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Comparison of methods to prevent restrictor plugging during off-line supercritical extraction

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ABSTRACT

Real-world environmental samples which contain high concentrations of water and/or extractable matrix components frequently cause intermittent or irreversible plugging of capillary flow restrictors during off-line supercritical fluid extraction. Heating the entire restrictor at 50°C produces a constant extraction flow-rate (±0.03 ml/min) for such samples, but poor collection efficiencies (30–65% recovery for polycyclic aromatic hydrocarbons) were obtained because the supercritical fluid could not be depressurized directly into the collection solvent. While the collection efficiency was improved (80–90%) by nebulizing an organic solvent with the restrictor effluent, a simpler method was to heat all but the last 3 cm of the restrictor and to depressurize the extract directly in the collection solvent. Depending on the sample matrix, restrictor heater temperatures ranging from 50 to 200°C were required to avoid restrictor plugging. With proper heating, constant extraction flow-rates (±0.07 ml/min) and high collection efficiencies (90–100%) for polycyclic aromatic hydrocarbons and *n*-alkanes as volatile as *n*-octane were achieved.

INTRODUCTION

Efforts to reduce the use of potentially hazardous solvents and decrease sample preparation time has led to supercritical fluid extraction (SFE) becoming a popular alternative to conventional solvent extraction methods. A good deal of emphasis has been placed on the applications of SFE, but less has been reported about poor SFE flow rates which can occur from restrictor plugging during extraction and low collection efficiencies which can be associated with the methods (*e.g.*, heating) used to avoid restrictor plugging. Restrictor plugging can often occur during off-line SFE when the sample matrices contain high concentrations of water or extractable matrix components. Since the depressurization occurs at the restrictor tip and inside the restrictor [1], the reduction of the extraction fluid density within the restrictor can cause a decrease in the solubility of the analytes. The decrease in analyte solubility, combined with the Joule-Thomson cooling effect of the expanding extraction fluid at the restrictor exit, produces a subcritical solvent which may lead to analytes precipitating and, ultimately, plugging the inside of the restrictor. For example, cuticle waxes precipitate when supercritical CO_2 (99 atm, 40°C) is cooled to a subcritical liquid (69 atm, 0°C) [2]. In order to prevent such plugging, the restrictor can be heated to counteract Joule–Thomson cooling or constructed to minimize the pressure drop from the extraction cell to the restrictor outlet. Heating the restrictor may also increase the extraction fluid solubility of analytes having some volatility, since ex-

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traction fluid solubility (at a given density) generally mirrors analyte vapor pressure [3].

The most practical and popular method to prevent plugging during off-line SFE is to heat the restrictor using a linear flow restrictor generally consisting of silica capillary tubing [4–9] or a mechanical and/or electric feedback regulator [10–13]. The advantage of using an electric feedback regulator [12,13] is the reproducible flow achieved with a variable orifice. However, the equipment is expensive and not amenable to direct collection of extracted analytes in a small volume of organic solvent. Conversely, the simple linear restrictor has the advantage of being inexpensive and disposable, available with several inner diameters to achieve desired flow-rates, and the extracted analytes can be collected in a variety of collection systems. Unfortunately, the linear restrictors are more susceptible to plugging during the extraction of complex samples and are, therefore, frequently heated either directly with a heating element [4–9] or indirectly by warming the collection device [14]. Alternative methods include combining an organic solvent with the pressurized [15] or depressurized [16] extraction fluid, or maintaining the density of the extraction fluid in the linear restrictor by using a nitrogen- or argon-pressurized collection vessel [17–19].

In this study, three methods of heating a linear restrictor and their effects on analyte collection efficiencies were evaluated based on the criteria that the ideal system would eliminate restrictor plugging using cheap, disposable, fused silica restrictors which could easily be changed to vary the extraction flow-rate, but still produce quantitative collection efficiencies (*e.g.*, >90%) of the extracted analytes using only a few milliliters (2.5 to 5.0 ml) of organic collection solvent. The extraction flow rates and collection efficiencies of the various heater designs were determined by spiking polycyclic aromatic hydrocarbons (PAHs) onto silanized glass beads and performing SFE. The final design was further tested with a series of *n*-alkanes. The ability of the system to prevent restrictor plugging from the matrix components was ascertained by monitoring the SFE flow-rate while extracting several samples known to cause restrictor plugging.

EXPERIMENTAL

Supercritical fluid extractions

Supercritical fluid extractions were performed using SFC-grade carbon dioxide (Scott Gases; Plumsteadville, PA, USA) and an ISCO Model 260D syringe pump (ISCO, Lincoln, NE, USA) operated at 400 atm. The extraction cell and pre-equilibration coil [1 m × 0.76 mm I.D. × 1.6 mm (1/16 in.) O.D. coiled stainless-steel tubing placed before the extraction cell to pre-warm the CO_2 to the extraction temperature] were maintained at 50°C using a thermostatically-controlled tube heater. Extractions were performed using a 0.5-ml (30 mm × 4.6 mm I.D.) extraction cell from Keystone Scientific (Bellefonte, PA, USA). The flow-rate of the supercritical fluid through the extraction cell was measured as liquid CO_2 at the pump and was controlled by 11-cm-long restrictors (28 μm or 32 μm I.D. × 140 μm O.D.) cut from fused-silica tubing (Polymicro Technologies, Phoenix, AZ, USA).

Three restrictor heater designs were investigated. The first design was similar to the commercially available Dionex restrictor heater used in their model SFE-703 instrument [9] and consisted of a stainless-steel tube (110 mm × 0.25 mm I.D.), partially wrapped in flexible electrical heating tape which was insulated with Lytherm insulating material (Lydall, Rochester, NH, USA) and electrical insulation tape (Fig. 1). The heating system was regulated with a J thermocouple and a temperature controller unit (Model 6102; Omega, Stamford, CT, USA). The heating tape covered 9 cm of the 11-cm stainless-steel tubing, and the last 2 cm of tubing was heated only by conduction. All but the last 2 mm of the restrictor was encased in the heated stainless-steel tubing.

Extracted analytes were collected in a 7.4-ml collection vial (60 mm height × 10 mm I.D. neck) capped with a screw cap (possessing a hole) and two 15-mm diameter PTFE-faced silicone septa, into which was placed a 61-mm-long (5 mm O.D. × 3 mm I.D.) glass tube insert and a vent tube (Hypodermic needle, Stubs gauge 18), as shown in Fig. 1. No attempt was made to control the collection solvent temperature during SFE. Methylene chloride (5 ml, pesticide grade from Fisher, Springfield, NJ, USA) was the collection solvent. The solvent volume was maintained during SFE by introducing ad-

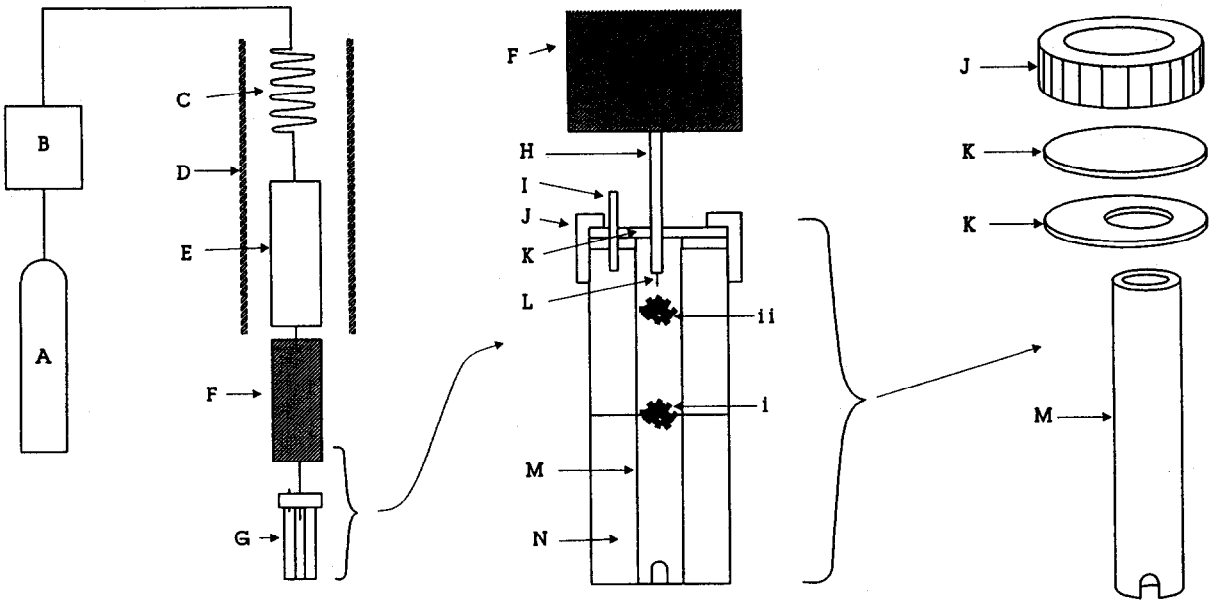

Fig. 1. SFE and restrictor heater apparatus. Components of extraction system are (A) CO_2 cylinder, (B) syringe pump, (C) pre-equilibration coil, (D) heating tube, (E) extraction cell, (F) heating tape wrapped around stainless-steel tubing and insulated with Lytherm insulating material and electrical insulating tape, (G) 7.4-ml collection vial, (H) stainless-steel tubing, (I) vent (hypodermic needle) (J) hole cap, (K) septum, (L) fused-silica restrictor, (M) glass tube, (N) 5 ml methylene chloride. Analytes deposit at points (i) and (ii) depending on the restrictor heater temperature, as discussed in the text.

ditional solvent through the septum with a hypodermic syringe. Using this arrangement, the restrictor effluent passed through the glass tube insert, into the collection solvent, and out the vent. To ensure a gas-tight seal between the insert and the collection vial septum, the glass tube was made *ca.* 1 mm longer than the length of the vial, thus, when the lid was screwed on, pressure was applied to the septum, forming a gas-tight seal.

The second restrictor heater design also encased the majority of the restrictor in heated stainless-steel tubing, using the same heating method as the first design. With the second design, an organic solvent was introduced at the tip of the restrictor and nebulized by placing a plastic tee-piece (3 cm long × 0.6 cm I.D.) between the restrictor and the glass tube. The three ends of the tee-piece were sealed with 6-mm rubber septa (Fig. 2). A single-piston reciprocating minipump (LDC Analytical, Riviera Beach, FL, USA) delivered organic solvent (0.3 ml/min) to the tee-piece. Extracted analytes were collected in the nebulized solvent which was transported through a 61-mm-long (5 mm O.D. × 3 mm I.D.) glass tube into a 7.4-ml collection vial (60 mm height × 10 mm I.D. neck) containing 5 ml methylene chloride (Fig. 2). The addition of the nebulizing solvent at 0.3 ml/min approximately balanced the collection solvent loss so that no further solvent addition was required during the extraction (solvent volume remained *ca.* 5 ml during SFE). No attempt was made to control the collection solvent temperature.

The third heated restrictor design (Fig. 3) used an insulated aluminum block (75 mm long × 20 mm diameter) with an electric cartridge heater (50 W, 40 mm long × 6 mm diameter). The temperature was regulated with a J thermocouple and a temperature controller unit (Model 6102, Omega). The restrictor was heated by inserting the fused-silica tubing through a 1-mm-diameter hole drilled through the heating block. Analytes were collected in a 3.7-ml collection vial (45 mm height × 8 mm I.D. neck) containing 2.5 ml of methylene chloride. Collection solvent volume was maintained by small additions

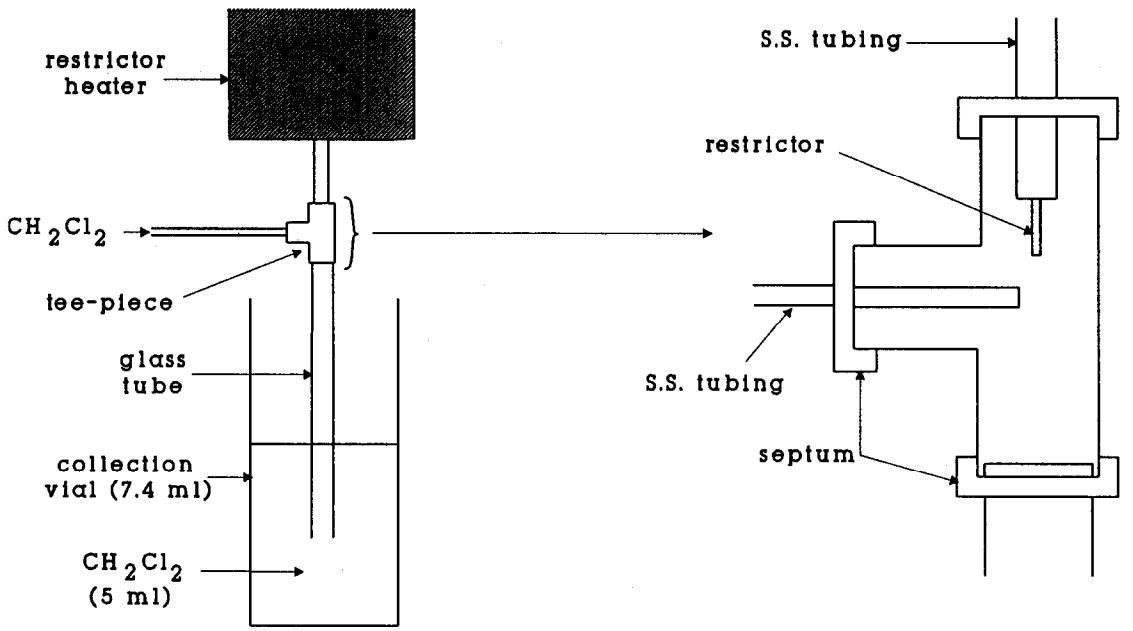

Fig. 2. Solvent nebulizer apparatus used in conjunction with the restrictor heater in Fig. 1 to introduce organic solvent (methylene chloride) to the tip of the capillary restrictor. See text for additional information. S.S. = stainless-steel.

of solvent during SFE. The collection vial was either free-standing in air (*i.e.*, no attempt to control collection solvent temperature) or placed in an aluminum block which contained a water-filled hole (26 mm deep × 23 mm I.D.) to accommodate the collection vial.

Standards and samples

Standards containing six PAHs ranging from naphthalene to chrysene (*ca.* 2.5 mg/ml each) or C_7 to C_{30} *n*-alkanes (*ca.* 1.7 mg/ml each) were prepared in methylene chloride and stored at −10°C until used. Spiking quantities for the individual PAHs and *n*-alkanes were at *ca.* 12.5 μg and 17 μg of each compound, respectively. Collection efficiencies were determined by filling the extraction cell with *ca.* 0.7 g of 70–80-mesh silanized glass beads (Analab, Norwalk, CT, USA) and spiking the PAH mixture (5 μl) or *n*-alkane mixture (10 μl) onto the top of the beads. The cell was immediately sealed to prevent any loss of the volatile components, placed inside the tube heater, equilibrated for 5 min, and then extracted for 10 min with CO_2 at 400 atm and 50°C. At the end of the extraction, the collection solvent was spiked with 5 μl (20 μg) of the internal standard *n*-heptadecane (for the PAHs) or 10 μl (26 μg) of the internal standard phenanthrene (for the *n*-alkanes) and analyzed using capillary gas chromatography (GC) with flame ionization detection (FID).

Five real-world samples with differing physical and chemical properties were chosen to test the ability of the restrictor heater to avoid restrictor plugging. The samples included railroad bed soil (Hastings, MN, USA), pine needles (Grand Forks, ND, USA), petroleum waste sludge (British Petroleum, USA), marine sediment standard reference material (SRM) 1941 [National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA], and elemental sulfur (99.999% pure, Aldrich, Milwaukee, WI, USA). Prior to SFE, the railroad bed soil was air-dried and sieved to <2 mm to remove any sticks and other debris, and 0.8 g of soil was placed in the extraction cell. The pine needles were freshly picked and cut into 10-mm lengths, and 0.35 g were immediately placed into the extraction cell. For the petroleum sludge, the extraction cell was initially half-filled with 70–80-mesh silanized glass beads and then filled with *ca.* 200 mg of sample. This ar-

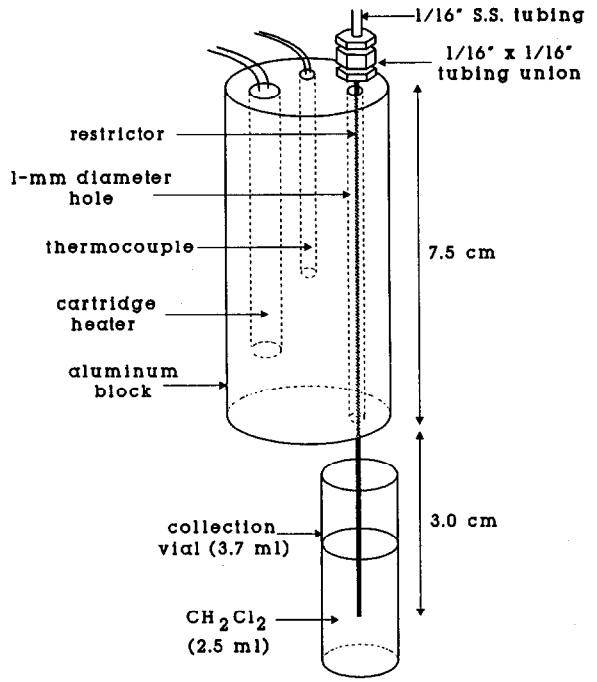

Fig. 3. Aluminum block restrictor heater apparatus. Fused-silica restrictor (11 cm long) was inserted through a 1-mm-diameter hole drilled through the alumininum heater block. The heater block was insulated with Lytherm insulating material and electrical insulating tape (for clarity, the insulating material and tape were omitted from the diagram). See text for additional information. S.S. = stainless-steel; " = inch.

rangement was required to prevent plugging of the 0.5 μm extraction cell frit, not the restrictor. The marine sediment (0.35 g) and elemental sulfur (0.4 g) were extracted without any preparation.

Gas chromatographic analysis

All GC analyses were done with a Hewlett-Packard 5890 gas chromatograph with FID and hydrogen as the carrier gas. The injections were performed in split mode with a 20:1 split ratio into a wide-bore (25 m × 0.32 mm I.D., 0.17 μm film thickness) HP-5 fused-silica capillary column. The injector and detector temperatures were maintained at 300°C. The oven temperature for the PAH analysis was 80°C at injection, followed by a temperature ramp at 8°C/min to 320°C. For the *n*-alkane analysis the oven temperature at injection was 35°C for 2 min followed by a temperature ramp at 8°C/min to 320°C.

RESULTS AND DISCUSSION

Depending on the nature of the sample, two different types of plugging have been encountered when using unheated capillary restrictors placed in a collection solvent. With some wet samples (more than *ca.* 1% water), the restrictor blocks as water freezes at the cooled restrictor outlet. Plugging from frozen water has previously been eliminated by maintaining the collection solvent temperature at 5°C with a thermostatically-controlled collection vial heating block [20]. The second type of plugging results from precipitated analytes and extracted matrix materials, and mostly occurs with samples containing very high concentrations of extractable components. Maintaining consistent SFE flow-rates with such samples requires the restrictor to be heated. Such heating has previously been achieved with a heat gun and produced reasonable extraction flow-rates, but also resulted in 20–50% loss of semi-volatile analytes [20].

In an effort to improve analyte collection efficiencies, a more controllable means of regulating the temperature of the restrictor was investigated by using a thermostatically-controlled restrictor heater with three restrictor heater designs (Figs. 1–3). The ability of the three designs to prevent restrictor plugging was assessed by extracting spiked PAHs from silanized glass beads. Since the spikes extracted very rapidly (within 2 or 3 void volumes of extraction system) and were present at a relatively high concentration (75 μg total PAHs), an unheated restrictor plugged very quickly upon commencing SFE. The PAH spike, therefore, proved to be a useful test for the ability of each restrictor heater design to prevent restrictor plugging. All three designs were able to maintain the extraction flow-rate, which could easily be varied by using the appropriate capillary restrictor. However, collection efficiencies varied for the three methods as discussed below.

Design 1, heating the whole restrictor

The initial restrictor heater design (Fig. 1) heated the whole restrictor (although the last 2 cm was indirectly heated as described in the experimental section). This eliminated restrictor plugging using either high (150°C) or low (50°C) restrictor heater temperatures. Reasonably constant extraction flow-

rates (*ca.* 0.75 ± 0.03 ml/min with the restrictor heater at 50°C) were obtained with a 28-μm I.D. restrictor, but the collection efficiencies were unacceptably low (*ca.* 30–65% recovery for the spiked PAHs), irrespective of analyte volatility or restrictor heater temperature (Table I). Visual inspection of the collection device indicated that the poor collection efficiencies were caused by the extraction fluid not depressurizing directly in the collection solvent, which led to some of the analytes depositing in the glass tube of the collection vial rather than in the collection solvent (i and ii in Fig. 1). Removing the crystallized analytes from the glass tube proved to be difficult as the collection vial had to be dismantled and the glass tube manually rinsed and/or sonicated with solvent. Simply shaking the vial to resolvate the analytes proved impractical as the solvent would leak out of the holes in the septum made by the restrictor heater and collection vial vent. The solvent rinse was combined with the collection solvent to produce a final collection volume of *ca.* 8 ml, and the combined solvent was used to obtain the collection efficiency values in Table I. Such deposition was most prevalent at the lower restrictor heater temperatures (50°C) where the majority of the analytes crystallized on the inside of the glass tube. In these instances, the tube was also sonicated in the collection solvent to remove the precipitated analytes.

TABLE I

COLLECTION EFFICIENCIES OF PAHs INTO METHYLENE CHLORIDE AT VARIOUS RESTRICTOR HEATER TEMPERATURES USING A 28-μm I.D. RESTRICTOR WITH THE GLASS TUBE INSERT COLLECTION VIAL (FIG. 1) OR THE SOLVENT NEBULIZER (FIG. 2)

PAH	Percent collected (R.S.D.)[a]			
	50°C[b]	100°C[b]	150°C[b]	50°C/CH_2Cl_2[c]
Naphthalene	55 (2)	63	64	95 (5)
Acenaphthylene	43 (4)	41	30	88 (5)
Fluorene	46 (13)	50	35	83 (4)
Phenanthrene	50 (16)	55	30	84 (3)
Fluoranthene	55 (12)	67	29	81 (3)
Chrysene	50 (1)	66	43	83 (3)

[a] Value in parentheses is the percent relative standard deviation (R.S.D.) of triplicate 10-min extractions. Recoveries for 100°C and 150°C restrictor heater temperatures were based on one extraction.

[b] Collection efficiencies achieved using the glass tube insert collection vial (Fig. 1). The recovery values were obtained from the combined solvent rinse and collection solvent. See text for additional information.

[c] Collection efficiencies obtained using the solvent nebulizer (Fig. 2).

Interestingly, the location of the crystallized analytes (i and ii in Fig. 1) was related to the physical state of the depressurizing extraction fluid. As the restrictor heater temperature was increased, the analytes were deposited further down the glass tube and further away from the restrictor outlet. Heating the restrictor heater above 100°C dramatically increased the effluent temperature (Fig. 4) and caused the disappearance of frozen CO_2 present at lower restrictor heater temperatures at the restrictor tip. The sudden increase in the restrictor effluent temperature corresponds to a previously reported [1] CO_2 phase change from a two-phase region of gas and solid to a single gaseous phase on expansion at temperatures of *ca.* >100°C. In the gas phase (restrictor heater 150°C), the analytes form very small solute particles (<0.2 μm [6]), leading to the formation of an aerosol. The aerosol is apparently swept along the glass tube until it reaches the cooled glass at the solvent boundary; at this location (Fig. 1, i), the less volatile analytes precipitated (*ca.* 20% fluoranthene and 40% chrysene precipitated in the glass tube; the rest of the PAHs including *ca.* 10% fluoranthene and 1% chrysene were recovered in the collection solvent). At lower restrictor heater temperatures (50°C), the majority of the analytes condensed in the glass tube near the restrictor outlet (Fig. 1, ii), and the collection solvent contained only the most volatile analytes (*ca.* 60% naphthalene and 45% acenaphthylene trapped in the collection solvent, the rest of the PAHs including *ca.* 5% acenaphthylene precipitated in the glass tube). It was also noted that small reversible changes in the flow-rate were obtained by heating the restrictor (Fig. 4), indicating that the restrictor heater has some potential to act as a fine SFE flow controller.

The restrictor heater design shown in Fig. 1 provides sufficient heat so that the collection solvent temperature was not significantly lowered during SFE (solvent temperature *ca.* 8°C after 10 min of extraction with the restrictor heater at 50 or 150°C), and resulted in an increase in solvent evaporation that may have caused the volatile analytes to be purged from the collection solvent. Because of the

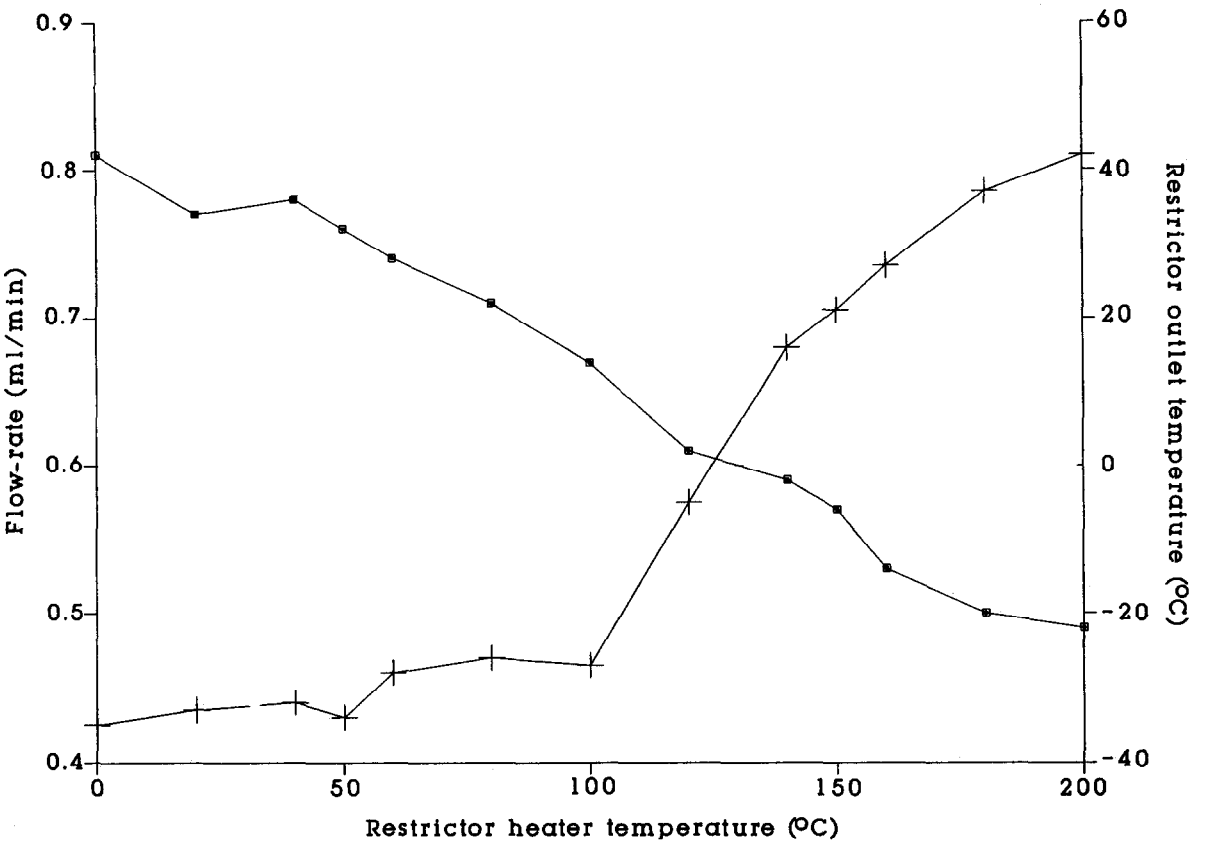

Fig. 4. Effect of restrictor heater temperature on the restrictor outlet temperature (+) and extraction flow-rate (⊡) using the glass tube insert collection vial (Fig. 1). Outlet temperature was measured with a J thermocouple placed at the restrictor exit. The large increase in restrictor outlet temperature corresponded to a phase change in the CO_2 exiting the restrictor. At restrictor heater temperatures of *ca.* > 100°C, the CO_2 was a gas, and at lower temperatures, the CO_2 was a mixture of gas and solid. SFE was performed at 400 atm and 50°C with a heated 11 cm × 28 μm I.D. capillary restrictor and a 0.5-ml Keystone extraction cell filled with silanized glass beads (70–80 mesh).

dimensions of the glass tube (3 mm I.D.), the extraction effluent escaped into the solvent as large bubbles. The formation of large bubbles in conjunction with a high gas flow (*ca.* 0.7 ml/min liquid CO_2, resulting in a gas flow of *ca.* 360 ml/min) and the small collection solvent volume (5 ml), apparently caused the poor trapping efficiencies. This was confirmed by analytes found deposited in the collection vial vent. A narrower glass tube insert (2 mm I.D.) was utilized in an attempt to reduce the bubble size; however, no improvement in collection efficiencies was obtained. A similar commercial system used by Dionex was able to obtain high collection efficiencies for PAHs (97% recovery for naphthalene [9]), using a larger solvent volume (15 ml), precooling of the collection solvent (cooled to *ca.* 0°C before the extraction), and lower extraction flow-rates (270 ml/min, *ca.* 0.5 ml/min liquid CO_2). Since the restrictor heater design shown in Fig. 1 did not meet all of the goals of good collection efficiencies, low solvent volumes and simplicity, other restrictor heater designs were investigated.

Design 2, post-extraction solvent nebulizer

The second design introduced an organic solvent (0.3 ml/min) at the tip of the restrictor (Fig. 2) in an attempt to increased solute/solvent contact, and increase the amount of analyte transported to the bulk collection solvent. The design also allowed for a simplified collection vial which only required a

relatively small (5 ml) collection solvent volume. The restrictor effluent nebulized the solvent introduced into the tee-piece to form a fine mist which was swept down the glass tube and into the bulk collection solvent. Using this method, no analyte deposition was seen along the glass tube and no additional solvent was required to maintain the solvent volume in the collection vial (solvent volume remained *ca.* 5 ml during SFE). The collection efficiencies for the PAHs were greatly improved (81–95%, Table I) and were attributed to increased solvent contact with the depressurized extract at the restrictor oulet. Low (50°C) restrictor heater temperatures were still sufficient to avoid restrictor plugging, since the solvent did not come in direct contact with the restrictor, thus reducing restrictor cooling. The nebulizer design produced constant extraction flow-rates (*ca.* 0.7 ± 0.05 ml/min) at low restrictor heater temperatures (50°C), but still did not meet the goals of simplicity (*i.e.*, an additional pump was required) and quantitative collection efficiencies (*e.g.*, >90%).

Design 3, heated restrictor placed in collection solvent

In an attempt to improve the collection efficiencies and further simplify the collection apparatus, the third design placed the restrictor directly into the collection solvent without any transfer device (Fig. 3). To minimize the non-heated zone of the restrictor (*i.e.*, the restrictor tip in the collection solvent), the restrictor length was kept to a minimum (11 cm), high restrictor heater temperatures (100 to 200°C) were applied, and small (3.7 ml) collection vials with small collection solvent volumes (2.5 ml) were used. This design used an aluminum heating block to heat the restrictor, as the heating block was less of a fire hazard in the presence of evaporating solvents than the heating tape used in designs 1 and 2.

The restrictor block heater produced reasonable extraction flow-rates (0.7 ± 0.07 ml/min) for the spiked PAHs, but required higher restrictor heater temperatures (100–150°C) to eliminate restrictor plugging due to Joule–Thomson cooling of the restrictor tip in the collection solvent. Quantitative collection efficiencies (*ca.* 90–95%, Table II) were obtained, presumably because direct depressurization of the extraction fluid into the collection solvent increased the solute–solvent contact and greatly reduced the solvent evaporation as the collection solvent temperature was quickly lowered to below 0°C during the extraction (Fig. 5). Very small bubbles were observed at the restrictor outlet, the increased viscosity of the cooled solvent possibly reducing the size of the bubbles which increases the solute–solvent resonance time [21]. Increasing the extraction flow-rate from 0.6 to 0.7 ml/min liquid

TABLE II

COLLECTION EFFICIENCIES OF PAHs INTO METHYLENE CHLORIDE AT VARIOUS RESTRICTOR HEATER TEMPERATURES AND SFE FLOW-RATES BY DIRECT DEPRESSURIZATION OF THE EXTRACTION FLUID INTO THE COLLECTION SOLVENT (FIG. 3)

PAH	Percent collected[a]					
	28-μm I.D. restrictor[b]			32-μm I.D. restrictor[c]		
	50°C	100°C	150°C	50°C	100°C	150°C
Naphthalene	Blocked[d]	Blocked	90.8 (1.3)	Blocked	89.9 (2.1)	91.1 (3.0)
Acenaphthylene	Blocked	Blocked	94.0 (0.9)	Blocked	91.7 (2.1)	90.8 (5.1)
Fluorene	Blocked	Blocked	93.7 (3.0)	Blocked	93.1 (1.8)	91.9 (5.1)
Phenanthrene	Blocked	Blocked	95.5 (1.6)	Blocked	95.3 (0.2)	94.1 (1.4)
Fluoranthene	Blocked	Blocked	95.7 (1.8)	Blocked	95.6 (0.5)	99.4 (2.0)
Chrysene	Blocked	Blocked	90.1 (1.1)	Blocked	96.1 (2.1)	92.4 (2.0)

[a] Value in parentheses is the percent relative standard deviation of triplicate 10-min extractions.
[b] Flow-rate *ca.* 0.61 ml/min liquid CO_2 at pump.
[c] Flow-rate *ca.* 0.85 ml/min at restrictor heater temperature of 100°C and *ca.* 0.69 ml/min at restrictor temperature of 150°C.
[d] Restrictor becomes blocked after a few minutes so that no flow is present.

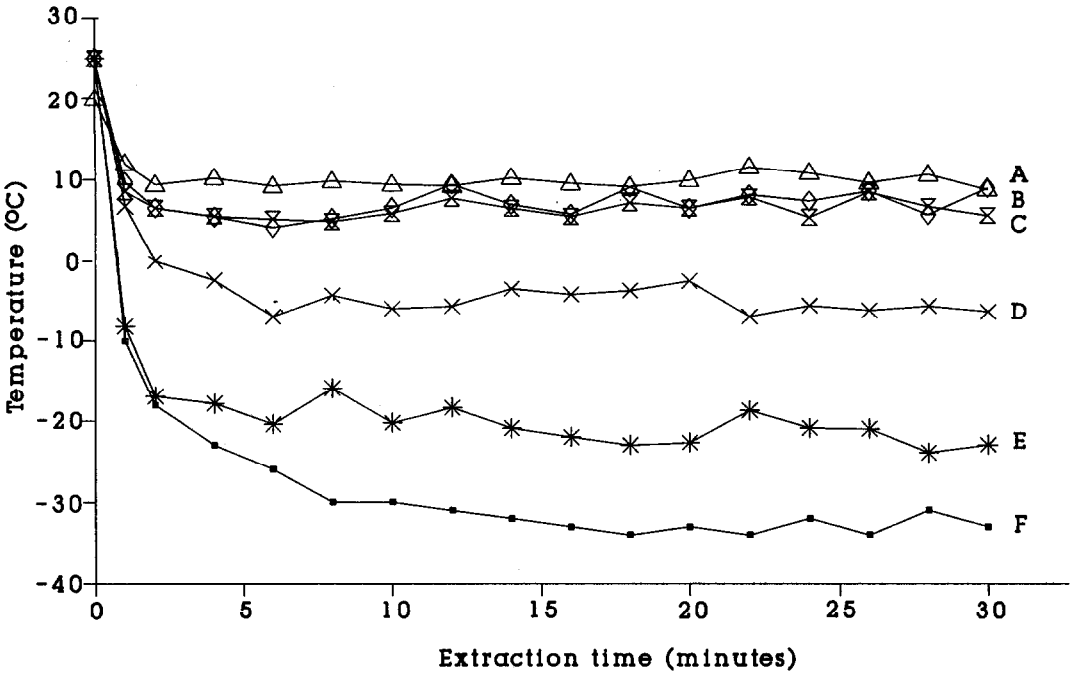

Fig. 5. SFE collection solvent temperature at various restrictor heater temperatures, with the extraction fluid being directly depressurized into the collection solvent (Fig. 3). Temperature profiles are shown for the collection solvent (2.5 ml) in a 3.7-ml vial standing in water with an 11 cm × μm I.D. restrictor heated to 200°C (A), restrictor heated to 100°C (B), no restrictor heating (C), or with the collection solvent vial in air with an 11 cm long × 28 μm I.D. restrictor heated to 200°C (D), restrictor heated to 100°C (E), and no restrictor heating (F).

CO_2 (*i.e.*, using 28- and 32-μm I.D. restrictors, respectively) enabled a lower restrictor heater temperature (100°C) to be used, which still eliminated restrictor plugging and produced quantitative (*ca.* 90–95%) collection efficiency (Table II).

The collection efficiencies using the restrictor block heater were further investigated using a test mix of *n*-alkanes possessing a large range of volatilities. At low restrictor heater temperatures (50 and 100°C) analytes as volatile as *n*-octane could be efficiently collected (>90%). However, at higher restrictor heater temperatures (200°C), *n*-decane was the most volatile species that was efficiently collected (Table III). The decrease in collection efficiencies with increasing restrictor temperature was presumed to be due to an increase in aerosol formation at the restrictor outlet and purging of volatile components due to an increase in the collection solvent temperature (Fig. 5).

Since previous work had shown that maintaining the solvent temperature above 0°C improved the extraction flow-rate for wet samples [20], a collection vial water bath was combined with the restrictor heater to assess the influence of collection solvent temperature on collection efficiencies. By placing the collection vial in a container of water initially at room temperature, the cooling effect of the expanding fluid in the solvent was reduced, so that the collection solvent temperature was stabilized at *ca.* 5–10°C (Fig. 5), and reasonable flow-rates were attained. Maintaining the collection solvent temperature at 5–10°C significantly reduced the collection efficiencies of the very volatile analytes (*ca.* 40% recovery for *n*-heptane, Table III) and also increased solvent evaporation. However, *n*-decane could still be efficiently trapped (*ca.* 90%) at all the restrictor heater temperatures investigated, even with the collection solvent temperature maintained above 0°C.

Since depressurizing the heated restrictor directly

TABLE III

COLLECTION EFFICIENCIES OF *n*-ALKANES INTO METHYLENE CHLORIDE (2.5 ml) AT VARIOUS RESTRICTOR HEATER TEMPERATURES USING A 28-μm I.D. RESTRICTOR DEPRESSURIZED DIRECTLY INTO THE COLLECTION SOLVENT (FIG. 3)

Collection vial in	*n*-Alkane		Percent collected[a]				
			No heating[b]	50°C	100°C	150°C	200°C[c]
Air	Heptane	(C_7)	78.1 (1.8)	73.9 (3.3)	71.8 (6.9)	71.5 (5.9)	56.5 (15.9)
	Octane	(C_8)	90.6 (0.8)	92.3 (1.5)	90.8 (7.9)	88.7 (6.3)	79.9 (9.3)
	Nonane	(C_9)	94.8 (0.9)	92.4 (2.1)	93.3 (8.7)	94.5 (5.2)	89.4 (6.9)
	Decane	(C_{10})	98.2 (0.7)	96.1 (3.0)	96.6 (8.7)	97.7 (3.5)	93.8 (6.2)
	Pentadecane	(C_{15})	97.1 (1.6)	101.5 (5.3)	99.0 (7.7)	95.5 (3.4)	93.2 (2.9)
	Eicosane	(C_{20})	97.7 (2.2)	103.4 (3.7)	102.3 (5.2)	95.1 (2.8)	95.0 (3.4)
	Pentacosane	(C_{25})	100.8 (1.1)	104.5 (2.0)	98.4 (5.0)	98.3 (3.2)	94.0 (9.1)
Water	Heptane	(C_7)	44.0 (13.1)	42.2 (15.7)	38.1 (8.0)	34.0 (8.6)	34.2 (16.2)
	Octane	(C_8)	73.0 (5.8)	71.8 (6.8)	71.9 (5.3)	68.8 (3.8)	70.0 (7.0)
	Nonane	(C_9)	85.6 (2.9)	85.5 (5.9)	88.1 (4.7)	81.5 (4.0)	86.4 (5.0)
	Decane	(C_{10})	94.2 (1.7)	90.7 (5.0)	93.0 (4.4)	87.9 (4.2)	92.2 (3.9)
	Pentadecane	(C_{15})	97.5 (2.7)	97.0 (4.1)	96.0 (5.5)	92.8 (2.2)	93.4 (1.7)
	Eicosane	(C_{20})	97.0 (1.4)	97.7 (5.3)	93.1 (6.8)	94.0 (0.9)	96.5 (2.5)
	Pentacosane	(C_{25})	99.0 (3.6)	93.8 (3.3)	101.3 (3.7)	100.0 (3.8)	95.5 (4.4)

[a] Value in parentheses is the percent relative standard deviation of triplicate 10 minute extractions.
[b] Flow-rate *ca.* 0.81 ml/min liquid CO_2.
[c] Flow-rate *ca.* 0.59 ml/min liquid CO_2.

into the collection solvent appeared to meet the goals of simplicity, small collection solvent volumes (*ca.* 2.5 ml), quantitative collection efficiencies, and reasonable extraction flow-rates (*ca.* 0.7 ± 0.07 ml/min), a range of environmental samples was chosen to assess the restrictor heater's ability to avoid restrictor plugging. The samples were selected from over a hundred different samples, and the majority represented the worst cases of restrictor plugging encountered during past studies. The samples included (i) an air-dried railroad bed soil (*ca.* 1%, w/w, water) which is fairly typical of soils in regard to restrictor plugging; (ii) pine needles (*ca.* 80%, w/w, water) containing cuticle wax and producing intermittent restrictor plugging; (iii; petroleum waste sludge (*ca.* 45%, w/w, water) contaminated with *ca.* 10% (w/w) extractable hydrocarbons and causing intermittent/complete blockage of the restrictor; (iv) a NIST marine sediment (SRM 1941) with *ca.* 2% elemental sulfur [22] and causing intermittent/complete blockage of the restrictor; and (v) elemental sulfur which causes rapid blocking of an unheated restrictor.

For the majority of the samples, a continuous flow was achieved by heating the restrictor to the experimentally-determined temperature, which in some cases was as high as 200°C (Table IV). To avoid restrictor plugging, none of the samples except elemental sulfur required the collection solvent to be temperature controlled by placing the collection vial in water, which is advantageous since allowing the collection solvent temperature to drop below 0°C during the extraction improves the collection efficiencies of very volatile analytes, as shown in Table III. A constant flow (0.7 ± 0.1 ml/min) was attained for most of the test samples during the 30-min extraction (Fig. 6). However, for the petroleum waste sludge which contained a large concentration of extractable material, the flow-rate initially decreased and then stabilized with time. Reasonable flow-rates were also obtained for samples containing large amounts of water, such as fresh pine needles (80%, w/w, water) and petroleum waste sludge (45%, w/w, water). It appeared that the temperature inside the heated restrictor was sufficient to avoid water freezing at the restrictor tip,

TABLE IV

EFFECT OF RESTRICTOR HEATER TEMPERATURE ON SFE FLOW-RATES WITH SEVERAL SAMPLES KNOWN TO CAUSE RESTRICTOR PLUGGING USING A 30-μm I.D. RESTRICTOR DEPRESSURIZED DIRECTLY INTO THE COLLECTION SOLVENT (FIG. 3)

Sample	Qualitative flow[a]				
	No heating	50°C	100°C	150°C	200°C
Railroad bed soil	Blocked	Continuous	Continuous	Continuous	Continuous
Pine needles	Blocked	Blocked	Continuous	Continuous	Continuous
Marine sediment	Blocked	Blocked	Intermittent	Continuous	Continuous
Petroleum waste sludge	Blocked	Blocked	Blocked	Intermittent	Continuous
Elemental sulfur	Blocked	Blocked	Blocked	Blocked	Continuous[b]

[a] The flow-rates are assessed as continuous (constant flow ± 0.1 ml/min), intermittent (flow varies and may temporarily stop for 1 or 2 s), or blocked (no flow). SFE conditions: 0.5-ml Keystone extraction cell filled with sample, exposed for 30 min to 400 atm and 50°C CO_2 with a heated 11 cm × 30 μm I.D. capillary restrictor. Collection vial in air unless otherwise indicated.

[b] Collection vial in water (initially at room temperature).

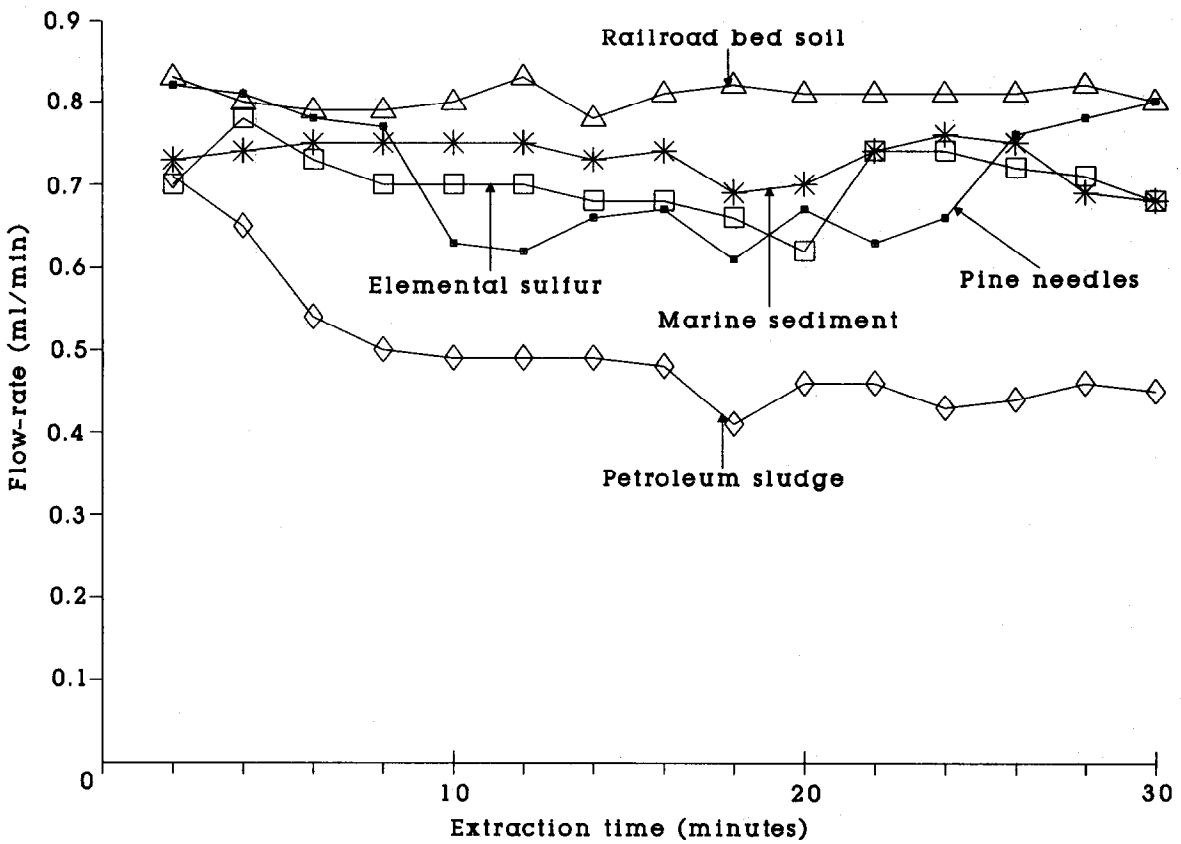

Fig. 6. Changes in flow-rate during SFE of railroad bed soil (0.8 g), marine sediment (0.35 g) and petroleum sludge (200 mg), with the extraction fluid being directly depressurized into the collection solvent (Fig. 3). SFE was performed at 400 atm and 50°C with a heated (150°C) 11 cm × 30 μm I.D. capillary restrictor and a 0.5-ml Keystone extraction cell. Flow-rate measured as liquid CO_2 at pump.

even when the collection vial was not placed in water and the collection solvent was allowed to cool below 0°C.

In this study, there was no evidence of thermal degradation of analytes, as no qualitative differences could be found between SFE extracts obtained with and without a heated restrictor. Since the time spent in the heated restrictor is short, thermal degradation seems unlikely, particularly for species that are thermally stable enough to be analyzed by GC. In the worst case, where no density decrease along the restrictor is assumed, an analyte requires only *ca.* 10^{-2} s to be transported through an 11 cm × 28 μm I.D. restrictor at 0.5 ml/min liquid CO_2 flow-rate (this value may be halved if the density decrease along the restrictor is included [1]). In the unlikely event that thermal degradation does become a problem for extremely sensitive analytes, then the nebulizer design which operated at lower restrictor heater temperatures (50°C) may be more appropriate. The results of this study demonstrate that the restrictor heater design which allowed direct depressurization of the SFE extract into the collection solvent best achieved the goals of simplicity, low collection solvent volume, quantitative collection efficiencies, and the elimination of restrictor plugging.

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