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Estimating flow-rates for sub- and supercritical fluid extractions with linear restrictors

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Abstract

The fluid flow-rate through a linear capillary restrictor depends on the type, pressure and temperature of the fluid as well as the length and internal diameter of the restrictor. A simple mathematical correlation was established for calculating the flow-rate of CO_2 and water through a capillary restrictor during dynamic flowing sub- and supercritical fluid extractions. Calculated flow-rate values compared favorably with the experimentally determined values for three cases: supercritical CO_2 extraction with the entire restrictor out of the supercritical fluid extraction oven, supercritical CO_2 extraction with restrictor inlet inside the supercritical fluid extraction oven, and sub- and supercritical water extraction.

1. Introduction

Since supercritical fluid extraction (SFE) is mostly performed under dynamic flowing extraction conditions [1], flow-rate is one of the important parameters which can influence extraction efficiencies for both supercritical CO_2 [2,3] and subcritical water extraction [4,5]. Because of their low cost, linear restrictors made from fused-silica tubing are often used for flow control in SFE. While there are several reports on estimating fluid flow-rate in supercritical fluid chromatography (SFC) [6–8], the calculations are frequently complex and fail to predict flow-rates for SFE. For example, differences between calculated and measured SFE flow-rates using the methods in Refs. [6–8] were typically up to ± 100%, possibly because in SFC, the restrictor is inside the SFC oven or heated detector (therefore, restrictor temperature $\geq$ SFC oven temperature); while for SFE, the entire restrictor (or at least the outlet of the restrictor) is outside the SFE oven during the extraction (restrictor temperature $\leq$ SFE oven temperature). Another reason might be that SFE flow-rates (ml/min) are normally much higher than SFC flow-rates (μl/min). In the present study, a simple mathematical correlation was developed for calculating fluid flow-rates through linear restrictors during sub- and supercritical fluid extractions with CO_2 and water.

2. Experimental

2.1. CO_2 extractions

CO_2 was pressurized by an ISCO (Lincoln,

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NE, USA) Model 260D syringe pump into a 0.8-ml cell (50 mm × 4.6 mm I.D., Keystone Scientific, Bellefonte, PA, USA). The extraction temperature was controlled by placing both the extraction cell and a 1-m-long preheating coil made from 1/16 in. O.D. × 0.020 in. I.D. (1 in. = 2.54 cm) stainless-steel tubing inside a Hewlett-Packard 5890 Series II gas chromatograph. Fused-silica tubing with 9 to 50 μm I.D. (Polymicro Technologies, Phoenix, AZ, USA) was used for outlet restrictors to obtain flow-rates of ca. 0.005 to 5 ml/min (measured as liquid CO_2 at the pump). Exact internal diameters of the restrictors were measured and specified by the manufacturer. Since it takes ca. 10 min to get flow-rate equilibrium after refilling the pump or filling the extraction cells, an accurate CO_2 flow-rate can only be read after this equilibrium time. CO_2 flow-rates were determined for two different arrangements for the restrictor. The first approach had the entire restrictor outside the SFE oven (there is a shut-off valve between extraction cell and restrictor). In the second approach, the restrictor was directly connected to the extraction cell, which means that the restrictor inlet was inside the SFE oven, and the restrictor outlet was outside the SFE oven.

2.2. Water extractions

The setup for water extractions was similar to CO_2 extractions with the entire restrictor outside the SFE oven except that an ISCO Model μLC-500 pump was used instead of an ISCO Model 260D pump. Because the polyimide seals used in the SFE cells failed at high temperatures, empty HPLC columns (30 mm × 4.6 mm I.D., 0.48 ml; Keystone Scientific) were used as extraction cells for the higher extraction temperatures (250–400°C). Water flow-rate was measured as liquid water at the pump.

3. Results and discussion

3.1. Flow-rate dependence on pressure

Fig. 1 shows that flow-rates obtained experimentally are directly proportional to pressure; therefore, an equation expressing flow-rate in terms of pressure can be delivered as follows:

$$F = \chi_p P \qquad (1)$$

where F is flow-rate in ml/min (liquid CO_2 or liquid water); P is pressure in atm (1 atm = 101 325 Pa); χ_p is a constant which is dependent on the type and temperature of the fluids, and the length and internal diameter of the restrictor. χ_p can be experimentally determined. Please note that χ_p is different if one of the parameters (the type and temperature of the fluids; the length and internal diameter of the restrictor) is changed [e.g.: the χ_p values in Fig. 1 (bottom) are $3 \cdot 10^{-3}$, $1.8 \cdot 10^{-3}$ and $4.8 \cdot 10^{-4}$ for restrictor lengths 10, 20 and 50 cm, respectively]. Flow-rate can be estimated by Eq. 1 with the help of experimentally determined χ_p. The calculated flow-rates using Eq. 1 are also shown in Fig. 1 (solid lines) which indicates a good agreement with experimental values. Once χ_p is known, Eq. 1 is applicable for all three extraction cases: CO_2 extraction with the entire restrictor outside the SFE oven, CO_2 extraction with the inlet of the restrictor inside the SFE oven, and water extraction.

3.2. Flow-rate dependence on internal radius of the restrictor

Restrictor internal radius (I.D./2) has a very strong influence on flow-rate for both CO_2 and water. Based on the experimental values as shown in Fig. 2, functions between flow-rate and restrictor internal radius can be established as below

$$F = \chi_r R^3 \qquad (2)$$

for CO_2 and

$$F = \chi_r R^5 \qquad (3)$$

for water, respectively;

where R is the internal radius of the restrictor in μm; χ_r is a constant dependent on the type, pressure and temperature of the fluids, and restrictor length. Using experimentally determined χ_r, Eqs. 2 and 3 give very close values

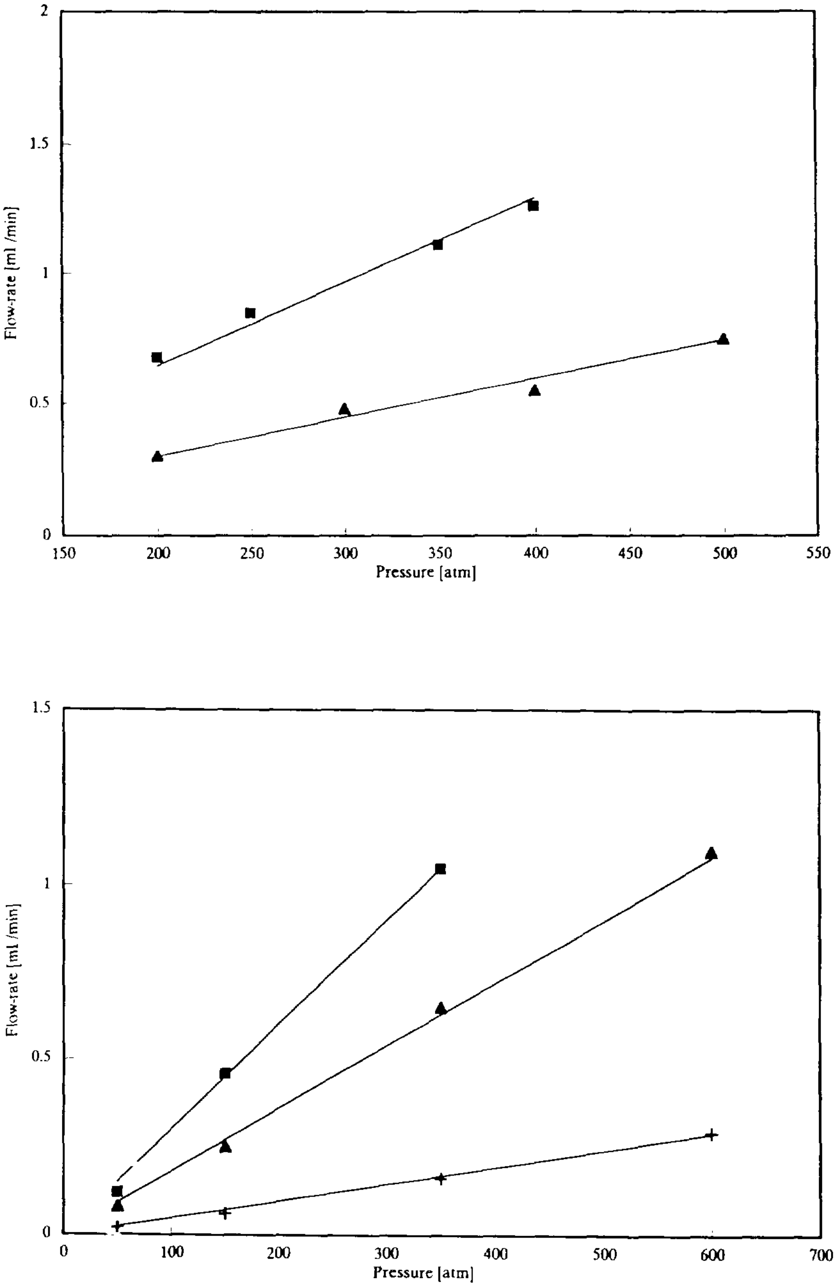
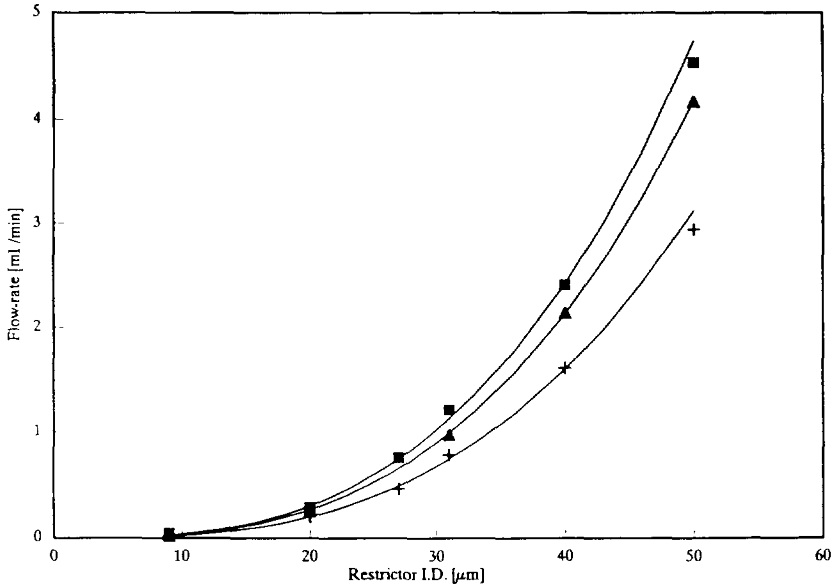


Fig. 1. Influence of pressure on flow-rate of CO_2 (top) and water (250°C, bottom). Experimental and calculated flow-rates are shown in symbols and lines, respectively. Top: ■ = 10 cm × 30 μm I.D. restrictor, outside the oven, 200°C; ▲ = 10 cm × 25 μm I.D. restrictor, inlet inside the oven, 80°C. Bottom: ■ = 10 cm × 30 μm I.D. restrictor; ▲ = 20 cm × 30 μm I.D. restrictor; + = 50 cm × 30 μm I.D. restrictor.



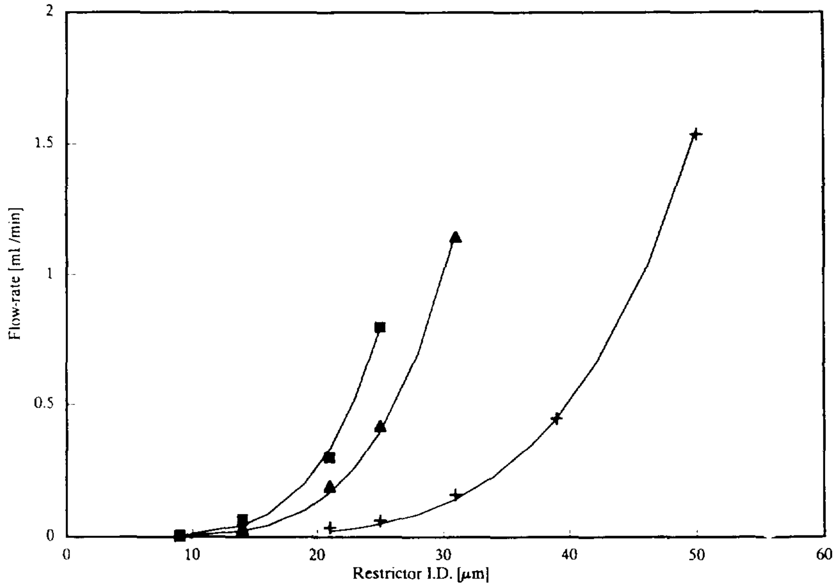


Fig. 2. Influence of internal diameter of restrictor on flow-rate of CO_2 (80°C, top) and water (250°C, bottom). Experimental and calculated flow-rates are shown in symbols and lines, respectively. Top: ■ = 10 cm restrictor (outside the oven), 400 atm; ▲ = 10 cm restrictor (inlet inside the oven), 400 atm; + = 10 cm restrictor (inlet inside the oven), 200 atm. Bottom: ■ = 10 cm restrictor, 600 atm; ▲ = 10 cm restrictor, 350 atm; + = 10 cm restrictor, 50 atm.

(solid lines) compared to experimental flow-rates (Fig. 2).

3.3. Flow-rate dependence on the length of the restrictor

Inverse proportional relationships between flow-rate and restrictor length were found and expressed by following equations

$$F = \chi_l / L^{0.5} \tag{4}$$

for CO_2 and

$$F = \chi_l / L \tag{5}$$

for water, respectively;

where L is restrictor length in cm; χ_l is a constant dependent on the type, pressure and temperature of the fluids, and the internal radius of the restrictor. χ_l can be determined by experimental flow-rates. Fig. 3 shows both experimental and calculated flow-rates using restrictors having different lengths.

3.4. Flow-rate dependence on temperature

The flow-rate of CO_2 extractions with the entire restrictor outside the SFE oven remained unchanged at extraction temperatures from 50 to 250°C (Fig. 4, top). The reason might be that the entire restrictor is out of the SFE oven (the temperature being much lower than that inside the oven), so that the flow-rate is much less influenced by extraction temperature. Once the restrictor inlet is directly connected to the extraction cell (the inlet of the restrictor is inside the SFE oven and the outlet of the restrictor is outside the oven), the extraction temperature does influence the CO_2 flow-rate (Fig. 4, top). In this case, the influence of temperature on CO_2 flow-rate can be expressed as

$$F = \chi_t / T \tag{6}$$

where T is extraction temperature in K; χ_t is a constant dependent on the pressure CO_2, and the length and internal radius of the restrictor and can be experimentally determined.

Like the flow-rate of CO_2 with the entire restrictor outside the SFE oven, water flow-rate is almost constant for high-temperature (200–450°C) extractions. However, at temperatures lower than 200°C, water flow-rate was decreased by lowering extraction temperatures (Fig. 4, bottom). Since a temperature around or higher than 250°C is required to extract non-polar organics using water [4,5], the mathematical correlation given below is established for a temperature range of 200–450°C. However, it should be easy to correct water flow-rates at temperatures lower than 200°C based on the relationship between water flow-rate and temperature (50–200°C) shown in Fig. 4, bottom (as discussed below).

3.5. Mathematical correlation of flow-rate

CO_2 flow-rates with the entire restrictor out of the SFE oven

Since the flow-rate of CO_2 is constant at a temperature range of 50–250°C, only Eqs. 1, 2 and 4 need to be considered. Thus, the expression of CO_2 flow-rate can be given by

$$F = 2.8 \cdot 10^{-6} PR^3 / L^{0.5} \tag{7}$$

where the constant $2.8 \cdot 10^{-6}$ was determined by experimental flow-rates, F is the flow-rate in ml/min, P is pressure in atm, R is the internal radius of the restrictor in μm and L is the restrictor length in cm. Table 1 gives some calculated flow-rates using Eq. 7 in comparing with experimental values, and good agreement was obtained.

CO_2 flow-rates with the restrictor inlet inside the SFE oven

In this case, we have to consider the influence of temperature on CO_2 flow-rate. To do this, we need to combine Eqs. 6 and 7, and obtain CO_2 flow-rate by

$$F = 7.6 \cdot 10^{-4} PR^3 / (TL^{0.5}) \tag{8}$$

where the constant $7.6 \cdot 10^{-4}$ was experimentally

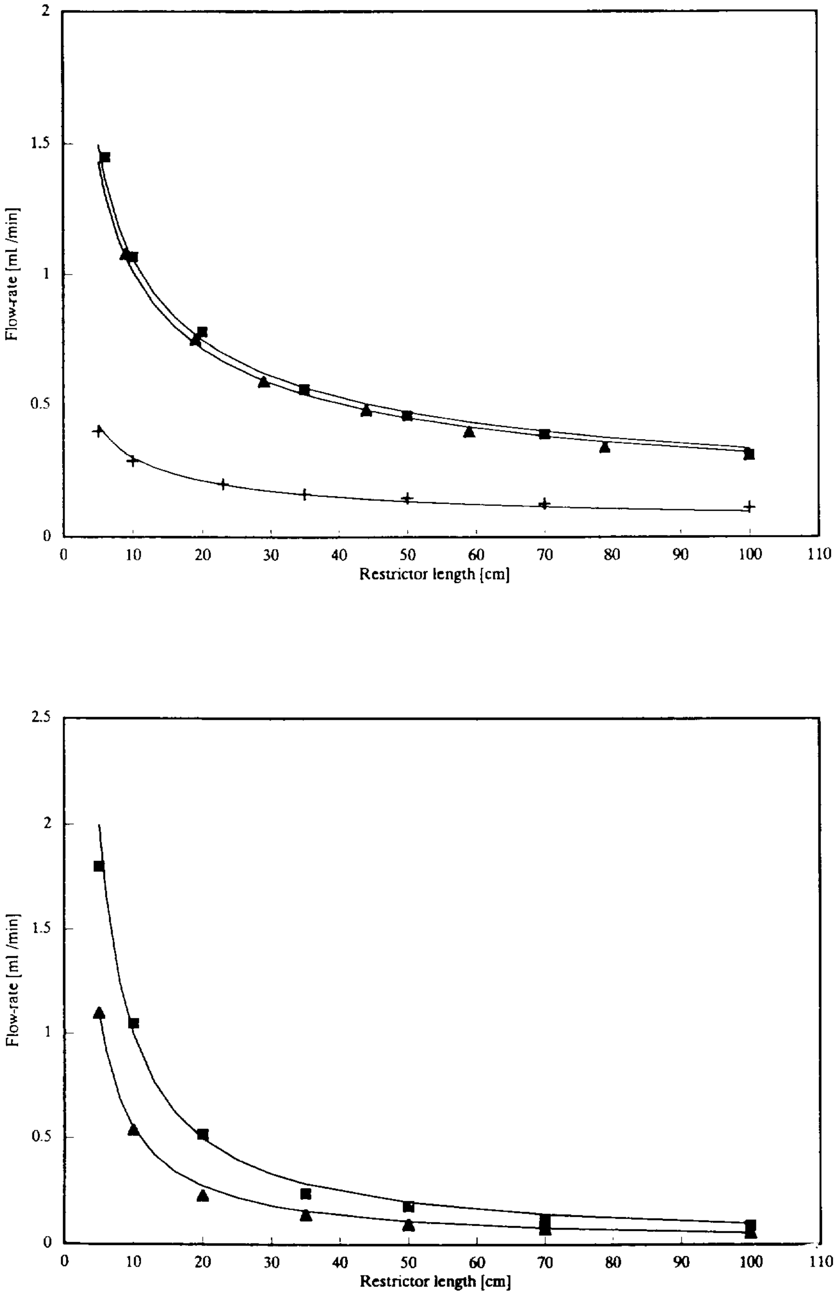
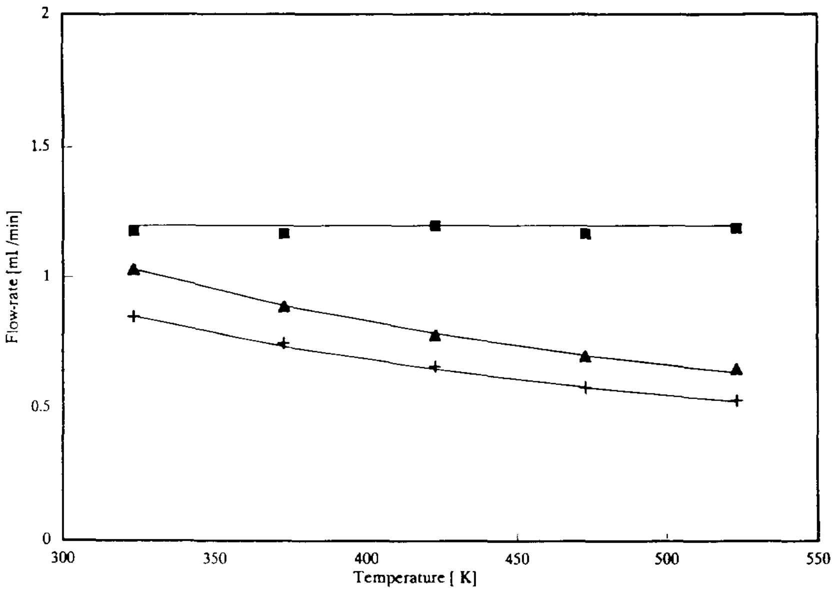


Fig. 3. Influence of restrictor length on flow-rate of CO$_2$ (top) and water (250°C, 350 atm; bottom). Experimental and calculated flow-rates are shown in symbols and lines, respectively. Top: ■ = 30 μm I.D. restrictor (outside the oven), 250°C, 350 atm; ▲ = 30 μm I.D. restrictor (inlet inside the oven), 80°C, 400 atm; + = 20 μm I.D. restrictor (outside the oven), 80°C, 400 atm. Bottom: ■ = 31 μm I.D. restrictor; ▲ = 26 μm I.D. restrictor.



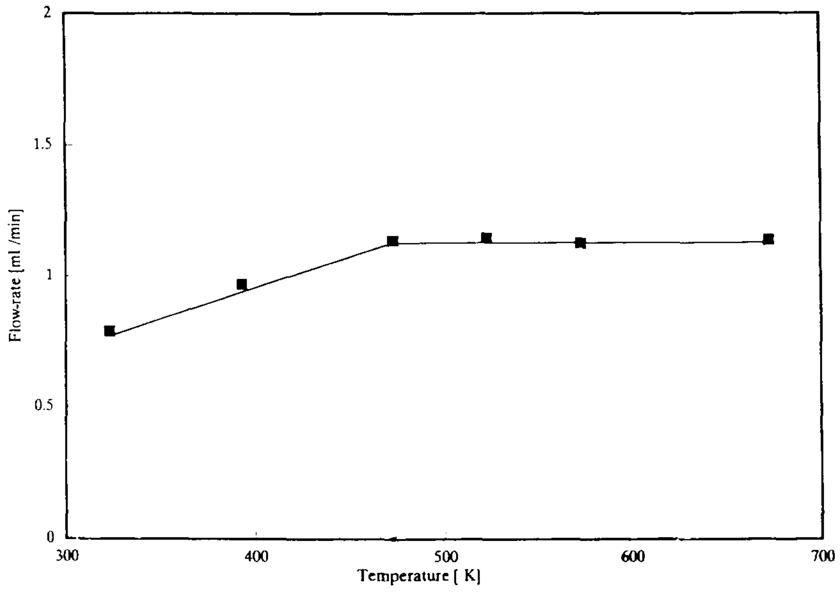


Fig. 4. Influence of temperature on flow-rate of CO_2 (400 atm, top) and water (350 atm, 10 cm × 31 μm I.D. restrictor; bottom). Experimental and calculated flow-rates are shown in symbols and lines, respectively. Top: ■ = 10 cm × 30 μm restrictor (outside the oven); ▲ = 10 cm × 30 μm I.D. restrictor (inlet inside the oven); + = 15 cm × 30 μm I.D. restrictor (inlet inside the oven).

Table 1
Comparison of calculated and experimental flow-rates for supercritical CO_2 extractions

Entire restrictor outside the SFE oven													
Pressure (atm)	200	200	200	200	350	350	350	350	400	400	400	450	600
Temperature (°C)	80	80	80	80	200	200	200	250	50	150	250	200	80
Restrictor length (cm)	10	10	10	10	20	50	100	10	10	10	10	10	10
Restrictor I.D. (μm)[a]	9	20	40	50	30	30	30	14	30	30	30	30	30
Calculated flow-rate (ml/min)	0.016	0.18	1.42	2.77	0.74	0.47	0.33	0.11	1.20	1.20	1.20	1.34	1.79
Experimental flow-rate (ml/min)[b]	0.022	0.20	1.61	2.92	0.76	0.46	0.33	0.16	1.18	1.20	1.19	1.23	1.45
Restrictor inlet inside the SFE oven													
Pressure (atm)	200	400	400	400	400	400	400	400	400	400	400	400	500
Temperature (°C)[c]	80	50	80	80	80	80	80	80	150	200	250	300	80
Restrictor length (cm)	10	10	10	10	10	10	50	100	10	10	10	10	10
Restrictor I.D. (μm)[a]	26	30	9	20	40	50	30	30	30	30	30	30	30
Calculated flow-rate (ml/min)	0.30	1.00	0.025	0.27	2.18	4.26	0.41	0.29	0.77	0.69	0.62	0.57	1.15
Experimental flow-rate (ml/min)[b]	0.31	1.03	0.023	0.27	2.15	4.19	0.40	0.29	0.77	0.69	0.65	0.60	1.08

[a] Values used in the correlation are internal radii (I.D./2).
[b] Experimental flow-rates were obtained by triplicate measurements, and the R.S.D. was less than 10%.
[c] Values used in the correlation are in K.

determined. As shown in Table 1, calculated flow-rates using Eq. 8 compared favorably with the experimentally determined values.

Water flow-rates

Based on Eqs. 1, 3 and 5, a mathematical correlation for water flow-rate can be expressed as

$$F = \chi PR^5/L \tag{9}$$

where χ is a temperature-dependent constant. For temperatures at or higher than 200°C, χ equals $3.6 \cdot 10^{-8}$ (determined by experimental flow-rates) if F is in ml/min, P is in atm, R is in μm and L is in cm. Thus, Eq. 9 can be changed into

$$F = 3.6 \cdot 10^{-8} PR^5/L \tag{10}$$

for $T \geq 200°C$ (473 K)

For water extractions at temperatures lower than 200°C, the calculated flow-rate in Eq. 10 need to be corrected by a factor of $T/473$, where T is the extraction temperature in K. As shown in Table 2, the correlation for water flow-rates gives very close values compared with experimental flow-rates.

Table 2
Comparison of calculated and experimental flow-rates for sub- and supercritical water extractions

Pressure (atm)	50	50	350	350	350	350	350	350	350	350	600	600	600
Temperature (°C)[a]	250	250	50	120	200	250	400	250	250	250	250	250	250
Restrictor length (cm)	10	10	10	10	10	10	10	20	50	100	10	10	10
Restrictor I.D. (μm)[b]	39	50	31	31	31	31	31	31	31	31	9	21	31
Calculated flow-rate (ml/min)	0.51	1.76	0.77	0.94	1.13	1.13	1.13	0.56	0.23	0.11	0.004	0.28	0.97
Experimental flow-rate (ml/min)[c]	0.45	1.54	0.79	0.97	1.14	1.15	1.14	0.52	0.18	0.09	0.006	0.30	1.05

[a] Values used in the correlation are in K.
[b] Values used in the correlation are internal radii (I.D./2).
[c] Experimental flow-rates were obtained by triplicate measurements, and the R.S.D. was less than 10%.

3.6. General expression for predicting flow-rates

Eqs. 7, 8 and 10 are the practical calculating equations for flow-rates in the three cases discussed above. We can still combine Eqs. 7, 8 and 10; and the flow-rate for all three cases can be expressed by one general form

$$F = \chi_a PR^b/(T^c L^d) \quad (11)$$

For CO_2 with entire restrictor outside the oven, CO_2 with restrictor inlet inside the oven. and water, χ_a is $2.8 \cdot 10^{6}$, $7.6 \cdot 10^{-4}$ and $3.6 \cdot 10^{-8}$; b is 3, 3 and 5; c is 0, 1 and 0; d is 0.5, 0.5 and 1, respectively. Eq. 11 is valid for: pressure from 150 to 500 atm (CO_2), and from 50 to 600 atm (water); restrictor internal diameter from 9 to 50 μm; restrictor length from 5 to 100 cm; temperature from 50 to 250°C (CO_2), and 200 to 450°C (water). For water flow-rates at temperatures lower than 200°C, the calculated flow using Eq. 11 need to be multiplied by $T/473$. As shown in Tables 1 and 2, this expression can be used to calculate flow-rates of CO_2 and water to ± 10% in most cases.

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