.100
ABU
0.0
Hqt
Co
Pb
Zn
Co
Fe
Cu
Ni
Hg
(A)
max
0 2 4 6 8 10 12 14 16 18 20 22 24
Time (min)
0.200
ABU
0.0
Co
Zn
Co
Ds
Fe
Cu
Ni
Hg
(B)
max
0 5 10 15 20 25 30
Time (min)
0.200
ABU
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Co
Hqt
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Co
Cu
Fe,Ni
Hg
(C)
max
0 5 10 15 20 25 30
Time (min)
0.200
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Fig. 3.

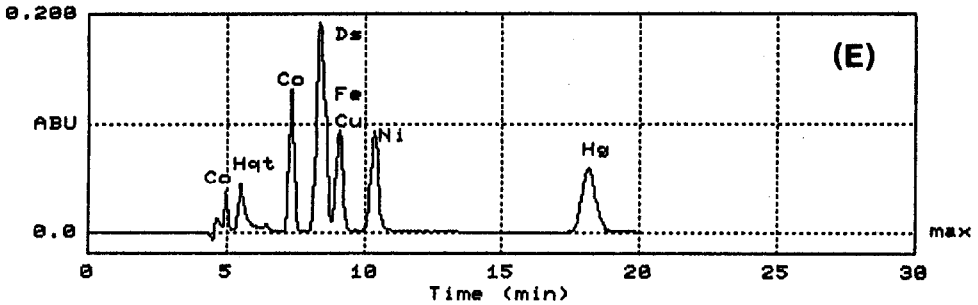

Fig. 3. Chromatogram of Hqt complexes. Mobile phase (A) methanol–water–chloroform (75:20:5, v/v/v) containing 1.0×10^{-3} *M* Hqt; (B) ethanol–water (65:35); (C) ethanol–water–chloroform (60:35:5); (D) methanol–water (82:18); (E) methanol–water–chloroform (77:18:5); mobile phases B–E contained 5×10^{-5} *M* EDTA. Flow-rate: (A,D,E) 0.8; (B,C) 0.6 ml min^{-1}. Amounts of metal injected: Co, 0.12; Pb, 0.41; Zn, 0.13; Fe, 0.11; Cu, 0.13; Ni, 0.12; Hg, 0.40 μg.

form–water, methanol–water and methanol–chloroform–water were examined as eluents. Typical chromatograms are shown in Fig. 3B–E. With acetonitrile–water, all the peaks broadened, whereas alcohol–water mixtures gave sharp peaks. The effects of methanol and ethanol content on the capacity factors are shown in Fig. 4A and B, respectively. The separation between Ds and the Fe complex was not good with ethanol–water. With methanol–water, better resolution was obtained in a shorter time. A methanol content of 82% (v/v) gave the best resolution and reasonable retention times. When 5% chloroform was added to methanol–water or ethanol–water, the Co and Fe complexes were retained stronger, whereas the retention of the Hg complex decreased (see Figs. 3C and E).

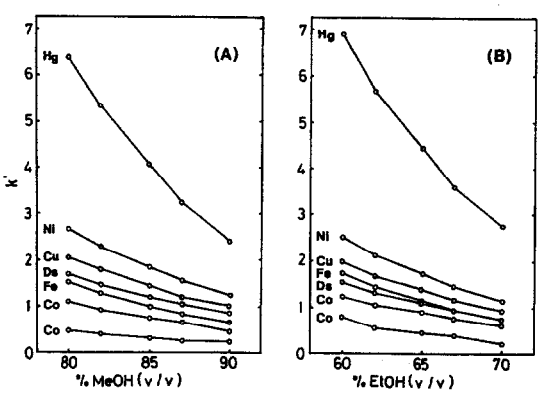

Fig. 4. Effect of alcohol content on capacity factors (*k'*). Mobile phase: (A) methanol (MeOH)–water; (B) ethanol (EtOH)–water. Flow-rate: (A) 0.8, (B) 0.6 ml min^{-1}.

With Hmqt, the complexes of Co(II), Ni(II), Zn (II) and Cd(II) were extracted into chloroform. In HPLC, however, only small peaks were observed for Co, Ni and Zn.

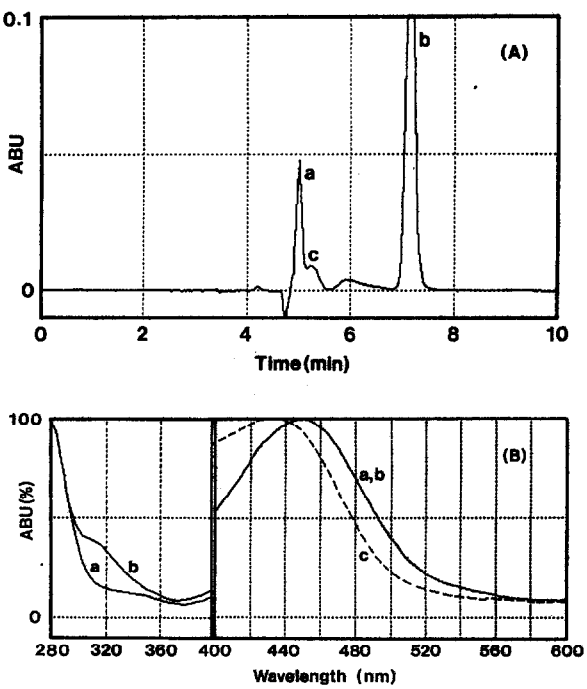

Fig. 5. (A) Chromatogram of cobalt–Hqt complexes and (B) their absorption spectra. Complex: (a) *fac*(*S*)-$Co^{III}(qt)_3$; (b) *mer* (*S*)-$Co^{III}(qt)_3$; (c) $Co^{II}(qt)_2$. Wavelength, 448 nm; mobile phase, methanol–water (80:20, v/v).

Complexes formed in Co–Hqt system

The chloroform extracts of Co complexes gave two major peaks, labelled (a) and (b), having a height ratio of 1:4 (Fig. 5A). Such peak splitting was also found in normal-phase HPLC of Co and Cr complexes, but has not been clearly explained [10,11]. In our previous study [2], benzene extracts of Co complexes gave only one peak in RP-HPLC. The complex dissolved in benzene has been assigned as *mer*(*S*)-$Co^{III}(qt)_3$ by ^{13}C NMR spectrometry. From the retention time, the complex for peak b in chloroform extracts is assigned as *mer*(*S*)-$Co^{III}(qt)_3$. The separation of such geometric isomers has been extensively studied for Co(III) and Cr(III) complexes with other ligands [13–16].

The absorption spectrum of peak a was almost the same as that of b in the visible region (Fig. 5B), but different in the UV region. The lower solubility in benzene and less retention in the reversed-phase HPLC together with the spectral characteristics suggest the assignment of the complex for peak a to *fac*(*S*)-$Co^{III}(qt)_3$, which is more polar than a *mer*(*S*)-isomer.

A third small peak (c) was occasionally found close to peak a. The absorption spectrum of the complex for peak c has a maximum at a shorter wavelength than those of *mer*(*S*)- and *fac*(*S*)-$Co^{III}(qt)_3$ and is close to that of $Co^{II}(mqt)_2$, for which an oxidation state of 2 is exclusively stabilized because of the steric hindrance in the tris complex [2]. This suggests the assignment of the complex for peak c as $Co^{II}(qt)_2$.

Application

This method can be applied to the separation and determination of the metals in spite of peak splitting for Co. The calibration graphs based on peak height and area were linear in the range $2.0 \cdot 10^{-5}$–$1.0 \cdot 10^{-3}$ *M* for Fe, Cu, Hg and Co [*mer*(*S*)-isomer], whereas the upper limit for Ni was restricted to $1.0 \cdot 10^{-4}$ *M* because of the limited solubility of its complex in chloroform. The detection limits of these metals (peak height-to-noise ratio = 3) are Cu 1.2, Ni 1.4, Fe 0.60, Hg 5.8 and Co 0.94 ng.

The proposed method was applied to the analysis of a standard steel sample (NBS 364) after the usual treatment [17]. The results are as follows (metal, % observed, % recommended): Co, 0.156, 0.15; Cu, 0.233, 0.249; and Ni, 0.139, 0.14.

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