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## Note

### Contribution to the application of the compressibility factor in programmed-temperature, programmed-flow and double-programmed (temperature and flow) gas chromatography

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It is well known that in classical gas chromatography (GC), where the column temperature, the inlet pressure of the carrier gas and different GC parameters are constant, the compressibility correction factor  $j$  (ref. 1) is also constant. However, this is not so in programmed-temperature, programmed-flow and double-programmed (temperature and flow) gas chromatography (PTGC, PFGC and DPGC, respectively), where both the inlet pressure of the carrier gas and  $j$  change. Although in practice this can be allowed for by taking the arithmetical mean value of the values of  $j$  at the initial and final times of programming, this procedure cannot be justified theoretically. From the literature<sup>2-4</sup>, it seems that there is no solution to this problem, which is of concern in important theoretical research.

In the present paper, the determination of the exact value of the compressibility correction factor  $j$  in PTGC, PFGC and DPGC is described.

#### THEORETICAL

Consider the fundamental definition described by James and Martin<sup>1</sup>:

$$j = \frac{3}{2} \left( \frac{P^2 - 1}{P^3 - 1} \right) \quad (1)$$

where

$j$  = compressibility correction factor<sup>1</sup>  
 $P$  = relative pressure drop of column:

$$P = \left( \frac{p_i}{p_o} \right) \quad (2)$$

$p_i$  = inlet pressure of carrier gas  
 $p_o$  = outlet pressure of carrier gas.

Divide the numerator and the nominator of the fraction on the right-side of eqn. 1 by  $(P-1)$ :

$$j = \frac{3}{2} \left( \frac{P+1}{P^2+P+1} \right) \quad (3)$$

Multiply the numerator and the nominator in eqn. 3 by 2:

$$j = \frac{3}{4} \left( \frac{2P+2}{P^2+P+1} \right) \quad (4)$$

and separate the right-hand side of eqn. 4 into two parts:

$$j = \frac{3}{4} \left( \frac{2P+1}{P^2+P+1} \right) + \frac{3}{4} \left( \frac{1}{P^2+P+1} \right) \quad (5)$$

Integrate eqn. 5 between the limits  $P_0$  and  $P_e$ , where  $P_0$  is the initial value of  $P$  and  $P_e$  is the final value of  $P$ , but first transform the second term on the right-side of eqn. 5 as follows:

$$\left( P + \frac{1}{2} \right)^2 + \frac{3}{4} = P^2 + P + 1 \quad (6)$$

Then,

$$\int_{P_0}^{P_e} j \cdot dP = \frac{3}{4} \int_{P_0}^{P_e} \frac{2P+1}{P^2+P+1} \cdot dP + \frac{3}{4} \int_{P_0}^{P_e} \frac{1}{P^2+P+1} \cdot dP \quad (7)$$

$$\int_{P_0}^{P_e} j \cdot dP = \left[ \frac{3}{4} \ln(P^2+P+1) + \frac{\sqrt{3}}{2} \operatorname{arc} \operatorname{tg} \frac{(2P+1)}{\sqrt{3}} \right]_{P_0}^{P_e} \quad (8)$$

It must be noted that eqn. 8 can be used only if

$$\frac{dp_t}{dt} \neq 0 \quad (9)$$

where  $t$  is time.

## EXPERIMENTAL

Of the experimental results, an example may be given of the calculations on SE-30 as stationary phase, emphasizing once more the theoretical significance of the fact that the arithmetical mean value mentioned in the introduction can give good results in most instances.

The initial inlet pressure of carrier gas was 1.53  $\text{kp/cm}^2$  and  $j = 0.7791$  at the initial column temperature. At the end of the temperature programming, the inlet pressure of the carrier gas was 1.56  $\text{kp/cm}^2$  and  $j = 0.7690$ . Therefore:

$$\begin{aligned}
 j_{PTGC} &= \frac{\int_{P_0}^{P_e} j \cdot dP}{P_e - P_0} & (10) \\
 &= \left[ \frac{0.75 \cdot 2.3 \cdot \log(P^2 + P + 1) + \frac{\sqrt{3}}{2} \cdot \text{arc tg} \frac{(2P + 1)}{\sqrt{3}}}{0.03} \right]_{1.53}^{1.56} \\
 &= 0.7740.
 \end{aligned}$$

The arithmetical mean value was:

$$\begin{aligned}
 &\frac{0.7791 + 0.7690}{2} \\
 &= 0.77405.
 \end{aligned}$$

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