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

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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 CO_2 extraction or liquid CO_2 of organic compounds from environmental samples. Coupled with a fluid modifier such as toluene, dry ice-originated supercritical CO_2 (Sc CO_2) 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.

Keywords: Supercritical fluid carbon dioxide extraction; Dry ice; Environmental pollutants

1. Introduction

Supercritical carbon dioxide (Sc CO_2) 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 CO_2 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) elimination 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 CO_2 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 CO_2 tank for performing SFE.

The dry ice-originated supercritical and liquid CO_2 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

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stainless steel vessels, one for packing dry ice and the other for containing the sample of interest, two water bathes for temperature control purpose, and a box of dry ice. Supercritical and liquid CO_2 are readily produced using this device which provides satisfactory extractions of PAHs, PCBs, and *n*-alkanes.

Although using dry ice as a CO_2 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 (CO_2 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 $\leq 4\,^{\circ}C$.

2.4. Extraction

Fig. 1 illustrates the set-up of the dry ice extraction apparatus. The CO_2 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 CO_2 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 CO_2 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.

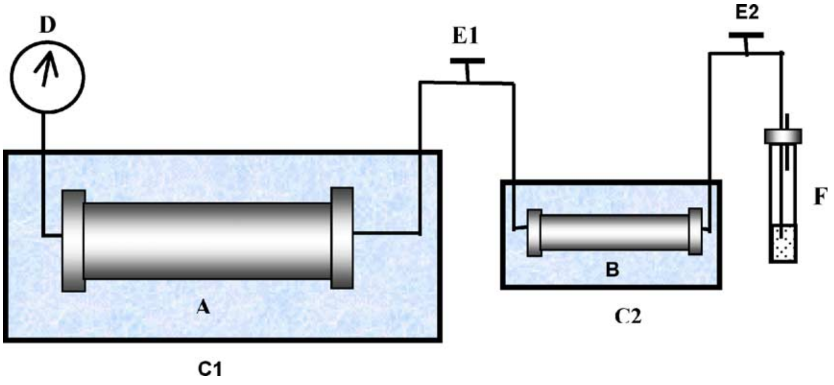

Fig. 1. Dry ice extraction set up: (A) vessel for storage of dry ice; (B) vessel for sample extraction; (C) water baths; (D) pressure gauge; (E) valves; (F) collection vial.

2.5. Analysis

After extraction, exactly 5 μg of squalane was spiked into each of the samples as an internal standard. Approximately 1 μL of the samples was injected into the GC for quantification. The injector and detector temperatures were set at 280 and 300 °C, respectively. The oven temperature program started from 1-min hold at 40 °C, followed by a ramp of 5 °C min^{-1} to 310 °C, where it is held for 15 min. The peaks were identified by comparison of retention times with authentic PAHs, PCBs and *n*-alkanes, and further verified with GC–MS. Peak areas were used for quantifications.

3. Results and discussion

3.1. Recovery tests

Standard D-PAHs (acenaphthene, phenanthrene, chrysene and perylene), *n*-alkanes (C_{24}, C_{26}, C_{28} and C_{30}) and PCBs [4-monochlorobiphenyl (BZ# 3); 2,2′,5-trichlorobiphenyl (BZ# 18); 2,2′,5,5′-tetrachlorobiphneyl (BZ# 52); 2,2′,6,6′-tetrachlorobiphenyl (BZ# 54) and 2,2′,4,4′,6,6′-hexachlorobiphenyl (BZ# 155)] were used for the recovery tests. The standard compounds were spiked onto 5 g of Fisher sea sand, and air-dried in a clean laboratory hood over night. After a sample was loaded into the 7.5-mL extraction vessel, the remaining space was filled with glass beads to minimize void volume. The same extraction procedure was used for both spiked samples and real-world samples. The extraction results of the standard compounds are listed in Table 1. These analytical results were obtained either on the same day as the SFE experiments or on the following day after the SFE. If the GC analysis was conducted on the following day, the samples would be kept in a refrigerator at ≤4 °C.

One can observe from Table 1 that although the lower molecular weight PAHs (naphthalene and 2,4-dichlorobenzene) and PCBs (BZ# 3) were partially or completely lost, most of the other spiked compounds were quantitatively recovered. The relative standard deviation (R.S.D.) was in the range of 1.1–7.9%. The loss of the lower molecular weight compounds were most likely due to their higher volatilities and probably happened either during the solvent evaporation process after spiking on the sand, or being purged during the depressurization of the CO_2. This phenomenon is identical to that of a conventional SFE operation with commercial equipment, and in this case a liquid–solid trap collection method [1] or a cryogenic trap collection method [28] should be employed if the volatile compounds are the analytes of interest.

Lower flow rate, e.g. 1–2 mL min^{-1}, was also investigated using a 100-μm diameter capillary restrictor. Although loss of the lower molecular weight compounds was slightly reduced, the overall recovery of the other compounds became obviously lower (ca. 50%) than those performed at higher flow rate (e.g. 4–5 mL min^{-1}) via a 320-μm diameter fused silica capillary as the restrictor. As was discussed in a previous article, a higher flow rate invariably produces higher recoveries for nonvolatile or semivolatile analytes [24]. This is due to the fact that higher flow rates can significantly reduce the mixing effect of the incoming fresh CO_2 with the bulk CO_2 that is already in the extraction vessel at any given time. This bulk CO_2, which contains the dissolved organic compounds, can exit the extraction vessel without being further "diluted" by the fresh CO_2 and therefore, enhance the extraction efficiency for a given volume of liquid CO_2.

Among a variety of modifiers, toluene was reported as one of the most effective organic solvents that could enhance the SFE recovery of PAHs [3,6]. For simplicity, toluene was also used as the modifier for extraction of the hydrocarbons and PCBs. As shown in Table 1, most of the analytes were quantitatively extracted and recovered.

Table 1
Recovery test results of perdeuterated PAHs, *n*-alkanes and PCBs (μg)

	Spiked	1	2	3	4	5	Average	Recov.(%)	R.S.D. (%)
D-PAHs									
Acenaphthene	40.0	18.3	16.3	17.6	22.8	20.6	19.1	47.8	6.5
Phenanthrene	40.0	39.7	41.4	38.1	38.9	36.4	38.9	97.3	4.6
Chrysene	40.0	40.1	43.3	39.8	43.6	45.1	42.4	106.0	5.8
Perylene	40.0	37.9	36.8	37.5	37.2	37.6	37.4	93.5	1.1
n-Alkanes									
C_{24}	20.0	19.2	19.6	21.1	22.0	21.6	20.7	103.4	6.3
C_{26}	20.0	18.8	21.6	19.9	20.9	21.3	20.5	102.4	5.7
C_{28}	20.0	18.2	18.0	18.1	19.0	20.5	18.8	93.9	5.3
C_{30}	20.0	20.4	20.0	18.2	20.1	21.2	20.0	100.0	5.5
PCBs									
BZ# 3	130	78.3	52.2	60.9	58.3	54.8	60.9	46.9	7.9
BZ# 18	91	78.2	74.9	77.4	75.7	82.2	77.7	85.4	3.2
BZ# 52	96	94.9	92.0	85.7	88.4	101.6	92.5	96.4	6.4
BZ# 54	100	94.4	87.3	94.7	87.5	105.9	94.0	94.0	7.6
BZ# 155	132.6	123.5	121.4	128.2	115.3	114.7	120.6	91.0	4.3

Table 2
Analytical results of *n*-alkanes in road dust and garden soil ($\mu g\,g^{-1}$)

Cn	Road dust					Garden soil				
	Test 1	Test 2	Test 3	Mean	R.S.D. (%)	Test 1	Test 2	Test 3	Mean	R.S.D. (%)
C_{19}	1.59	1.61	1.42	1.54	6.8	0.04	0.06	0.04	0.05	24.7
C_{20}	1.43	1.62	1.41	1.49	7.7	0.07	0.09	0.06	0.07	20.8
C_{21}	1.83	2.08	1.78	1.90	8.5	0.27	0.30	0.24	0.27	11.1
C_{22}	2.57	2.69	2.39	2.55	5.9	0.15	0.18	0.16	0.16	9.4
C_{23}	3.12	3.37	3.09	3.19	4.8	0.24	0.29	0.20	0.24	18.5
C_{24}	4.25	4.42	4.13	4.27	3.4	0.17	0.19	0.20	0.19	8.2
C_{25}	0.94	1.13	0.95	1.01	10.6	0.14	0.15	0.13	0.14	7.1
C_{26}	2.36	2.67	2.22	2.42	9.4	0.24	0.28	0.21	0.24	14.4
C_{27}	3.49	3.76	3.61	3.62	3.7	3.47	3.73	3.15	3.45	8.4
C_{28}	1.35	1.44	1.21	1.33	8.9	0.58	0.64	0.57	0.60	6.3
C_{29}	2.62	2.98	2.76	2.79	6.5	4.46	4.69	4.32	4.49	4.2
C_{30}	0.87	0.91	0.67	0.82	16.1	0.23	0.22	0.18	0.21	12.6
C_{31}	2.24	2.46	2.48	2.39	5.6	2.94	3.01	2.83	2.93	3.1
C_{32}	1.19	1.46	1.22	1.29	11.3	0.19	0.23	0.20	0.21	10.1
C_{33}	1.03	1.17	0.94	1.05	11.1	0.65	0.74	0.59	0.66	11.4
C_{34}	0.62	0.87	0.75	0.75	16.7	0.03	0.04	0.03	0.03	17.3
C_{35}	0.52	0.66	0.61	0.60	11.9	0.05	0.06	0.05	0.05	10.8

A temperature of about 35 °C was found to be the optimum condition for the sample vessel. Higher temperatures above this value showed an adverse effect on the recoveries of all the compounds. As the temperature of the sample vessel was increased to 50 °C, the extraction efficiencies would be reduced to about 2/3 of those conducted at 35 °C. It is well documented that at fixed pressure, higher temperatures lead to lower Sc CO_2 densities, which in turn lower the solvation power and result in lower extraction efficiencies [29]. Extraction at room temperature with liquid CO_2 was also investigated, the results showed no statistically significant differences as compared to those performed at 35 °C (Sc CO_2). These results show that both liquid CO_2 and lower temperature Sc CO_2 are suitable for this reported technique.

3.2. Analytical results of real-world samples

In order to investigate the feasibility of using dry ice for real-world sample extractions, one garden soil sample and one road dust sample were collected for the test. *n*-Alkanes and PAHs in the soil sample and the road dust sample were extracted and analyzed. Perdeuterated chrysene (D-chrysene) was spiked into the sample as a surrogate compound and, after extraction, squalane was added into the sample as an internal standard for GC quantification. Quantitative recovery was observed for the spiked D-chrysene from both the soil and the dust samples (95–105%), demonstrating that this technique is capable of quantitatively extracting semivolatile organic compounds.

Tables 2 and 3 show the analytical results of *n*-alkanes and PAHs in these samples. In the garden soil sample, no detectable PAHs were observed. In the road dust sample, only trace amounts of PAHs were detected. *n*-alkanes were relatively more abundant in both samples (Fig. 2). The R.S.D. for three repeated trials ranges from 3.4 (C_{24}) to 16.7% (C_{34}) for the road dust sample and from 3.1 (C_{31}) to 24.7% (C_{19}) for the garden soil (Table 2). The medians for these ranges are 8.5 and 10.8%, respectively, for the road dust and for the garden soil.

Different origins of *n*-alkanes were observed in the garden soil and the road dust samples. From the carbon preference index (CPI) values, the main contribution sources of the *n*-alkanes in these two different types of samples can be assessed. Repeated studies have shown that if CPI is close to unity, it is a good indication of high maturity suggesting a major anthropogenic contribution from petroleum product origin. For a CPI value greater than 6, it indicates a significant biogenic input from higher plants [30,31]. The road dust demonstrated a strong input from the anthropogenic source since its CPI value is close to 1.1, which implies the majority of the *n*-alkanes input comes from petroleum products (e.g. automobile exhausts, spilled or leaked lubricating oils, etc.). On the other hand, the *n*-alkanes in the garden soil sample showed a major contribution from biogenic source such as grass and tree leaves, since the CPI value is about 7.0.

The big “bump” under the *n*-alkanes peaks in road dust sample is another good indication of significant input from anthropogenic source, mainly petroleum products. This “bump” is from “unresolved complex matter” (UCM), which is a typical characteristic of man-made pollutants [31].

Table 3
Analytical results of PAHs in road dust ($\mu g\,g^{-1}$)

PAHs	1	2	3	Mean	R.S.D. (%)
Naphthalene	0.29	0.40	0.27	0.32	21.9
Fluorene	0.10	0.11	0.14	0.12	17.8
Phenanthrene	0.09	0.13	0.14	0.12	22.0
Fluorancene	0.52	0.56	0.48	0.52	7.7
Pyrene	0.74	0.68	0.61	0.68	9.6
Chrysene	0.33	0.43	0.37	0.38	13.4

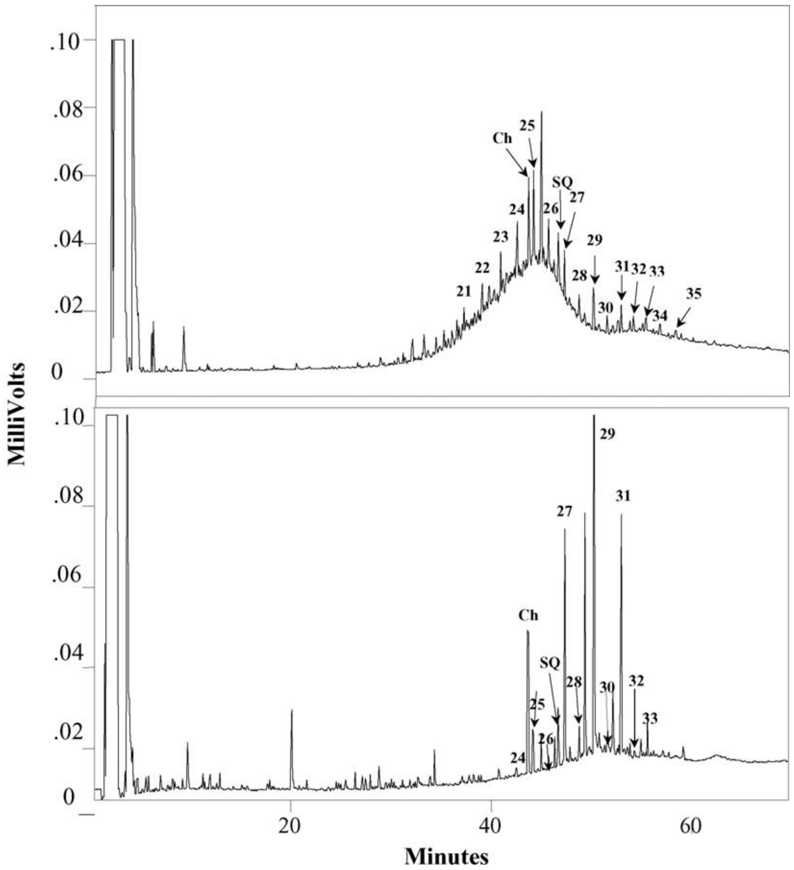

Fig. 2. Chromatograms of the dry ice SFE extracts from a road dust sample (upper) and a garden soil sample (lower). Ch: perdeuterated chrysene as a surrogate compound for extraction; SQ: squalane as an internal standard for GC analysis; numbers on peaks are the carbon numbers of the major *n*-alkanes.

For PAHs, only the most abundant fluorene, phenanthrene, fluoranthene, pyrene and chrysene were detected (Table 3). This result demonstrates exactly the same characteristics of PAHs in road dust samples reported by Rogge et al. [32]. Although naphthalene has a high vapor pressure, it was still detectable in this road dust sample. The R.S.D. for three repeated extractions is between 7.7 (fluorancene) and 22.0% (phenanthrene), with the median of the range lying at 15.6%. In the garden soil sample, no detectable PAHs were observed.

4. Conclusions

We have described a simple and effective supercritical or liquid carbon dioxide extraction technique that requires only two high-pressure stainless steel vessels (one for packing dry ice and the other for containing the sample of interest), two water bathes for temperature control purpose, and a box of dry ice. Coupled with a fluid modifier such as toluene, dry ice-originated supercritical or liquid CO_2 achieves quantitative extraction of several volatile organic compounds and semivolatile organic compounds including polycyclic aromatic hydrocarbons, *n*-alkanes, and polychlorinated biphenyls from sand, road dust, and garden soil. This technique has the advantages of requiring very low initial investment in equipment, being very economical to maintain and operate, and having high versatility and mobility for field or laboratory operations. 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 immediately in the field.

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