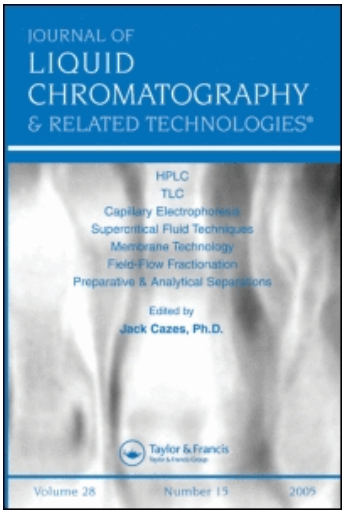

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

STUDY OF THE METHOD OF COMPLEXATION-SUPERCRITICAL FLUID EXTRACTION OF COPPER IONS WITH 8-HYDROXYQUINOLINE

Juncheng Liu[a]; Zhaojie Cui[a]; Wei Wang[a]; Ganzuo Li[a]
[a] Institute of Colloid and Interface Chemistry, Shandong University, Jinan, P. R. China

Online publication date: 20 December 2000

To cite this Article Liu, Juncheng , Cui, Zhaojie , Wang, Wei and Li, Ganzuo(2000) 'STUDY OF THE METHOD OF COMPLEXATION-SUPERCRITICAL FLUID EXTRACTION OF COPPER IONS WITH 8-HYDROXYQUINOLINE', Journal of Liquid Chromatography & Related Technologies, 23: 20, 3109 — 3117
To link to this Article: DOI: 10.1081/JLC-100102371
URL: http://dx.doi.org/10.1081/JLC-100102371

J. LIQ. CHROM. & REL. TECHNOL., 23(20), 3109–3117 (2000)

STUDY OF THE METHOD OF COMPLEXATION-SUPERCRITICAL FLUID EXTRACTION OF COPPER IONS WITH 8-HYDROXYQUINOLINE

Juncheng Liu, Zhaojie Cui, Wei Wang, Ganzuo Li

Institute of Colloid and Interface Chemistry
Shandong University
Jinan 250100, P. R. China

ABSTRACT

8-Hydroxyquinoline, methanol, and Triton X-100 were first used together in the extraction of metal ions by supercritical fluid. In the new system, the effects of pressure, temperature, and the volume of supercritical CO_2 used on the efficiency of supercritical fluid extraction (SFE) were systematically investigated. The recovery of Cu^{2+} was only 17.7% by pure supercritical CO_2 while the recovery increased significantly (83.6%, RSD=3.64%, n=5) with the addition of a suitable amount of methanol (v/v=5%).

In order to further enhance the recovery, a suitable amount of Triton X-100 was added to the samples, and the results were favorable (96.6%, RSD=2.76%, n=5).

INTRODUCTION

The primary advantages of SFE over liquid-phase extraction are the lower viscosity and variable density of the supercritical fluid. Mass transfer occurs more quickly and efficiently in supercritical fluid than in liquid. Driven by the desire to limit in both solvent usage and solvent waste generation, reduce analysis times, and increase extraction efficiency, the practice of SFE has been growing at a rapid rate for several years.

To date, most of the published SFE works have focused on organic compounds,[1-4] and studies have been published on SFE of metal ions.[5-13]

Direct extraction of metal ions by supercritical CO_2 is highly inefficient because of the charge neutralization requirement and the weak solute-solvent interactions. One suggested approach of extracting metal ions by supercritical CO_2 is to convert the charged metal ions into neutral metal complexes by using chelating agents. Important requirements for the selection of suitable chelating agents used in the complexation-SFE of metal ions includes high stability constant of the metal complex, good solubility of the chelating agent, and their metal complex in supercritical CO_2. Moreover, the metal complex must be easy to desorpe from the active sites on the solid matrices and must be easy to be transported in the supercritical CO_2.

A variety of organic chelating agents such as thiocarbamate, β-diketones, and crown ether have been used in SFE of metal ions. 8-Hydroxyquinoline contains double coordination atoms (N, O^-), which is easy to react with Cu^{2+} and form stable neutral chelates. So, 8-Hydroxyquinoline was investigated as a chelating agent in the complexation-SFE of Cu^{2+} in our laboratory and satisfactory results were obtained.

This paper represents, that under the condition which 8-Hydroxyquinoline was selected as chelating regent and the methanol was used as modifier, the recovery of Cu^{2+} was achieved at 83.6% (R.S.D=3.64%, n=5). Adding surfactant to the samples is also presented in this paper as a new way of enhancing the solubility of the metal chelates in supercritical CO_2. The recovery of Cu^{2+} can be further enhanced by using a non-ionic surfactant (Triton X–100).

EXPERIMENTAL

Reagent and Materials

8-Hydroxyquinoline (Reagent Station of Shanghai of China) was used as the chelating agent, $CuCl_2$ $2H_2O$ (Reagent Station of Jinan of China) as the source of Cu^{2+}, and ethanol (95%) (Reagent Station of Jinan of China) as collecting solvent.

Triton X-100 (Reagent Factory of Beijing of China) was used as surfactant and silica (100-120 mesh) as solid matrices, which were obtained from Reagent Factory of Shanghai of China.

Apparatus

All experiments were carried out in a supercritical fluid extraction apparatus, which was made in Shandong University and Shangdong Lunan Chemical

Instrumental Plant. SFC-grade CO_2 or CO_2 with 5% methanol was delivered to the system by using a high pressure injecting pump, which was controlled by a computer.

The extractor consists of an on/off valve connected to a 2.5 mL extraction cell. The extraction cell was placed in an oven where temperature was controlled by a computer. A fused-silica tube (50 μm i.d and 20 cm in length) was used as the pressure restrictor for the exit gas. The SFE system allowed static and dynamic extraction to be performed by using the on/off valves. The scheme diagram of the SFE is shown in Figure 1.

The concentration of metal chelates obtained by complexation–SFE was determined by an ultraviolet and visible spectrophotometer (made in the Third Analytical Instrumental Plant of Shanghai of China).

Preparation of Sample

Because the apparatus in our laboratory can only extract solid matrices, we carried out the complexation first in the solution and then the metal chelates were extracted by supercritical CO_2. A known amount of $CuCl_2$ $2H_2O$ reacted with 8-Hydroxyquinoline in the solution of ethanol (95%). The mole ratio of Cu^{2+} to 8-Hydroxyquinoline is 1 to 2.5. Then Cu(8-Hydroxyquinoline)$_2$ was coated on the surface of silica.

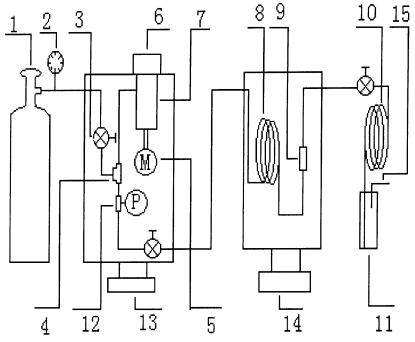

Figure 1. The scheme diagram of the SFE. (1) CO_2 steel cylinder (2) high pressure meter (3) high pressure on-off valve (4) tee-joint (5) electric machinery (6) cooling equipment (7) SB-2 injecting pump (8) preheating pipe (9) extraction cell (10) restrictor (11) collector (12) pressure sensor (13) the system of controlling pressure (14) the system of controlling temperature (15) exhaust.

After the samples were added to the extraction cell, 20% Triton X-100 (20% Triton and 80% methanol) was injected into the extraction cell and the samples were saturated by the 20% Triton X-100 in the extraction cell.

Extraction Procedures

In order to find the optimum condition of the extraction of Cu^{2+}, experiments at different pressures, temperatures, and total volumes pump displaced have been undertaken. Under the condition found above, supercritical CO_2 containing 5% (v/v) methanol was used in the extraction. 20% and Triton X-100 was added to the samples. The Cu(8-Hydroxyquinoline)$_2$ was collected in 10 mL ethanol (95%), and was determined by spectrophotometry.

RESULTS AND DISCUSSION

Complexation-SFE of metal ions from the solid matrices is a partitioning of the metal chelates between the matrices and the supercritical fluid. Clearly, the equilibrium is driven to favorable solvation of the metal chelates either if the metal chelates is made more soluble in the supercritical fluid or if the metal chelates is driven off the matrices. As with adding chelating reagent, modifier and surfactant may drive the equilibrium in both of two ways, but their functions are different.

In order to extract Cu^{2+}, 8-Hydroxyquinoline was used as chelating reagent during complexation-SFE. Little information is available in the literatures about this new system. So, it is necessary to study the optimum extraction condition in this experiment.

Effect of Pressure on the Recovery of Cu^{2+}

The effect of pressure on the recovery of Cu^{2+} at 60°C was shown in Figure 2. As the other conditions were fixed, the density of CO_2 increases with the increase of the pressure of CO_2 and the solubilizing ability of supercritical CO_2 increases correspondingly, which leads to the increase of the solubility of Cu(8-Hydroxyquinoline)$_2$ in supercritical CO_2.

But, as the density nears its maximum value, additional pressure is not able to increase density. So the solubility of Cu(8-Hydroxyquinoline)$_2$ in supercritical CO_2 also approaches a limit as suggested by Figure 2. 30 Mpa was selected as the optimum pressure.

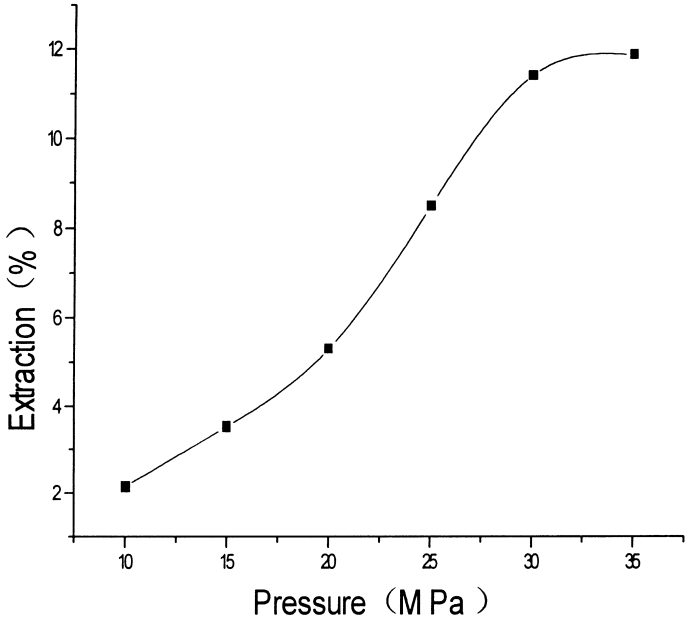

Figure 2. Effect of CO_2 pressure on the recovery of Cu^{2+} at 60°C, 10 mL supercritical CO_2 used, and 20 min static extraction.

Effect of Temperature on the Recovery of Cu^{2+}

The effect of temperature on the recovery of Cu^{2+} was shown in figure 3. As the other conditions were fixed, according to the opinion of kinetics, the higher the temperature is, the more intensive the heat motion of solutes on the active sites of the matrices is. It is beneficial for the solutes to overcome the adsorbing energy fortress of the matrices and to be desorped by supercritical CO_2. In view of the thermodynamics, when temperature increases, the saturated vapor-pressure increases correspondingly, which made the solutes dissolve in the supercritical CO_2 more easily.

When temperature is increased at constant pressure, the density of supercritical CO_2 decreases, thus reducing the partition coefficient, therefore, the solubility of metal chelates in supercritical CO_2 decreases. These three functions compete with each other. Figure 3 shows that the most efficient extraction was obtained at 60°C, so 60°C was selected as the optimum temperature.

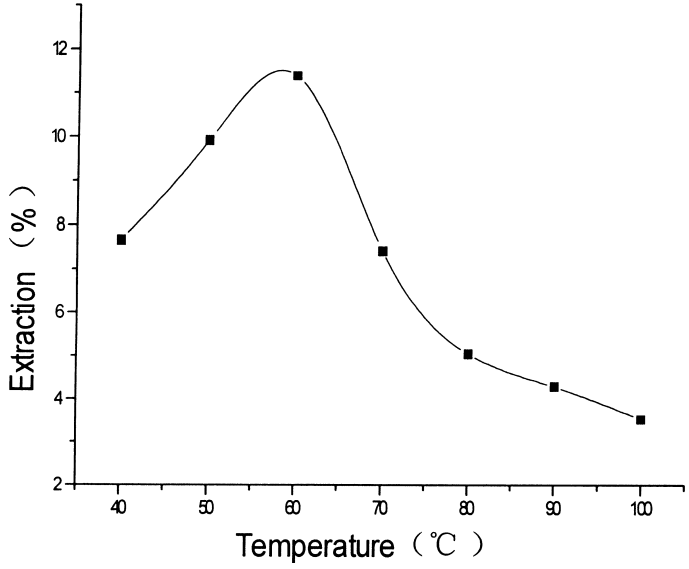

Figure 3. Effect of temperature on the recovery Cu^{2+} at 30 mpa, 10 mL supercritical CO_2 used, 1mL/min flow rate of supercritical CO_2 in the dynamic extraction and 20 min static extraction.

Effect of the Total Volume of the Supercritical CO_2 Pump Displaced on Recovery of Cu^{2+}

The effect of the total volume of the supercritical CO_2 the pump displaced during the experiment on the recovery of Cu^{2+} was shown in figure 4. When the total volume increases, the balance of extraction shifts to the direction of increasing extraction of Cu (8-Hydroxyquinoline)$_2$. With the increase of the total volume, the CO_2 emitted from the restrictor increases, which leads to the increase of the loss of collection of analytical sample due to volatilization and the formation of aerosols. It is not beneficial to increase the recovery. In the range of 5 mL - 25 mL supercritical CO_2 pump displaced, the recovery increases incessantly and in the range of 25 mL-40 mL, the recovery decreases slowly. So the 25 mL was selected as the optimum total volume.

Effect of Modifier on the Recovery of Cu^{2+}

Improved solvent characteristics and extraction efficiency can be obtained if polar solvent such as methanol is added to the supercritical CO_2. Polar mod-

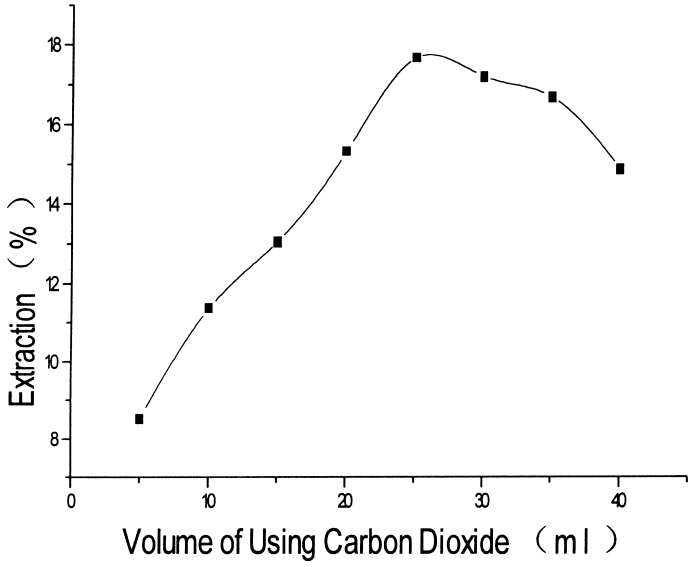

Figure 4. Effect of volume of using CO_2 on the recovery of Cu^{2+} at 60°C, 30 Mpa, 1 mL/min flow rate of supercritical CO_2 in the dynamic extraction and 20 min static extraction.

ifier is thought to enhance extraction in two ways; increasing the solubilizing ability of supercritical $CO_{2,}$, as well as promoting rapid desorption of Cu (8-Hydroxyquinoline)$_2$ from the solid matrices to the supercritical CO_2. as As we know, the carbon dioxide is nonpolar but Cu (8-Hydroxyquinoline)$_2$ is polar metal complex.

Suitable amounts of modifier can improve the polarity of supercritical CO_2 solvent, which increases the interaction between polar solutes and modified solvent. The methanol was chosen in the current experiment because of its high polarity, and its ability to deactivate the active sites on the surface of solid matrices. The recovery of Cu^{2+} using a commercially available SFC grade CO_2 containing 5% methanol are summarized in table 1. The methanol-modified CO_2 increased the recovery of Cu^{2+} by 17.7 % to 83.6 %.

Effect of the Surfactant on the Recovery of Cu^{2+}

The recovery of Cu^{2+} by using supercritical CO_2 modified with methanol was further improved in the presence of a non-ionic surfactant Triton X-100.

Table 1

Effect of the Methanol on the Recovery of Cu^{2+} at 60°C, 30 Mpa, 25 mL Supercritical CO_2 Used, 1 mL/min Flow Rate of Supercritical CO_2 in the Dynamic Extraction and 20 min Static Extraction

Number	Modifier	Efficiency of Extraction (%)
1	Methanol (5%)	80.4
2	Methanol (5%)	85.8
3	Methanol (5%)	83.3
4	Methanol (5%)	87.5
5	Methanol (5%)	81.0

RSD = 3.64% n = 5, Average value 83.6%.

Triton X-100 serves as solubilizer. It is beneficial for the dissolution of the Cu (8-Hydroxyquinoline)$_2$ in the supercritical CO_2 and desorption of Cu(8-Hydroxyquinoline)$_2$ from the active sites of the matrices to the supercritical CO_2. The result are shown in Table 2.

Table 2

Effect of the Surfactant TritonX-100 on the Recovery of CU^{2+} at 60°C, 30 Mpa, 10 mL Supercritical CO_2 Used, 1 mL/min Flow Rate of Supercritical CO_2 in the Dynamic Extraction and 20 min Static Extraction

Number	Modifier	Surfactant	Efficiency of Extraction (%)
1	Methanol (5%)	TritonX-100	93.1
2	Methanol (5%)	Triton X-100	95.3
3	Methanol (5%)	Triton X-100	100.0
4	Methanol (5%)	Triton X-100	96.4
5	Methanol (5%)	Triton X-100	98.3

RSD = 2.76% n = 5. Average value = 96.6%.

SPECTROPHOTOMETRIC ANALYSIS

The calibration graph was run by measuring photometrically Cu(8-Hydroxyquinoline)$_2$ standard solutions. The largest absorption wavelength of Cu (8-Hydroxyquinoline)$_2$ standard solutions is 407.8 nm with the ethanol (95%) as the reference solution. The range of linearity is 1.905-15.237 μg/mL of Cu^{2+}. The equation obtained is:

$$Y = 0.05796X - 0.00116$$

where Y is the absorbance and X is the concentration of Cu^{2+} in μg/mL, and the regression coefficient R = 0.99995.

REFERENCES

1. M.Y. Ding, Vol.15, No.6, 527-529 (1997).

2. L. H. Yue, C. M. Wai, Trends Anal. Chem., **14(3)**, 123-132 (1995).

3. C. Von Holst, B. W. Wenclawiak, Anal. Chem., **69**, 601-606 (1997).

4. Y. Meguro, S. Lso, T. Sasaki, Z. Yoshida, Anal Chem., **70**, 774-779 (1998).

5. K. E. Laintz, C. M. Wai, Anal. Chem., **64**, 2875-2878 (1992).

6. C. M. Waind, L. H. Yue, Talanta, **40(9)**, 1325-1330 (1993).

7. Y. Liu, V. Lopaz-Avila, M. Alcaraz, J. Chromatogr. Sci., **31**, 310-316 (1993).

8. Y. Lin, R. D. Brauer, K. E. Laintz, C.M. Wai, Anal. Chem., **65**, 2549-2551 (1993).

9. Y. In, C. M. Wai, Anal. Chem., **66**, 1971-1975 (1994).

10. J. Wang, W. D Marshall, Anal. Chem., **66**, 1658-1663 (1994).

11. S. Wang, S. Elshanl, C. W. Wai, Anal. Chem., **67**, 919-923 (1995).

12. M. D. Luque de Castro, M. T. Tena, Trends Anal. Chem., **15(1)**, 32-37 (1996).

13. K. E. Laintz, C. D. Hale, C. L. Rouquette, Anal. Chem., **70**, 400-404 (1998).

Received September 5, 1999 Author's Revisions August 12, 2000
Accepted December 27, 1999 Manuscript 5167