Inexpensive Fluid Delivery System for Supercritical Fluid Extraction

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1 Introduction

Supercritical fluid extraction, a process well accepted by chemical engineers [1, 2], has recently attracted deserved attention on the part of analytical chemists [3–12]. This separation technique exploits the properties of the compressed gas, in most cases inexpensive and non-toxic carbon dioxide, at temperatures and pressures above its critical point.

Very often the major limitation to the wide application of analytical supercritical fluid extraction systems is associated with the use of expensive high pressure pumps. Syringe, membrane, and dual piston pumps designed to supply liquids have been reported for this application. In addition to the high cost, these devices are often unreliable for the delivery of fluids whose critical temperatures are below (Xe) or slightly above (CO_2, N_2O) room temperature. The main reason for this is that the supercritical fluid has a much lower viscosity than a "normal" liquid and therefore the pump "leaks" if its head is above the critical temperature of the fluid. In order to prevent these problems, cooling of the heads is necessary [13, 14].

This paper describes an alternative low-cost method for supercritical fluid delivery based on high pressure vessels. The method is able to provide a continuous supply of well-controlled high pressured fluid for extraction. The other advantage of this approach over pumps includes its potential application in the more selective static rather than the commonly used dynamic (leaching) method of extraction.

2 Experimental

The high pressure vessels were constructed of stainless steel in the Science Machine Shop at the University of Waterloo [15] or purchased (High Pressure Equipment Co., Erie, Pennsylvania). Their volumes are about 200 mL and the vessels are made to withstand pressures in excess of 1,400 atm. The vessel is equipped with a safety valve containing disks which rupture at 7,000 atm. This type of safeguard is extremely important to protect the operator in the case of manual and/or electronic temperature control failure. The 0.25" inside diameter copper

tubing is welded to the outside surface of the vessel. This system is used to pass liquid nitrogen to cool the vessel to below the critical point of the fluid during servicing, just before filling it up with liquid fluid. The liquid nitrogen is supplied from a single stainless steel thermos. The vessel is heated using a beaded heater (Cole Palmer, Chicago, IL). The pressure is monitored visually by using a pressure gauge (Linde, Union Carbide, Toronto, Ont.) and electronically by a pressure transducer (Model AB, Data Instruments, Lexington, MA.) interfaced to PC-AT compatible computer (Trillium AT, Waterloo, Ont.) equipped with an IBM-DACA acquisition board (IBM, Danbury, CT) and ASYST software (ASYST Software Technologies, Inc., Rochester, N.Y.). The temperature in the high pressure vessel and extraction vessel is monitored using thermistors (Radio Shack, Barrie, Ontario). The pressure in the extraction system is controlled by using the simple electronic circuit shown in **Figure 1** and timer circuit. The pressure is first set by adjusting the position of the variable resistor (Figure 1). When the output voltage from the pressure transducer exceeds a set value, the state of the comparator output changes, switching off the supply of the power to the heater. The switching on and off is done with the help of a solid state relay (Model EOM-1DA42-3/32, Potter and Brumfield, Princeton, IN). A similar circuit was designed to control the temperature in the extraction vessel. The continuous mode of operation of the supercritical fluid delivery system was achieved by connecting outputs of two high pressure vessels to a single electronically
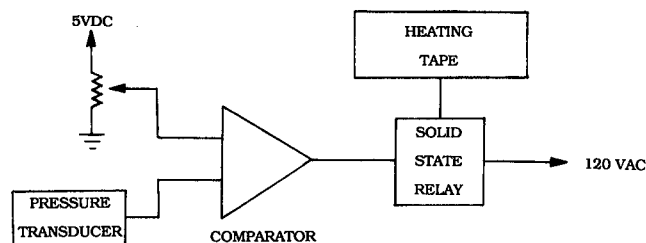

Figure 1

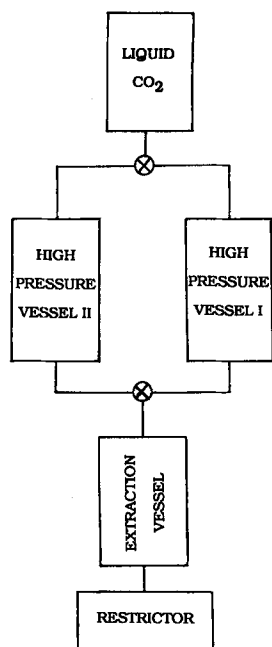**Electronic circuit to control extraction pressure.**

Figure 2

Continuous source of fluid using two high pressure vessels.

Figure 3

Schematic of fluid source for supercritical fluid extraction based on high pressure vessel.
1 high pressure vessel; 2 safety valve; 3 pressure/electrical transducer; 4 temperature/electrical transducer; 5 heating/cooling jacket; 6 electrical heater; 7 extraction vessel; 8 restrictor; 9 source of cooling fluid; 10 source of heating fluid; 11 activated carbon trap.

controlled valve (Valco Instrument Co., Inc. Houston, TX) (**Figure 2**). Initially, one of the vessels supplied the fluid to the extraction system while the other vessel was serviced and then stabilized at the extraction pressure. After a period of time, when the supply of fluid from the first vessel was low (as indicated by its high temperature), the valve was switched to allow use of the second vessel.

3 Discussion

Figure 3 outlines the principle of the design and operation of the high pressured fluid source based on the heated pressure vessel. In the first step, the high pressure container (1) is cooled to below the critical temperature of the fluid (for CO_2, t_c is 32 °C), using a source of coolant (9). The vessel is then filled with liquid fluid from a high pressure cylinder. In the next step, the vessel is heated. This significantly increases the pressure in the vessel. The pressure is monitored and regulated electronically by using a pressure transducer (3) coupled to the thermostat (10) which controls the temperature of the vessel. Supercritical fluid at a well regulated pressure is then supplied to the extraction vessel (7).

It should be emphasized that the density of the fluid in the extraction vessel (7) and therefore its solubility and extraction properties [2] are independent of that which exists, in a high pressure container (1). Only the extraction pressure is determined by the conditions in the larger volume vessel (1). The extraction temperature which determines the density of the fluid is regulated independently by using a heater (6). This approach is significantly different from that used in batch extractors where the liquid fluid is poured directly into the extraction vessel [16]. The system illustrated in Figure 3 applies a separate high pressure vessel and allows much better control of extraction conditions which are required in analytical applications.
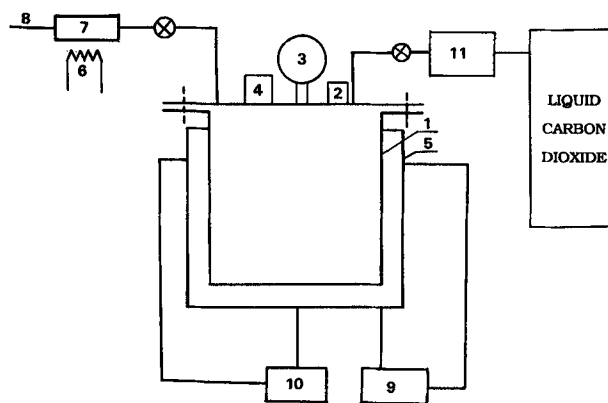
The actual design of the high pressure vessel is not crucial. For example, in our initial investigations we used a vessel which had originally been designed for preparing slurry packed columns for HPLC. This allowed us to initiate research in supercritical fluid extraction virtually without any initial instrumentation cost. It must be ensured, however, that the vessel will withstand pressures several times higher than determined by the rupture disk to allow for safety margin. In practice, the heating of the vessel is best achieved by resistive heating and the cooling by passing the ice water and/or liquid nitrogen through the metal tubes welded to the surface of the vessel.

The high pressure vessel (Figure 3) is supplied with liquid gas from a bottle containing high purity grade fluid. The amount of liquid transferred to the vessel from the bottle is closely related to the temperature to which the high pressure container is cooled. The density of the fluid increases significantly with decrease in the temperature close to critical pressure [2].

Figure 4 shows a typical relationship between the pressure of carbon dioxide contained in the high pressure vessel and its temperature. As expected the pressure increases with temperature increase. Three different curves correspond to different initial temperatures of the high pressure vessel at which the device was filled with liquid CO_2. If the vessel is charged at temperatures close to room conditions ($\approx$20 °C, Figure 4 A) then it must be heated to about 45 °C to supply fluid at extraction conditions which are usually close to 300 atm. On the other hand, by cooling the vessel below –15 °C (Figure 4 C) the same pressures can be achieved below 0 °C. The density of the liquid carbon dioxide is about 0.8 g/mL at room temperature and at –15 °C it is about 1.0 g/mL. The amount of CO_2 in the vessel cooled to –15 °C is approximately 30 % more compared to the same container kept at a temperature close to room conditions. Therefore, the larger amount of CO_2 can be provided for extraction. It should be remembered, however, that it is difficult to control temperatures below ambient conditions. Accidental increase of the tempera-
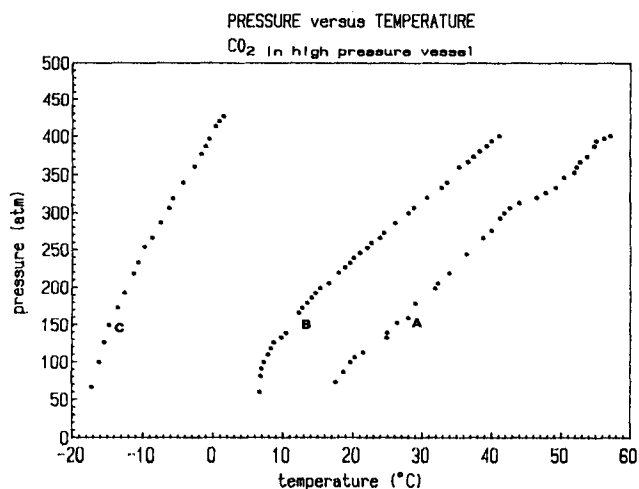
PRESSURE versus TEMPERATURE

CO$_2$ In high pressure vessel

Figure 4

Pressure _vs._ temperature relationship for different initial temperatures.
A) Vessel was filled with liquid carbon dioxide at 19 °C. B) 7 °C. C) −17 °C.

ture of the vessel associated with Figure 4 C might cause crossing the safety pressure determined in our system by the rupture disk.

The pressure slowly drops when the fluid is used for extraction. This is compensated by raising the temperature of the high pressure vessel. The amount of fluid which is available in a single cycle for extraction is determined by the volume of the high pressure vessel and its maximum temperature. In our design this limit was at 140 °C. The density of the carbon dioxide at this temperature and the extraction pressure of 400 atm is about 0.5 g/mL. Therefore, we are able to use 30–50 % of carbon dioxide depending on the initial and final temperature. In our application the vessel was usually cooled to −15 °C and its final temperature was set to 60 °C. This narrow temperature range ensured the constant temperature of the fluid reaching the extractor. 50 cm of $^1/_{16}''$ stainless steel tubing connecting the high pressure vessel and the extraction vessel was used to allow equilibration of the fluid temperature under ambient conditions. This permitted constant temperature at the extraction vessel independent of the state of the high pressure vessel. This temperature was within 1 °C from the set value even at flow rates of expanded gas in excess of 300 mL/min.

The small diameter of the fused silica capillary ($\approx$20 μm) ensures that all pressure drops occur at the restrictor and not at the transfer lines. The pressure in the extraction vessel was identical to the condition of the high pressure vessel in the investigated flowrate ranges between 0–300 mL/min. Using a simple control circuit (indicated on Figure 1) we were able to obtain stable pressure output with very low frequency ripple (cycle length of about 10 min) of magnitude of about ±8 atm at nominal pressure of 400 atm. This effect corresponded to an on/off state of the heater. No other variation of the pressure was detected. The magnitude of the ripple is reduced substantially if a commercially available proportional-integral-derivative (PID) controller (Ome-

ga Engineering, Stanford, CT) replaces the simple circuit from Figure 1. However, this upgrade significantly increases the overall cost of the delivery system.

The 200 mL vessel used in this study can supply about 50 L of CO$_2$ gas at ambient pressure. This corresponds to about 5 h of continuous supercritical fluid extraction with the 20 μm restrictor (the CO$_2$ flow rate is close to 150 mL/min). This time is much longer compared to a few minutes it takes to complete a single supercritical extraction process [3–12]. Continuous supply of the fluid can be ensured by using two vessels connected "in parallel" to the extraction system (Figure 2). While the first high pressure container is being used to supply the fluid to the extraction vessel the other vessel is serviced. The pressure in the second vessel is then brought to the required extraction pressure. After a set maximum temperature is reached in the first vessel the valve is switched. Now, the fluid is supplied from the second vessel while the first vessel undergoes a service. This involves a cooling process, refilling, and heating to achieve the required pressure. This cycle repeats as long as a continuous supply of CO$_2$ is required.

The system can be easily miniaturized by replacing the high pressure vessels with pieces of stainless steel tubing. However, in this case, the amount of supercritical fluid available from a single piece of tubing for extraction will be limited. This might be sufficient for the extraction of small amounts of sample followed by direct deposition onto a capillary column [10, 17]. If a continuous supply of supercritical fluid is necessary, the system made from two pieces of tubing connected in a parallel configuration (similar to Figure 2) supplied with the check valves can be applied. This system is much safer, considering the small diameters of the tubes. The tubes can be made very small, however, this would require rapid heating/cooling cycles to supply the needed flow rate of the fluid for extraction. This necessitates development of good electronic control [18].

The cost of the fluid delivery system based on the principle described in this paper can be negligible since it can be constructed from parts readily available in most analytical laboratories and certainly should not exceed the $ 1,000 mark, even when a large volume high pressure vessel is purchased commercially. The specific design of such a device is related to the availability of parts and the imagination of the researcher. We are presently involved in research to improve the performance design of such a device based on this general concept. Some initial results describing the application of supercritical fluid extraction and this fluid delivery system to the isolation of organic material from fly ash matrix has been described in reference [19].

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Further Applications of Permethylated β-Cyclodextrin Capillary Gas Chromatographic Columns

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1 Introduction

The development of derivatized cyclodextrin capillary columns represents an important advance in gas chromatography. *Casu et al.* [1] first investigated the use of permethylated cyclodextrins as gas chromatographic stationary phases either pure or dissolved in methyl silicone in packed columns. They utilized hydrocarbon solutes and suggested an inclusion phenomenon was operative. *Tanaka et al.* [2] used permethylated β-cyclodextrin packed columns to separate alkanes, alcohols, and alkylbenzenes. The use of glass capillary columns coated with permethylated β-cyclodextrin was reported by *Juvancz et al.* [3]. These workers prepared van Deemter plots for the column at different temperatures. Compared to 200 °C the column efficiency dramatically decreased at 140–150 °C which they attributed to slow mass transport in the supercooled liquid (permethylated β-cyclodextrin has a melting point of 175 °C [4]). To improve chromatographic properties *König* and co-workers [5] prepared per-pentylated cyclodextrins which are liquids below room temperature. Using 2,3,6-tri-O-pentylated and 3-O-acetylated 2,6-di-O-pentylated