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Application of Carbon Dioxide Supercritical Fluid Extraction of Heavy Metals from Ambient Aerosols

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The possibility of using carbon dioxide supercritical fluid for extraction of trace heavy metals including; Pb, Cd, Cr, Cu, Ni and Zn from airborne particulate matter has been investigated. The effects of pressure, extraction time and mixed modifier on the extraction efficiencies of heavy metals were studied and the results showed that although all of these parameters enhance the extraction efficiencies, but using surfactants has improved the extraction efficiency considerably. Two different chelating agents were used for making complex from the heavy metals and it was cleared that diethyl dithiocarbamate (Na DDC) along with mixed modifier can be effectively used for extraction of Pb, Cd, Cu and Zn while dithizone (DT) along with mixed modifier showed capability for extraction of Cd, Cu and especially for Cr.

Key Words: Airborne particulate matter, Supercritical fluid extraction, Air pollution, Heavy metals in urban air, Extraction of metals.

INTRODUCTION

Carbon dioxide supercritical fluid extraction (SFE) has become an important technique in sample preparation due to the common effort to reduce the consumption, disposal and long term exposure to organic solvents[1]. In comparison with conventional solvent extraction, supercritical fluid extraction is quite fast and it's efficiency for extraction of different organic compounds can be enhanced by using modifiers. In addition, carbon dioxide supercritical fluid that commonly used for extraction is chemically inert, non-toxic, non-flameable, low cost, non-polluting and has the moderate critical temperature (31 °C) and critical pressure (73 atm). In spite of the advantages, supercritical fluid extraction offers low efficiency for extraction of polar compounds. The efficiency of supercritical fluid extraction for extraction of polar compounds can be developed by addition of complexing agents and modifiers onto the sample matrix[2-6].

Complex making and then extraction with supercritical fluid extraction could be a novel technique for extraction of metals from solid matrices. The nature of the matrix and its physico-chemical characteristics are of prime importance for performing an effective extraction[7]. The parameters such as extraction time, pressure and modifier

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are all important in enhancement of the extraction efficiency. So, these parameters should be optimized and adjusted carefully for performing a successful extraction[8].

Supercritical fluid extraction is usually used as a popular technique for the extraction of a wide range of pollutants such as organometallic compounds, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and even inorganic species from environmental samples[9,10]. Metals in atmosphere are mostly associated with airborne particulate matter. The extraction of heavy metals from airborne particulate matter is of great interest[11].

To obtain the effective metal recoveries by supercritical fluid extraction using chelating agents are necessary and it should be noted that; (a) the chelating agent must be soluble and stable in supercritical fluid conditions, (b) the metal ion must be efficiently reacts with the chelating agent and a neutral complex should be achieved and (c) the metal complex must be quantitatively trapped in the collection solvent[12]. It has been reported that the solubility and stability of fluorinated organic chelating agents in supercritical fluid is much higher than the non-fluorinated ones. As a result, the extraction efficiency with these reagents is higher and these compounds have usually been used for extraction of metals from different environmental samples[13]. It should be noted that fluorinated reagents are unavailable, expensive and their synthesis is complicated and has a tedious procedure. Therefore, development of a method based on using other reagents which are easily available could be useful for development of SFE for extraction of heavy metals from environmental samples.

Although, the carbon dioxide supercritical fluid is able to extract neutral organometallic compounds from airborne particulate matter, the direct extraction of metal ions has been far less successful, because charge neutralization of the ion is required in order to significantly enhance the solubility of the metals in supercritical fluid[12]. Chelating agents such as dialkyl dithiocarbamates[14-16], β-diketonates[17,18], organophosphates[19,20] and crown ethers[21] have so far been reported for making complex from metal ions. Modifiers have also been extensively used to enhance the extraction efficiency and it could be very useful for metal extraction with SFE[22,23].

In the present work, the possibility of using carbon dioxide supercritical fluid for extraction of toxic heavy metals including; Pb, Cd, Cu, Cr, Ni and Zn from airborne particulate matter with using sodium diethyldithiocarbomate (NaDDC) and dithizone (DT) as chelating agents was investigated. The effects of pressure, extraction time and modifier on the extraction efficiencies of trace heavy metals were investigated.

EXPERIMENTAL

Collection of samples: Airborne particulate matter from the atmosphere of the city of Isfahan was collected on quartz fiber filter (Whatman, QM-A) using a high volume air sampler (Greaseby, PS2, USA). Samples were collected from a height of 1.5 m above the ground level. Sampling flow rate and sampling period were 1 m^3 min^{-1} and 12 h, respectively.

All of the reagents used were of analytical grade. Dithizone (DT) was purchased from Merck chemical company (Germany). Sodium diethyldithiocarbamate (NaDDC) was prepared from Aldrich chemical company (USA) and used without further purification. Carbon dioxide with a purity of 99.5 % was purchased from Zam Zam Co. Ltd (Isfahan, Iran). Standard stock solutions (1000 mg/L) of Pb, Cd, Cr, Cu, Ni and Zn for atomic absorption spectrometry (BDH, Ltd) were used. Working range standard solutions were prepared from the stock standard solution by proper diluting with 0.1 M nitric acid.

The extractions were performed by carbon dioxide supercritical fluid. The SFE instrument was consisted of the following parts. The liquid carbon dioxide was pressurized, by a JASCO, Model PU-980 reciprocating pump through a preheating coil located in an oven. The temperature was monitored using a thermocouple-temperature controller device (Alton Ray model TC14, Tehran, Iran). A back-pressure regulator (JASCO BP 1580-81) depressurized the solvent after extraction. Fig. 1 shows the schematic diagram of the SFE apparatus used.

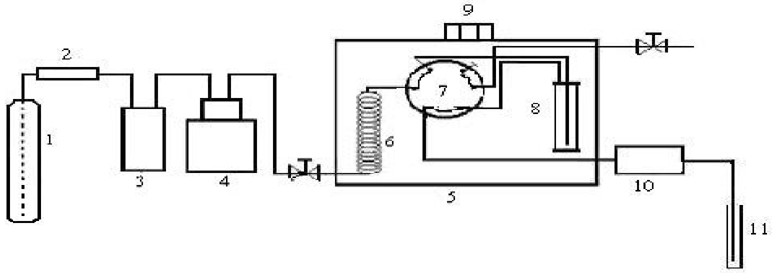

Fig. 1. Schematic diagram of supercritical fluid extraction apparatus used for extraction; 1 = cylinder of CO_2, 2 = purifier, 3 = cooling bath, 4 = pump, 5 = oven, 6 = pre-heating coil, 7 = six port valve, 8 = equilibrium cell, 9 = thermocouple, 10 = back pressure regulator, 11 = collection vial

Determination of Pb, Cd, Cr, Cu, Ni and Zn were carried out on a Varian atomic absorption spectrometr, Model AA-220. The system was linked to a Varian GTA-110 graphite furnace and auto-sampler system. The standard Varian hollow cathode lamps of the elements were used. The wavelengths used for the determination of heavy metals were 283.3 nm for lead, 228.8 nm for Cd, 357.9 nm for Cr, 324.7 nm for Cu, 232.0 for Ni and 213.9 nm for Zn.

Extraction procedure: The exposed filter was folded and placed into the stainless steel extraction cell and 3 mL of solution of 2×10^{-3} M chelating agent (dithizone or sodium diethyldithiocarbamate) was added on that. The extraction was then performed with supercritical CO_2 using methanol or methanol-surfactant (Triton-X-100) as mixed modifiers at 60 °C and at 200 atm pressures and an extraction time protocol of 0.5 h static and 1 h dynamic extraction with a flow rate of 0.5 mL min^{-1}. The extract was collected in a test tube containing 5 mL methyl isobutyl ketone (MIBK) and used for analysis of metals.

Wet digestion of airborne particulate matter: The digestion of airborne particulate matter is described in detail in previous paper[24]. The exposed filter was folded several times and placed in a PTFE beaker, moisturized with a few mL of de-ionized distilled water and 10 mL of concentrated nitric acid and 5 mL of hydrofluoric acid were then added on that. The lid of the beaker was replaced and the beaker was heated at 90 ºC for 4 h. The lid of the beaker was then unscrewed and the beaker was heated at 90 °C on a hot plate until its volume was reduced to a half. 5 mL more nitric acid was added and the mixture was heated and evaporated to near dryness to remove the excess HF. The digest was finally extracted in 5 mL, 3 M, nitric acid, filtered into a 10 mL volumetric flask and made to the volume by distilled de-ionized water.

RESULTS AND DISCUSSION

In order to investigate the effect of pressure on the extraction efficiency, the extraction of heavy metals from airborne particulate matter was performed at 150 and 200 atm. pressures. Sodium diethyldithiocarbomate and dithizone were used as chelating agents. The extraction was carried out in presence of 10 % methanol as modifier. The extraction temperature was adjusted to 60 ºC to prevent any possible thermal decomposition of the metal complexes. The amount of each metal extracted was compared with that obtained from wet digestion procedure. Figs. 2 and 3 show the recovery of heavy metals extracted at the two different pressures. The results showed that for both sodium diethyldithiocarbomate and dithizone, the extraction efficiencies of metals were fairly increased at higher pressure.

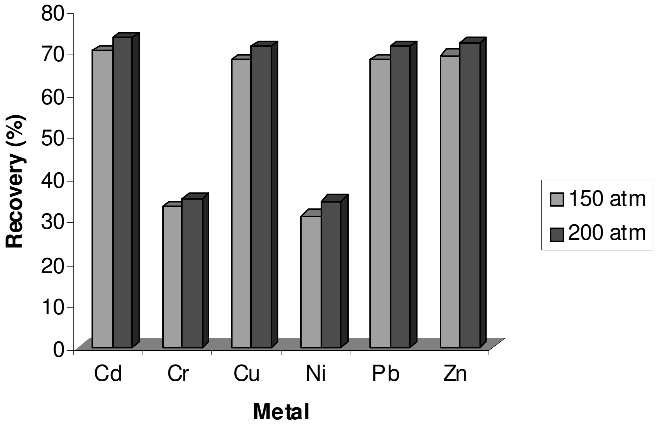

Fig. 2. Recovery percentage of heavy metals from airborne particulate matter by supercritical fluid extraction using sodium diethyldithiocarbamate (NaDDC) as chelating agent, methanol modifier 10 % (v/v), supercritical fluid flow rate = 0.5 mL min^{-1}, supercritical fluid pressures were 150 and 200 atm., chamber temperature = 60 °C, back pressure regulator temperature = 50 °C, static extraction time = 0.5 h and dynamic extraction time = 0.5 h

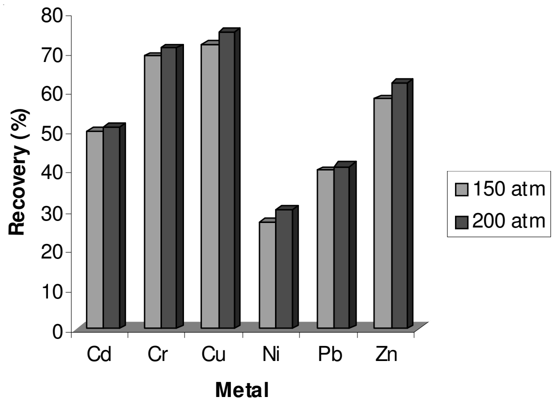

Fig. 3. Recovery percentage of heavy metals from airborne particulate matter by supercritical fluid extraction extraction, using sodium dithizone as chelating agent, methanol modifier 10 % (v/v), supercritical fluid flow rate = 0.5 mL min^{-1}, supercritical fluid pressures were 150 and 200 atm., chamber temperature = 60 °C, back pressure regulator temperature = 50 °C, Static extraction time = 0.5 h and dynamic extraction time = 0.5 h

The extraction of heavy metals was also performed under two different extraction time protocols. The protocol **1** was 0.5 h static and 0.5 h dynamic extraction and protocol **2** was 0.5 h static and 1 h dynamic extraction. Figs. 4 and 5 show the results obtained from this investigation for sodium diethyldithiocarbamate and dithizone respectively. The results indicate that for both chelating agents the higher dynamic extraction time resulted in fairly higher extraction efficiency.

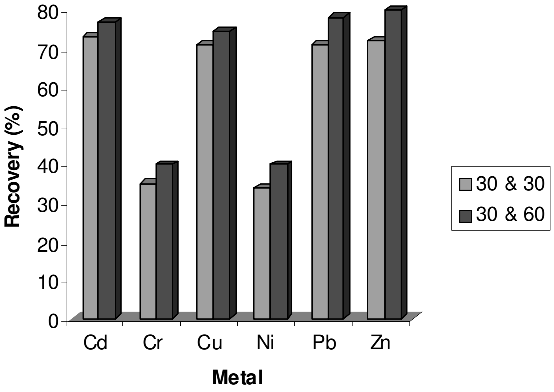

Fig. 4. Recovery percentage of heavy metals from airborne particulate matter by supercritical fluid extraction using sodium diethyldithiocarbamate as chelating agent, methanol modifier 10 % (v/v), supercritical fluid flow rate = 0.5 mL min^{-1}, supercritical fluid pressures 200 atm. chamber temperature = 60 °C, back pressure regulator temperature = 50 °C, Static extraction time = 0.5 h and dynamic extraction times of 0.5 and 1.0 h, respectively

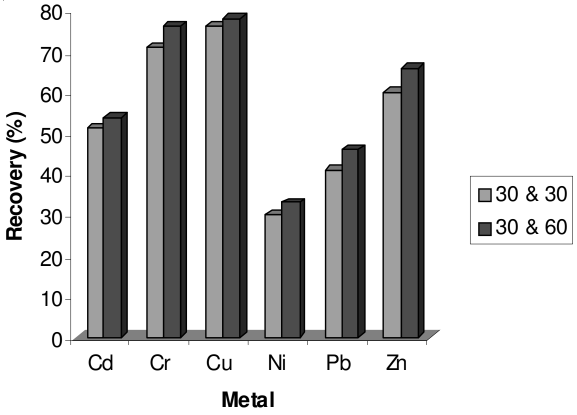

Fig. 5. Recovery percentage of heavy metals from airborne particulate matter by supercritical fluid extraction extraction, using sodium dithizone as chelating agent, methanol modifier 10 % (v/v), supercritical fluid flow rate = 0.5 mL min^{-1}, supercritical fluid pressures was 200 atm, chamber temperature = 60 °C, back pressure regulator temperature = 50 °C, Static extraction time = 0.5 h and dynamic extraction times of 0.5 and 1.0 h, respectively

In order to investigate the effect of surfactant on the extraction efficiencies of heavy metals from airborne particulate matter was also investigated at optimized conditions of time and pressure, but using a combination of methanol (10 % v/v) and surfactant (Triton-X-100, 5 % v/v) as mixed modifier. Table-1 shows the results obtained from this investigation and indicate that using surfactant-methanol mixed modifier is able to enhance the extraction efficiencies considerably not only for NaDDC but also for DT.

TABLE-1
EXTRACTION EFFICIENCIES OF HEAVY METAL COMPLEXES WITH METHANOL 10 % (v/v) AND WITH A COMBINATION OF METHANOL 10 % (v/v) AND SURFACTANT 5 % (v/v) AS MIXED MODIFIER

Element	Sodium diethyldithiocarbomate		Dithizone	
	Methanol	Methanol + Surfactant	Methanol	Methanol + Surfactant
Cd	76.9 ± 1.3	91.6 ± 0.7	54.9 ± 1.6	89.1 ± 2.1
Cr	39.9 ± 1.5	51.3 ± 1.1	75.5 ± 1.4	88.9 ± 1.3
Cu	74.2 ± 2.3	93.4 ± 1.9	78.0 ± 2.3	91.0 ± 2.5
Ni	40.1 ± 2.3	57.8 ± 2.2	32.9 ± 2.1	44.6 ± 2.8
Pb	78.5 ± 1.7	91.4 ± 1.9	45.9 ± 1.4	85.6 ± 1.5
Zn	81.3 ± 2.3	91.2 ± 1.8	64.7 ± 2.6	81.7 ± 2.9

Pb, Cd, Cu and Zn were effectively extracted by using NaDDC and mixed modifier, while DT showed relatively better extraction efficiency for Cu, Pb and Cr. Dithizone showed an excellent capability for extraction of Cr. Although the extraction of Ni with the both chelating agents was improved by using mixed modifier, it is still not properly explored and needs to be more development.

The proposed method was applied for the extraction and determination of trace heavy metals in urban and rural areas. Table-2 shows the results obtained from this study.

TABLE-2
MEAN CONCENTRATIONS OF HEAVY METALS IN URBAN AND RURAL AREAS (ng/m^3)

Element	Urban area	Rural area
Cd	5.9	1.0
Cr	34	12
Cu	268	119
Pb	197	104
Zn	624	308

Values are reported without standard deviation because of huge variation in concentrations of elements in different samples collected in different dates.

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