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Rational inlet design for a portable atmospheric pressure ionization–mass spectrometer (API–MS)

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ABSTRACT

Equations are derived that describe the gas-dynamic flow through three types of high pressure inlets into a vacuum system: (1) a sonic orifice inlet, (2) a sonic capillary inlet and (3) a pulsed sonic capillary inlet. These equations can be used for rational inlet design for portable atmospheric pressure ionization–mass spectrometers (API–MS) taking into account the optimum operating pressure of the mass filter and the pumping characteristics of the system.

1. Introduction

It is a great honor to participate in this special issue recognizing the scientific contributions of John Bennett Fenn. Although best known in the field of mass spectroscopy for his contributions to electro-spray ionization for mass analysis of large bio-molecules, he is almost as well known in the field of molecular beam chemistry for his insight that using a free molecular sample of a supersonic flow instead of a free molecular sample of a stagnant gas as the source for a collimated molecular beam provides substantial advantages and makes possible a wealth of important scientific experiments. This insight and John's contributions to understanding sonic free jets and supersonic nozzle beams form the foundation for a large body of fundamental chemical research especially on the rotational/vibrational characteristics of polyatomic molecules and on molecular collisions with surfaces and with other molecules.

A delightful review of John's life and scientific achievements can be found in his Nobel lecture [1] and the autobiography he wrote on the occasion of receiving the 2002 Nobel Prize in Chemistry [2]. While Yale features prominently, as it should, his years at Princeton receive less attention. It was while he was at Princeton that the original work on sonic free jets and supersonic nozzle beams was done and it was at Princeton where I had the great good fortune to work with him and the Princeton Beam Group consisting of John, myself, Jim Anderson, John Bittner, and David Marsden.

I arrived at Princeton as a potential PhD candidate in the Department of Chemical Engineering in 1959 the same year John accepted a research position in the Department of Mechanical Engineering. My PhD adviser was Michel Boudart and because of his interest in what John was proposing to do with a huge vacuum system incorporating not one but two 32 in diameter oil diffusion pumps I became involved with John first as an observer and then as an acolyte. After my first year at Princeton, Michel left to accept a position at Berkeley and John became my surrogate research mentor. I owe a tremendous debt to Michel Boudart and am proud to be one of his academic sons, but I owe at least as much, particularly in how I conceive of research ideas, to John Fenn.

The size of the "Princeton Beam Apparatus" was impressive. I later built a similar apparatus at Princeton incorporating only one 32 in diameter diffusion pump, and when I brought this system to Purdue, my students labeled it the "Pumposaurus". The ability to run experiments in an apparatus with great pumping speed is a decided advantage when studying free jet expansions into a vacuum and free molecular sampling of a supersonic flow using a conical "skimmer". However, what is learned in these studies has wide applicability for any experiment that involves sampling from a high density gas into a vacuum environment, e.g., a API–MS.

One of the most exciting current areas in mass spectroscopy is the development of small portable mass spectrometers for atmospheric sampling. The weight and size of such a mass spectrometer is largely determined by the size of the vacuum pump that must

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be used. In what follows equations will be derived for the rational design of the inlet of such a mass spectrometer with the goal of minimizing vacuum requirements and pump size.

2. Results

It will be assumed that the mass spectrometer samples an atmospheric pressure mixture consisting of the ions of interest entrained in a carrier gas of neutral molecules, which in the case of atmospheric sampling are largely nitrogen. Given a minimum detectable ion signal, I_{min} (ions per second), the mole fraction, f, of a given ion in the inlet flow and the overall efficiency, φ, at which ions entering through the atmospheric inlet are detected, it is possible to calculate the smallest inlet flow, N_{min}(molecules per second), for detection of that ion.

$$N_{\mathrm{min}} = \frac{I_{\mathrm{min}}}{f\varphi} \tag{1}$$

The focus of most mass spectrometer design innovation is to maximize f by designing an efficient atmospheric ionizer and to maximize φ by improving the design of the mass filter. Whether the mass spectrometer is a time-of-flight ($\sim 10^{-6}$ torr), quadrupole ($\sim 10^{-5}$ torr), or quadrupole ion trap ($\sim 10^{-3}$ torr) there is a critical pressure, p_{crit} (torr), at which collisions of the desired ions with background molecules in the mass spectrometer adversely affect the operation of the mass filter. This p_{crit} and the molecular flow, N (molecules per second), entering the vacuum chamber determine the required pumping speed, S (liters per second).

$$S = 3.07 \times 10^{-20}\,\frac{N}{p_{\mathrm{crit}}} \tag{2}$$

Multistage or differential pumping can be employed to decrease N relative to the total flow entering through the atmospheric inlet. This approach serves to decrease the size of vacuum pump employed to evacuate the chamber containing the mass filter, however, this approach requires a second vacuum pump and is not a viable option for a portable mass spectrometer. In what follows it will be assumed that N is the total molecular flow entering through the atmospheric inlet. Equations to calculate N for three types of atmospheric inlets will be derived with the goal of designing N to equal N_{min} and thereby minimizing S.

2.1. Sonic orifice inlet

When a high pressure gas expands through a sharp edge orifice into a vacuum the gas forms a free jet flow downstream from the orifice. If the mean free path in the gas is small with respect to the diameter of the orifice, this flow is termed a sonic free jet and the expansion downstream of the orifice is supersonic. This supersonic expansion is characterized by the adiabatic conversion of the thermal energy of the gas into a directed mean flow velocity along the axis of the orifice. Energy conservation yields the relation

$$\left(\frac{1}{2}\right) m u^2 = C(T_0 - T) \tag{3}$$

Here m (g) is the mass of a gas molecule, u (cm/s) is the mean velocity of the flow along the axis of the free jet, C (erg/K) is the molecular heat capacity of the gas, T_0 (K) is the initial temperature of the gas, and T (K) is the temperature in the flow. Eq. (3) assumes that a single temperature T is adequate to describe the translational, rotational, and vibrational energy modes of the molecules and that the molecular heat capacity is constant. These assumptions fail at some point in the expansion when the collision frequency in the gas is no longer sufficient to maintain equilibrium energy conversion. First the vibrational modes become frozen, then the rotational modes, and finally even the translational temperature in the flow becomes frozen. For the purposes of the present discussion, however, Eq. (3) is an adequate model. For nitrogen expanding from room temperature (298 K) the molecular heat capacity is

$$C = 3.5\ k \tag{4}$$

k is the Boltzmann constant (1.38×10^{-16} erg/K).

At the plane of the orifice the mean velocity of the flow is equal to the speed of a pressure wave in the gas, i.e., the speed of sound. This is termed the sonic condition.

$$u = u_{\mathrm{sonic}} = \left(\frac{\gamma k T}{m}\right)^{0.5} \tag{5}$$

γ is the specific heat ratio of the gas. For nitrogen $\gamma = 7/5$ and when $T = 298$ K, $u_{\mathrm{sonic}} = 3.5 \times 10^4$ cm/s. Upstream of the orifice the gas expands in an isentropic manner and at the plane of the orifice

$$T = T_0\left[\frac{\gamma+1}{2}\right]^{-2} \tag{6}$$

$$n = n_0\left[\frac{1+\gamma}{2}\right]^{-2/(\gamma-1)} \tag{7}$$

Thus, the molecular flow through a sonic orifice is a function only of T_0, n_0, and the diameter, d (cm), of the orifice. When $\gamma = 1.4$,

$$N = 0.33\ n_0\left(\frac{\gamma k T_0}{m}\right)^{0.5}\left(\frac{\pi d^2}{4}\right) \tag{8}$$

For nitrogen initially at $p_0 = 760$ torr and $T_0 = 298$ K

$$N = 2.2 \times 10^{23} d^2 \tag{9}$$

Far downstream from the orifice the mean flow velocity reaches an asymptotic limit. If it is assumed that in this limit $T = 0$, $u = u_{\mathrm{max}}$ where

$$u_{\mathrm{max}} = \left(\frac{2 C T_0}{m}\right)^{0.5} \tag{10}$$

For nitrogen when $T_0 = 298$ K, $u_{\mathrm{max}} = 7.9 \times 10^4$ cm/s. In an actual expansion the asymptotic value of T is finite and the asymptotic mean velocity lies between u_{sonic} and u_{max}. The asymptotic molecular flux along the centerline of a sonic free jet is

$$F = \frac{N}{2\pi x^2} \tag{11}$$

F is the flux in molecules/cm^2 s and x is the distance from the orifice in cm.

John Fenn made two important predictions with regard to this sonic free jet expansion [3]. The first was that, although the flux through a collimation orifice located a distance downstream from a sonic orifice or a free molecular orifice follows the same relation, i.e., Eq. (11), the centerline intensity of the molecular beam resulting from such collimation can be orders of magnitude greater in the case of the sonic orifice because of the what he termed “Mach number focusing” [3]. The second was that, if a heavy molecule is introduced as a trace component in a light carrier gas, this heavy molecule will be accelerated by collisions with the carrier gas molecules and can achieve the same terminal velocity as the light carrier gas in a free jet expansion. This leads to an increase in the kinetic energy of the heavy species equal to the ratio $m_{\mathrm{heavy}}/m_{\mathrm{light}}$ [4]. Both of these predictions have been shown to be achievable. An excellent review of this literature is the chapter by Miller in the book on experimental molecular beam methods edited by Scoles [5].

When considering a sonic orifice as an atmospheric inlet for a portable mass spectrometer, the key relation is Eq. (9), which defines the inlet flow, N, and thereby the required pumping speed, S, from Eq. (2). Assuming an orifice diameter of 0.01 cm (100 microns), yields a value for N of 2.2×10^{19} molecules per second. For a

$p_{\text{crit}} = 10^{-3}$ torr this flow requires S to be 6.8×10^2 l/s while for a $p_{\text{crit}} = 10^{-6}$ torr the required pumping speed equals 6.8×10^5 l/s. Decreasing the orifice diameter by a factor of 10 decreases N by a factor of 100, however, the relatively large values for N predicted by Eq. (9) suggest that a sonic orifice may not be the best atmospheric inlet for a portable mass spectrometer.

2.2. Sonic capillary inlet

If a sharp edge orifice is replaced by a capillary tube, it is possible to reduce the flow because of the pressure drop through the capillary. Such a sonic capillary inlet retains the benefits of the free jet expansion while substantially decreasing N. As long as there is a negligible loss of ions due to gas phase reactions and reactions taking place at the capillary wall, the mole fraction of any ion in the flow from a sonic capillary inlet is the same as that for a sonic orifice inlet. For the case of a dilute population of ground state ions entrained in a carrier gas like nitrogen this assumption appears to be reasonable.

Assume isothermal, laminar flow in a cylindrical capillary with a length, L, and a diameter, d, both in cm. Conservation of mass requires that $N = n_0\, u_0\, \pi\, d^2/4 = n_l\, u_l\, \pi\, d^2/4 = n\, u\, \pi\, d^2/4$, where n and u are the molecular density and mean velocity averaged over the cross-section of the capillary, the subscript 0 denotes the atmospheric inlet to the capillary and the subscript l denotes the vacuum outlet. The classical Hagen–Poiseuille equation for flow through a cylindrical capillary states that

$$u_0 = u_l = \frac{(p_0 - p_l)d^2}{32\,\mu \text{L}} \tag{12}$$

p (g/cm s^2) is the pressure and μ (g/cm s)is the viscosity of the gas. This expression, however, assumes that the density of the gas remains constant, which is not the case for a gas passing from atmospheric pressure into a vacuum. The gas density, $n = p/kT$, decreases along the capillary as the pressure decreases and the mean velocity increases. In the case of a sonic orifice the expansion upstream of the orifice is abrupt and isentropic while in the case of a sonic capillary the expansion is slow and isothermal.

There are two critical boundary conditions. The density at the inlet of the capillary, n_0, is fixed at the atmospheric condition, and the velocity at the exit is fixed at the speed of sound, $u_l = (\gamma k T_0/m)^{0.5}$. It will prove useful to introduce a variable, $W = u_l/u_0 = n_0/n_l$, which describes the inverse relation between the density and mean velocity. Thus, the total molecular flow through a sonic capillary inlet is

$$N = n_0\ u_0 \left(\frac{\pi d^2}{4}\right) = \left[\frac{1}{w}\right] n_0 \left(\frac{\gamma k T_0}{m}\right)^{0.5} \left(\frac{\pi d^2}{4}\right) \tag{13}$$

Conservation of momentum along the capillary requires that

$$\frac{\partial}{\partial x}\left[\left(\frac{4}{3}\right) m\, n\, u^2 + n\, kT\right] + \frac{4\tau_{\text{wall}}}{d} = 0 \tag{14}$$

$(4/3)\, u^2$ is the square of the flow velocity averaged over a cross-section of the capillary, $n\, kT = p$ is the pressure in the capillary, and τ_{wall} is the shear stress at the wall.

$$\tau_{\text{wall}} = \frac{8\,\mu\ u}{d} \tag{15}$$

Substituting $[N/u\, \pi\, d^2/4]$ for n in Eq. (14) and making use of Eq. (15)

$$\frac{\partial}{\partial x}\left[\left(\frac{4}{3}\right) m\, N\, u + \frac{N\, kT}{u}\right] + 8\pi\, \mu\, u = 0 \tag{16}$$

Integrating Eq. (16) from $x = 0$ to $x = L$ yields

$$\left(\frac{4}{3}\right) m\, N\, \ln\left(\frac{u_l}{u_0}\right) + \left(\frac{1}{2}\right) N\, kT[u_l^{-2} - u_0^{-2}] + 8\pi\mu\, L = 0 \tag{17}$$

Introducing W and setting $u_l = (\gamma\, kT_0/\text{m})^{0.5}$ in Eq. (17)

$$N\left[-\left(\frac{4}{3}\right)\ \ln W + \frac{W^2 - 1}{2\gamma}\right] = \frac{8\pi\,\mu\, L}{m} \tag{18}$$

When $W > 20$, Eq. (18) becomes simply

$$\frac{NW^2}{2\gamma} = \frac{8\pi\,\mu\, L}{m} \tag{19}$$

For nitrogen at $T = 298$ K, Eq. (19) becomes

$$N = 2.7 \times 10^{20}\ \frac{L}{W^2} \tag{20}$$

For nitrogen initially at $p_0 = 760$ torr and $T_0 = 298$ K Eq. (13) becomes

$$N = 6.8 \times 10^{23}\ \frac{d^2}{W} \tag{21}$$

Eqs. (20) and (21) yield

$$W = 6.8 \times 10^{23}\ \frac{d^2}{N} \tag{22}$$

$$\text{and}\ \ L = 3.7 \times 10^{-21}\ NW^2 \tag{23}$$

Setting $N = 1 \times 10^{17}$ molecules per second for a capillary with $d = 0.01$ cm (100 microns), W is 680 and $L = 1.7$ meters. Since the flow is subsonic and laminar, the capillary tube can be coiled without compromising its operation as long as its exit is aligned along the axis of the mass spectrometer. Decreasing the diameter of the capillary by a factor of 10, decreases W by a factor of 10^2 and decreases L by a factor of 10^4. For $p_{\text{crit}} = 10^{-3}$ torr a molecular flow of 10^{17} molecules per second requires a S of only 3 l/s and for $p_{\text{crit}} = 10^{-6}$ torr, S becomes 3000 l/s. This example illustrates the potential benefits of a sonic capillary inlet. By proper choice of d and L the total flow, N, through such an inlet can often be set equal to N_{min}, thereby minimizing the required pumping speed, S.

Murphy and Miller [6] have shown that the free jet expansion from a sonic capillary is identical to that from a sharp edged orifice having the same Reynolds number, and unpublished results from my laboratory at Purdue have verified the predictions of Eq. (18) over a wide range of capillary lengths and molecular flows [7]. In effect the use of a sonic capillary inlet allows one to decrease the inlet flow, N, of an atmospheric pressure ionization–mass spectrometer to a desired value, N_{min}, while retaining the positive attributes of a free jet expansion. However, two caveats must be taken into consideration when considering a sonic capillary inlet for a portable atmospheric pressure ionization–mass spectrometer. The first is that the long residence time the ions experience passing through the capillary increases the possibility of ion reactions both in the gas phase and on the walls. The second is that, if the Reynolds number of the capillary becomes too small, the assumption of continuum flow in the capillary and a sonic free jet expansion from its exit cease to be valid. The Reynolds number of a sonic capillary is

$$Re = \frac{4m\ N}{(\pi\,\mu\, d)} \tag{24}$$

For nitrogen at $T_0 = 298$ K

$$Re = 3.3 \times 10^{-19}\ \frac{N}{d} \tag{25}$$

Thus, a capillary with $d = 0.01$ cm and $N = 10^{17}$ molecules per second has a Re = 3.3. Supersonic nozzle beam experiments typically have Reynolds numbers in the range of 1–10.

2.3. Pulsed sonic capillary inlet

Operating a sonic capillary inlet in a pulsed manner rather than as a continuous flow is another way to reduce pumping requirements. Gao et al. [8,9] have employed this scheme terming it a "discontinuous atmospheric pressure interface". These authors introduce a flexible silicone tube at an intermediate point in the capillary and use a pinch value to open the flow for a short time and then shut it off allowing the background pressure in the mass spectrometer to return to a base level. If the dynamics of the vacuum system are neglected, it appears that such pulsed operation should lower the required pumping speed, S, by the ratio of the open time over the time between pulses

$$S = 3.07 \times 10^{-20}\left(\frac{N}{p_{\text{crit}}}\right)\left[\frac{\Delta_{\text{open}}}{\Delta}\right] \tag{26}$$

Δ_{open} (s) is the open time and Δ (s) is the time between pulses. In practice, however, Eq. (26) is only valid if the volume of the chamber containing the mass filter is extremely large. A finite volume chamber exhibits a more complex behavior. An input pulse of molecules into the mass spectrometer produces a sharp pressure rise that is sensitive to the volume, V (liters), of the vacuum chamber. This pressure pulse decays exponentially with a time constant $\tau = V/S$. The ratio of the pressure right after the input pulse and the pressure just before the next input pulse is

$$\frac{p_{\text{initial}}}{p_{\text{final}}} = \exp\left(\frac{-\Delta}{\tau}\right) = exp\left(\frac{-\Delta S}{V}\right) \tag{27}$$

If operation of the mass spectrometer requires that $p < p_{\text{crit}}$,

$$p_{\text{initial}} = 3.07 \times 10^{-20}\left(\frac{N\Delta_{\text{open}}}{V}\right)\left[1 - \exp\left(\frac{-\Delta S}{V}\right)\right]^{-1} < p_{\text{crit}} \tag{28}$$

From Eq. (28) it is seen that no matter what the value of S

$$3.07 \times 10^{-20}\left(\frac{N\Delta_{\text{open}}}{V}\right) < p_{\text{crit}} \tag{29}$$

In a sense V/Δ_{open} replaces S as the key variable in the operation of a pulsed inlet mass spectrometer. This is seen in the data of Gao et al. [9] where the authors find that the operation of their mass spectrometer is quite insensitive to pumping speed, S, but highly sensitive to Δ_{open}.

The vacuum requirements of a pulsed mass spectrometer then are quite different from those of a mass spectrometer with a continuous inlet flow. Given the number of ions in a pulse needed to obtain a detectable signal, M_{ion},

$$N\Delta_{\text{open}} = \frac{M_{\text{ion}}}{f\varphi} \tag{30}$$

$\Delta S/V$ should be chosen to give a desired ratio between the pressure in the mass spectrometer right after an input pulse and the base pressure just before the next input pulse. Given a p_{crit} at which background molecules in the mass spectrometer adversely affect its operation, Eq. (28) with $p_{\text{initial}} = p_{\text{crit}}$ can be used to determine $N\Delta_{\text{open}}$.

$$N\Delta_{\text{open}} = 3.26 \times 10^{19}(p_{\text{crit}}V)\left[1 - \exp\left(\frac{-\Delta S}{V}\right)\right] \tag{31}$$

Judicious choice of Δ and V largely eliminates the need for large pumping speed and increasing the ratio of V/Δ_{open} increases the allowable N for a given p_{crit}.

A pulsed capillary inlet provides an opportunity for gas-dynamic gating of the mass spectrometer. If the pinch valve is located near the atmospheric inlet to the capillary, the gas filling the capillary tube will form a shock wave traveling through the capillary at the speed of sound (3.5×10^4 cm/s in the case of nitrogen). This will produce a sharp onset of the free jet flow in the mass spectrometer. The falling edge of the pulse will be much less abrupt, but the sharp onset of the ion signal may be used to advantage.

3. Conclusion

Flow equations for three different atmospheric inlets have been derived. Each of the cases studied assumes a sonic free jet expansion into the mass spectrometer. This supersonic flow has been well studied as a source for high intensity molecular beams [5]. Two aspects of this literature deserve special mentioning. The high mean velocity and lowered translational temperature of the molecules in the jet provide potential gains in the operating efficiency, φ, of whatever type of mass spectrometer is employed. However, if a solid surface is placed normal to the flow and too close to the source of the free jet, molecules scattered from this surface will produce a local background much larger than that in the rest of the vacuum chamber and these backscattered molecules can severely attenuate the flow. It is for this reason that conical skimmers are used to collimate supersonic molecular beams [5]. The strong cooling that takes place in a free jet expansion can also cause problems due to condensation of low vapor pressure species. Ions are effective nucleating agents for this process. Heating the inlet is an effective way to control this problem.

The equations derived in this paper provide a basis for the rational design of an atmospheric inlet for any mass spectrometer that does not use multistage or differential pumping. Of the three types of inlets studied the pulsed sonic capillary inlet appears to be particularly attractive when the goal is minimization of pumping requirements for a portable atmospheric pressure ionization–mass spectrometer (API–MS). Although this scheme has not been used extensively, the pinch valve employed by Gao et al. [8,9] seems to be a practical way of introducing short gas pulses through a sonic capillary. It is expected that the pulsed sonic capillary inlet will find wide acceptance for portable API–MS's.

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