Some new light on the study of fluid flow in closed conduits: An experimental protocol to identify the value of a misconstrued constant

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Abstract

In this paper, the experimental protocol which we disclose is designed to identify the values for both the *constant* in the Kozeny/Carman model, which relates to the *linear* component of permeability, and the *variable* kinetic coefficient in the newly minted Q- modified Ergun model, which relates to the *non-linear* components of permeability, without involving any new theoretical development. Moreover, kinetic contributions to measured pressure gradient, which are not accounted for in some currently accepted empirical fluid flow equations, such as Poiseuille's for flow in empty conduits and Kozeny/Carman for flow in packed conduits, but which nevertheless contribute to measured pressure drop and thus hamper the identification of the value of the constant relative to the laminar component, are captured and lumped together into a single variable kinetic parameter-the kinetic coefficient.

Keywords: Bed Permeability: Kozeny/Carman: Ergun: Friction Factor: Porosity: UHPLC.

1. **Introduction**

Beginning with the work of Darcy in packed conduits circa 1856 and continuing to this very day, extraordinary amounts of energy has been expended by authors of scientific publications in an attempt to shed light on an understanding of underlying contributions to permeability, not only in packed conduits, but also in empty conduits [1].

Azevedo et al focused their attention on turbulent flow of water in corrugated pipes [2]. Baker et al studied the flow of air through packed conduits containing spherical particles [3]. Erdim et al studied the pressure drop-flow rate correlation of spherical powdered metal particles in packed conduits [4]. Dukhan et al, studied pressure drop in porous media with an eye to reconciliation with classical empirical equations [5]. Anspach et al reported results relating to very high pressure drops in very narrow id HPLC columns using small fully porous particles [6]. Zhong et al. studied air flow through sintered metal particles in the context of the Ergun flow model [7]. Tian et al reported experimental results with sintered ore particles in packed conduits [8]. Mayerhofer et al studied the permeability of irregularly shaped wood particles [9]. Pesic et al studied the effect of temperature on permeability of packed conduits containing spherical particles [10]. Abidzaid et al discusses water flow through packed beds in light of some modified equations [11]. Mirmanto et al studied friction factor of water in micro channels [12]. Capinlioglu et al focused his work on simplified correlations of packed bed pressure drops [13]. Yang et al made comparisons of superficially porous particles in packed HPLC columns [14]. Lundstrom et al used sophisticated analysis techniques to evaluate transitional and turbulent flow in packed beds [15]. Sletfjerding et al reported on flow experiments with high pressure natural gas in empty pipes [16]. Langeiandsvik et al studied pipeline permeability and capacity [17]. De Stephano et al studied the performance characteristics of small particles in packed conduits for fast HPLC analysis [18]. Pereira reported on expected pressure drops in commercial HPLC columns [19]. Van Lopik et al studied grain size on nonlinear flow behavior [20]. Li et al discussed particle diameter effects in sand columns [21]. An in depth evaluation of each one of the references above can be found on our web site;www.wranglergroup.com/UPPR

In our appreciation for the historical record regarding the work of renowned contributors in the field of permeability as applied to flow in closed conduits, we have given equal consideration to all classical works in both packed and empty conduits. Because the field of general engineering in empty conduits is so vast, it is beyond the scope of this paper. Nevertheless, it is part of the same fundamental science and any serious fluid dynamic assessment must include it in its repertoire, especially when challenging conventional wisdom, as we are doing here. Accordingly, as part of our foundation in challenging conventional wisdom with regard to permeability in packed conduits, and particularly in chromatographic columns, and even more particularly, in the recent vintage so-called sub 2 micron high throughput analytical columns, we will briefly mention it in passing as part of our supporting material. As part of our research on this topic reported elsewhere, we have reviewed the classic work of Nikuradze (circa 1930) pertaining to flow through smooth [22] and roughened pipes [23] as well as the much more recent work which we will refer to here as the Princeton study (circa 1995) [24]. Since these classical works in empty conduits are directly supportive of our thesis herein concerning permeability in packed conduits, we include as part of our assessments herein the teaching of Poiseuille's which is broadly accepted as the governing equation underlying permeability in empty conduits in the laminar flow regime, which is a specific target of this paper.

We would be remiss herein however, if we did not single out for special mention the works of two popular authors whose work in packed chromatographic columns we consider legendary. Those authors are Sabri Ergun [25,26] and Georges Guiochon [27].

Firstly, we believe that, with respect to the values of his equation "constants", Ergun got it completely wrong for a variety of reasons which we go into in great detail in another publication [28]. Suffice it to say in this writing that, although we acknowledge that Ergun made a unique, significant and lasting contribution to the underpinnings of fluid dynamics, by virtue of his putting together two distinct elements of viscous and kinetic expressions for energy dissipation in packed conduits, his work has been memorialized by many for the wrong reasons- his erroneous assignment of the now famous values of 150 and 1.75 for the "constants" of his now equally famous Ergun equation.

Guiochon, on the other hand, although he published a prestigious amount of experimental data, is famous for taking one step forward and two steps backward in his continuous flip-flop assertions concerning the value of the constant in the Kozeny/Carman equation [29]. His work will be remembered for his contention that the value of the constant could be anything from 120 to 300 and, despite the fact that, occasionally, he would assign a very specific value depending on the results of a particular experiment in hand, he would often times, either revert backwards to the safety of Darcyism or further seek shelter in the vague proclamation that the value of the constant was a complete mishmash of undetermined variables [30].

In order to facilitate a comprehensive understanding of fluid flow in closed conduits, therefore, one must develop a common language which crosses the chasm between *empty* and *packed* conduits, on the one hand, and *laminar* and *turbulent* flow regimes, on the other. Let us begin with the language of a typical chromatographer who invariably invokes the permeability parameter K_0, a dimensionless mathematical construct.

Conduit permeability may be expressed, as follows;

$$\frac{\Delta P}{L} = \frac{\mu_s \eta}{K_0} \tag{1}$$

Where, ΔP is the pressure differential between the inlet and outlet of the conduit; L is the length of the conduit; μ_s is the superficial fluid velocity; η is the fluid absolute viscosity and K_0, is conduit permeability based upon the use of superficial fluid flow velocity, μ_s, and where superficial velocity, μ_s, in turn, is defined as:

$$\mu_s = \frac{4q}{\pi D^2} \tag{2}$$

Where, D = conduit diameter and q = fluid volumetric flow rate.

Let us define the term "friction factor", f, which is widely used jargon relating to flow in conduits, as a dimensionless mathematical construct which normalizes pressure drop in a conduit for the various individual contributions to that pressure drop value and is the reciprocal of K_0. In the case of an empty conduit and when the flow regime is confined to that of laminar flow, it is defined as;

$$f_P = \frac{\Delta P}{\mu_s \eta L} \tag{3}$$

$$= \frac{1}{K_0} \tag{4}$$

Where, f_p is the Poiseuille's type friction factor.

1.1 The Poiseuille's and Kozeny/Carman Models

Readers familiar with fluid dynamics will recognize that when it comes to laminar flow, Poiseuille's equation is generally considered the governing permeability equation in an empty conduit and the Kozeny/Carman equation is generally considered the governing permeability equation in a packed conduit. Let us further examine these two relationships.

Poiseuille's equation can be written as;

$$\frac{\Delta P}{L} = \frac{32 \mu_s \eta}{D^2} \tag{5}$$

Rearranging gives:

$$\frac{\Delta P D^2}{\mu_s \eta L} = 32 \tag{6}$$

Substituting K_0 in equation (1) into equation (6) gives:

$$\frac{D^2}{K_0} = 32 \tag{7}$$

$$= K_P \tag{8}$$

Where, K_p, is defined as Poiseuille's constant for laminar flow.

Similarly, the Kozeny/Carman equation can be written as:

$$\frac{\Delta P}{L} = \frac{K_c \Psi_v \mu_s \eta}{d_p^2} \tag{9}$$

Where, K_C = Kozeny/Carman constant, d_p = the average spherical particle diameter equivalent and Ψ_v = the viscous porosity dependence term.

And where, the porosity dependence term, Ψ_v, in turn, is refined as:

$$\Psi_v = \frac{(1-\varepsilon_0)^2}{\varepsilon_o^3} \tag{10}$$

Where, ε_o = the external porosity of the packed conduit, also defined as;

$$\varepsilon_o = \frac{V_e}{V_{ec}} \tag{11}$$

Where, V_e = the volume external to the particle fraction and V_{ec} = the empty volume of the conduit in the packed column.

We point out here that variations in specific surface area are accommodated within our concept of spherical particle diameter equivalent, i.e., the value of d_p.

Similarly, as in the case of the Poiseuille model, the Kozeny/Carman model maybe expressed as a dimensionless friction factor. This is accomplished by normalizing the pressure drop term in equation (9), on the left hand side of the equality sign, for the individual contribution terms, on the right hand side of the equality sign, as follows:

$$\frac{\Delta P d_p^{\,2}}{\Psi_v \mu_s \eta L} = f_K \qquad (12)$$

Where, f_K is the Kozeny/Carman type friction factor.

Isolating the term $K_{c,}$ as a dimensionless mathematical construct, by rearranging equating (9) gives:

$$K_c = \frac{\Delta P d_p^{\,2}}{\Psi_v \mu_s \eta L} \qquad (13)$$

Substituting K_0 into equation (13) gives:

$$K_c = \frac{d_p^{\,2}}{K_0 \Psi_v} \qquad (14)$$

Note that there is an embedded numerical coefficient, 32, in the Poiseuille model which we have written as equation (7) and in equation (8) assigned the symbol K_P and the label Poiseuille's constant. However, in equation (13) for the Kozeny/Carman model, although we have the term K_C which we label the Kozeny/Carman constant, there is no numerical value assigned to it. Since both equations purport to represent permeability in a closed conduit when the fluid flow is laminar, let us assume that they both represent the same functional concept in each equation and that they are, therefore, related.

Accordingly, let us functionally equate the formulae embedded in the Poiseuille model and in the Kozeny/Carman model as follows:

$$\frac{K_c}{K_P} = \frac{d_p^{\,2}}{D^2 \Psi_v} \qquad (15)$$

Substituting for K_P into equation (15) and rearranging gives;

$$K_c = \frac{32 d_p^{\,2}}{D^2 \Psi_v} \qquad (16)$$

Where, functional equivalency between the two fluid flow models is dictated by two internally consistent boundary conditions as follows:

The term d_p in the Kozeny/Carman model = the term D in the Poiseuille model, and the term Ψ_v in the Kozeny/Carman model has the constant numerical value of 0.125 (1/8) in the Poiseuille model.

We can now derive a more specific version of both the Poiseuille and the Kozeny/Carman models by, on the one hand, importing the concept of porosity from the Kozeny/Carman model into the Poiseuille model, and, on the other hand, importing the numerical value of the constant from the Poiseuille model into the Kozeny/Carman model. Thus, we can represent our equalizing and reciprocating boundary conditions as:

$$d_p = D; \quad \Psi_v = 1/8 \tag{17}$$

Incorporating this assumption into equation (16) gives:

$$K_c = \frac{K_P}{\Psi_v} = \frac{32}{(1/8)} = 256 \tag{18}$$

Equation (18) would appear to suggest, however, what appears to be a contradiction in terms, i.e. the value of the constant in the Poiseuille model, K_P, has two confliction values, i.e. 32 and 256. To demonstrate that these two numerical values do *not* represent a contradictory interpretation of the Poiseuille model, let us further articulate the meaning of what our equivalency proposition actually represents. We do this by recasting the Poiseuille model in both of its now *dual* dimensionless friction factor formats. To accomplish this, we initially express the Poiseuille model in terms of the Poiseuille type friction factor as follows:

$$f_P = \frac{\Delta P D^2}{\mu_s \eta L} = 32 \tag{19}$$

Note that in this format, the characteristic dimension of the conduit is expressed in terms of its diameter D.

Similarly, we may now express the Poiseuille model in terms of a Kozeny/Carman type friction factor by incorporating our equalization assumptions, as follows:

$$f_P = \frac{\Delta P D^2}{\Psi_v \mu_s \eta L} = 256 \tag{20}$$

How can we justify that equations (19) and (20) are two equivalent renditions of the same entity? The answer lies in the Conservation Laws of Nature sometimes referred to as the Laws of Continuity when they involve moving entities. In any conduit packed with particles, the total free space contained within the conduit is proportioned between the volume fraction taken up by the particles and the volume fraction taken up by the fluid. Accordingly, the characteristic dimension of the particles contained in a conduit and the *resultant* conduit porosity are *not independent* variables, meaning *the one depends upon the value of the other.*

In the case of a conduit packed with particles, since the particle diameter, d_p, may vary independently of the conduit diameter, D, the ratio of the conduit diameter to the particle diameter, D/d_p, may vary over a very wide range of values, and accordingly, the value of the packed column external porosity, ε_0, also may vary over a very broad range of values. The first functional boundary conditions which we imposed upon the Poiseuille model - which applies only to an empty conduit- simply demonstrates that resultant porosity, in the case of an empty conduit, is *always* a constant because we defined the ratio of conduit diameter to particle diameter to be a constant, i.e. $D/d_p = 1$ (unity). Therefore, the permeability of an empty conduit is represented in terms of (a) its diameter in conjunction with a numerical coefficient in which the constant value of its porosity is embedded where $K_P = 32$ or (b) its diameter in conjunction with a numerical coefficient which does not contain the constant value of porosity embedded but, instead, the constant value of the porosity is expressed in the separate term Ψ_v where $K_P = 256$. In the case where the conduit porosity is expressed in the separate term Ψ_v whose value = 1/8, the value of 256 is greater because the external porosity, ε_0, in an empty conduit is not only constant but it is also *greater* than unity. In fact, the value of the porosity dependence term Ψ_v in an empty conduit (1/8) is the correlation coefficient between these two numerical values representing the constant in the respective dimensionless formats for an empty conduit.

1.2 The Ergun Model

Having established a frame of reference for hydrodynamics between an empty and a packed conduit in the regime of *laminar* flow, where permeability is a *linear* function of fluid flow velocity, we shall now proceed to widen our frame of reference to accommodate the *turbulent* flow regime in which the relationship between permeability and fluid velocity is *nonlinear*. Accordingly, we look now to the Ergun equation for a model which includes a term purporting to describe the pressure drop/fluid flow relationship when the fluid flow regime is other than laminar [31].

The Ergun equation may be written as:

$$\frac{\Delta P}{L} = \frac{A\Psi_v\mu_s\eta}{d_p^2} + \frac{B\Psi_k\mu_s^2\rho_f}{d_p} \qquad (21)$$

The first term on the right hand side of equation (21) is identical to the Kozeny/Carman model for laminar flow and where, A is the same constant as the Kozeny/Carman constant (K_C), and the second term on the right hand side of equation (21) is an expression for kinetic flow, but B is merely a coefficient valid for a given experiment. Where, ρ_f = the fluid density and Ψ_k is the kinetic porosity dependence term, defined as;

$$\Psi_k = \frac{(1-\varepsilon_0)}{\varepsilon_0^3} \qquad (22)$$

We point out that the concept of fluid tortuosity is captured as a kinetic contribution only in this paper and is therefore reflected in the value of the coefficient B.

Employing the friction factor methodology which we used above by normalizing the pressure drop, first on the left hand side of the equation (22), for the individual contributions contained in the first term, on the right hand side of the equation, gives:

$$\frac{\Delta P d_p^2}{\Psi_v \mu_s \eta L} = A + \frac{B \Psi_k \mu_s^2 \rho_f d_p^2}{\Psi_v \mu_s \eta d_p} \qquad (23)$$

Substituting, f_v, a normalized dimensionless Ergun *viscous* type friction factor for the term on the left hand side of equation (23) and simplifying the second term on the right hand side of the equation gives:

$$f_v = A + \frac{B \mu_s d_p \rho_f}{(1-\varepsilon_0)\eta} \qquad (24)$$

$$= A + B R_{em} \qquad (25)$$

Where, R_{em} represents the modified Reynolds number, defined as;

$$R_{em} = \frac{\mu_s d_p \rho_f}{(1-\varepsilon_0)\eta} \qquad (26)$$

Let us now establish a universal frame of reference by connecting the concept of a friction factor with that of the flow "constants" referred to above by stating that, in the limit, as the flow rate through any conduit tends to zero (fluid at rest); the Ergun viscous type friction factor (f_v) becomes equivalent to what we have defined herein as the Kozeny/Carman constant (K_C), which also happens to represent the Kozeny/Carman type friction factor f_K.

We can write this relationship algebraically as:

$$\underset{(\text{Lim } q \to 0)}{f_v} = \underset{(\text{Lim } q \to 0)}{(A + BR_{em})} = A = K_C \qquad (27)$$

(when $q \rightarrow 0$, $BR_{em} \rightarrow 0$)

1.3 **The Hydrodynamic Equivalency Assumption**

We now backtrack somewhat to clarify that our assumption stated above concerning the hydrodynamic equivalency between an empty and a packed conduit requires some modification. We now suggest that the classical Poiseuille equation for flow in an empty conduit is not totally accurate. As we have previously stated, the equation is valid only for laminar flow and, thus, it should reflect only linear contributions to measured pressure drop. We postulate, however, that the empirical procedure, by which the value for its constant was identified, was contaminated by kinetic contributions which the equation did not isolate. This resulted in the value of 32 being a *little* too low to properly correlate measured pressure drop when only *linear* contributions are considered. Since *kinetic* contributions, however small, are a function of the second power of the fluid velocity, which makes the relationship *quadratic* rather than *linear*, the effect of small contributions can be significant.

As reflected hereinafter, we assert that the true value for the Kozeny/Carman constant is approximately 268, which is also the value for A in our Q-modified Ergun model. This value is approximately 5% larger than the value of 256, which we derived above as the Kozeny/Carman type friction factor. Accordingly, the corresponding corrected value for the Poiseuille constant in an empty conduit, when expressed as a Poiseuille type friction factor, is approximately 5% greater than the accepted value of 32, i.e. 33.5. We further represent that we have *independently* validated this value using third party published data and refer the reader to our web site for a description of this validation process [32].

Finally, we note that a discrepancy of circa 5 % in the value of the Poiseuille constants above is within the measurement error of many experimental protocols and especially in the case of historical measurements before the advent of accurate pressure measuring devices, such as modern day pressure transducers, for instance. Thus, one could argue that the genesis of this discrepancy resides in the lack of accurate measurement techniques especially in experimental results which are now dated.

We call the relationship described by equation (25) the "Q-modified Ergun equation" where the value of A is *always* 268 approx.

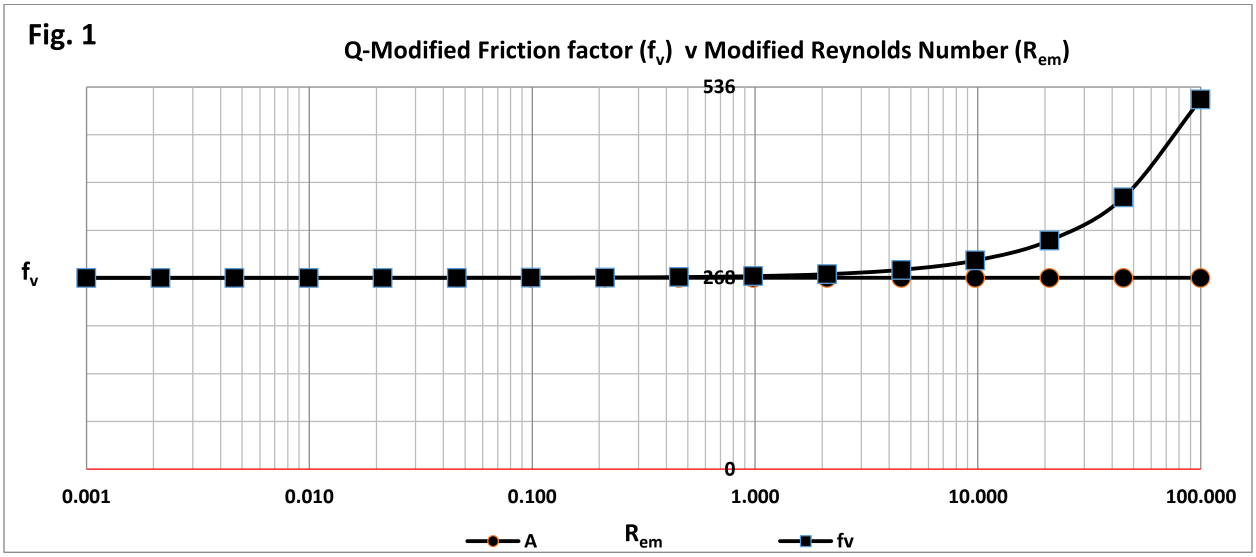

Fig.1 f_v is our Q-modified Ergun type friction factor. A is the constant in our Q-modified Ergun type friction factor. R_{em} is the modified Reynolds number.

As shown in Fig. 1, the numerical value of f_v and A are virtually identical (268) at values of the modified Reynolds number close to zero and deviate increasingly as the value of f_v increases continuously with the value of the modified Reynolds number, above the value of unity.

1.4 Giddings' Empirical Validation of the Value of 268 for K_C

We focus our attention now on arguably the most important work relating to fluid flow in packed chromatographic columns, which is the now famous first text book of J.C Giddings published in 1965 [33]. At page 198 of the text book, in a footnote, he teaches; "It is impossible to make an absolute distinction between inter-particle and intra-particle free space in connection with flow. All inter-particle space is not engaged in flow because the velocity approaches zero at all solid surfaces and at certain stagnation points. Conversely, all intra-particle space is not totally impassive to flow". Further on in the text, at page 208, when discussing packed bed permeability in the context of the Kozeny-Carman equation, Giddings further opines in relation to the precise value of the constant in that equation; "If it is assumed that for $f_0 = 0.4$, this equation yields $\phi' = 202$. The empirical value, as mentioned earlier, is closer to 300. *The same magnitude of discrepancy has been noted by Bohemen and Purnell and by dal Nogare and Juvet for gas chromatographic supports*. Hence the factor 300 would appear to be quite reasonable for most chromatographic materials with $f_0 \sim 0.4$" (emphasis added). We note that Giddings' nomenclature for f_0 corresponds to our nomenclature of ε_0, which represents the external porosity of a packed column. Accordingly, Giddings identifies (in 1965) a basic boundary condition of permeability in packed columns by defining the value of his ϕ' parameter to be 300 when the external porosity of the chromatographic column under study, ε_0, is 0.4

By announcing the revised value of 300 for his ϕ' parameter, Giddings was clearly rejecting the previously accepted *lower* value of 202 corresponding to the value of 180 for $K_{C,}$ the constant in the Kozeny/Carman equation [34], an assertion which he says was clearly supported by *four* other authors in the field of gas chromatography as far back as 1965. This adjustment in the value of his ϕ' parameter amounts to an increase of a factor of 1.5 (300/202 = 1.5) which when applied to Carman's identified value of 180 in Giddings' equation (5.3-10), corresponds to the new value of 267 (180x1.5 = 267). Accordingly, since this Giddings modified value for the Kozeny-Carman constant was first disclosed in 1965, it is of a more recent vintage than either Carman's value of 180, derived in 1937, or the even more recent value of 150 derived by Ergun in 1952. For an in depth analysis of the basis upon which we believe that Giddings got it right and that this adjustment is justified, see the paper by H.M. Quinn [35].

In order to comprehend fully the ramifications of Giddings' teaching for his ϕ' parameter and to demonstrate that his experimental results validate our value of 268 for K_C, we must take a closer look at how Giddings' nomenclature for terms and experimental protocols lines up with ours. In order to connect the dots, therefore, between his methodology and ours, we include herein in our Table 1 an elaboration of Giddings' Table 5.3-1 on page 209 of his 1965 textbook which contains his reported experimental results.

Table 1	ε_t	Φ	ϕ	ϕ_i	ϕ_o	ϕ'	Ψ_γ	K_C
Particle/Column Description		ε_0	$\Delta P_m d_p^2$	$\Delta P_m d_p^2$	$\Delta P_m d_p^2$	ϕ_i	$(1-\varepsilon_t\Phi)^2$	$2\phi'$
		ε_t	$\mu_t \eta L$	$\mu_i \eta L$	$\mu_s \eta L$	2	$(\varepsilon_t\Phi)^3$	$\Psi_\gamma \varepsilon_t \Phi$
Units	none	none	none	none	none	none	none	none
Nonporous Particles								
Giddings' traditional nonporous column	0.4000	1.00	601	601	1,502	300	5.625	267
Gidding's Table 5.3-1								
50/60 mesh glass beads	0.4222	1.00	500	500	1,184	250	4.436	267
50/60 mesh glass beads	0.4085	1.00	560	560	1,371	280	5.133	267
Porous Particles								
Giddings' traditional porous column	0.6000	0.67	900	600	1,500	300	5.625	267
Gidding's Table 5.3-1								
30/40 mesh alumina	0.8031	0.50	1,204	600	1,499	300	5.616	267
50/60 mesh alumina	0.8373	0.50	1,043	520	1,246	260	4.665	267
60/80 mesh chromasorb W (5% DNP)	0.7659	0.50	1,404	700	1,833	350	6.867	267
60/80 mesh chromasorb W (20% DNP)	0.7850	0.50	1,333	660	1,698	330	6.358	267
Giddings' empty conduit equivalent	1.0000	2.00	33	67	33	33	0.125	267

Table 1 This Table represents an elaboration of Giddings' Table 5.3-1 published in his 1965 text book.

Giddings eliminated the uncertainty of the measurement of external porosity, ε_0, in columns packed with porous particles by employing the chromatographic technique of injecting small unretained solutes into his packed columns under study. This measurement technique resulted in an accurate value for ε_t, the total porosity of a column packed with *porous* particles, but it also provided an accurate value for the external porosity, ε_0, when the particles in the column were *nonporous*.

The term ε_t, in our nomenclature, is defined as;

$$\varepsilon_t = \varepsilon_0 + \varepsilon_i \qquad (28)$$

Where ε_t = the conduit *total* porosity and, ε_i is defined, in turn, as;

$$\varepsilon_i = \underline{V_i} \qquad (29)$$

V_{ec}

Where ε_i = the conduit *internal* porosity and V_i = the cumulative pore volume of all the particles.

Let us define the term ε_0, *alternatively*, in the context of Giddings' experimental permeability methodology:

$$\varepsilon_0 = 1 - \rho_{pack}(S_{pv} + 1/\rho_{sk}) \tag{30}$$

$$\rho_{pack} = \frac{M_p}{V_{ec}} \tag{31}$$

Where, ρ_{pack} = the column packing density; M_p = mass of particles in a given column; S_{pv} = the specific pore volume of the particles, ρ_{sk} = the skeletal density of the particles.

Let us now derive the definition for particle porosity, as follows:

$$\varepsilon_p = S_{pv}\rho_{part} \tag{32}$$

Where, ε_p = the particle porosity; ρ_{part} = the apparent particle density;

In order to identify the value of ε_0 in columns packed with porous particles, Giddings did not rely *directly* on chromatographic measurements of *column* external porosity. Rather he used the *independently* determined value of the *particle* porosity, ε_p, and supplemented his measured value for ε_t with gravimetric measurements of the amount of particles packed into each column. This experimental technique allowed him to identify the value of his Φ parameter, defined as the ratio of both porosity parameters, i.e. $\Phi = \varepsilon_0/\varepsilon_t$. Moreover, he eliminated the uncertainty of measuring the particle diameter of porous particles, d_p, by using well-defined particle sizes (smooth spherical glass beads) of nonporous particles, which he used in combination with his accurately determined values of ε_t (equivalent to ε_0 in columns packed with nonporous particles) and by the technique of cross- correlating the pressure drops measured in these columns with pressure drops measured in columns containing porous particles with identical particle diameter values, he grounded his permeability conclusions relative to particle size and column external porosity in the bedrock of measurements made with nonporous spherical particles. Thus Giddings' methodology is based upon the dependent relationship between particle size, d_p and column external porosity, ε_0, through the correlation factor, n_p, which is the actual number of spherical particle equivalents packed into any given column based upon its value of d_p.

We can express this relationship algebraically, as follows;

$$\frac{n_p \pi d_p^3}{6} = V_{ec}(1-\varepsilon_0) \tag{33}$$

Where, n_p = the number of spherical particle equivalents packed into any given column.

It follows that we may now algebraically express the external porosity, ε_0, as follows;

$$\varepsilon_0 = 1-(2n_p d_p^3)/(3D^2L) \tag{34}$$

In addition, in his studies relating to column permeability, Giddings used the concept of the flow resistance parameter $\phi = \Delta P_m d_p^2/(\mu_t \eta L)$, rather than the permeability parameter K_0. This is significant because his ϕ parameter identifies *separately* the value of the particle diameter, d_p, which in contrast, the permeability parameter, K_0, does not. The symbol ΔP_m represents his *measured* values of the pressure drop as opposed to the theoretically *calculated* value. Accordingly, it is obvious that use of the permeability parameter, K_0, would leave the value of the particle diameter, d_p, embedded in the measured value of ΔP_m and, in the absence of measuring the mass of particles packed into a given column under study, would not provide the additional degree of intelligence of identifying, *simultaneously and independently*, the *measured* values of particle diameter, d_p and column external porosity, ε_0, which is a *prerequisite* to validate the value of K_C from experimental measurements of pressure gradient. On the contrary, Giddings was careful to identify the value of d_p *independently* from measurements of pressure differential, thus setting a reference value against which he titrated his measurement technique for column resultant porosity following the Laws of Continuity.

Thus, Giddings was ahead of his peers in using a fundamentally superior technique for defining the components of permeability and, accordingly, he was able to identify the *correct* value of the embedded constant, K_c, which was something that eluded his peers. For instance, Istvan Halasz, one of Giddings' most well respected peers, took a decidedly different approach to identifying the fundamentals of permeability. Because of the difficulty of measuring precisely the particle size of irregular silica particles, Halasz made the startling proclamation that the particle size is defined by the permeability [36]. In so doing, unlike Giddings, he essentially buried his head in the sand relative to particle size and adapted the teaching that one ought to start with an *assumption* relative to the value of K_c and use the Kozeny/Blake equation to back-calculate for the value of the particle size, using Carman's value of 180 for its constant. The problem with this approach, unfortunately, is that Carman's value of 180 was erroneously derived in the first instance [37] and, accordingly, Halasz is responsible for "putting the rabbit in the hat" relative to the value of K_C, which is a practice that his disciples have continued to this very day [44] p. 85.

By using his resistance parameter methodology in his permeability studies of packed columns, however, Giddings had to content with the reality that his measurement of column total porosity, ε_t, resulted in his identification of the *mobile phase velocity, μ_t,* which in the case of columns packed with porous particles was a major complicating factor relative to third party empirical permeability equations, such as Poiseuille's for flow in an empty conduit and Kozeny/Carman for flow in a packed column, in as much as it contains a contribution from molecular diffusion within the stagnant pores of the particles, which is not driven by pressure differential. Accordingly, since the aforementioned third party equations were both defined based upon the use of *superficial fluid velocity, μ_s*, with a corresponding flow resistance parameter $\phi_0 = \Delta P_m d_p^2/(\mu_s \eta L)$, he was forced to come up with a frame of reference which would connect his methodology to theirs. Moreover, on the one hand, there was the additional complicating factor that the *actual* velocity that exists in a packed column is neither the mobile phase nor the superficial but rather the *interstitial fluid velocity, μ_i*, with yet another corresponding flow resistance parameter $\phi_i = \Delta P_m d_p^2/(\mu_i \eta L)$ but conversely, on the other hand, interstitial velocity does not ever exist in an empty conduit, which always contains the superficial velocity. This means that he had to invent a methodology which would enable an apples-to-apples comparison between permeability in *all* flow embodiments at a comparable velocity frame, i.e. interstitial velocity, μ_i, which is the only *fluid* velocity frame that actually exists in packed conduits when pressure drops are recorded and, superficial velocity, μ_s, which is the only *fluid* velocity frame that actually exists in empty conduits when pressure drops are recorded and, the remaining *mobile phase* velocity, which is not a fluid velocity term at all, but rather the velocity of a small unretained solute which penetrates the inner pore volume of the particles in the column, a mechanism driven by solute concentration, *not pressure gradient.*

Therefore, Giddings devised a *specifically tailored* definition of his dimensionless flow resistance parameter, to which he gave the symbol ϕ', and which would render an approximate constant value no matter what combination of fluid velocity, (μ_s, μ_i, μ_t), particle porosity type (porous, nonporous) or conduit type (packed or empty) a practitioner wanted to employ.

Accordingly, his ϕ' parameter represents the dimensionless "constant" in Giddings' equation which can be applied to a wide variety of different experimental protocols and can include any one of the three distinctly different types of fluid linear velocity encountered in the study of packed conduits containing either porous or nonporous particles, on the one hand, and empty conduits, which contain no *solid* particles at all, on the other hand. Although its value varies somewhat between 250 and 350 for the packed columns reported in his Table 5.3-1, it does represent a meaningful benchmark within the context of permeability in packed chromatographic columns, to the extent that it incorporates a great variety of particle types, both nonporous and porous, of various particle porosities.

As can be seen from our Table 1 herein, our elaboration of Giddings Table 5.3-1 contains our supplemental definitions for Giddings' terms, which ties together his measured results with his reported values for his ϕ' parameter for his nonporous glass beads as well as his porous particles of Alumina and Chromasorb.

Note in particular, that we have included at the bottom of our Table 1 a line item labeled "Giddings' empty conduit equivalent" which has a ϕ' value of 33. This clarifies the meaning of his ϕ' parameter with respect to an empty conduit, inasmuch as it identifies it as our Poiseuille's type friction factor and confirms that, just as we have independently concluded herein, Giddings had also concluded in 1965 that the numerical value of 32 contained in Poiseuille's equation is just a little too low to correlate accurately empirical data. This line item in the Table also identifies the correlation coefficient for an empty conduit, $\Psi_v = 0.125$, which relates a Poiseuille's type friction factor and a Kozeny/Carman type friction factor. Therefore, Giddings' use of his ϕ' parameter normalized all fluid velocities in an apples-to-apples comparison to that in an empty conduit in which the value of $\phi_0 = \phi' = K_{P,}$ i.e. the "constant" in Poiseuille's fluid flow model.

Note also, as shown in our Table 1, that Giddings' methodology of using his ϕ' parameter to identify the value of K_c, does *not* require the identification of the value of ε_o by itself, but includes it in the ratio, which is his Φ parameter. When the particles are nonporous, on the one hand, this ratio is unity and so measuring ε_t by itself is sufficient to define the value of Φ. When the particles are porous, on the other hand, one simply back-calculates for the value of ε_0 by using his ϕ' parameter, in order to correlate the measured data, and, thus, establish the value of ε_0 embedded in the value of Φ. Therefore, Giddings' methodology, in the case of porous particles, is in conformance with the Laws of Continuity to the extent that he uses the value of, $d_{p,}$ which has been measured independently of the column under study and the *INDEPENDENT* measurement of both particle porosity, ε_p, and the mass of the particles, M_p, packed into any given column. He assigns his independently measured value of d_p as his *independent column* variable and the value of, ε_0, as his *dependent column* variable. Accordingly, by the use of his ϕ' parameter, Giddings' *also* found a way to "engineer" around the difficulty of measuring accurately the value of external porosity, ε_o, in columns packed with porous particles, *without putting a rabbit in the hat with respect to the value of K_C*, as was the method chosen by Halasz to solve *his* unique dilemma, a direct consequence of choosing to work with irregularly shaped particles, in the first instance.

Finally, as is also apparent in our Table 1, the value of 267 for K_C which represents our Q-modified Ergun viscous type friction factor (also the modified Kozeny/Carman type friction factor) compares favorably to our independently asserted value of 268.

2. Experimental

The major objectives of the experimental protocol outlined in this paper are to:

a. Design a fluid flow experiment which meets the standards of a properly configured fluid dynamics experiment, i.e. all contribution to energy dissipation is captured.
b. Minimize/eliminate any and all *uncertainty* related to the experimental variables of particle diameter, d_p, and packed bed external porosity, ε_0.
c. Validate empirically the value of the Kozeny/Carman constant, i.e. the remainder in this empirical equation after all measurable entities have been accounted for.

Since a major source of the uncertainty in the value of K_C relative to modern day HPLC packed columns has to do with the accurate measurement of diameter of *fully porous* particles, d_p, and a determination of the column external porosity, ε_0, two critical parameters involved in the determination of packed column permeability, we use empty conduits (capillaries) in our experiments to eliminate this particular issue. In this way, we replace the difficult-to-measure diameter of fully porous particles, typically less than 2 microns in modern day UHPLC columns, with that of the diameter of a capillary which is several orders of magnitude greater in characteristic dimension. In addition, we use capillaries of different lengths in conjunction with various fluids of varying viscosity to further insure the integrity of our measured values. By invoking the well-known/established Poiseuille's flow model for empty conduits, which does *not* possess a porosity term on its face, (porosity being embedded in the "constant" value of 33), we "engineer" a way around the uncertainty associated with the measurement of porosity in packed columns. Once we establish the value of the residual constant in empty conduits in which we have minimized the uncertainty associated with the measurements of characteristic dimension and conduit porosity, we use it as a "given" when we turn our attention to packed conduits wherein we avoid the use of small, fully porous particles in favor of large, nonporous particles which will, once again, minimize the uncertainty associated with the measurement of particle diameter and packed column external porosity.

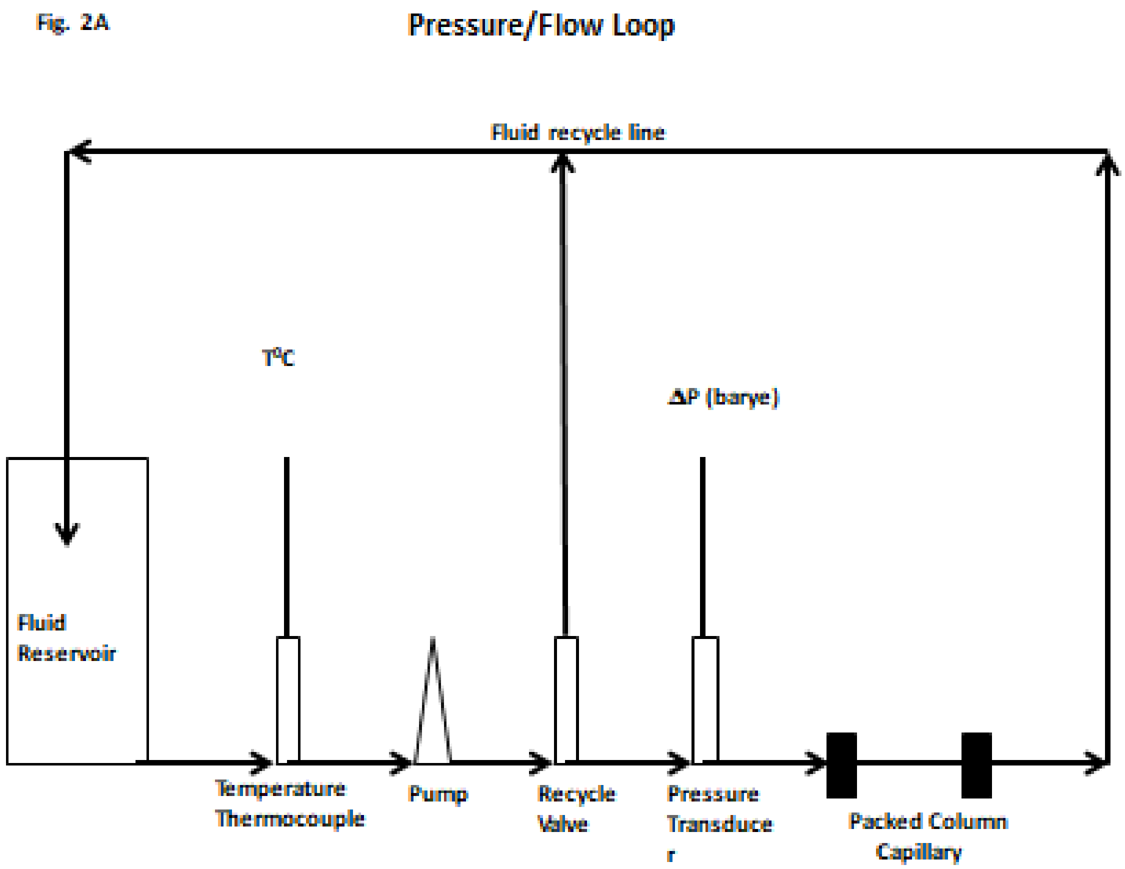

Fig. 2A Pressure/Flow loop used in our experiments to determine the permeability of empty and packed conduit

In Fig. 2A we show a schematic block diagram of the experimental apparatus that we used to measure the permeability in both empty and packed conduits. In every experiment, we measured the temperature, flow rate and pressure drop at as many flow rates as was reasonably possible given the constraints of the pump, i.e. maximum pressure, minimum flow rate and pump power. The pressure drop was recorded by means of a calibrated pressure transducer purchased from Omega, Model # PX409-250DWU5V. It had a pressure range of 0-250 psi and run under a 24V DC power supply. The flow rate was measured for each recorded pressure drop by means of a stop watch and graduated cylinder. The time interval over which the measurement was taken varied with the flow rate-larger for low flow rates and smaller for high flow rates. The temperature of the fluid was recorded by means of a thermocouple purchased from Omega, Model # TCK-NPT-72.

The liquid pump was manufactured by Fluid-o-Tech (Italy), Model # FG204XDO(P.T)T1000. It is an external gear pump, 0-5V, 300-5,000 rpm delivering *pulseless* flow rate under a constant pressure. The flow rate of the pump was controlled by means of a lap top computer running under a software control package manufactured by National Instruments. The pump had a flow rate range of 100-1600 mL/min and a pressure maximum rating of circa 200 psi. This range of flow rates was further enhanced at lower flow rate values by the use of our recycle valve, which was used to shunt the flow between the devise under study and the recycle line.

The Air pump was a 3L Calibrated Syringe type pump manufactured by Hans Rudolf Inc., Shawnee, KS, USA., and Model # 5630, serial # 553.

3. Results and discussion

3.1 Empty Conduits

Experiment # 1

In our experiment # 1, we chose to evaluate the permeability of a commercially available empty capillary made of Peek plastic, an article of commerce in the HPLC industry, which had a nominal diameter of 0.02 inches. We chose to evaluate two different lengths, 100 cm and 726 cm, in order to be able to exploit different modified Reynolds number ranges of the fluid flow regime and we have captured our results in Fig.2.

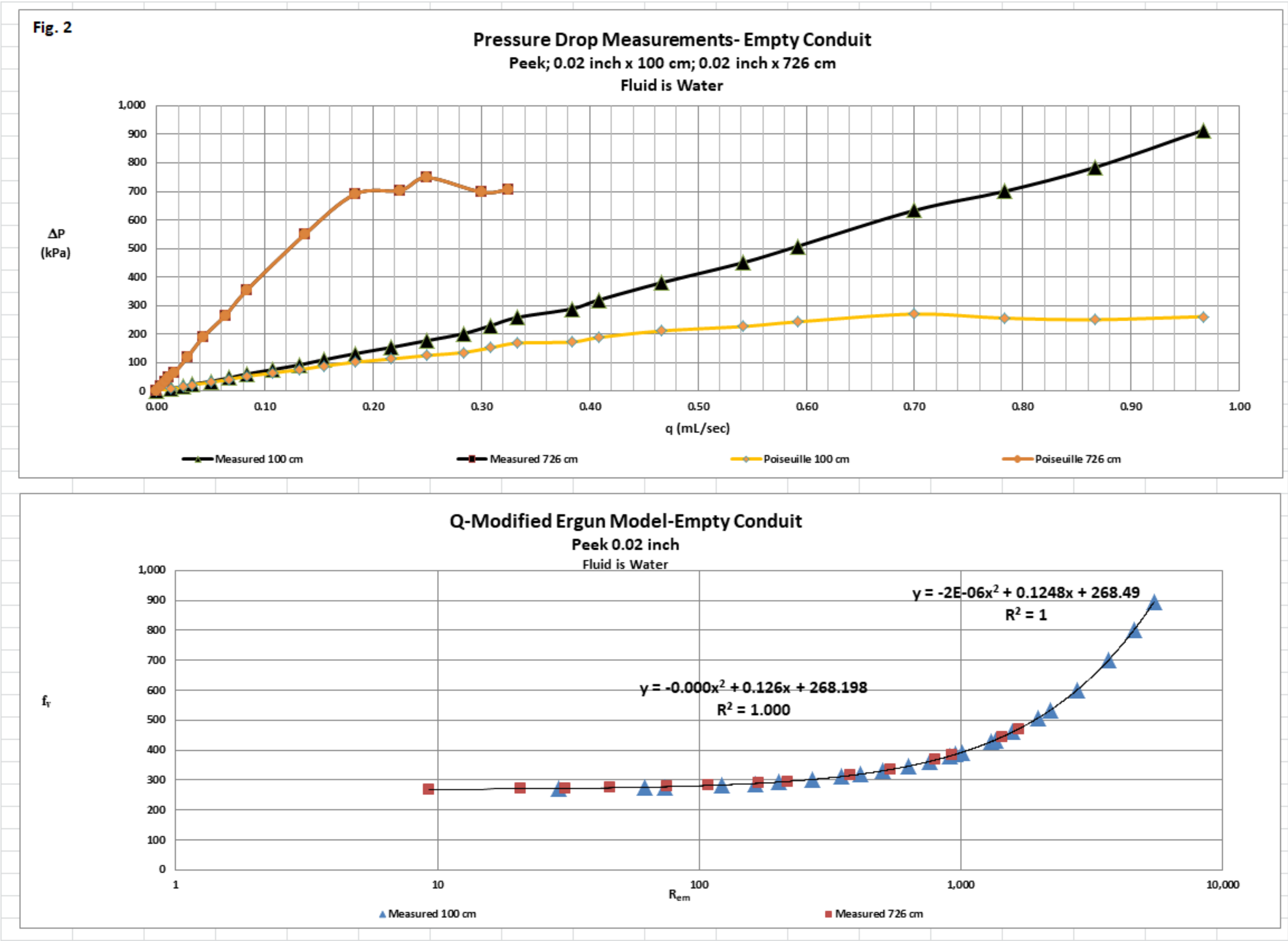

Fig. 2 The measured results for flow capillary with dimensions 0.02 inches in diameter and 100 and 726 cm in length. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As can be seen from Fig.2 in the dimensional plot, Poiseuille's equation, as expected, deviates increasingly from the measured results as the flow rate increases. In the dimensionless plot in Fig. 2, we show a plot of f_v on the y axis and R_{em} on the x axis. Using a logarithmic scale on the x-axis and a quadratic equation of the line for the measured data, we demonstrate that the intercept on the y-axis for the measured data is 268 (approx.) for both capillaries. Finally, as also shown on the dimensionless plot, the Poiseuille's equation does not correlate the measured data at the higher Reynolds number values and is slightly too low, even at the lowest values of the modified Reynolds number.

Experiment # 2.

In our experiment # 2, we chose a Peek capillary of nominal diameter 0.03 inches and lengths of 100 and 700 cm. In this experiment we also included in our measurements two different fluids, water and Glycol, and captured the measured results in Fig. 3. The viscosity of the water was 0.01poise and the density was 1.0 g/mL. The viscosity for the Glycol solution was 0.38poise and the density was 1.14 g/mL.

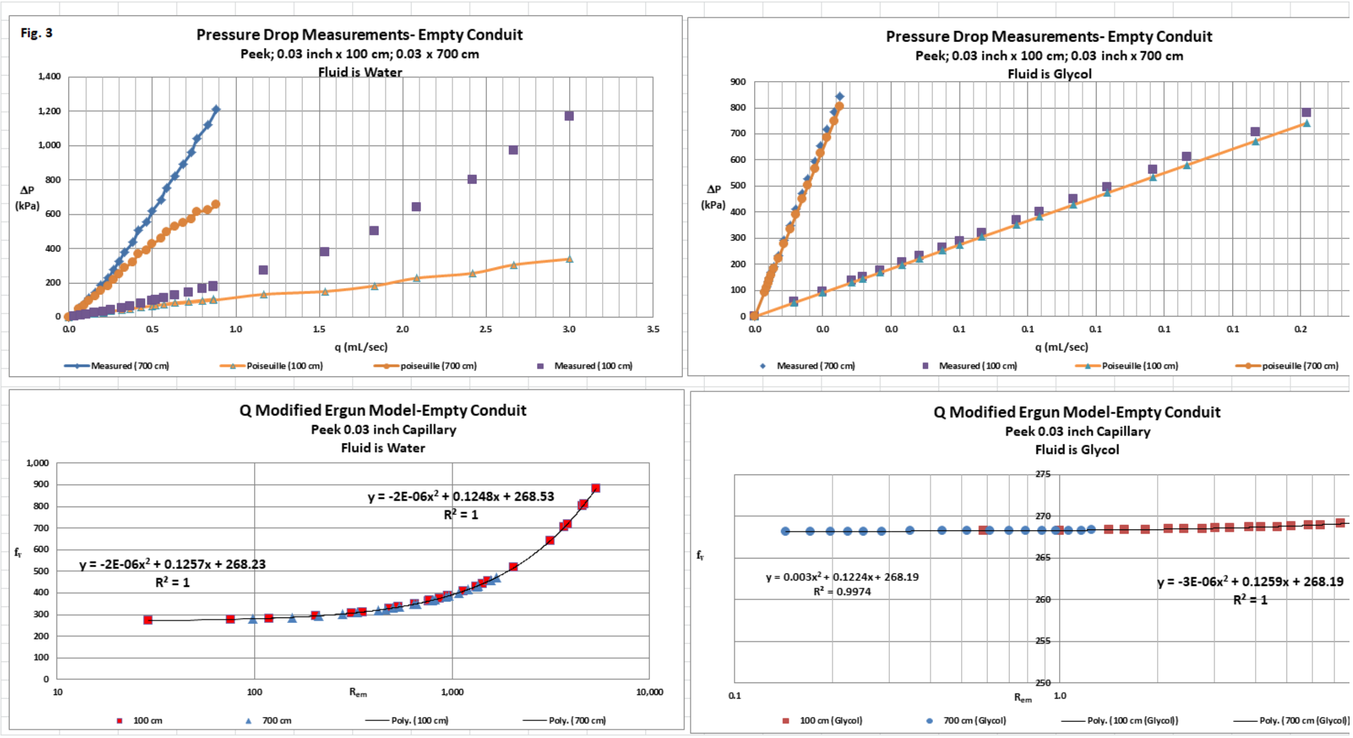

Fig. 3 The measured results for flow capillary with dimensions 0.03 inches in diameter and 100 and 700 cm in length. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As can be seen from Fig.3, by including the measurements in the higher viscosity fluid, Glycol, we are able to focus on the deviations of the Poiseuille's model at lower modified Reynolds number values. This experiment again identifies the universal value of the residual constant as 268 under all measurement conditions.

Experiment #3.

In our experiment # 3, we chose a stainless steel capillary of nominal diameter 0.07 inches x 66.5 cm in length and captured our results in Fig. 4.

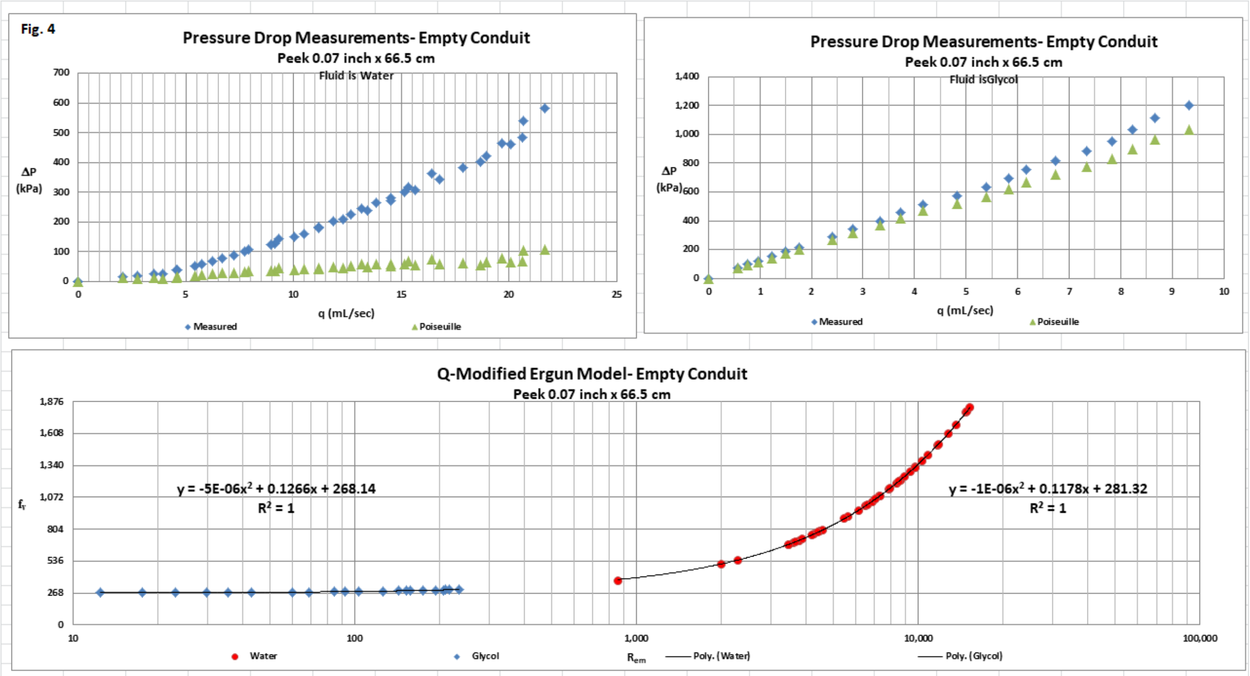

Fig. 4 The measured results for flow capillary with dimensions 0.07 inches in diameter and 66.5 cm in length. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As shown in Fig. 4, the results for this simple one length capillary shows that a practitioner may use it in conjunction with Glycol as the fluid to easily demonstrate the universal value of 268 for the residual constant. This experiment also teaches the practitioner that the intercept is sensitive to the range of Reynolds number covered in the measurements- as shown in the plot an intercept value of 281 represents a higher range of Reynolds numbers.

Experiment #4.

In our experiment # 4, we chose a stainless steel capillary of nominal diameter 0.08 inches x 31.75 cm in length and captured our results in Fig. 5.

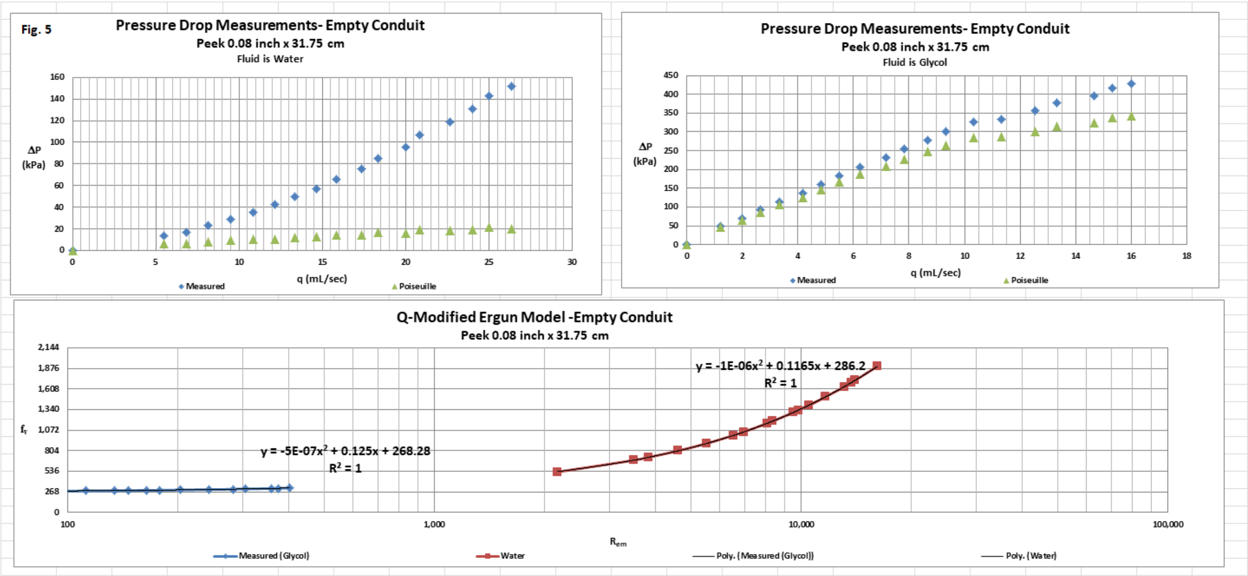

Fig. 5 The measured results for flow capillary with dimensions 0.08 inches in diameter and 31.75 cm in length. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As shown in Fig. 5, the results for this simple one length capillary shows that a practitioner may use it in conjunction with Glycol and water as the fluid to easily demonstrate the universal value of 268 for the residual constant.

3.2 Packed Conduits

In our experiments with packed conduits, we wanted to eliminate issues related to the accuracy of measuring particle size and packed column external porosity. We accomplished this by using very large electro-polished (smooth) stainless steel non porous ball bearings. In addition, by counting the number of particles in each packed column (76 in one case and 45 in the other) and by knowing the exact volume of each particle, we were able to eliminate any uncertainty relating to external column porosity. This particular choice of experimental variables means that our packed columns had extraordinarily *high* values of external porosities and correspondingly *low* values for column to particle diameter ratios, from a chromatographic column utility point of view. However, although such packed columns may not be of great utility in solving modern day separation problems, there is nothing unusual about these packed columns from a hydrodynamic point of view and, accordingly, they easily overcome our experimentally challenging permeability objectives from an accuracy of measurement point of view. Another consequence of this set of experimental variable choices, however, is that our measurements have to be made at relatively high values of the modified Reynolds number, where kinetic contributions play a dominant role in the overall contributions to measured pressure drop. Accordingly, in order to experimentally identify the value of A in this flow regime, we must normalize our measured pressure drops for kinetic contributions which dictate that we must first identify the value of B in our dimensionless manifestation of the Q-modified Ergun viscous type friction factor.

We begin by repeating our equation (25) which represents the friction factor in the Q-modified Ergun viscous type friction factor;

$$f_v = A \quad + BR_{em} \tag{25}$$

We now make use of our determination of the value of 268 for A above, by substitution this numerical value into equation (25). Thus we may write:

$$f_v = 268 \quad + BR_{em} \tag{35}$$

Rearranging equation (35) to isolate the value of B gives:

$$\frac{f_v - 268}{R_{em}} = B \tag{36}$$

Since we have experimentally measured every variable on the left hand side of equation (36) for each data point in our study, we can calculate the value of B corresponding to *each recorded pressure drop* by using equation (36). Accordingly, the value of B represents a lumped parameter which, when combined with the value of the modified Reynolds number, contains *all* the individual kinetic contributions, whatever they may be. We can now further exploit the relationship in equation (25) to determine the value of A in any experimental packed column under study. To accomplish this objective we make a plot of f_v on the y axis and BR_{em} on the x axis and using a *linear* equation as a fit to the measured data in the experimental column, we can identify the value of A as the intercept on the y axis. This procedure normalizes for kinetic contributions by setting the slope of the straight line in this plot equal to unity.

In reality, therefore, in the case of a *packed* conduit, our methodology to identify the value of A normalizes the *flow term* for *kinetic* contributions in the *non-linear* component of the pressure flow relationship. This is in contrast to our methodology to identify the value of A in an *empty* conduit, which normalizes the *pressure drop term* for *viscous* contributions in the *linear* component of the pressure flow relationship. Accordingly, our methodology is *orthogonal* with respect to its identification of the value of A in empty and packed conduits, respectively, as well as in laminar and non-laminar flow regimes, respectively.

Experiment # 5.

In our experiment number 5, we placed 76, nominal 4 mm stainless steel perfectly spherical ball bearings into a 0.46 x 30 cm peek column. The particles were touching each other at a single point in the packed column array. The column end-fittings were custom-drilled to accommodate large diameter end fittings. We used both water and Glycol as the fluid and captured our measured results in Fig. 6.

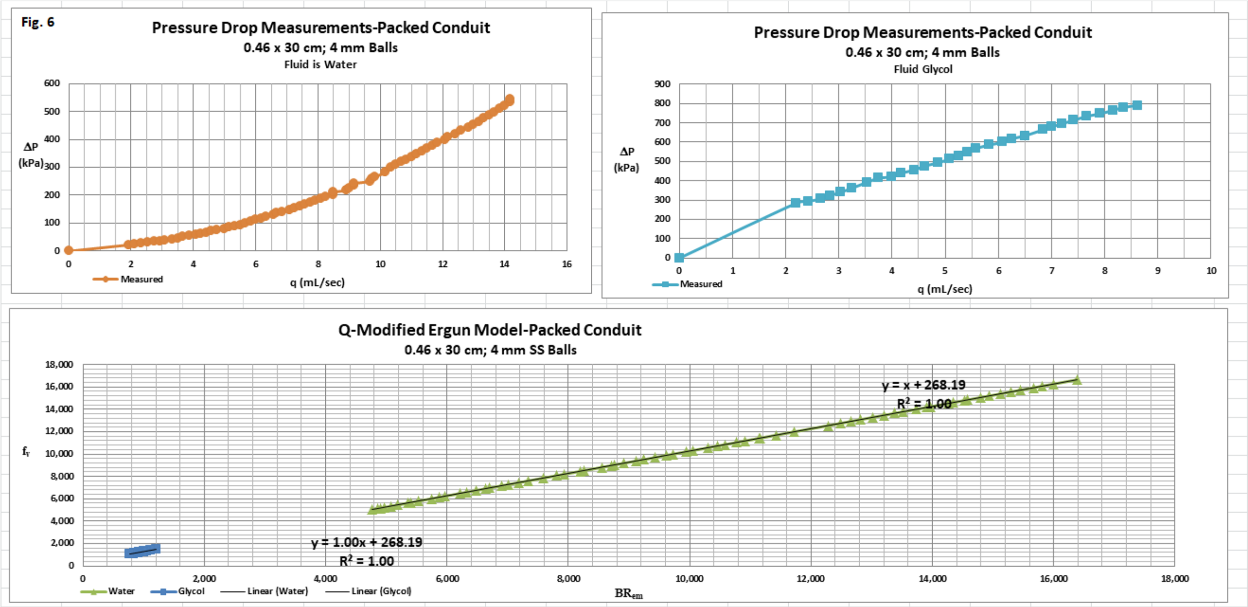

Fig. 6 The measured results for the packed conduit with dimensions 0.46 cm diameter and 30 cm in length. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as normalized modified Reynolds number versus friction factor.

The measured external porosity of the column, ε_0, was 0.499 and the value of the particle diameter, d_p, was 3.975 mm. As can be seen in the dimensionless plot in Fig. 6, the data points in both lines representing the measured data fall on a straight line of slope unity and intercept 268, thus validating the value of A.

Experiment # 6.

In our experiment number 6, we used two different values of external porosity in the experiment. The column that we used with air as the fluid had 41 particles and the other column which we used with both light oil and glycol had 45 particles. These particles were nominal 10 mm stainless steel perfectly spherical ball bearings in a 1.07 x 40.6 cm stainless steel column. The particles were touching each other at a single point in the packed column array. The column end-fittings were custom-drilled to accommodate large diameter end fittings. We used both light oil and Glycol as the fluid in one column and air as the fluid in the other and we captured our measured results in Fig. 7. In the experiments with the light oil, we used the value of 0.153poise, for the absolute viscosity of the fluid, and a value of 0.80 g/mL for fluid density.

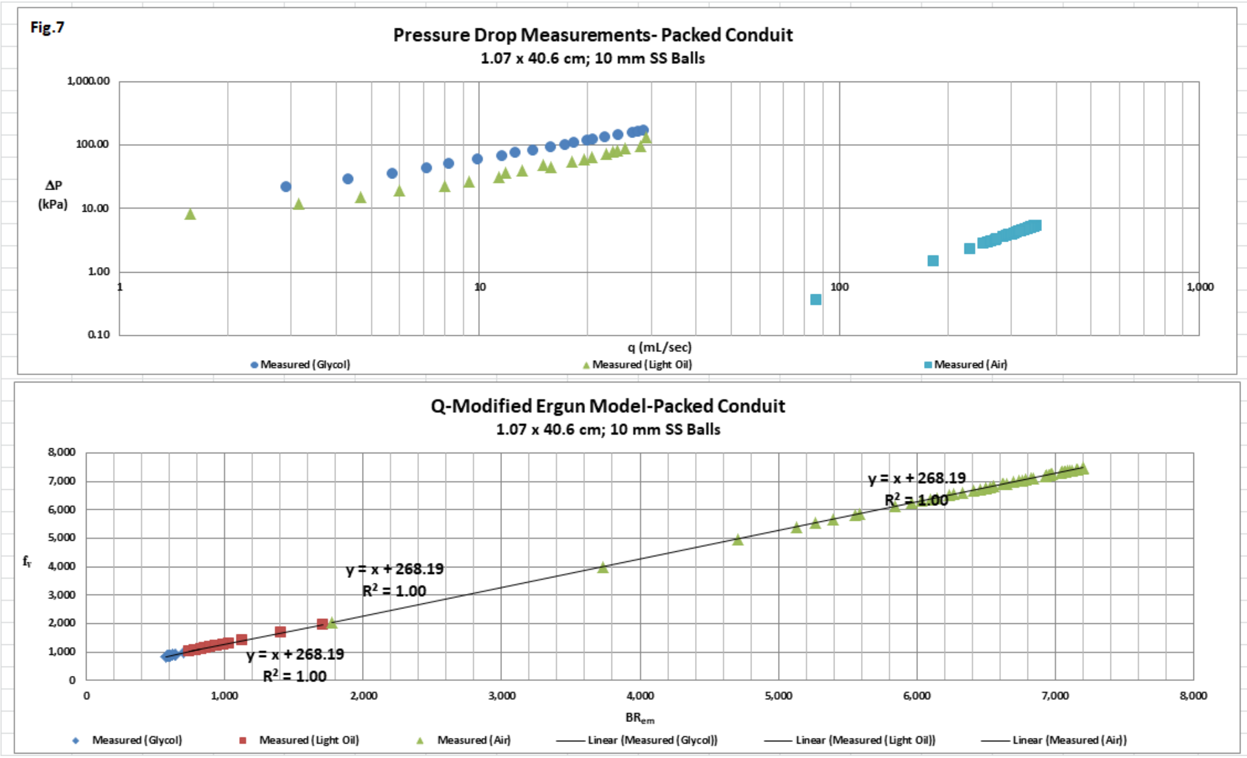

Fig. 7 The measured results for the packed conduit with dimensions 1.07 cm diameter and 40.6 cm in length. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as normalized modified Reynolds number versus friction factor.

The measured external porosity of this larger volume column, ε_0, was 0.44 corresponding to the column with 45 particles, and 0.49 corresponding to the column which contained the 41 particles. The value of the particle diameter, d_p, was 9.525 mm. As can be seen in Fig. 7 the data points in all three lines representing the measured data fall on a straight line of slope unity and intercept 268, thus validating the value of A.

3.3 Third Party Independent Validation of experimental Protocol

Whenever one seeks to challenge conventional wisdom, as we are doing in this paper, one must be vigilant to guard against criticism of all different kinds. In order to defend our methodology against those who may suggest that it is based solely upon measurements made in our own laboratory, which is true, and consequently may not be repeatable or reproducible, which is *not* true, we look to validate using independent means. To this end we include in this section the experiment of Sobieski and Trykozko published relatively recently (2014)[38].

In their experiment, they used non porous smooth spherical glass beads of diameter 1.95 mm. Their column was 90 cm in length and 8 cm in diameter. Accordingly, the empty column volume was about 4.5 L, all of which translates into very manageable measurements from an accuracy point of view. They used water as the fluid and were careful to measure the temperature of the fluid when recording the pressure drops. They reported the results of their experiments in

Table 1 and 2 in the paper as well as providing a plot of pressure drop against fluid velocity in Fig.8. We have captured their results in our Fig. 8.

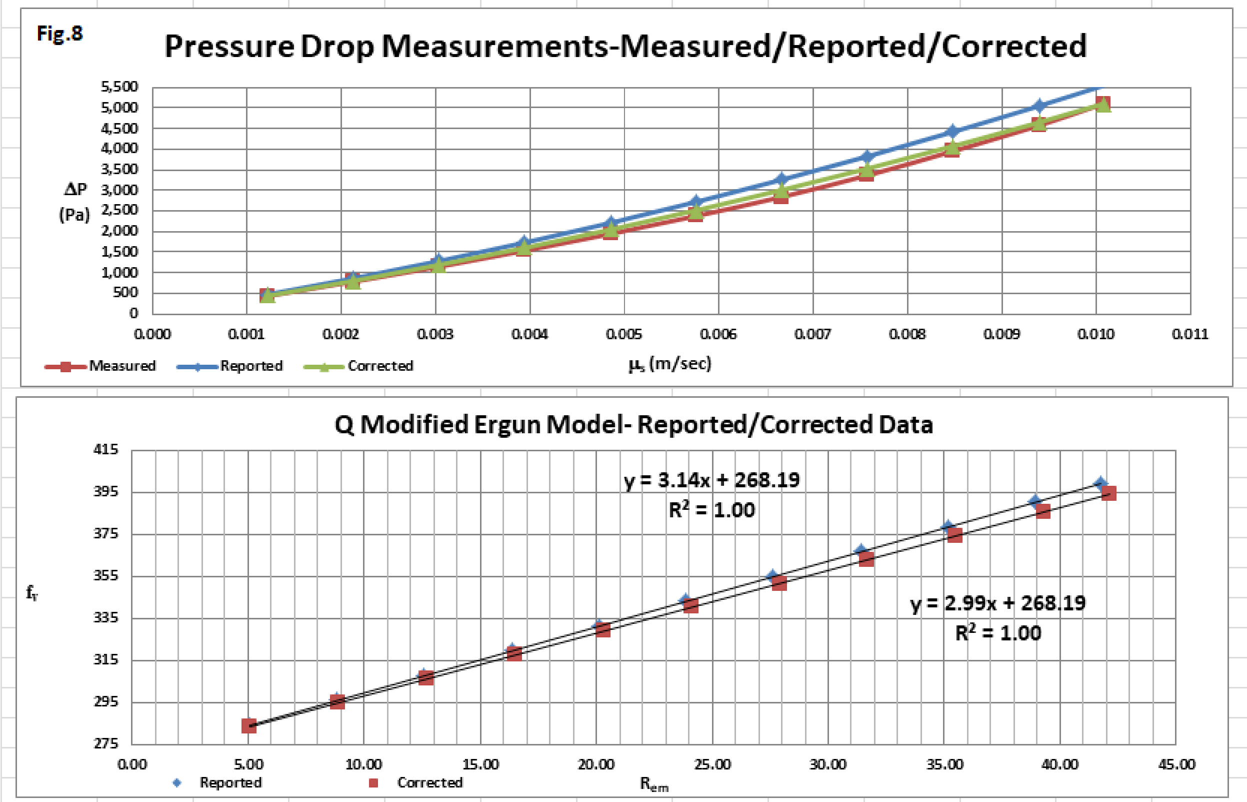

Fig. 8 Experimental results of Sobieski et al. Upper plot is pressure drop against velocity. Lower plot is dimensionless plot of f_v against Rem

We point out initially that the experimental design parameters in this experiment represent a "special case" of our teaching protocol herein, to the extent that the measurements were all taken over a range of modified Reynolds numbers in which the value of B is virtually constant. Accordingly, we may use a linear regression analysis in our plot of f_v against R_{em} to validate *both* components of our methodology, i.e. validate the value of A and identify the correct value of the kinetic coefficient, B. As is shown in Fig 8, in the dimensional plot, the measured pressure drop values do not line up exactly with the calculated pressures based upon the reported underlying variables. In the dimensionless plot, the reported underlying variables validate the value of 268 for A and a value of 3.14 for B. This value of B is not accurate, however, because it does not correlate the data perfectly, especially at the higher values of the modified Reynolds number. We have adjusted the value of ε_0, reported as 0.37, to the value of 0.376 in order to correlate the measured data. This represents an increase of 1.7% in the value of ε_0. The corrected data in the dimensionless plot, which correlates the measured values perfectly, generates a value of 2.99 for B which is a decrease of 4.8%.

Accordingly, our protocol outlined in this paper, when applied to the experiment of Sobieski et al, validates the value of 268 for A and a value of 2.99 for B, with an uncertainty of less than 2% in the value of the external porosity, ε_0, and less than 5% in the value of B.

4. Some Worked Examples.

Now that we have disclosed a methodology to enable a practitioner to identify the value of A in a packed column, let us demonstrate the utility of the teaching from the perspective of a potential researcher who wants to use it to evaluate the credibility, or lack thereof, of third party published permeability experiments.

Example 1.

In this example, we evaluate our own measured permeability results for column number HMQ-2 which was manufactured circa the year 2000, approximately 18 years ago, in the author's laboratory in Franklin, Ma. This column consisted of a stainless steel column 248 cm (8 ft.) in length and 1.002 cm in diameter. The column was manufactured by placing the empty conduit upright in a holding devise and this author, by means of a step ladder, placed 1 mm diameter spherical glass beads into the column by pouring the dried beads into the column slowly, while at the same time, vibrating the column with a hand-held mechanical vibrator, a typical dry-packing technique well-known in conventional HPLC circles. After the column was filled with the glass beads, water was poured into the column slowly until it overflowed. The amount of water in took to fill the column (76 ml) represents the volume of fluid external to the particles in the packed column and, when divided by the empty column volume of 196 mL, results in an external porosity value, ε_0, for this nonporous particle column, of 0.39. The choice of this large internal volume column in combination with nonporous glass beads of 1 mm nominal diameter, was driven by the design objective to, once again, minimize the measurement uncertainty in the measured values of particle diameter, d_p, and column external porosity, ε_0. We used a preparative HPLC pump, manufactured by Ranin Corp., to flow water through the column and the pressure drops were measured by means of a calibrated pressure transducer over a flow rate range of 300 to 500 mL, approx. We have plotted our measured results in Fig. 9, herein.

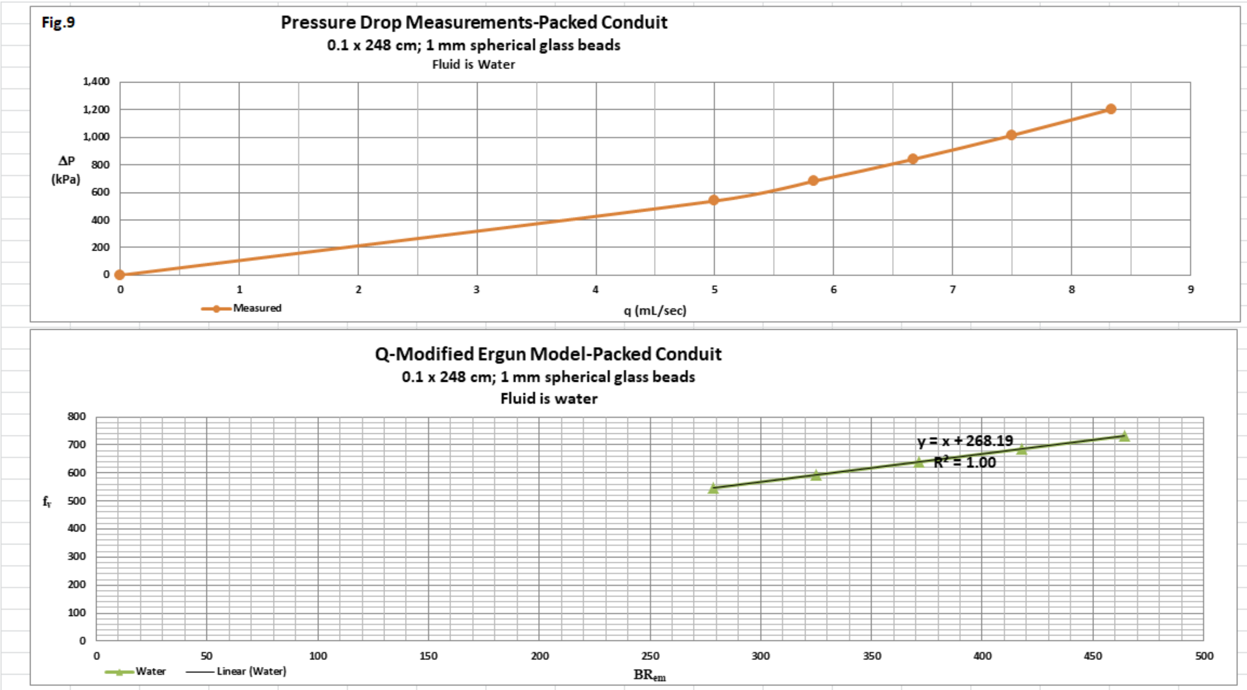

Fig. 9 The measured results for column HMQ-2. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as normalized modified Reynolds number versus friction factor.

As can be seen from Fig.9 the measured data points on the dimensionless plot all fall on a straight line of slope unity and intercept 268 which validate the value of A.

Example 2.

In this example, we examine a published scientific article in the Journal of Chromatography by Cabooter et al (2008) [39]. This publication represents one example of what we have referred to above regarding the value of the Kozeny/Carman constant, K_C, being used as a tool to justify false separation performance claims pertaining to the modern chromatography columns containing the so-called sub 2 micron particles. In this paper, the authors report 6 different values for K_C supposedly based upon their experimental assessment of 6 different commercially available chromatographic columns. We will use our methodology disclosed herein, however, to demonstrate that, not only did the authors not experimentally validate their erroneous values for K_C by using credible scientific principles, but also, the values of their underlying combinations for the parameters of d_p and ε_0, are demonstrably false. In our Fig. 10 herein, we have captured the authors' reported results and applied our methodology reported herein to demonstrate that, not only is our teaching herein effective in identifying substandard scientific publications, but also, it can be used effectively to correct the reported data and present a true picture of what the experimental results really identify as the underlying values for the various equation variables.

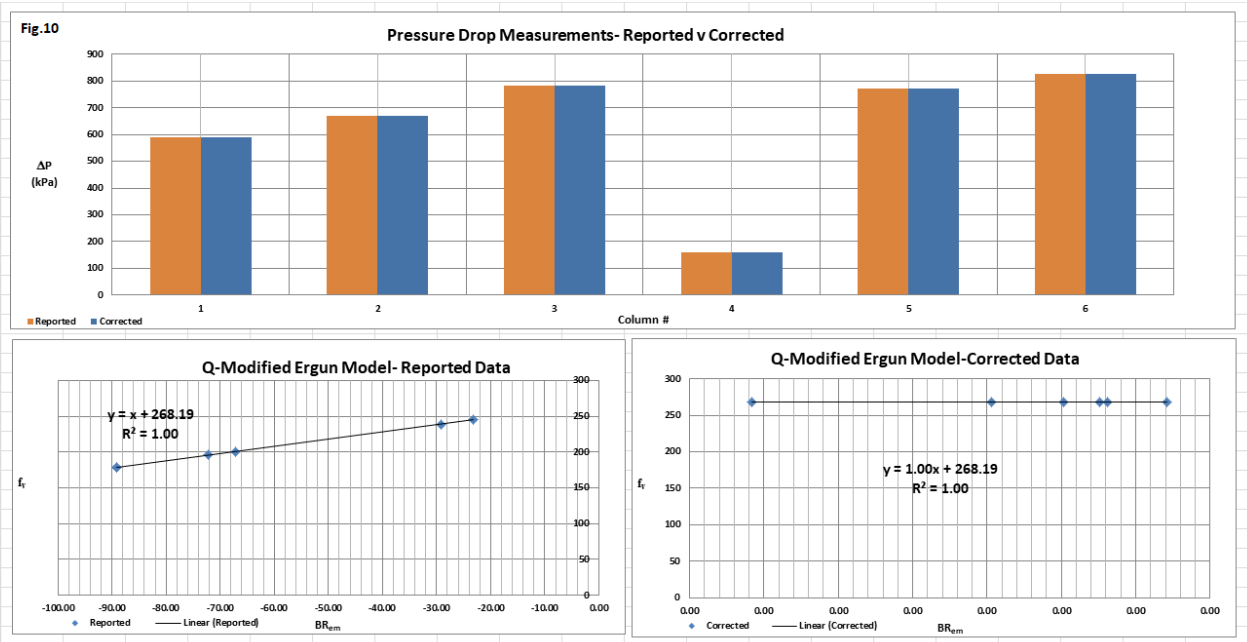

Fig. 10 The measured results for the Cabooter et al paper. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as normalized modified Reynolds number versus friction factor.

As can be seen in the dimensionless plot in Fig. 10 representing the *reported* results, the values of f_v on the y axis are identical to the values of K_C reported by the authors for each of the 6 columns, but when their reported modified Reynolds numbers values are normalized for kinetic contributions on the x axis, the intercept of the straight line has a value of 268, thus validating the *true* value of K_C. However, *all* the plotted values on the x axis are negative (less than zero). On the other hand, as can also be seen in the dimensionless plot in Fig. 10 representing the *corrected* results, all 6 values of f_v on the y axis have the same value of 268 and all the corresponding modified Reynolds number values when normalized for kinetic contributions on the x axis, are positive (greater than zero). We have also included in Fig. 10, a dimensional plot of the measured pressure drop versus fluid flow rate for both the reported results as well as our corrected results to demonstrate that our correction methodology does not alter any of the measured values which are not subject to measurement uncertainty.

The only scientifically valid explanation for the negative values of BR_{em} on the x axis for the reported results is that the fluid in the column was moving backwards *against* the pressure gradient when the pressure drops were recorded within the column, a phenomenon which all knowledgeable scientists will agree is physically impossible. Accordingly, we know that the values of the modified Reynolds numbers derived based upon the reported results are in error. Since the modified Reynolds number parameter is comprised only of 5 discrete variables, μ_s, d_p, ρ_f, ε_o, and η, all of which values we do not question except, d_p and ε_o, we conclude that the combination of these two variables reported by the authors for each of the 6 columns was in error.

This conclusion is also supported by the erroneously reported values for the particle porosity, ε_p, for each of the 6 columns. The authors erroneously determined the value of ε_p, an independent *column* variable, by computing it (erroneously) with their equation (13) which contains all *column* measured variables, $\varepsilon_p = (\varepsilon_t-\varepsilon_0)/(1-\varepsilon_0)$. Their reported values for ε_p for the 6 columns were, 0.402, 0.366, 0.286, 0.245, 0.408, and 0.371 for columns numbered 1 through 6, respectively. The correct values for ε_p, on the other hand, which *must* be determined *independently* of the column measured parameters and which are typically available from the manufacturers of the particles, are 0.623, 0.623, 0.623, 0.623, 0.579, and 0.579, respectively.

In a given fixed volume of free space, the internal volume of a given empty column, for instance, the Laws of Continuity dictate that for a given mass of particles packed into that column, there is but one *unique* combination of the values of ε_p, d_p, ε_0, ΔP and q, all other variables being held constant, that establishes a valid correlation between calculated and measured permeability. Since the authors of this paper did not measure or report the mass of the particles packed into each of the columns under study, reporting measured values of underlying equation variables, such as d_p and ε_0, which is what these authors did, does *not* by itself, constitute a validation process for *any* value of K_C. Moreover, since the authors got the value of ε_p wrong for each column in the study, by virtue of their use of an invalid procedure using their equation (13) in the paper, we know *for certain* that, their values reported for d_p and ε_o are entirely arbitrary.

Our corrected values, on the other hand, are based simply upon the independently derived correct value of ε_p for each of the columns, which we obtained from the manufacturers of the particles. By identifying a specific mass of particles packed into each column corresponding to the specific particle porosity in that particular column, we are able to deduce a *valid combination of* d_p and ε_0 (not necessarily the *correct* combination because the authors never measured/reported the mass of particles in the actual columns under study) underlying the reported permeability results for each column. Since these two values are *dependent* variables, in the absence of other specific knowledge, we used the reported value for d_p as the independent variable and the value of ε_0 as the dependent variable, in our correction methodology. Our resultant corrected values for ε_o were 0.376, 0.379, 0.413, 0.415, 0.394, and 0.384 for columns numbered 1 through 6, respectively. These corrected values for external porosity are all larger than those reported in the paper and range from an increase of 2% in the lowest case to 10% in the case of the largest, which are columns 5 and 6 manufactured by Waters Corp. These are significant discrepancies in the context of permeability since the relationship between pressure drop and external porosity is close to the power of 4 for packed conduits. Curiously, a fictitiously low value for external porosity in a modern small-particle chromatographic column can easily explain *all* of the so- called enhanced separation efficiency claims made for these products, both related to reduced plate height, on the one hand (inaccurate value for d_p), and velocity shift of the minimum of the Van Deemter plot, on the other hand (inaccurate value for ε_0).

Thus, we conclude that the authors of this paper erroneously derived their values for K_C reported in the paper. This invalid result was based upon flawed science in combination with inferior experimental protocol/technique which can be cataloged as;

1. By reporting their permeability results in the form of K, the permeability parameter, rather than the flow resistance parameter ϕ, they left wiggle room for the values of d_p and ε_0, to accommodate their objectives with respect to unverified efficiency in the form of reduced plate height claims. As pointed out above, with respect to the permeability parameter, K, there are an *infinite number of combinations* of values for d_p and ε_0, which will satisfy the same value for K.
2. The authors practice of reporting their permeability parameter K, however, turns out to be a fatal error, when combined with their erroneously determined values of ε_p, which they did not determine independently.
3. Finally, they ignored the Laws of Continuity.

Example 3.

In this example, we examine another published scientific article, again, in the Journal of Chromatography by Gritti et al (2014) [40]. This publication represents a second example of what we have referred to above regarding false chromatographic performance claims. In this paper, the authors report 4 different values for K_C supposedly based upon their experimental assessment of 4 different commercially available chromatographic columns. Similarly, as in example 2 above, we demonstrate that, although the values reported for K_C in this paper are different from the values reported in the Cabooter paper, they are equally invalid and for the same underlying reasons of poor science in combination with inappropriate experimental protocol/technique. In our Fig. 11 herein, we have captured the authors' reported results and, once again, made our own corrections to the reported data.

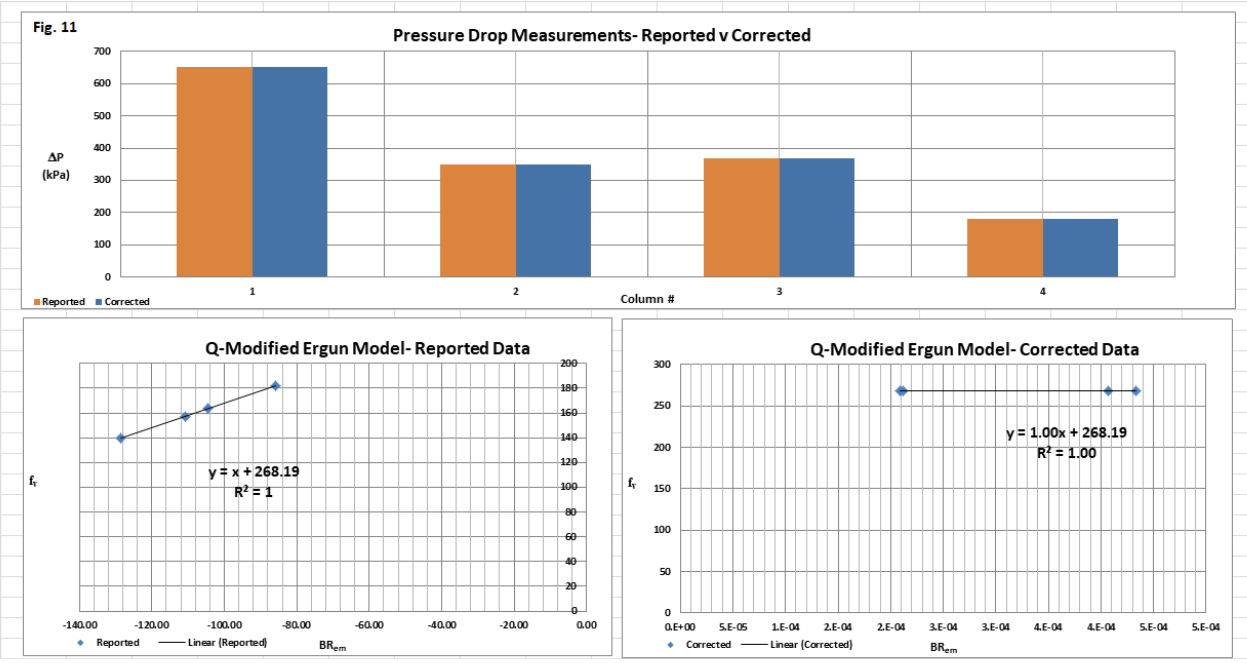

Fig. 11 The measured results for the Gritti et al paper. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As can be seen in the dimensionless plot in Fig. 11 representing the *reported* results, the values of f_v on the y axis are identical to the values of K_C reported by the authors for each of the 4 columns, but when their reported modified Reynolds numbers values are normalized for kinetic contributions on the x axis, the intercept of the straight line has a value of 268, thus validating the *true* value of K_C, and again *all* the plotted values on the x axis are negative (less than zero). On the other hand, as can also be seen in the dimensionless plot in Fig. 11 representing the *corrected* results, all 4 values of f_v on the y axis have the same value of 268 and all the corresponding modified Reynolds number values when normalized for kinetic contributions on the x axis, are positive (greater than zero). We have also included in Fig. 11, a dimensional plot of the measured pressure drop versus fluid flow rate for both the reported results as well as our corrected results to demonstrate that our correction methodology does not alter any of the measured values which are not subject to measurement uncertainty.

The authors in this paper followed the identical erroneous procedure as in the Cabooter paper to determine the value of ε_p, which were reported as 0.379, 0.348, .375, and 0.367 for columns numbered 1 through 4, respectively. The correct value for ε_p for all 4 columns has the unique value of 0.626 since all 4 columns were packed with particles from two different manufacturing batches of the *same* particle type. Using the same correction procedure as we used in the case of the Cabooter paper, our corrected values for ε_o were 0.440, 0.431, 0.428, and 0.428 for columns numbered 1 through 4, respectively. These corrected values for external porosity compare to the reported values of 0.390, 0.385, 0.368 and 0.392, respectively, and are all larger by approximately 9-13 % which represents an even greater discrepancy than in the Cabooter paper.

Thus, we conclude that similarly to the Cabooter paper, the authors of this paper erroneously derived their values for K_C based upon the same flawed methodology.

Example 4.

In this example, we examine another published scientific article in the Journal of Chromatography, by K.K. Unger (2008) [41]. This publication is in stark contrast to both the Cabooter and Gritti papers, in as much as the author, a world renowned expert in the synthesis and characterization of porous particles used for chromatographic analysis for more than 50 years, and who is also, interestingly, a contemporary of J.C Giddings, *expertly* discloses a teaching concerning chromatographic HPLC columns which is comprehensive in nature and specifically applies to the modern day category of chromatographic columns. Unlike the teaching in the Cabooter and Gritti papers, however, Unger includes in his teaching the independently derived values for the particle porosity, ε_p, dictated by his expressed value for silica skeletal density, which when combined with his expressed values for the mass of silica packed into each individual column specified in his Table 4, defines *uniquely* the value of the external porosity, ε_0, for each column, which happens to be almost exactly 0.4 representing, as it does, the typical column packing density in a well-packed column [33]. We have captured his teaching in Table 4 of the paper in our Fig 12.

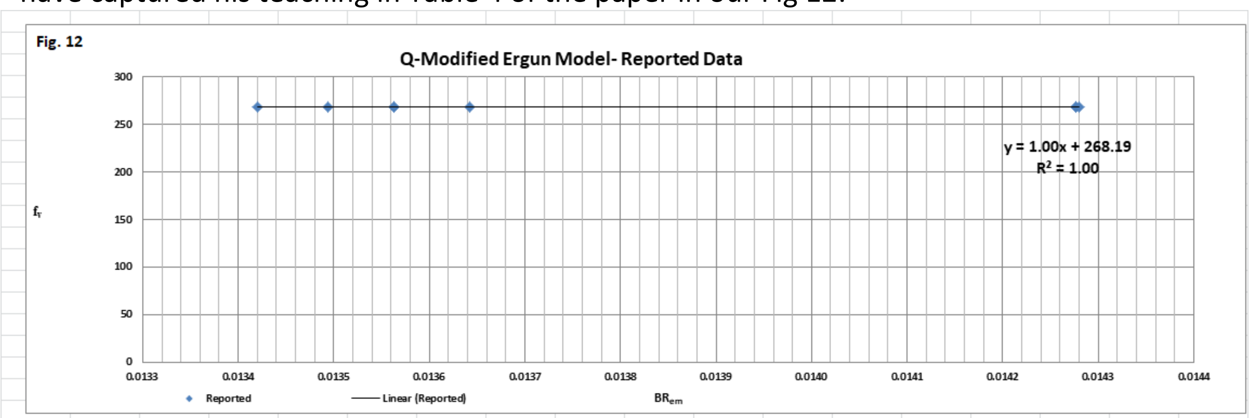

Fig. 12 The measured results for the Unger paper. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As can be seen in Fig. 12, we have used Unger's teaching contained in Table 4 of his paper as a basis upon which to apply our methodology to identify the value of K_C endemic to his teaching for all 8 columns specified in his Table of data. Clearly his teaching validates the value of 268 (approx.) for K_C.

Example 5.

In this example, we examine another published scientific article, also in the Journal of Chromatography by Farkas et al (1999) [42]. This paper was co-authored with Georges Guiochon whose extensive publications on this topic we have commented on above. We consider this paper to be one of the most credible publications in the entire literature on permeability in closed conduits. We assign it this lofty importance because the degree of difficulty that the authors went to in making pressure drop measurements at such low values of the modified Reynolds number is most impressive. We have selected the data from Fig 2 in the paper which represents permeability measurements taken on an HPLC column packed with nominal 10 micron silica C18 particles using Glycol as the fluid and extremely low flow rates. In addition, the pressure drops recorded were in the range of 100 to 2,000 psi which increases the accuracy of the overall pressure/flow relationship. We have captured the reported data in Fig 2 of the paper in our Fig 13.

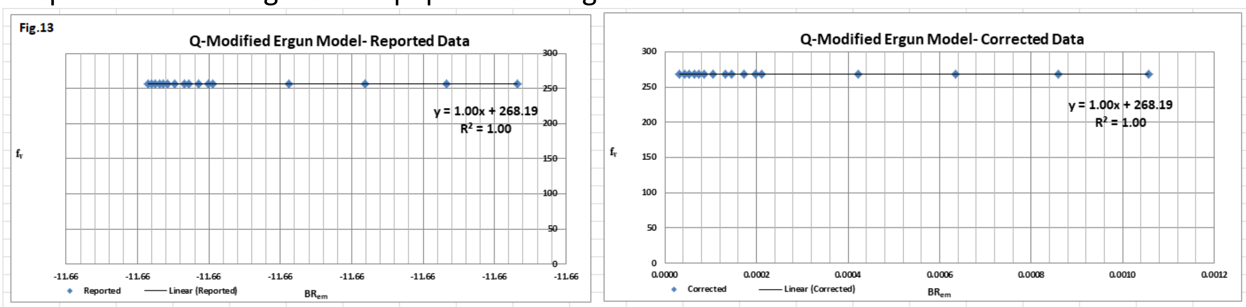

Fig. 13 The measured results for the Farkas et al paper. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As can be seen from Fig.13, the reported data had values for K_C of 258 (approx.) which is a bit on the low side and is responsible for the slightly negative value of -11.6 on the x axis of the dimensionless plot for the reported data. The discrepancy between the reported value for the external porosity of 0.399 and our corrected value of 0.401 represents a discrepancy of 0.5% which is within the measurement error of any well-designed experimental set up. Accordingly, we conclude that the Farkas paper *independently* validates our value of 268 for K_C.

Importantly, in this paper, the authors made enlightening comments regarding the accuracy of underlying variables used in the determination of column permeability, when they stated, “The nominal particle sizes given by manufacturers of silica adsorbents used in chromatography are often approximate averages which *cannot* be used for accurate calculations of column permeabilities”(emphasis added).

Example 6.

In this worked example, we review a published article by Neue et al published in Analytical Chemistry in 2005 [43]. We have selected this paper for review because it fits into this permeability-driven expose and because it discloses critical information concerning the measured value underlying the particle porosity of Acquity BEH particles from Waters Corp., which is referenced above in relation to the Cabooter paper and, in addition, it allows us to address two very important issues associated with, (a) the Handbook teaching of Uwe Neue concerning the value of the Kozeny/Carman constant (185), and (2) the fictitiously low values for external column porosity advertised by Waters Corporation for their so-called sub 2 micron particle columns. The publication contains 4 experiments relating to a comparison between the so-called sub 2 micron Acquity BEH particles and the more conventional format of a nominal particle diameter of 5 micron. For ease of description we designate them based upon their column dimension, and numbered 1 through 4 as follows;

1. Acquity BEH C18 particles 1.7 micron; 0.21 x 5 cm column
2. Acquity BEH C18 particles 4.8 micron; 0.21 x 5 cm column
3. Acquity BEH C18 particles 1.7 micron; 0.21 x 3 cm column
4. Acquity BEH C18 particles 4.8 micron; 0.21 x 10 cm column

Firstly, we focus on page 465 of the paper in which the authors disclose the independently measured characteristics of the particles; S_{pv} = 0.68 mL/g, ρ_p = 0.85 g/mL, the product of which represents the value of the particle porosity, ε_p, (0.68 x 0.85 = 0.579). Secondly, we focus on Neue's Handbook at page 30 in which he discloses a value of 185 for the constant in the Kozeny/Carman equation [44]. The authors did not report any measured values for partial column porosities in this paper including the value of external porosity, ε_0, nor did they disclose any value for K_C, but did report the values of their measured pressure drops. In Fig. 14 herein, we show a comparison of the reported results for measured permeability in this paper and our *calculated* values for f_v assuming Neue's Handbook value of 185 for K_C, on the one hand, and our validated value of 268, on the other hand, to facilitate an analysis of the impact on the discrepancies in Waters advertising for particle size value and external porosity value of their so-called sub 2 micron chromatographic columns.

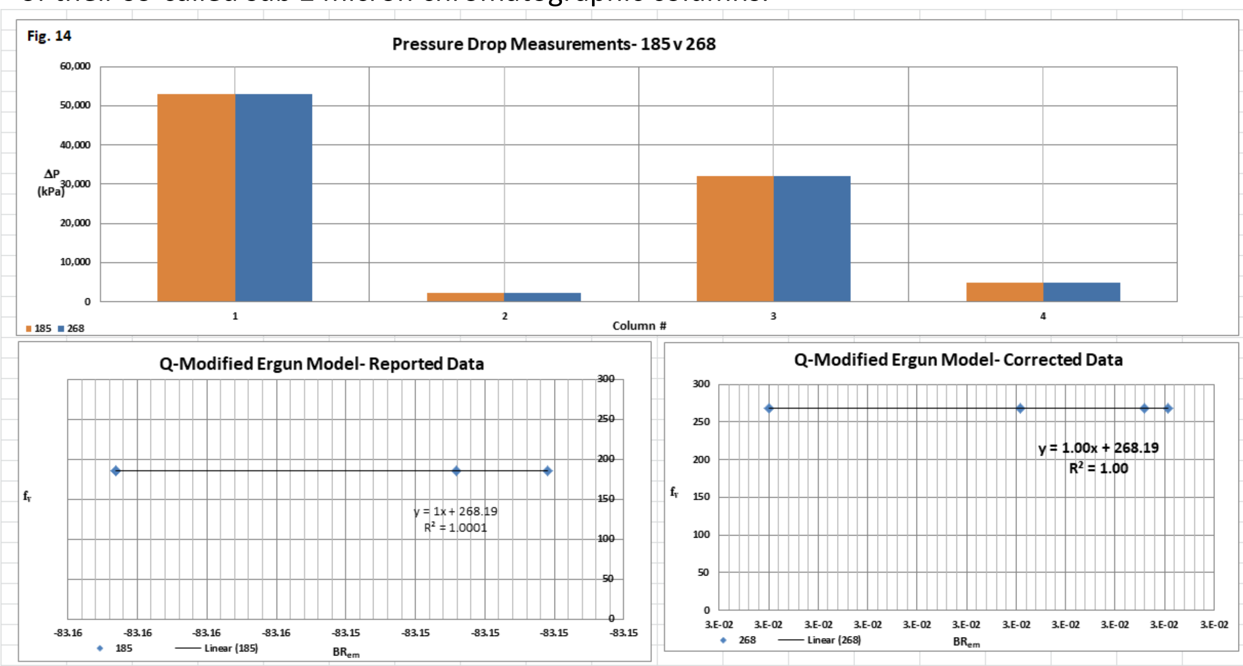

Fig. 14 The measured results for the Neue et al paper. The upper plot is the results in dimensional format plotted as flow rate versus pressure drop. The lower plot is the Q-modified Ergun type friction factor plotted as modified Reynolds number versus friction factor.

As can be seen in Fig 14, the negative values on the x axis dictate that our assumption of the value of 185 for the value of K_C is invalid. Moreover, it is critically important to emphasize that the value of 185 in Neues's Handbook for the Kozeny/Carman constant, K_C, is based upon an *unsupported* assertion in the book since no reference to any corroborating evidence is provided for its genesis. Our calculated values for external porosity based upon our assumption of a value of 185 for K_c are 0.366, 0.359, 0.365 and 0.359 for columns numbered 1 through 4, respectively. On the other hand, our calculated values for external porosity based upon our validated value of 268 for K_c are 0.400, 0.398, 0.399 and 0.392 for columns numbered 1 through 4, respectively. This discrepancy in the values of the external porosity translates, on a percentage basis, to an increase of 9%, 11%, 9% and 9%, respectively.

Accordingly, since commercially advertised high-throughput low internal volume columns, such as column numbered 1 and 3 in this paper manufactured by Waters Corp., are not suitable for making *direct* meaningful chromatographic partial porosity measurements, we conclude that the *fictitiously low values* for column external porosity, ε_0, advertised by Waters Corp. for their columns containing these so-called sub 2 micron particles, are based upon the unsupported incorrect value of 185 for the constant in the Kozeny/Carman equation referenced on page 30 in Neue's Handbook, a direct consequence of the teaching of Halasz, which understates the external porosity by approximately 10%, and that, therefore, the chromatographic separations claims for these columns are correspondingly inaccurate.

Example 7.

We now focus on a very recent example, which is based upon a series of papers published in the Journal of Chromatography between 2016 and 2017 by Reising et al, [45, 46, 47, 48]. In this series of papers, the authors detail packing methodologies using fused silica capillaries packed with C18 BEH particles manufactured by Waters Corp. In addition, Waters Corp. are given credit, in all 4 papers, for participating in the study and providing both the BEH particles and, in some cases, the packed columns under study. The major finding disclosed in these papers from a permeability point of view is that the packed capillaries had much larger external porosities than that taught by Giddings in 1965 for well-packed columns [33] in which he states "From these results it is safe to conclude that f_0 will only occasionally vary by more than 0.03 from a normal value of 0.40 for well-packed granular materials in chromatography" (page 209). The authors of these referenced papers, however, expressed the sentiment that the high external porosity values were *unexpected* and went on to give their explanations as to why the packed bed structures, *apparently surprisingly*, produced such high values for porosity.

In one of these papers [46], the authors published measured pressure drops for 6 capillary columns packed with BEH particles of circa 2.0 micron, Fig. 3 in the paper. We have captured the reported data in our Fig. 15.

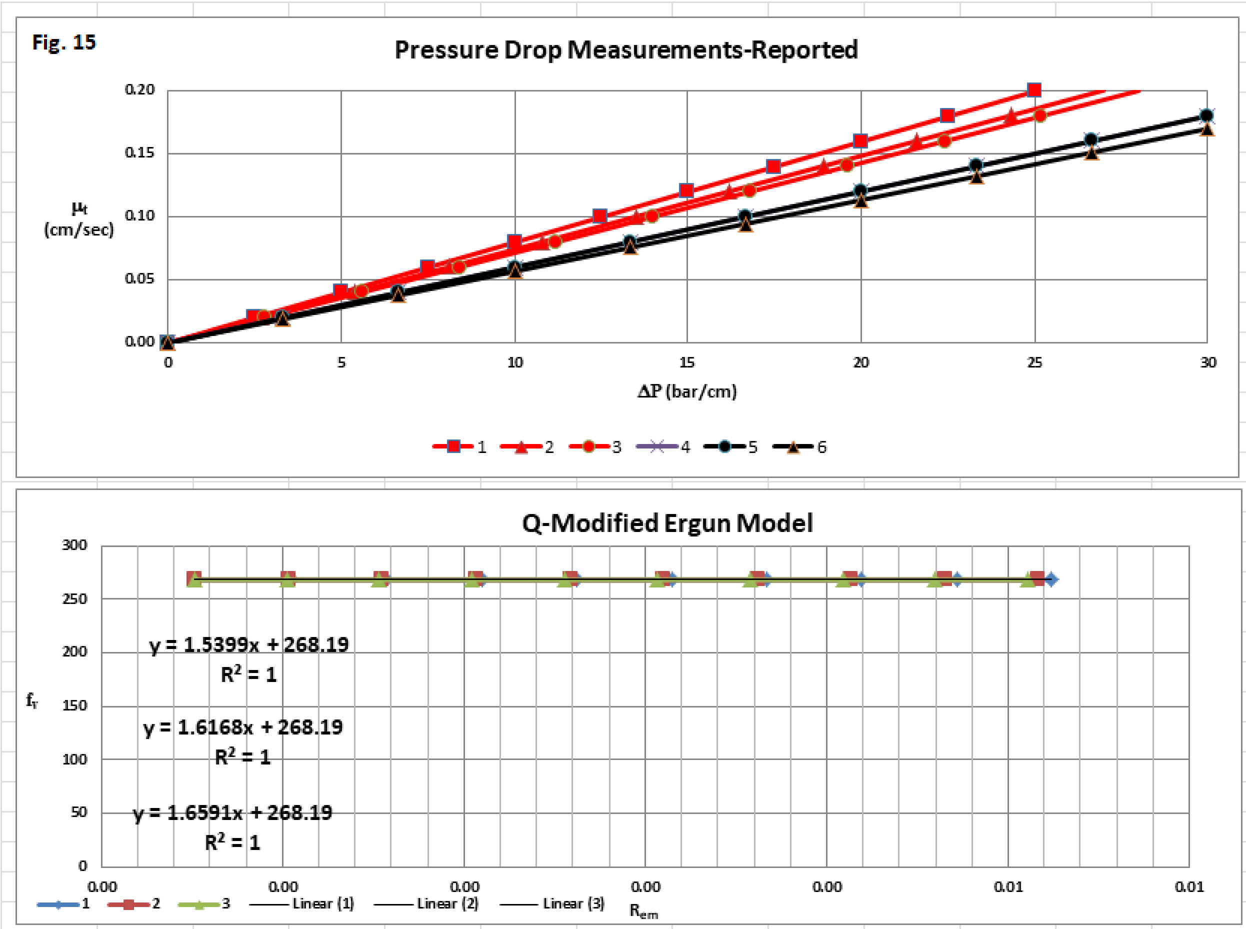

Fig. 15 This represents the reported results in the Reising et al 2016 paper. The upper plot is the reported permeability data in Fig. 3 of the paper for all 6 columns and the lower plot is our protocol to identify the values of A and B in the Q-modified Ergun model using just the 3 columns in which sonication was used in the slurry preparation.

As can be seen from our Fig. 15 herein, the permeability of the 3 columns in which sonication was used in the slurry preparation, numbered 1 through 3 in our plot, demonstrates a value of 268 for A, for all 3 columns, and a value for B which is slightly different for each of the columns. Accordingly, our protocol disclosed herein may also be used to identify the external porosity of a given column when its permeability has been measured carefully. We have determined that the external porosity, ε_0, for the three columns shown in our dimensionless plot was 0.469, 0.462 and 0.458, respectively. These values would appear to be consistent with the experimental results reported by the authors in all 4 referenced papers, using their *highly sophisticated imaging technology* to measure *directly* external porosity, ε_0, in low volume columns. Accordingly, what is novel in this collection of papers is the *imaging technology* used to confirm the relatively high values of external porosity in the chromatographic columns under study.

In yet another one of the papers referred to herein [45], the authors reported their result of a value for external porosity which in our nomenclature, ε_0, corresponds to a value of 0.512, in Table 2 of that paper. The authors, however, reported the value as ε_{ext} = 0.488. This is because these authors are practicing the use of an *archaic* nomenclature which has been the source of enormous confusion down the years in published literature on bed permeability. As is evident from equations (4) through (8) in the paper, their nomenclature for terms is, at best, extremely confusing. For instance, they define in their equation (8) their term for external porosity as $\varepsilon_{ext} = 0.49$ and refer to it as the "external porosity of the packing". This terminology is inappropriate at best and is, in fact, technically incorrect. This definition represents the particle volume fraction in the packed column and corresponds to our term $(1-\varepsilon_0)$ which is actually not a "porosity" term at all. Giddings, in his exemplary text at page 197 defines porosity as follows; "Porosity f is defined as the fraction of free (nonsolid) space within a certain volume element of porous material. It is a measure of the room available for the mobile phase. This parameter is basic to most studies of porous materials"[33]. Accordingly, the space occupied by the particles in a packed conduit, *excludes* all mobile phase when the particles are nonporous, and also excludes, partially, the mobile phase when the particles are porous. Therefore, the particle fraction in a packed column represented by the term $(1-\varepsilon_0)$ does not represent *any* kind of porosity, either *external* or *internal*. In addition, their use of the word "external" has the connotation of porosity *external* to the particles, which in the context of their definition, constitutes a contradiction in terms.

The author's equation (7), on the other hand, to which they give the symbol, ε_{intra}, is in fact the porosity of the *particles* which is an independent *column* parameter. This creates the *illusion*, based upon the symbol used, that it represents the internal porosity of the *column*, i.e. a *column* porosity term, which in our nomenclature is, ε_i, and which unfortunately and counter intuitively, it is *not*. Accordingly, the author's nomenclature can only be described as "organized confusion" because their equation (6) for ε_t, represents the total porosity of the column, i.e. a *column* porosity term; their equation (7), for ε_{intra}, represents the particle porosity, i.e. a *particle* porosity term; and their equation (8), for ε_{ext}, represents the volume fraction taken up by the particles which is *not* even a porosity term at all in any reasonable interpretation of the meaning of porosity.

Although the external porosity value of $\varepsilon_0 = 0.512$ reported in Table 2, is an extraordinarily high value for a chromatographic column, the authors, curiously, did not report their permeability measurements for this column in the paper. Accordingly, we cannot apply our methodology *directly* in this case to validate the value of A. However, in the interests of full disclosure, we can actually apply our methodology *in reverse* and identify our *calculated* values for permeability for this column, which we show in our Fig. 16.

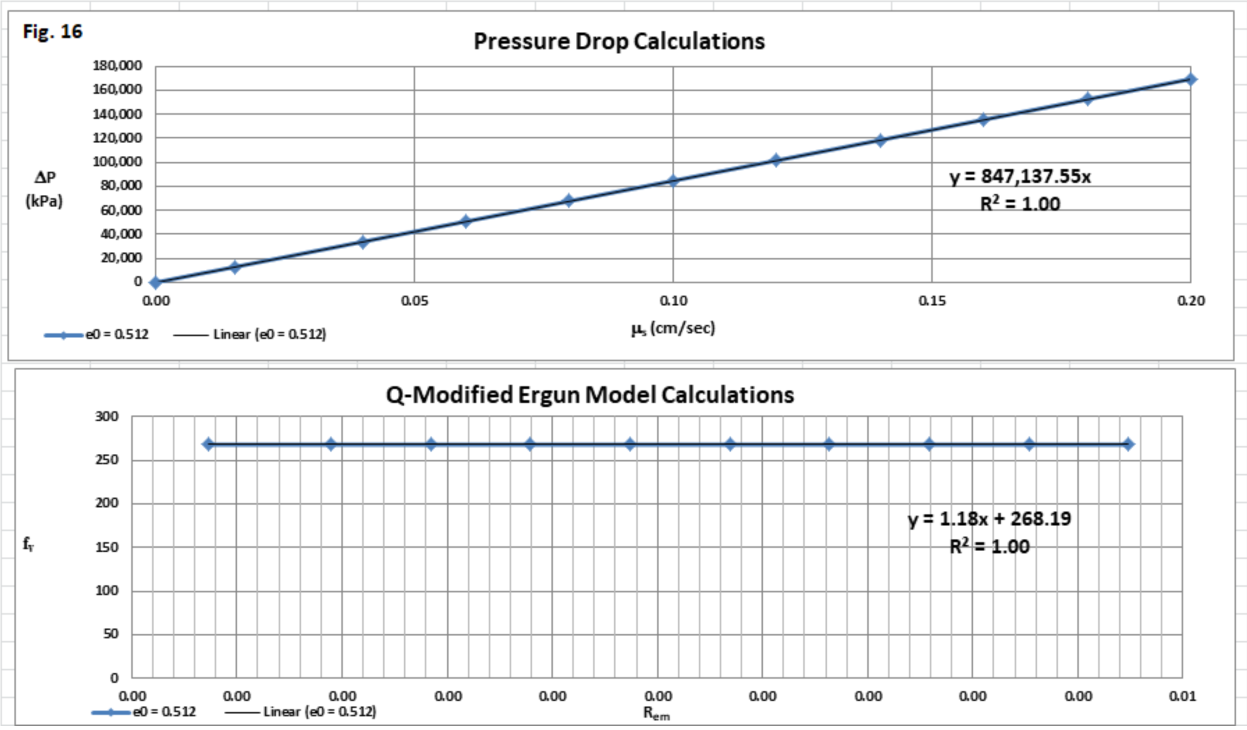

Fig. 16 This plot represents our calculations for permeability underlying the column reported in Table 2. The upper plot is our calculated pressure drop versus velocity and the lower plot is our calculated values for the Q-modified Ergun model.

As shown in Fig. 16, our calculated values for pressure drop, in units of psi, and superficial linear velocity, in units of cm/sec., indicate a linear relationship with a slope of 122,868. We used as our fluid in this exercise the same mobile phase of Water/ Acetonitrile, 50/50, which was used by the authors to run their standard separation mix. In addition, our Q-modified Ergun model identifies the calculated values of 268 for A and 1.18 for the kinetic coefficient B.

Example 8.

Finally we include our last example, which was published simultaneously with the writing of this paper in 2018 [49]. The authors of this paper studied the heat generated in a chromatographic column when three different fluids are pumped through it using an imaging technique involving infrared cameras. Their experiments were carried out on a Kinetex 1.3 μm C18 100A^0 LC column 50 x 2.1 mm purchased from Phenomenex in Australia. The three fluids were all chromatographic grade and included Methanol, Isopropyl Alcohol and Acetonitrile. For each fluid the authors took eight flow rate measurements and they recorded the pressure drops for each flow rate in conjunction with their imaging measurements for temperature gradient. They reported their permeability results in Table 1 in the paper as flow rate in units of mL/min and pressure drop in units of psi. The particles in this example were fully porous silica based, in contrast to the BEH particles manufactured by Waters Corp., which were a hybrid of inorganic silica and organic polymer. We have captured the authors permeability results in our Fig. 17 herein.

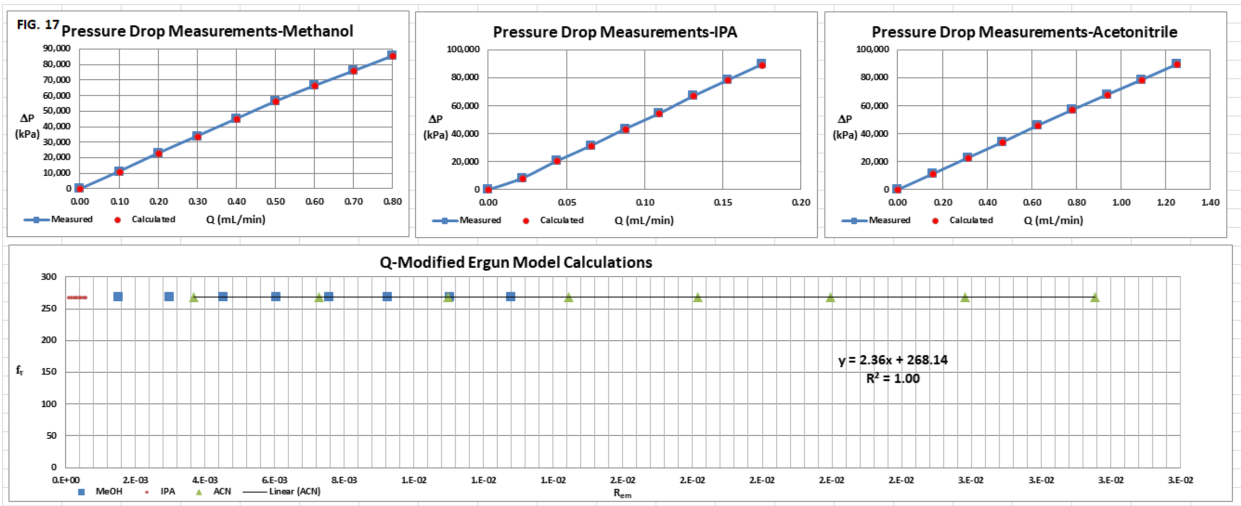

Fig. 17 This plot represents the reported results in the 2018 paper. The upper plot is the reported permeability data in Fig. 1 of the paper for all 3 fluids used in the study and the lower plot is our protocol to identify the values of A and B in the Q-modified Ergun model.

As can be seen in our Fig. 17 herein, in the upper dimensional plot, there is an excellent agreement between the measured values and our calculated values. In fact, we made them identical by adjusting the viscosity of the fluid in our calculations to account for the temperature changes due to increased resistance at higher flow rates. Our viscosity values were as follows; Methanol had an average value of 0.0054 (poise) with a standard deviation of 2.4% for all eight measurements; IPA had an average value of 0.0234 (poise) with a standard deviation of 9% for all eight measurements; Acetonitrile had an average value of 0.0035 (poise) with a standard deviation of 0.8% for all eight measurements. Incidentally, we believe that the value of 0.021 (poise) reported by the authors for IPA, is in error.

As can also be seen in Fig. 17 in the lower dimensionless plot, our protocol validates the value of A at 268 and the value of B at 2.36 for all three fluids.

However, the dimensionless plot also reveals an issue not raised by the authors in arriving at their conclusions. As is obvious from the plot, the authors did not take their temperature measurements at comparable values of the modified Reynolds number. Accordingly, the data for Acetonitrile has the lowest standard deviation of viscosity value, 0.8%, because the measurements were taken at much higher values of the modified Reynolds numbers, where trans-column mixing is significantly better. This results in a much more constant temperature within the column, which is reflected in the permeability results. Methanol showed the next best performance with a standard deviation value for viscosity of 2.4% because its' modified Reynolds numbers were lower than those of Acetonitrile but higher than those for IPA. Lastly, the IPA standard deviation value for viscosity was the worst amongst the three fluids at a value of 9% because it had the lowest modified Reynolds number values. The conclusions reached by the authors are not supported by our methodology herein, which we have used to accurately assess the role of fluid dynamics in the heat generated within the column under study.

Finally, we point out that our protocol identifies the value of 0.404 for, ε_0, the external porosity in this column, which represents that of a well-packed column according to the teaching of Giddings referred to above.

We conclude from this example that our protocol is also valuable for evaluating the mass transfer characteristics of chromatographic columns and, more specifically, in the case of heat transfer, it would appear to be even a superior technique to infrared cameras, which is what the authors used in this paper.

5. Conclusions

The Laws of Nature dictate a particular relationship between the flow rate of a fluid and the pressure generated by that fluid as it percolates through a closed conduit whether that conduit is empty or is filled with solid obstacles. Many of the variables involved in this relationship are identified in conventionally accepted empirical equations, but some are not. In these empirical equations, when all the known variables are accounted for, there remains a residual fixed “constant” whose value does not change depending upon the relative value of certain of the known variables. The value of this “residual” constant is not self-evident and unfortunately, its value has been sometimes used to justify self-serving conclusions regarding the value of difficult-to-measure variables, as part of a plan to project favorable performance characteristics colored to favor the originator, such as packed column particle diameter, particle porosity, column porosity and column separation efficiency and productivity. Such proclamations have been made by some manufacturers involved in the production of the so-called sub 2 micron chromatographic columns as well as other interested parties involved in the periphery of the chromatographic industry worldwide.

In fact, the nomenclature of “sub 2 micron” is an unusual and novel nomenclature to represent particle size, *never used in the chromatography world heretofore*, and is a contrived label designed to obscure the true values of the related column permeability parameters of particle size and column external porosity, and which, in turn, enables false claims of separation productivity in chromatographic columns. The Laws of Nature do not lend themselves to manipulation by man and, just because it is extremely difficult to differentiate between the free space *between* the particles and the free space *within* the particles, in chromatography columns packed with porous particles, manufacturers of these particles do *not* have the right to *knowingly* misrepresent the reality existing within chromatographic columns in which the particle diameters maybe substantially less than 2 micron in combination with external porosity values greater than about 0.45. This conclusion is supported, for instance, in the case of Acquity BEH particles, by the many publications, all admittedly in the Journal of Chromatograhy A, in which the *same* BEH particles are reported to have particle diameters of 1.30 μm (ref. 45), 2.05 μm (ref. 39), 1.70 μm (ref. 50) and 1.99 μm (ref. 51), a reality which is obviously impossible.

Moreover, particle size distribution is accommodated within the Kozeny/Carman model via *the combination of* the values of the average spherical particle diameter equivalent, d_p, and the packed conduit external porosity, ε_0, which, in turn, are related through the number of particles packed into a given column. The Laws of Continuity dictate that for a given conduit packed with particles, any value of d_p will have a corresponding combination of values of n_p and $\varepsilon_{0,}$ which means that chromatographic columns of a given physical dimension when packed with different particle size distributions, will contain varying numbers of particles, even if the external porosity value is kept constant. Accordingly, regardless of what the particle size distribution is that exists within any packed conduit, the value of the Kozeny/Carman constant, K_c, does not change. Furthermore, it can only be *validated experimentally* when all variables including the three variables of d_p, ε_o and n_p are reconciled *simultaneously.* Since counting the number of particle equivalents, $n_{p,}$ can be a daunting task, especially when they are numbered in the millions, as is the case for chromatographic columns packed with particles of circa one micron in diameter, measuring the mass of the particles, $M_{p,}$ in combination with the independently determined particle porosity value, ε_p, is a viable experimental alternative. Thus, in order to unambiguously identify empirically the value of K_c in packed columns, one must know the number of particle equivalents, n_p, (or alternatively the mass of particles, M_p) packed into a given column under study, in combination with, the value of the average spherical particle diameter equivalent, d_p, and the independently derived value of the particle porosity, $\varepsilon_{p,}$ (or alternatively the particle specific pore volume, S_{pv}, in combination with the particle skeletal density, ρ_{sk}). Therefore, one may argue about the merit of the relative *combination and/or permutation* values of d_p, ε_o and n_p which exist within a given column under study, based upon various experimental protocols and/or techniques used to identify them, but one *cannot* argue about the value of K_c, because it is *always* the same. Accordingly, since the external porosity, ε_0, is a function of not only the value of d_p and the conduit dimensions, D and L, but also the value of, $n_{p,}$ the number of particle equivalents present in any column under study, as demonstrated in our equation (34) herein, the conclusions expressed relative to the values of K_c in the reviewed papers herein by Cabooter et al and Gritti et al, are without scientific foundation or experimental corroboration.

Importantly, in more recent publications by academicians focused on chromatographic applications, the use of a so-called "pore blocking" technique has been offered as a panacea to overcome measurement uncertainty related to packed column permeability reconciliation. This proclamation is without merit. The reason for the discrepancy in their claimed validation of their numerous and erroneous values for the constant in the Kozeny/Carman model, in the first instance, is due to the fact that there is a mismatch built into their measurement techniques. In some cases, apparently, the porous particles under study may have "liquid isolated" internal pores which have no opening to allow *liquid* to penetrate. Accordingly, their measurement technique generates measured values for column total porosity, ε_t, which are *too low* because there is a substantial component of liquid "inaccessible" pores. Thus, their methodology regarding permeability reconciliation within columns packed with the so-called sub 2 micron particles violates the Laws of Continuity because, on the one hand, their measured values for particle diameter, d_p, which *does not* depend on internal liquid pore volume accessibility, reflects the existence of such isolated pockets within the particles but, on the other hand, their measured porosity values, which *does* depend on internal liquid pore volume accessibility, do not. Furthermore, since their "pore blocking" methodology is only effective at blocking liquid "accessible" pores, it does nothing to address this mismatch of measurement techniques between measured particle size, on the one hand, which captures *all of the free space* within the particle exterior envelope and, on the other hand, resultant column porosity which dictates the need to include *all of the free space* which is not occupied by solid matter and which includes pore volume *between* the particles and pore volume *within* the particles both *accessible* and *non-accessible*, a feature their porosity measurement technique *may not* and *cannot* deliver. Of course, one could make the alternative argument that the sub 2 micron particles in question have *no* inaccessible pores, but then this would cast doubt on the other side of their measurement technique ledger, i.e. the particle size, since under this scenario the Laws of Continuity would force one to make the corresponding argument that the particle diameters in question are significantly smaller with correspondingly larger *external* porosity values even. Accordingly, any reference to "pore blocking" techniques in the context of permeability reconciliation in columns packed with the so-called sub 2 micron particles, is merely a distraction when made in the context of experimental verification of the value of K_c.

The teaching in this paper underscores the fundamental errors made by chromatographers and engineers alike, which have been compounded down the years, pertaining to the role of the kinetic term in the pressure flow relationship. Since not all kinetic contributions are captured in the value of the conventionally defined Reynolds number, assumptions concerning the lack of relative importance of kinetic contributions at low values of the Reynolds number, a concept steeped in conventional folklore, are *not* valid. To remedy this stunning lack of understanding of fluid dynamics in closed conduits, we have demonstrated an experimental protocol, which unambiguously validates the value of 268 approx. for the constant in the Kozeny/Carman equation, as well as isolating the value of the kinetic coefficient, B, which when combined with the modified Reynolds number, completely defines bed permeability in packed conduits over the entire fluid flow regime including laminar, transitional and turbulent.

The experimental protocol and associated teaching herein, sets the groundwork for a novel new theory of fluid dynamics in closed conduits, which will be the subject of a follow on paper. In it we will define from first principles *all* the variables contained in the pressure flow relationship including those not identified in some conventionally accepted empirical equations and including, in particular, those variables which we have chosen, in the interests of simplification in this paper, to combine in our lumped parameter, B. Furthermore since this new disclosure will include all regimes of fluid flow in closed conduits including laminar, transitional and turbulent, it is projected that it will shed some much needed light on the well-known Navies-Stokes equation, which as of this writing, stands without an analytical solution, at least one that can be validated in the real world.

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