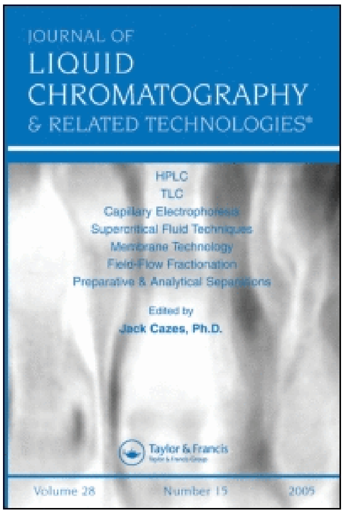

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Supercritical Fluid Extraction of Hazardous Metals from Urban Total Suspended Particles

Shiyong Du[a]; Guoying Zhang[bc]; Zhaojie Cui[c]
[a] Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P.R. China [b] Shandong University of Traditional Chinese Medicine, Jinan, P.R. China [c] School of Environmental Science and Engineering, Shandong University, Jinan, P.R. China

To cite this Article Du, Shiyong , Zhang, Guoying and Cui, Zhaojie(2005) 'Supercritical Fluid Extraction of Hazardous Metals from Urban Total Suspended Particles', Journal of Liquid Chromatography & Related Technologies, 28: 10, 1487 — 1495

To link to this Article: DOI: 10.1081/JLC-200058335

URL: http://dx.doi.org/10.1081/JLC-200058335

Journal of Liquid Chromatography & Related Technologies®, 28: 1487–1495, 2005

ISSN 1082-6076 print/1520-572X online
DOI: 10.1081/JLC-200058335

Supercritical Fluid Extraction of Hazardous Metals from Urban Total Suspended Particles

Shiyong Du
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou, P.R. China

Guoying Zhang
Shandong University of Traditional Chinese Medicine, Jinan,
P.R. China and School of Environmental Science and Engineering,
Shandong University, Jinan, P.R. China

Zhaojie Cui
School of Environmental Science and Engineering, Shandong University,
Jinan, P.R. China

Abstract: This paper describes the procedure for supercritical fluid extraction (SFE) of hazardous metals (Cu, Pb, Zn, Cd, Cr, and Ni) from urban total suspended particles (TSP) with supercritical CO_2 and several different types of chelating agents, under optimum extraction conditions of 20MPa, 60°C, and surfactant-methanol modified supercritical CO_2. Efficient extraction of metal ions from simulate samples was achieved. Only trifluoracetylacetone (TFA) is a general chelating agent to efficiently extract all of the target metal ions from TSP (83.2–99.3%). Sodium diethyldithiocarbamate (NaDDTC) can extract Cu, Pb, Zn, and Cd effectively (80.6–94.9%). 8-Hydryquinoline (8-HOx) can selectively extract Cu and Zn, with recoveries of 90.1% and 78.7%, respectively. Dithizone (H_2Dz) is capable of extracting Cu, Zn, and Cr with recoveries of 93.8, 79.8, and 94.5%, respectively. The results showed that, under optimized extraction conditions, and with suitable selection of chelating

Address correspondence to Zhaojie Cui, School of Environmental Science and Engineering, Shandong University, Jinan, 250100, P.R. China. E-mail: cuizj@sdu.edu.cn

agent, SFE for pretreating metals in TSP can yield results comparable to chemical digestion methods much more quickly and conveniently.

Keywords: Supercritical fluid extraction, TSP, Hazardous metals, Modifier

INTRODUCTION

A large number of studies of PAHs and PCB have been reported in relation to the total suspended particles (TSP, particles with a diameter of less than 100 μm). But, very little data are available on the content of hazardous metals in the urban TSP. These are often well above natural background levels, owing to anthropogenic processes, such as the production of iron and steel, nonferrous metal production, etc. Because the fine particulates can be absorbed into human lung tissues during breathing, when this fact results in enhanced metal concentrations, it can do great harm to human health. As the first stage in an analytical procedure, despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry (AAS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES), there is a crucial need for sample pretreatment. Supercritical fluid extraction has been proven to be a good technology for extraction of heavy metals from solid matrices. This new approach offers several outstanding benefits:

(i) the supercritical fluids have diffusivities and viscosities similar to gases and densities similar to liquids, thus enabling rapid mass transfer.[1]

(ii) by adjusting the system pressure, the solubility of a solute can be varied by several orders of magnitude.[2,3]

Supercritical CO_2 has been preferred for both analytical and technical applications, due to its convenient critical point (304.2 K; 7.3 MPa), low cost, and low toxicity. Thus, it can reduce solvent usage and exposure, disposal costs, and extraction times.[4]

Supercritical CO_2, as a medium to transport metal ions, has been investigated by many research facilities. Since metal ions are only partly soluble in this non-polar medium, appreciable solubility of the metal can be achieved only with a suitable derivatisation of the metal ions. Chelating with fluorinated and non-fluorinated isologues of dialkyldithiocarbamates[5–7] and of β-diketonates,[8,9] organophosphates,[10,11] and crown ethers[12] has been exploited for complex metal ions. In this work, we studied SFE of Cu, Pb, Zn, Cd, Cr, and Ni from simulated samples and urban TSP with four kinds of widely used chelating agents, namely, trifluoracetylacetone (TFA), Sodium diethyldithiocarbamate (NaDDTC), 8-hydryquinoline (8-HOx), and Dithizone (H_2Dz) with surfactant-methanol modified supercritical CO_2. The selected chelating agents are commercially available and inexpensive, and their coordination chemistry is well understood.

The objective of this research was to establish a fast and useful pretreatment and analytical method for determination and elimination of metal ions in TSP.

EXPERIMENTAL

Reagent and Materials

Organic film filters (200 × 250 mm) were purchased from Oriental Green Technology Co. of Tianjin. The supercritical grade carbon dioxide (99.99%) was supplied by Jinan Gas Factory of Shandong Province in China. H_2Dz, 8-HOx, and NaDDTC were contributed by Shanghai Chemical Reagent Company of the Medicine Group of China, and TFA was supplied by Acros Organics. Methylisobutylketone (MIBK, Shanghai Chemical Reagent Co., Ltd.) was used as collecting solvent. HPLC grade methanol (TEDIA Co., America) and surfactant Triton X-100 (Reagent Factory of Beijing of China) were used as modifier. The surfactant was diluted with methanol. Silica gel (Ocean Chemical Factory of Qingdao of China) was used to simulate samples.

An aqueous metal ion solution was prepared by dissolving a known amount of solid metal ion in tri-distilled water, and the simulated sample was prepared as follows: A known amount (10 μg for each type of metal ion) of mixed metal ions was spiked onto 2.0 g silica gel. Then, a 10-fold molar excess amount of chelating agent was added to the silica gel to overcome degradation or dissociation of the metal chelates. Then, the sample was mixed rapidly.

All other chemicals used were analytical grade reagents.

Apparatus

TSP was collected with a high-volume sampling system (Qingdao Hengyuan Instruments Co., Ltd., Model HY-1000).

All extractions were carried out using a supercritical fluid extraction system (Applied Separation Co., USA). The schematic diagram of the system is shown in Fig. 1. Modifier was added by a high-performance liquid chromatography (HPLC) pump (WellChrom K-501, Germany). Two 10 mL stainless-steel extraction vessels were fitted with stainless-steel needle valves which can process two samples at the same time. Two micrometering valves are used as restrictor valves to control the flow rate of the supercritical CO_2 to the solvent collection. Extraction temperatures were monitored using a thermocouple, and were found to be accurate to within ± 1°K. The precision of the pressure measurement is ± 1Pa.

Metal extracts were analysed using a graphite furnace absorption spectrophotometer (FAAS, Z-800, Japan) after being disposed. The FAAS

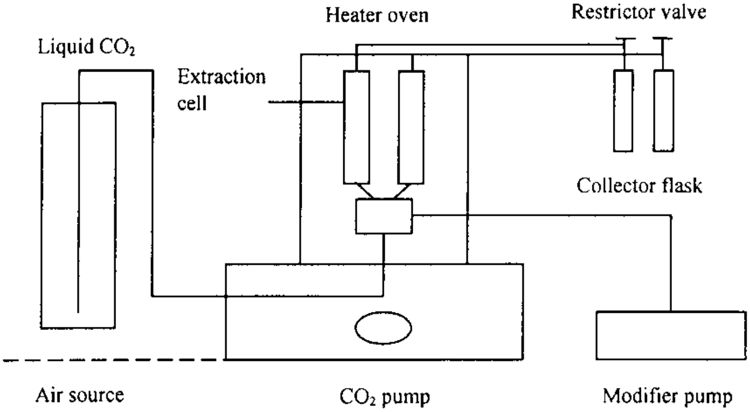

Figure 1. The scheme diagram of the SFE system.

measurements were carried out using an air acetylene flame. Standard solutions for FAAS were freshly prepared from 1000 mg/L stock solution of metal nitrates and/or metal complexes with concentrations of 1–50 mg/L.

Collection of TSP; Chemical Digestion Method

The TSP samples were trapped by organic filter films with a flow rate of 1.05 m^3/min, during 48 h, by a high-volume sampling system located at the campus of Shandong University. The filter films with TSP samples were cut into small pieces, and then separated into approximately five equal portions. One part was processed by a chemical digestion method. Another four parts were treated by SFE with different chelating agents. To obtain the initial contents of the metals, the same amount of original TSP sample as those pre-treated with the SFE technique was digested with concentrated sulfuric acid and perchloric acid in beakers that were heated on hot-plates to temperatures slightly below the boiling points of the sample solutions. The acid solution was then diluted to a standard volume. The digestion procedure was according to the guidelines laid down in GB/T17137 (1997). Then, the metal contents in the collection solvent were determined by graphite furnace absorption spectrophotometer at wave lengths of 324.8, 283.3, 213.9, 228.8, 359.3, and 232.0 nm for Cu, Pb, Zn, Cd, Cr, and Ni, respectively. The results are shown in Table 1.

Extraction of Metal Chelates from Simulated Samples

To research the optimum extraction conditions for extracting metal ions from TSP samples, simulated samples were studied first, at different pressures and temperatures; the effects of modifier were also studied.

Table 1. Metal contents in TSP pretreated by chemical digestion method ($\mu g/m^3$)

Content	$\mu g/m^3$
Cu	0.086
Pb	0.487
Zn	0.421
Cd	0.008
Cr	0.039
Ni	0.058

n = 3, RSD = 1.2 ~ 4.6%.

One of the end-fittings was removed and a plug of polypropylene wool was pushed into the closed end of the extraction vessel with a tamping rod. A 10 ml-vessel was filled with the prepared sample and the bed was tamped. It is essential to pack the sample bed firmly to ensure that supercritical CO_2 diffuses uniformly through the sample matrix. The remainder of the cell volume was filled with additional polypropylene wool. The vessel was inserted into the oven to perform the extraction. As modifier, surfactant-methanol solution (5%, v/v) was added into the extraction cell by the HPLC pump.

Under the optimum conditions found above, a 3 mL aliquot of microemulsion, containing Triton X-100, was directly added to the extraction cell to study the effect of surfactant on the extraction efficiency.

The metal chelates were collected in 5 mL MIBK and were analyzed by AAS.

Triplicate determinations were made in each experiment to ensure reproducibility of the system.

Extraction efficiencies of metals from TSP were determined under the optimum extraction conditions found with the simulated samples. The chelating sequence was completed prior to the extraction. After 2.0 g of the TSP sample was added to the extraction cell, about a 10-fold molar excess amount (calculated by the result obtained from the chemical digestion method and AAS analysis) of chelating agent was injected into the extraction cell. The sample was mixed sufficiently to ensure the metal ions in the matrix could react with the chelating agent efficiently. Aqueous methanol (5%, v/v) was added to the extraction cell by the HPLC pump as modifier and a 3 mL aliquot of microemulsion containing Triton X-100 was added directly to the extraction cell. The SFE procedure was performed in the same manner as for the simulated samples. The extracts were collected in 5 mL MIBK and were analyzed by AAS after treatment.

The percent recoveries of metal ions from TSP were calculated by comparing the result obtained by the SFE technique with the metal contents obtained with chemical digestion method.

RESULTS AND DISCUSSION

Extraction of Metal Ions from Simulated Samples

For each kind of chelating agent, effects of pressure (15–35 MPa), temperature (313 K–353 K), dynamic extraction time (10–60 min), and flow rate of the supercritical CO_2 on the extraction efficiency for the hazardous metals were studied systematically. The experimental results showed that, for most metal ions, 20 MPa, 333K, a 10-min static extraction followed by a 20-min dynamic extraction, and a liquid flow rate of 1.0 mL/min for the supercritical CO_2 in dynamic extraction process are the optimized extraction conditions. Under the optimum conditions found above, the addition of suitable amounts (5%, v/v) of methanol can improve the recoveries of the metal chelates, noticeably. The extraction efficiency with TFA as chelating agent is higher than with the other three chelating agents, which which corroborates the reports of Wai and co-workers.[13–16] The main reason is that the solubility of TFA is much higher than the other three non-fluorinated chelating agents. It is also known that fluorination of β-diketones improves the stability and volatility of the metal complexes which, in turn, increase the solubility in supercritical fluids. The efficiency of the extraction of metal chelates by methanol modified supercritical CO_2 was further improved by the presence of microemulsion containing Triton X-100. The result is agreement with our former study, which dealt with the extraction of Cu from solid matrices.[17] However, the role of the surfactant in the SFE of metals is not well understood. Maybe the microemulsion is beneficial for lowering the analyte polarity, enhancing the analyte solubility, and stimulating desorption kinetics. It was reported that the surfactant can be fully solubilized by adding the polar methanol modifier to the supercritical fluid, but there was no synergistic effect between surfactant and methanol.[14,18]

The experiments showed that, with a microemulsion containing Triton X-100, similar results can be gained as when using LiFDDTC as chelating agent, which has proven to be quite an efficient chelating agent for most metal ions.[13] While LiFDDTC is not available commercially, its common use in SFE is currently limited because it is costly to synthesize in small quantities. So, the method of adding microemulsion containing surfactant to modify both the matrices and supercritical CO_2 is a much more practical way to enhance the extraction efficiencies.

The results are summarized in Table 2.

Extracting Metal Ions from TSP

On the basis of the optimized extraction conditions found with the simulated samples, the metal chelates in the TSP samples were extracted by the SFE technique. The results are shown in Table 3.

Table 2. Recoveries of metal ions from simulated samples (%)

	TFA		8-HOx		H_2Dz		NaDDTC	
	a	b	a	b	a	b	a	b
Cu	96.3	99.4	79.2	103.4	79.5	102.1	84.6	106.8
Pb	88.5	92.6	75.8	95.6	76.1	86.9	79.2	97.4
Zn	94.5	96.7	82.1	103.8	77.8	105.5	85.7	102.3
Cd	94.7	92.1	84.9	97.3	63.4	82.1	81.8	92.5
Cr	78.6	101.2	71.8	78.1	74.9	95.6	67.3	81.7
Ni	82.5	99.8	76.3	89.6	66.3	83.7	71.3	82.9

Extractions were performed at 20 MPa and 333K, 10 min static followed by 20 min dynamic. a: Recoveries with methanol modified supercritical CO_2; b: Recoveries with surfactant-methanol modified supercritical CO_2. RSD $= 1.3 \sim 3.4\%$ ($n = 3$).

The result showed that TFA is the best chelating agent in our experiments at 20 MPa and 333K with methanol and Triton X-100 modified supercritical CO_2. Nearly all of the six kinds of metals can be extracted efficiently. The outcome was similar to the results obtained with simulated samples. The lower extraction efficiencies for some metal ions with NaDDTC, 8-HOx or H_2Dz indicated that the active sites and natural chelating agents present in real sample systems may bind strongly to certain metal ions, hindering their complexation with added chelating agent. In real samples, native metals can also be in highly insoluble forms, such as oxides and sulfides. Dissolution and extraction of these insoluble metal compounds from TSP depends upon the chelating ability of the chelating agents and the accessibility of the compound sites. Consequently, a certain fraction of native metals in solid samples may not be completely extractable by the chelating agents.[19]

Table 3. Recoveries of metal ions from TSP (%)

	TFA	8-HOx	H_2Dz	NaDDTC
Cu	95.6	90.1	93.8	94.9
Pb	83.2	73.5	37.2	84.9
Zn	88.4	78.7	79.8	89.6
Cd	80.5	71.0	68.9	80.6
Cr	99.2	62.9	94.5	46.8
Ni	98.7	64.1	38.3	53.9

Extractions were performed in duplicate at 20 MPa and 333 K, 10 min static followed by 20 min dynamic with methanol and Triton X-100 modified supercritical CO_2. RSD $= 1.7 \sim 8.6\%$ ($n = 3$).

The data for the method are compatible with the requirement of environmental monitoring quality control; it is suitable for the determination of metal ions in TSP.

CONCLUSION

SFE of hazardous metals from urban air particles, using supercritical CO_2 with polar surfactant and methanol modifiers, provides quantitative extraction under reasonable extraction conditions on an analytical scale (20 MPa, 333K). TFA turned out to be the best chelating agent in our experiments. Nearly all of the six kinds of metals can be extracted efficiently. But, for some metal ions, the recoveries were a little poor with NaDDTC, 8-HOx, or H_2Dz as chelating agents. Triton X-100 has been proven to be a useful modifier for supercritical CO_2, for it can lower the polarities of the analytes and increase the solubilities of the extracts based on reverse micelle formation. But, a great deal of work (including the investigation of micelle formation for surfactants in supercritical CO_2) still has to be done in order to clarify this behavior.

The chelating-SFE technique described in this paper provides a new method for extracting trace metals from urban TSP. This sample preparation method avoids the use of a chemical digestion method and organic solvent extraction required for separation and concentration of trace metals in conventional methods. Our work shows evidence that, with the supercritical fluid extraction method, a similar result was obtained as with the chemical digestion method. Therefore, the developed SFE method could improve and possibly replace the standard method for metal preconcentration in environmental solid matrices.

REFERENCES

1. Yang, Y.; Gharaibeh, A.; Hawthorne, S.B.; Miller, D.J. Anal. Chem. **1995**, *67*, 641–646.
2. Weber, W.T., Jr.; Young, T.M. Envir. Sci. Technol. **1997**, *31*, 1686–1691.
3. Miller, D.J.; Hawthorne, H.B.; Clifford, A.A.; Zhu, Sh. J. Chem. Eng. Data **1996**, *41*, 779–786.
4. Porschmann, J.; Blasberg, L.; Mackenzie, K.; Harting, P. J. Chromatogr. A **1998**, *816*, 221–232.
5. Lainz, K.E.; Wai, C.M.; Yonker, C.R.; Smith, R.D. Anal. Chem. **1992**, *64*, 2875.
6. Liu, Y.; Lopez-Avila, V.; Alcaraz, M.; Beckert, W.F.; Heithmar, E.M. J. Chromatogr. Sci **1993**, *31*, 310.
7. Wang, J.; Marshall, W.D. Analt. Chem. **1994**, *66*, 1658.
8. Lin, Y.; Wai, C.M. Anal. Chem. **1994**, *66*, 1971.
9. Lainz, K.E.; Tachikawa, E. Anal. Chem. **1994**, *66*, 2190.
10. Smart, N.G.; Carleson, T.E.; Kast, T.; Clifford, A.A.; Burford, M.D.; Wai, C.M. Talanta **1997**, *44*, 137.

11. Smart, N.G.; Carleson, T.E.; Elshani, S.; Wang, S.F.; Wai, C.M. Ind. Eng. Chem. Res. **1997**, *36*, 1819.
12. Wang, S.F.; Elshani, S.; Wai, C.M. Anal. Chem. **1995**, *67*, 919.
13. Lin, Y.H.; Wai, C.M.; Jean, F.M.; Brauer, R.D. Envir. Sci. Technol **1994**, *28*, 1190.
14. Wai, C.M. Anal. Sci **1995**, *11*, 165.
15. Wai, C.M.; Wang, S.; Liu, Y. Talanta **1996**, *43*, 2083–2091.
16. Wai, C.M.; Wang, S. J. Biochem. Biophys. Meth. **2000**, *43*, 273–293.
17. Liu, J.; Wang, W.; Li, G. Talanta **2001**, *53*, 1149–1154.
18. Jimenez-Carmona, M.M.; Luque de Castro, M.D. Anal. Chim. Acta **1998**, *358*, 1–4.
19. Wai, CD.M.; Wang, S. J. Chromatogr. A **1997**, *785*, 369–383.

Received November 5, 2004
Accepted November 10, 2004
Manuscript 6534