

# Construction of a robust stainless-steel clad fused-silica restrictor for use in supercritical fluid extraction

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## ABSTRACT

Fused-silica restrictors used for off-line supercritical fluid extraction (SFE) frequently break when extractions are performed with polar supercritical fluids [*e.g.*,  $\text{CHClF}_2$  (Freon 22) or  $\text{CO}_2$  containing polar modifiers (*e.g.*, methanol)]. Securing the fused-silica restrictor inside a 1/16 in. (1.6 mm) O.D. stainless-steel tube with an epoxy resin eliminated the restrictor breakage and allowed restrictors to be connected to the extraction cell with conventional stainless-steel fittings. The stainless-steel clad fused-silica restrictor was simple and inexpensive to construct, physically robust, and proved ideal for SFE applications since no artifacts from the clad restrictor were detected in the collection solvent.

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## INTRODUCTION

The linear flow or capillary restrictor constructed of fused-silica tubing is the most common type of restrictor used in analytical-scale supercritical fluid extraction (SFE), because the restrictors are inexpensive, disposable, available with several inner diameters to achieve desired flow-rates, and can be used with a variety of collection systems. However, these restrictors often break when they are used with polar fluids such as  $\text{CHClF}_2$  (Freon 22) [1] and when polar modifiers such as methanol [2] are added to  $\text{CO}_2$ . Fused-silica restrictors clad in an external tube may reduce the breakage that occurs with polar fluids [3-5]. The aim of this study was to construct an inexpensive, simple, robust, and

disposable restrictor which could be used with a number of polar SFE fluids without breakage. This was achieved by using an epoxy resin to secure the fused-silica capillary restrictor inside a stainless-steel tube.

## EXPERIMENTAL

### *Construction of stainless-steel clad restrictor*

Stainless-steel clad restrictors were made from either 32  $\mu\text{m}$  I.D.  $\times$  145  $\mu\text{m}$  O.D. fused-silica tubing (Polymicro Technologies, Phoenix, AZ, USA) inserted into 1/16 in. (1.6 mm) O.D.  $\times$  0.02 in. (0.51 mm) I.D. stainless-steel tubing, or 29  $\mu\text{m}$  I.D.  $\times$  370  $\mu\text{m}$  O.D. fused-silica tubing inserted into 1/16 in. (1.6 mm) O.D.  $\times$  0.03 in. (0.76 mm) I.D. stainless steel tubing. A 5-ml disposable plastic syringe with a male Luer lock outlet (Becton Dickinson & Co, Rutherford, NJ, USA), the fused-silica restrictor, and the stain-

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less-steel tube were connected to a 1/16 in. (1.6 mm) stainless-steel tee-piece so that the fused-silica restrictor extended through the stainless-steel tube and the tee-piece (Fig. 1). The fused-silica restrictor was then secured inside the stainless-steel tube by injecting an epoxy resin "Epo-tek 353ND" (Epoxy Technology, Billerica, MA, USA) from the syringe into the metal tubing to fill the void space between the stainless-steel tube and the fused-silica restrictor. The epoxy-filled tube containing the restrictor was then disconnected from the tee-piece and placed in a 80°C oven for 2 h to cure the epoxy resin. Finally, the excess fused-silica protruding from the stainless-steel tubing was removed using a scoring tool (Supelco, Bellefonte, PA, USA), or the metal tubing was cut with an SSI tube cutter (SSI, State College, PA, USA) so that the fused-silica restrictor was flush with the tube. Note, when using the SSI cutter, cylinder pressure CO<sub>2</sub> (ca. 90 atm) was flowed through the restrictor to avoid blocking the restrictor tip with pieces of metal.

#### Evaluation of stainless-steel clad restrictors

The ability of the stainless-steel clad fused-silica restrictor to avoid restrictor breakage during SFE was evaluated using pure supercritical fluid chromatography (SFC)-grade CO<sub>2</sub>, CHClF<sub>2</sub> (Freon 22), premixed CO<sub>2</sub>-methanol (90:10, v/v), or CO<sub>2</sub>-toluene (90:10, v/v) (Scott Gases, Plumsteadville, PA, USA). Each fluid was pumped by an ISCO Model 260D syringe pump

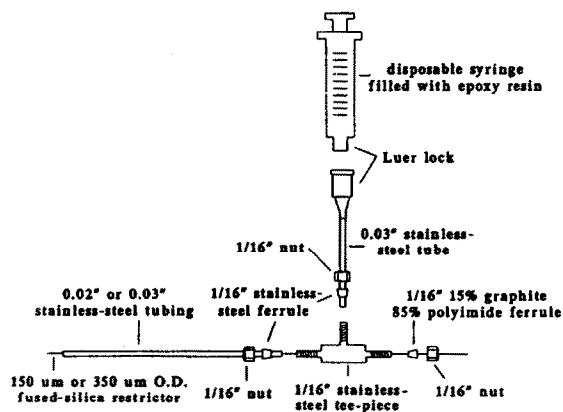


Fig. 1. Equipment used to construct stainless-steel clad fused-silica restrictors. " = inch.

(ISCO, Lincoln, NE, USA) which was connected to an empty 0.5-ml extraction cell (30 mm long × 4.6 mm I.D.) with 1/16 in. (1.6 mm) O.D. stainless-steel tubing and "Slip-free" fingertight connectors (Keystone Scientific, Bellefonte, PA, USA). A 1-m long coil of 1/16 in. (1.6 mm) tubing (placed before the extraction cell to pre-warm the fluid to the extraction temperature) and the extraction cell were placed inside a tube heater to maintain the extraction temperature. The flow-rate of the supercritical fluid through the extraction cell was controlled by a 10-cm long fused-silica restrictor or 10-cm long stainless-steel clad fused-silica restrictor connected to a "Slip-free" fingertight connector via a tubing union (1/16 in. × 1/16 in.). The outlet of the restrictor was inserted into a 7.4-ml vial containing 5 ml pesticide-grade methylene chloride [for GC-flame ionization detection (FID) analysis] or 5 ml Fisher "Optima Grade" acetone [for GC-electron-capture detection (ECD) analysis] to simulate normal SFE procedures. Collection solvent volume was maintained by small additions of solvent during SFE.

The 1-m long tubing and the empty 0.5-ml extraction cell were pre-heated in a tube heater for 15 min before SFE at 400 atm (1 atm = 1.01 · 10<sup>5</sup> Pa) was begun with pure CO<sub>2</sub> (60°C or 150°C), CO<sub>2</sub>-toluene (90:10) (80°C), CO<sub>2</sub>-methanol (90:10) (60°C), or CHClF<sub>2</sub> (100°C). The supercritical fluid was pumped through the extraction system until either the restrictor broke or until the complete 240 ml volume of pressurized fluid in the syringe pump had been used (ca. 4 h).

To determine whether the epoxy resin used in the construction of the stainless-steel clad restrictors could contribute artifacts to the SFE extracts, 500 mg cured epoxy resin (0.5–0.2 mm pieces) was placed on a bed of 80-mesh silanized glass beads inside a 0.5-ml extraction cell and extracted for 20 min with 400 atm CO<sub>2</sub>-methanol (90:10) at 60°C or 400 atm CHClF<sub>2</sub> at 100°C at a flow-rate of ca. 0.8 ml/min of compressed fluid (measured at the pump).

#### RESULTS AND DISCUSSION

Using the syringe device shown in Fig. 1, several of the clad restrictors can be made in one

hour. If wide bore (0.03 in. I.D.) stainless-steel tubing is used in the construction, up to 50 cm of the clad restrictor could be produced at one time and then cut into the desired lengths. For the smaller 0.02 in. I.D. stainless-steel tube only ca. 15 cm lengths of clad restrictor can be made because of the added pressure needed to inject the epoxy.

As shown in Table I, the conventional fused-silica restrictors did not break when pure CO<sub>2</sub> (60°C and 150°C) or CO<sub>2</sub>-toluene (90:10) were used as the extraction fluids. However, when the polar fluids CO<sub>2</sub>-methanol (90:10) or CHClF<sub>2</sub> were used with the conventional fused-silica restrictors, the restrictors soon became brittle and broke into two or more pieces. Restrictor breakage with CHClF<sub>2</sub> proved to be the worst for the supercritical fluids so far encountered [1]. Longer extraction times were possible using a thick walled (*i.e.*, 370 μm O.D.) instead of a thin walled (*i.e.*, 145 μm O.D.) fused-silica restrictor with the polar fluids, however within ca. 30 min even the thick walled restrictors had broken. Similar breakage problems have been encountered with several different batches of fused-silica tubing.

Examination of the broken fused-silica restrictor tip under the light microscope (×80 magnification) revealed an uneven break with fine cracks and grooves along the broken surface. Conversely, a freshly cut restrictor using a scor-

ing tool had a "clean" break and the cut surface had a smooth, uniform appearance. The presence of cracks and grooves in the restrictor may be related to the increased instability of glass and fused-silica in the presence of polar solvents like methanol [6]. Furthermore, the location of the break in the fused-silica restrictor was random, and the ability of the restrictor to withstand polar supercritical fluids varied. When breakages occur above the collection solvent, not only is the extract lost, but the analyst experiences a significant risk of exposure when toxic compounds are being extracted. Fortunately, by securing the fused-silica restrictor inside a stainless-steel tube, restrictor breakage due to polar fluids was eliminated for the maximum time tested (*e.g.*, ca. 4 h, Table I).

As shown in Figs. 2 and 3, the epoxy resin used to secure the fused-silica restrictor in the stainless-steel tube did not add significant contaminants to the extracts since none of the SFE [*e.g.*, 400 atm CO<sub>2</sub>-methanol (90:10) at 60°C and 400 atm CHClF<sub>2</sub> at 100°C] extractable components from the 0.5-g cured epoxy resin sample (Fig. 2iii, iv and Fig. 3iii, iv) were detected in the collection solvent from the blank extractions using the clad restrictors (Fig. 2i, ii and Fig. 3i, ii). However, trace amounts (ppb concentration) of several other components were found in the collection solvent from the clad restrictor evaluation, though the majority of

TABLE I

BREAKING TIMES FOR FUSED-SILICA RESTRICTORS AND STAINLESS-STEEL CLAD FUSED-SILICA RESTRICTORS WITH DIFFERENT SUPERCRITICAL FLUIDS

Supercritical fluid	Time <sup>a</sup>			
	29 μm I.D. × 370 μm O.D. restrictor	32 μm I.D. × 145 μm O.D. restrictor	29 μm I.D. × 370 μm O.D. stainless-steel clad restrictor	32 μm I.D. × 145 μm O.D. stainless-steel clad restrictor
400 atm 60°C or 150°C CO <sub>2</sub>	>4 h	>4 h	>4 h	>4 h
400 atm 80°C CO <sub>2</sub> -toluene (90:10)	>4 h	>4 h	>4 h	>4 h
400 atm 60°C CO <sub>2</sub> -methanol (90:10)	Broke (28 ± 5 min)	Broke (5 ± 2 min)	>4 h	>4 h
400 atm 100°C CHClF <sub>2</sub>	Broke (23 ± 3 min)	Broke (7 ± 5 min)	>4 h	>4 h

<sup>a</sup> >4 h is the time taken to pump the contents of a 260-ml syringe pump through the restrictor and the time in parentheses is the time elapsed before the restrictor physically broke. All the evaluations were carried out in triplicate.

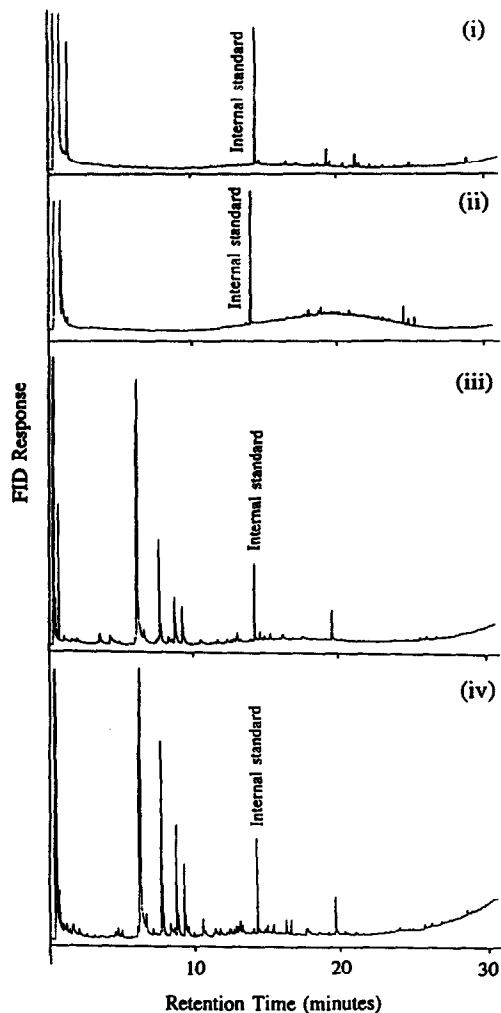


Fig. 2. Gas chromatography with flame ionization detection (GC-FID) analysis of the collection solvent used to collect the extracts from: (i) CO<sub>2</sub>-methanol (90:10) using a stainless-steel clad fused-silica restrictor; (ii) CHClF<sub>2</sub> (Freon 22) using a stainless-steel clad fused-silica restrictor; (iii) a 0.5-g sample of cured epoxy resin extracted with CO<sub>2</sub>-methanol (90:10); (iv) a 0.5-g sample of cured epoxy resin extracted with CHClF<sub>2</sub>. Analysis was performed on a 25 m × 0.32 mm I.D. (0.17 μm film thickness) HP-5 fused-silica capillary column with an oven temperature program of 40°C followed by a temperature ramp at 8°C/min to 300°C. Phenanthrene was the internal standard (54 μg was added to the 5 ml collection solvent used for the epoxy resin extract and 3 μg was added to the 5 ml collection solvent used for the restrictor evaluation). The detection limit for the internal standard was *ca.* 75 pg in the splitless mode (3:1 signal-to-noise ratio).

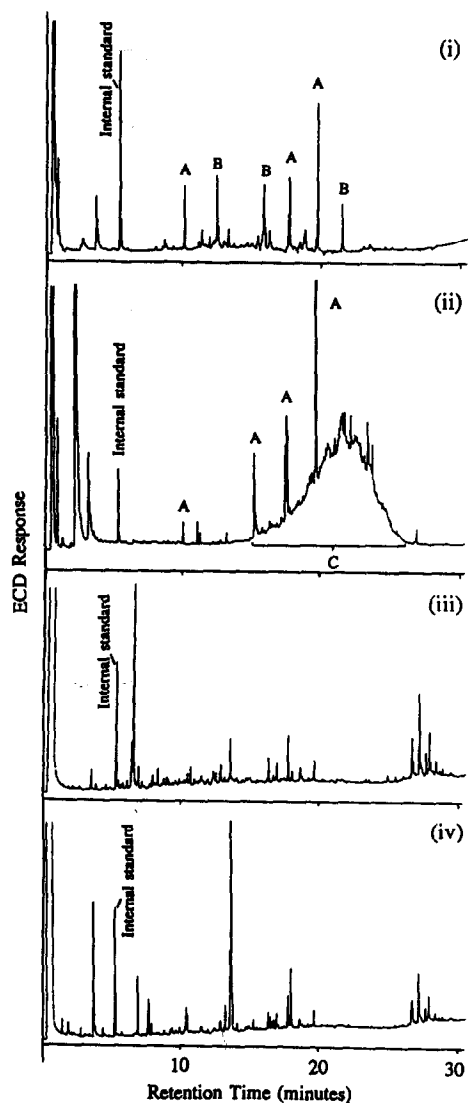


Fig. 3. Gas chromatography with electron capture detection (GC-ECD) analysis of the collection solvent used to collect the extracts from: (i) CO<sub>2</sub>-methanol (90:10) using a stainless-steel clad fused-silica restrictor; (ii) CHClF<sub>2</sub> (Freon 22) using a stainless-steel clad fused-silica restrictor; (iii) a 0.5-g sample of cured epoxy resin extracted with CO<sub>2</sub>-methanol (90:10); (iv) a 0.5-g sample of cured epoxy resin extracted with CHClF<sub>2</sub>. Peaks marked A were contaminants from the acetone collection solvent, B from the methanol-modified CO<sub>2</sub>, and C from the CHClF<sub>2</sub> extraction fluid. GC column and temperature program conditions were the same as Fig. 2. 1,2,4-Trichlorobenzene was the internal standard (2.0 μg added to the 5 ml collection solvent used for the epoxy resin extract and 0.2 μg added to the 5 ml collection solvent used for the restrictor evaluation). The detection limit for the internal standard was *ca.* 2 pg in the splitless mode (3:1 signal-to-noise ratio).

these were artifacts found to be from the collection solvent (acetone), the modifier (methanol), or the  $\text{CHClF}_2$  extraction fluid (Fig. 3i, ii). Furthermore, since the trace contaminants were also present in the collection solvent when using a conventional unclad fused-silica restrictor, it is clear that the epoxy resin used to construct the stainless-steel clad restrictors did not contribute detectable contaminants to the SFE extracts. (Note, Clark and Jones [7] also successfully used the epoxy resin "Epo-tek 353 ND" to secure a fused-silica restrictor to a capillary column in a SFC system, and no contaminants from the epoxy resin were detected in the chromatograms.)

#### CONCLUSIONS

The breakage of fused-silica restrictors which occurs with polar supercritical fluids was prevented by securing the restrictor inside a stainless-steel tube with an epoxy resin. The stainless-steel clad fused-silica restrictors are simple, inexpensive, several restrictors can be made in an hour, and the epoxy resin does not contribute significant contaminants to the SFE extracts. The clad restrictor is also easy to connect to the extraction apparatus since a standard 1/16 in. stainless-steel ferrule can be used.

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