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Simple and efficient methane-marker devices for chromatographic samples

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Abstract

Calculation of the most useful gas chromatographic retention parameters, such as net and specific retention volumes, relative retentions, and retention indices, requires that raw retention data be corrected for gas hold-up time or volume (sometimes called dead time or volume) of the chromatographic system. When a flame-ionization detector is used, a common technique (where it is physically appropriate) is to introduce methane into the sample as a marker to approximate unretained species to correct for hold-up. This is often done by bubbling methane (or natural gas) through the sample just before injection. In this paper, we describe two easily constructed devices that provide continuous release of methane into liquid samples, sustainable for several weeks or even months. This long-term feature makes the techniques especially suitable to extensive retention studies done at multiple temperatures on several stationary phases. Moreover, one of the devices described is applicable to commercially available automatic sampler vials. After a detailed description of the construction of the devices is provided, some applications are discussed.

Keywords: Retention times; Hold-up times; Methane-marker devices

1. Introduction

The measurement and application of derived gas chromatographic retention parameters provides reliable (although not always unequivocal) sample component identification [1–5], as well as access to important thermodynamic functions of solutions [6–8]. The primary derived retention parameters used in gas chromatography are the net and specific retention volumes, relative retentions, and retention indices [9]. The calculation of all these parameters requires that the experimentally-accessible retention parameter, the retention time, t_R, be corrected for the gas hold-up time or volume (sometimes referred to as the dead time or volume) of the chromatographic system, usually represented as t_m. The most common way that this has been done involves the subtraction of the retention time (or volume) of an unretained sample component from the retention time(s) or volume(s) of the component(s) of interest. When using a thermal conductivity detector (TCD), the air (or nitrogen) peak is often used for this purpose, since air is usually demonstrably unretained on most stationary phases.

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Since air does not cause a response in a flame-ionization detector (FID), other methods of correcting for gas hold-up have been devised for measurements made with this detector. A number of mathematical techniques have been devised to estimate or extrapolate the gas hold-up (see for example Refs. [10–20]). All of these methods require a significant investment of time, since a good deal of retention time (or volume) data are required for a series of *n*-alkanes in order to implement each technique. In addition to these extrapolation methods, hydrodynamic models of the chromatographic column have been devised to estimate t_m [21]. These methods require precise measurement of numerous chromatographic system parameters, a task that is usually not possible unless modifications are made to the instrument. This mathematical analysis and modeling problem is still a topic of active research and controversy, since a totally satisfactory and rigorous approach has been elusive [11].

The use of methane as a minimally retained marker (MRM) is a conceptually-simple and common way to approximate the gas hold-up under certain conditions [15]. It is especially useful when higher column temperatures (approximately 80–100°C or higher) are employed with somewhat polar open tubular columns or nonpolar open tubular columns that have relatively thin coatings (in the 0.1–0.3 μm range). At lower temperatures, some partitioning of methane in most stationary phases may be observed, and on packed columns, adsorption has been observed to contribute to the retention of methane. Moreover, it is advisable not to use the methane-marker method to approximate t_m for solutes that elute quickly, since the error associated with any methane partitioning will then be relatively higher. The onset of methane partitioning is dependent on the nature of the stationary phase, film thickness (or loading), and other instrumental variables.

Thus, the applicability of the methane-marker technique has to be evaluated for each application. When used properly and under the appropriate conditions, however, the methane-marker technique will produce minimal departures from the t_m values calculated using one of several mathematical approximations [12–17]. We have found, for example, that the values for gas hold up approximated with the methane MRM method are identical (within experimental error) to those calculated with several of the extrapolation or hydrodynamic methods when applied to some industrially important analyses. Specifically, we have studied the analysis of heavy contaminants in natural gas and natural gas liquids [22,23] analyzed on a 30-m open tubular column with 0.1-μm coatings of 5 percent phenyl-polymethylsiloxane and pure polymethylsiloxane [24].

Historically, the simplest way that the methane-marker technique has been implemented is by bubbling methane gas through the liquid samples just before injection [5]. This approach suffers from some major disadvantages, however. The methane marker introduced by bubbling methane into a liquid will last for only a short time, typically 30 min or less. Reintroducing methane into sample vials between runs is inconvenient, especially if crimp-closure automatic sampler vials are used. The reintroduction procedure also increases the likelihood of operator exposure to potentially dangerous analytes, and also increases the risk of sample contamination. Moreover, bubbling methane through such samples can itself be hazardous, and that technique would be impossible to implement in some laboratories that have explosion-proof ratings. Workers who use laboratory-utility natural gas as the methane source (an all too common practice) risk exposing their samples to the numerous non-methane constituents of natural gas [22]. Another difficulty caused by bubbling methane through the sample is the potential loss of the more volatile components of the sample. Some workers add methane to the syringe after drawing in the sample. While this is a serviceable technique, it is time-consuming, labor intensive, and cannot be automated.

In this paper, two approaches to long-term methane release in chromatographic samples will be described. These techniques address all of the above disadvantages, while providing some addi-

tional useful features. The methods are based on permeation tubes, well-known devices that have been used for the preparation of gaseous mixtures for a number of years [25,26]. A permeation tube is a short length (usually between 5 and 20 cm) of a polymeric tubing through which a fluid may pass at a relatively slow, constant rate (at a given temperature). Numerous polymers have been used for the preparation of the tubes used for such permeation devices. These polymers include polyethylene, polyvinyl acetate, polyamide, polyester, silicones, polyvinylidene chloride and polyethylene terephthalate. The most common materials are fluorinated ethylene propylene (FEP Teflon[1]) and tetrafluoroethylene (TFE Teflon). The most common use of permeation tubes is for the dynamic preparation of gas mixtures.

2. Theory

The operation of a polymeric permeation tube device is described fundamentally by Fick's law [25,26]:

$$q_d = (p_g \cdot A \cdot \Delta P)/L \quad (1)$$

$$p_g = D \cdot S \quad (2)$$

where q_d is the amount of material (methane in the present case) that passes through the permeation tube (in mass units per unit area per unit time), p_g is the gas permeability constant, D is the diffusion coefficient of the gas (in units of area per unit time), S is the solubility constant of the gas in the polymer (in concentration units divided by the permeating gas fugacity or pressure), A is the surface area of the material, ΔP is the pressure difference across the polymer, and L is the thickness of the polymer. The pressure difference ΔP is the difference in pressure of the permeating fluid on either side of the permeation tube. As these equations demonstrate, the main factors that affect passage of a gaseous material through a polymeric permeation tube are (1) the (vapor) pressure of the permeating fluid, (2) the solubility of the permeating fluid in the polymer, and (3) the wall thickness of the polymer. At constant temperature, the solubility of the fluid within the polymer is constant, and a steady-state condition exists. In the great majority of permeation tube applications, the fluid is contained within the inside of a sealed tube made from the polymer, and the desired concentration of fluid is achieved by appropriate mixing with a diluent flowing outside the tube. The concentration of the fluid in the diluent can be approximated by:

$$[c] = \frac{(v \times 10^6)(T/273)(P/0.101325)q_d}{q_D M} \quad (3)$$

where [c] is the concentration expressed in parts per million (that is, 0.0001 percent), T is the temperature of the permeation tube and fluid (in K), P is the pressure of the diluted gas stream (in MPa), q_D is the volumetric flow-rate of the diluent (in l/min), v is the molar volume of the permeating fluid (in l) and M is the relative molecular mass of the permeating fluid. A common approximation sometimes applied to Eq. 3 is to replace the molar volume v with 22.4 l, the molar volume of an ideal gas. In the present case, the "diluent" is actually the analytical sample, as will be shown in the experimental section.

The steady-state useful life of any device based upon a permeation tube depends on the volume of the tube, the mass of material in the supply portion of the tube, and the permeation rate through the tube. The lifetime can be approximated by:

$$L_s = 1465\varrho/q_d \quad (4)$$

where L_s is the lifetime of the device in months,

[1] Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for that purpose.

and ϱ is the density of the permeating component in grams per milliliter.

3. Experimental

The two approaches to chromatographic sample methane markers developed in this work are shown in Fig. 1a,b. The first marking device is a cartridge made from a 2-cm length of TFE Teflon permeation tubing (0.48 cm O.D., 0.32 cm I.D.), containing an activated carbon adsorbent that has an especially high capacity for storing methane. The relevant properties of this material are discussed more fully later in this section. Both ends of the tube are plugged with cylindrical disks consisting of 25 percent glass filled Teflon (hereafter referred to as Teflon-g) machined to provide three points of contact with the permeation tube [27]. The largest diameter of the disk is 0.40 cm, providing a leak tight interference fit with the tube. An interference fit exists when the outside diameter of the disk significantly exceeds the inside diameter of the permeation tube.

This cartridge is made by press-fitting a Teflon-g plug into one end of the TFE Teflon tube, and filling the tube through the opposite end with the adsorbent. We have found that a dental restoration amalgam carrier is the ideal tool to perform this task. These low-cost devices are readily available from medical/dental supply sources. The filled cartridge is then placed in a small pressure vessel, similar to vessels that have been used as sample reservoirs for supercritical fluid chromatography and extraction (SFC/SFE) [28]. These vessels, held in an upright position, can usually accommodate three such methane-marker cartridges at one time. The adsorbent is then charged by introducing methane (research grade, 99.99 percent purity) at approximately 4 MPa (580 p.s.i.), at ambient temperature. Lower methane pressures can and have been used satisfactorily in this application, but it appears that the adsorbent material achieves the highest measured methane storage after pressurization at 4 MPa. After an overnight pressurized exposure to methane, the pressure vessel is vented in a fume hood, and the open end of the permeation tube is promptly plugged with another Teflon-g disk.

To use this cartridge, it is simply placed in a vial containing the liquid sample. The methane will continuously desorb from the adsorbent and pass out of the permeation tube. An equilibrium concentration of methane will dissolve in the liquid and remain in solution as long as the sample vial is sealed. Methane that evaporates from the liquid during sampling will be replenished from the methane-marker cartridge during the useful life of the cartridge. Naturally, methane will also always be present in the head space of the closed vial.

The second approach to chromatographic sample methane marking is depicted schematically in Fig. 1b. This device consists of a commercially available automatic sampler vial equipped with an insert made from a 1.9-m length of TFE Teflon permeation tubing (0.48 cm O.D., 0.32 I.D.). This insert is held securely in the neck of the vial with a 0.48-cm long ring made from polyethylene (0.64 cm O.D., 0.32 cm I.D.). The bottom end of the permeation tube is plugged with a Teflon-g disk as described earlier. Incorporated between the polyethylene collar and the TFE Teflon permeation tube is a methane transfer line consisting of a single, short length (approximately 0.8 cm long) of polyamide-coated fused-silica capillary tubing (0.32 mm O.D., 0.010 mm I.D.). A capillary with a small inside diameter (such as those used as restrictors in SFC/SFC) was chosen for this transfer line to minimize subsequent loss of methane through the capillary [29]. Somewhat larger inside diameters will work satisfactorily, however.

This methane-marker device is assembled by first slipping the polyethylene collar around the permeation tube, with a short length of fused-silica capillary in place between the two. The relative positions of each component are shown in the detailed insets of Fig. 1b. The encircled inset shows the permeation tube and polyethylene collar in cross-section, with the transfer line in profile. A small piece of tape temporarily holding the fused-silica transfer line to the per-

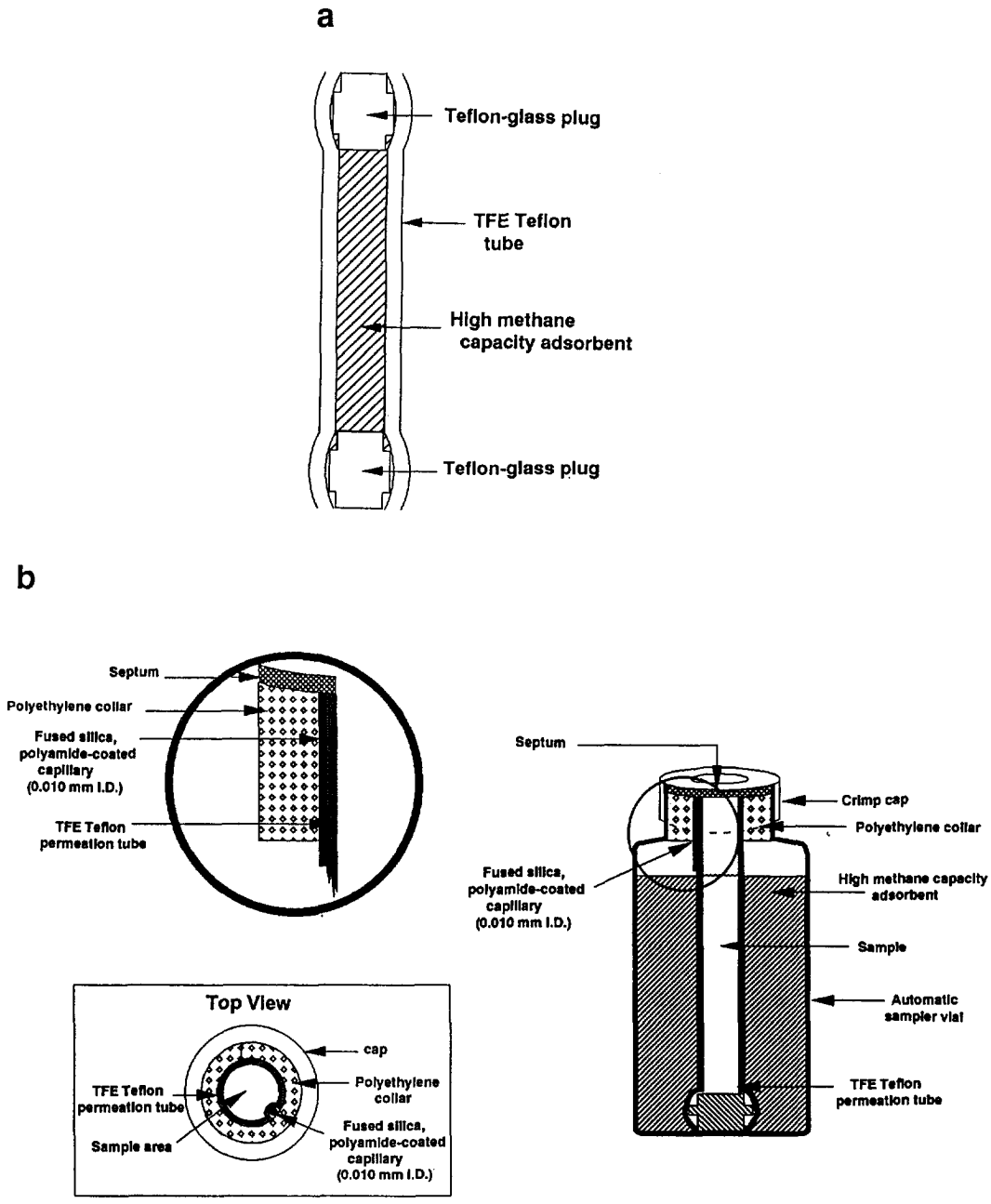

Fig. 1. (a) Cartridge methane-marker device consisting of a TFE Teflon permeation tube filled with methane-saturated adsorbent. (b) Methane-marker insert made from a TFE Teflon permeation tube contained within an automatic sampler vial. The two insets show in detail the position of the polyamide-coated fused-silica transfer line.

meation tube facilitates this operation. Both ends of the fused-silica tube are trimmed back with a quartz or ceramic knife, to ensure that any foreign material that may have entered the opening of the tube during assembly will not subsequently create a blockage. The capillary on

the top end of the insert is cut to be flush with the surface of the permeation tube and polyethylene ring. The bottom of the insert is plugged with a Teflon-g disk, as with the cartridge described earlier.

The automatic sampler vial is partially filled (to occupy approximately 3/4 of the volume of the vial) with the adsorbent, and the assembled insert is press-fitted into the neck of the vial on a laboratory press or an arbor press. This methane-marker device is activated by placing one or more of the prepared vials into a small pressure vessel, and pressurizing them overnight with methane, as described earlier for the cartridge. It is advisable to purge air from the adsorbent space of the vial with an iterative pressurize-and-vent process before the overnight exposure in order to remove air. After the pressurized exposure, the vessel is vented in a fume hood, and the vials are removed. The liquid sample is placed inside the permeation tube insert, and a septum-equipped cap is crimped on the vial. Methane will permeate into the sample space in a fashion similar to that of the cartridge. The septum of the crimped cap is held flush against the opening of the fused-silica capillary. In this way, it serves the additional role of minimizing methane loss (through the transfer line) from the adsorbent.

4. Adsorbent

The adsorbent used for the methane-marker devices presented here has been specially prepared to provide a high capacity for methane storage [30]. The material is available for adsorbed natural gas technology intended for use in natural gas vehicles. It is prepared from petroleum coke, and has a reported maximum methane storage capacity of 20.5 percent (mass/mass) at 4 MPa, at ambient temperature. In the application described in this paper, the material is not used under a significant pressure of methane. The methane that is introduced for sorbent saturation is vented after a suitable period of time. We have gravimetrically measured the maximum methane storage capacity under these conditions (ambient temperature and pressure) to be 0.35 ± 0.07 percent (mass/mass). This is greater than the methane storage capacity of many common carbon-based chromatographic adsorbents which were tried prior to choosing the petroleum coke material. Some representative properties of the material are provided in Table 1.

Table 1
Properties of high methane-capacity adsorbent

Source	Petroleum coke
Form	Powder
BET[a] surface area	3150 m^2/g
Total pore volume	1.75 ml/g
Particle size	57 μm
Measured methane capacity, 4MPa	20.5 percent (mass/mass)
Measured methane capacity, ambient pressure[b]	0.35 ± 0.07 percent (mass/mass)

[a] Braunauer–Emmett–Teller.
[b] Measured in this work.

5. Results and discussion

The major issues that concern the use of the methane-marker technique described above are the performance and lifetime of the methane-marker devices. This, of course, presumes that one has already considered the applicability of methane retention as an approximation for t_m. The chromatogram shown in Fig. 2 illustrates the typical response from the methane-marker devices shown in either Fig. 1a or b. This chromatogram was obtained with flame-ionization detection for a surrogate mixture of natural gas heavy components, run on a 30-m capillary column coated with a 5 percent phenyl-polymethylsiloxane (0.1 μm thickness). The first peak corresponds to approximately 2–3 ppm of dissolved methane, the retention time of which is identical to that obtained for pure methane, or for the solution of analyte that has had methane freshly bubbled through it.

To estimate the concentration of methane that can be made available to the sample, one could,

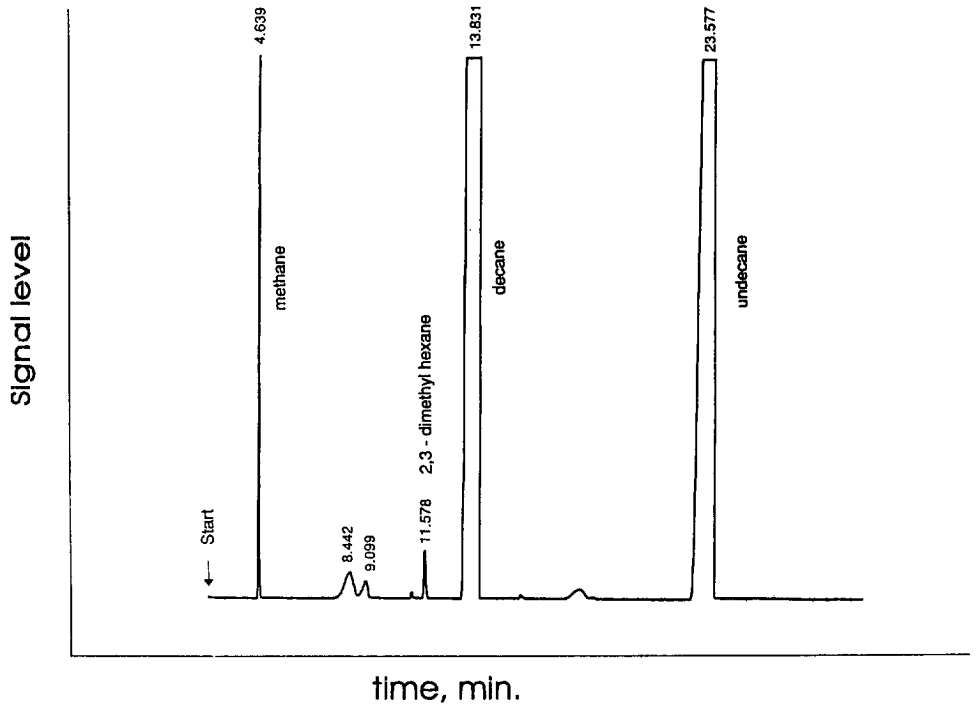

Fig. 2. Chromatogram of a mixture of surrogate of heavy natural gas components obtained from a sample contained in the vial shown in Fig. 1b. This chromatogram was obtained on a 30-m column with a 0.01 μm coating of 5 percent phenylpolymethylsiloxane obtained with flame-ionization detection.

in principle, use Eq. 3 to estimate an upper bound. In this case, q_D would simply be the sampling rate from the sample vial. In practice, however, one would also have to consider the solubility of methane in the analyte solution. This will invariably lower the methane concentration that will be present in the sample.

To estimate the useful life of either methane-marker device, one could, in principle, use either Eqs. 3 or 4 to estimate a lower bound. In practice, of course, the sampling rate will probably override equilibrium considerations. A rough calculation with Eq. 4 indicates that a freshly charged methane-marker device that is left opened in ambient air (that is, without the septum cap crimped in place) should last approximately 54 h. This figure can serve as a crude lower bound on the lifetime of a methane-marker device, since typical chromatographic sampling rates would result in a much lower rate of methane depletion. We have found in realistic sampling protocols that the cartridge devices (Fig. 1a) have a useful life of approximately 3 weeks, and the automatic sampler vial devices (Fig. 1b) have a useful life of approximately 6 weeks. We anticipate that the useful lifetime could be increased by the use of FEP Teflon as the insert material, although this has not been thoroughly explored. The lifetime could also be extended by future advances in adsorbent technology.

After the methane in the marker device has been depleted, the device can be reactivated by heating or simply disposed of as a laboratory waste. As the devices are used, vapors of the sample will permeate into the adsorbent. It is therefore important that the adsorbent be reactivated by heating before it is given a fresh charge of methane. The extent of permeation by the sample can be approximated with Eq. 3, used along with published tables of permeation measurements [25].

6. Conclusions

In this paper, two devices and approaches to continuous methane marking for chromatographic samples are presented. Such marking is needed for retention parameter measurement and application for sample identification. One of the approaches is suitable for use with automatic sampler vials. These devices are capable of functioning for up to 6 weeks in their present configurations. Additional work on adsorbent technology and permeation tube material have the potential of extending the useful lifetime even further.

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References

[1] J.M. Takacs, J. Chromatogr. Sci., 11 (1973) 210–215.
[2] B.J. Perrigo and H.W. Peel, J. Chromatogr. Sci., 19 (1981) 219–226.
[3] N.G. Johansen and L.S. Ettre, Chromatographia, 15 (1982) 625–630.
[4] P.C. Hays and E.W. Pitzer, J. Chromatogr., 253 (1982) 179–198.
[5] A.J. Lubeck and D.L. Sutton, J. High Resolut. Chromatogr. Chromatogr. Commun., 6 (1983) 328–332.
[6] R.J. Laub and R.L. Pecsok, Physicochemical Applications of Gas Chromatography, Wiley-Interscience, New York, 1978.
[7] J.R. Conder and C.L. Young, Physicochemical Measurement by Gas Chromatography, John Wiley, Chichester, 1979.
[8] T. Cserhati and K. Valko, Chromatographic Determination of Molecular Interactions: Applications in Biochemistry, Chemistry and Biophysics, CRC Press, Boca Raton, FL, 1993.
[9] R.L. Grob, Modern Practice of Gas Chromatography, Wiley-Interscience, 2nd ed., New York, 1985.
[10] F. Riedo, G. Fritz, G. Tarjan and E. sz. Kovats, J. Chromatogr., 126 (1976) 63–83.
[11] M.S. Wainright and J.K. Haken, J. Chromatogr., 184 (1980) 1.
[12] J.K. Haken, Adv. Chromatogr., 8 (1976) 367–407.
[13] J.F. Parcher and D.M. Johnson, J. Chromatogr. Sci., 18 (1980) 267–272.
[14] G. Castello, S. Vezzani and P. Moretti, J. Chromatogr. A, 677 (1994) 95–106.
[15] B. Koppenhoeffer, G. Laupp and M. Hummel, J. Chromatogr. A 547 (1991) 239–245.
[16] M.V. Budahegyi, E.R. Lombosi, T.S. Lombosi, S.Y. Meszaros, S. Nyiredy, G. Tarjan, I. Timar and J.M. Takacs, J. Chromatogr., 271 (1983) 213–307.
[17] M.B. Evans and J.K. Haken, J. Chromatogr., 472 (1989) 93–127.
[18] M.S. Wainwright and J.K. Haken, J. Chromatogr., 184 (1980) 1–20.
[19] L. Ambrus, J. Chromatogr., 294 (1984) 328–333.
[20] R.F. Strasburg, D.M. Scott and J.S. Fritz, Anal. Chim. Acta, 215 (1988) 311–316.
[21] G. Castello, P. Vezzani and P. Moretti, J. Chromatogr. A, 677 (1994) 95–106.
[22] T.J. Bruno, Constituents and Physical Properties of the C_6 + Fraction of Natural Gas, GRI Topical Report 94/0274, Gas Research Institute, Chicago, IL, 1994.
[23] T.J. Bruno and M. Huber, Extended Natural Gas Analysis (ENGA™) Database, Gas Research Institute, Chicago, IL, 1995.
[24] T.J. Bruno, in preparation.
[25] G.O. Nelson, Gas Mixtures: Preparation and Control, Lewis Publishers, Boca Raton, FL, 1992.
[26] J. Namiesnik, J. Chromatogr., 300 (1984) 79–108.
[27] T.J. Bruno, J. Chromatogr. A, 704 (1995) 157–162.
[28] T.J. Bruno, J. Res. Nat. Inst. Std. Tech., 93 (1988) 655–658.
[29] T.J. Bruno, in T.J. Bruno and J.F. Ely (Editors), Supercritical Fluid Technology: Reviews in Modern Theory and Applications, CRC Press, Boca Raton, FL, 1992.
[30] A.L. Chaffee, personal communication and transmittal, BHP Research, Melbourne Laboratories, Australia, 1994.