

Dry ice-originated supercritical and liquid carbon dioxide extraction of organic pollutants from environmental samples

Kong-Hwa Chiu^a, Hwa-Kwang Yak^b, Chien M. Wai^c, Qingyong Lang^{d,*}

^a Department of Natural Sciences, National Science Council, Taipei 10636, Taiwan, ROC

^b Department of Chemistry, Chung Yuan Christian University, Chung-Li 320, Taiwan, ROC

^c Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

^d Nutritional Laboratories International, 1001 S 3rd West, Missoula, MT 59801, USA

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Abstract

Packed in a high-pressure vessel and under calculated conditions, dry ice can be used as a source of carbon dioxide for supercritical CO₂ extraction or liquid CO₂ of organic compounds from environmental samples. Coupled with a fluid modifier such as toluene, dry ice-originated supercritical CO₂ (Sc CO₂) achieves quantitative extraction of many volatile organic compounds (VOCs) and semivolatile organic compounds (SOCs) including polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes, and polychlorinated biphenyls (PCBs) from solid matrices. Compared to contemporary manual or automated supercritical fluid extraction (SFE) technologies, this novel technique simplifies SFE to a minimum requirement by eliminating the need of a high-pressure pump and any electrical peripherals associated with it. This technique is highly suitable to analytical areas where sample preservation is essential but difficult in the sampling field, or where sample collection, sample preparation, and analysis are to be done in the field.

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1. Introduction

Supercritical carbon dioxide (Sc CO₂) extraction has been successfully used for removing a variety of organic compounds such as polycyclic aromatic hydrocarbons (PAHs), [1–12] polychlorinated biphenyls (PCBs) [13–15] and pesticide residues [16–18] from various environmental samples, from food composite [19], and for extraction of contaminants from recycled paper and board [20]. Compared to liquid solvent extraction, Sc CO₂ extraction has several advantages including: (1) faster extraction due to carbon dioxide's higher diffusivity and lower viscosity, thus faster mass transfer; (2) higher extraction efficiency due to continuous flow in of fresh fluid through the sample matrices; [21] (3) higher selectivity by manipulation of extraction temperature and pressure and/or addition of modifiers [22]; and (4) elimina-

tion of sample pre-concentration step and, in many cases, the sample cleanup process, which is typically time-consuming and often results in loss of volatile analytes. [23] In order to attain the supercritical state and to deliver Sc CO₂ to the sample vessel, a high-pressure pump is required for contemporary manual and automated SFE systems. A commercially available manual high-pressure pump typically costs a few thousand US dollars, while its more sophisticated, automated counterpart typically costs 10,000–30,000 US dollars. Although the manual high-pressure pumps do not require power supply, they are heavy and are not suitable for field operations. The automated high-pressure pumps are somewhat lighter but require power supply, thus limiting their field applications to those having power supply. Both pumps also require a liquid CO₂ tank for performing SFE.

The dry ice-originated supercritical and liquid CO₂ extraction techniques described in this article simplifies SFE to a minimum requirement by eliminating the need of a high-pressure pump and any electrical peripherals associated with it. This technique requires only two high-pressure

* Corresponding author. Tel.: +406 273 5493.

E-mail address: drlang@nutritionallabs.com (Q. Lang).

stainless steel vessels, one for packing dry ice and the other for containing the sample of interest, two water baths for temperature control purpose, and a box of dry ice. Supercritical and liquid CO₂ are readily produced using this device which provides satisfactory extractions of PAHs, PCBs, and *n*-alkanes.

Although using dry ice as a CO₂ source for SFE of pesticide residues from meat products [24], oil from spent bleaching clays [25], and spiked organic compounds from soil samples [26] has been reported, it is to our knowledge that its applications to real-world environmental samples have not been studied. This report demonstrates that the dry ice method can be successfully applied to SFE of various organic pollutants from environmental matrices.

2. Experimental

2.1. Materials

The chemicals used in the study are listed as follows: toluene (HPLC grade, Fisher), regular and perdeuterated PAH standards (GC standard, Ultra Scientific, N. Kingstown, RI), *n*-alkanes (GC standard, Alltech), polychlorinated biphenyls (PCBs, GC standard, Supelco), dry ice (Oxarc, Lewiston, ID), and silica gel (70–230 mesh, Aldrich).

2.2. Apparatus

Two high-pressure stainless steel vessels were used for the extractions. One was a 50-mL homemade vessel for dry ice (CO₂ source vessel), and the other (7.5-mL sample vessel) was purchased from Keystone (Philadelphia, PV). Two styrofoam buckets filled with warm water were used as water baths. A Hewlett Packard GC (model 5890) equipped with a flame ionization detector (FID) and installed with a DB-5 column (30 m × 0.32 mm × 0.25 μm) was used for quantitative analysis. A GC-MS (model 5890-5971A) installed with the same DB-5 column was used for peak verification of the real-world samples. Helium (Oxarc, Spokane, WA) was used as the carrier gas for both the GC and GC-MS.

2.3. Samples

A soil sample was collected from a garden behind an apartment building in Moscow, ID. A road dust sample was collected from a busy street (sixth Street) on the campus of University of Idaho. The samples were passed through a 45-mesh sieve, then carefully mixed, stored in clean glass bottles and kept in a refrigerator maintained at ≤4 °C.

2.4. Extraction

Fig. 1 illustrates the set-up of the dry ice extraction apparatus. The CO₂ source vessel (50 mL) was packed with dry ice while the sample vessel (7.5 mL) was loaded with sample. Approximately 1.0 g silica gel was placed at the bottom of the sample vessel for in situ fractionation. [27]. Before connecting the sample vessel to the system, a known amount of perdeuterated chrysene (e.g. 5.0 μg) was spiked onto the sample as the surrogate, and 1 mL of toluene was added into the vessel as a modifier. After the vessels were connected via stainless steel tubing and fittings, the CO₂ source vessel was placed into a water bath maintained at around 70 °C, and the sample vessel into a water bath maintained at about 40 °C. Pressure was monitored with the pressure gauge. When the pressure reached a stable value (usually >4000 psi if the dry ice was firmly packed), a 20-min static extraction was first conducted. After the 20 min of static extraction, the outlet valve was opened for a dynamic extraction. The flow rate was controlled at about 4–5 mL min⁻¹ by the outlet valve so that during depressurization no toluene would be splash out of the collection vial. When the pressure in the CO₂ source vessel had dropped down to near atmospheric pressure, the extraction was terminated. Typically >0.5 mL of toluene was collected in the collection vial. The extracted sample was transferred to a smaller vial for storage and the collected toluene was transferred to a clean vial. The collection vial was rinsed twice with fresh toluene that was subsequently added to the collected toluene to ensure quantitative transfer. The final solution was then brought to volume for GC analysis.

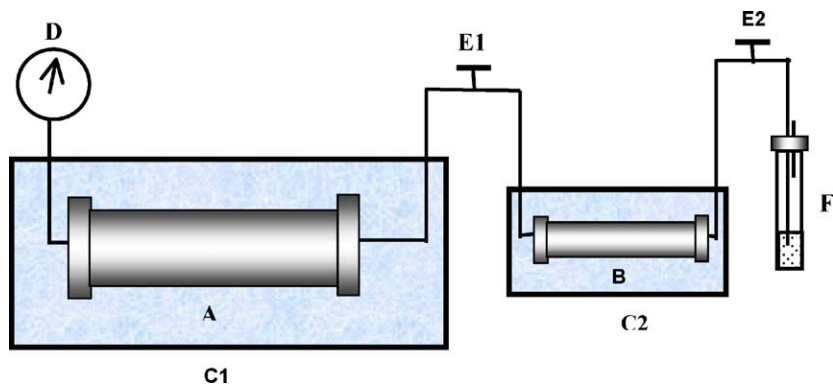


Fig. 1. Dry ice extraction set up: (A) vessel for storage of dry ice; (B) vessel for sample extraction; (C) water baths; (D) pressure gauge; (E) valves; (F) collection vial.

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