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Sampling and Analysis of Suspended Particles and Vapors by Continuum Source Particle Beams

Barton Dahneke

Departments of Radiation Biology and Biophysics

and of Chemical Engineering

University of Rochester

Rochester, New York 14642

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Abstract

Two continuum source particle beam methods are proposed for the on-line measurement of suspended particles or material which is suspendable in a gas. The first method can be used to size separate the various molecular and particulate species present in the beam. The second method is used to obtain a molecular composition analysis of individual beam particles or a composition distribution for a sample containing a large number of particles. The two methods are complimentary and can be used together to obtain molecular composition analyses of size-separated beam particles.

I. Introduction

The measurement of particles and large molecules suspended (or suspendable) in a gas is a problem of special interest because of their influences on meteorology, public health and process control engineering. The quantities important to their influences are the particle size (or molecular weight) and composition. Particle size completely controls or strongly influences the diffusion coefficient, sedimentation velocity, transport rate, residence time, inhalability, viability as a condensation nucleus, light scattering cross-section, and other factors. Moreover, particle size is related to the origin of the particle. For example, the particles of a photo-chemical smog are generally much smaller than wind blown soil particles or even power plant fly ash.

The measurement of particle composition should provide not only the elemental analysis but also the molecular structure, as the latter may have remarkable effect on the function of small particles as condensation nuclei, participants in chemical reactions and on their health effects.

For several years continuum source particle beams have been investigated in the author's and other laboratories as a tool in measuring the size and composition of suspended particles and vapor molecules. Some of the results of these investigations are summarized in references (1) and (2). The unique properties of continuum source particle beams that make them attractive in the on-line size and composition analysis of suspended particles and molecules are the properties that the sample particles are isolated from one another (as a consequence of the high speeds they obtain in the beam the linear number

density must be small for a given particle flux) and isolated from their suspending gas (by several stages of differential pumping). Thus, sensitive probes such as an electron beam can be used to detect and measure the individual beam particles.

Particle beam methods for measuring composition may also be useful as a general analytical tool. Simple techniques can be used to disperse liquid and, therefore, soluble solid samples in a stream of suspending gas. Techniques for dispersing insoluble solid samples are also available, though these are not so simple. Thus, although the focus of this paper is the analysis of particles and vapors already suspended in a gas, particle beam techniques may be useful over a wide range of analytical problems including analysis of air and water pollution, liquids, powders and biological samples.

Although various schemes seem promising in the on-line size and composition measurement of beam particles, attention is focused herein on two specific ones for the sake of brevity and also because, in the author's opinion, these schemes represent some of the most promising possibilities. Because some of the ideas have not yet been experimentally demonstrated in combination with one another, this investigation comprises a feasibility study of some promising particle beam techniques. Experimental data demonstrating the properties of these techniques is currently being sought in the author's laboratory.

Two basic approaches can be taken in the size/composition measurement of beam particles. In the first, the size and composition of individual beam particles are explicitly measured. This method is thus called an explicit measurement.

In the second, the beam particles are size-separated followed by the composition measurement of the total mass present within the selected size range, i.e., the composition measurement does not correspond to that of any individual particle (unless they are all identical) but rather represents the average composition of all particles in the selected size range. This method is, therefore, called a distribution measurement.

The explicit measurement approach is very powerful in identifying the exact properties of individual particles and, therefore, in determining their precise origins, histories and effects. However, any representative sample must contain a large number of particles. To make such detailed information comprehensible for a large sample, the data must be reduced to distribution form. The distribution measurement approach obtains data of this type directly. Of course, the most powerful method is the former as the explicit data can always be reduced to distribution form. However, the distribution measurement approach is useful in the substantial simplicity it affords in both system apparatus and data reduction. An ideal system could be operated in either mode.

The accurate sizing of an individual beam particle is readily accomplished by measurement of the particle TOF in the vacuum chamber as has been demonstrated experimentally (1) and theoretically (2). The method has also been patented (3). One problem that remains in the application of this method in the size measurement of small particles ($<0.5\mu\text{m}$ dia.) is the development of a suitable detection technique, a problem that is considered below in connection with the composition analysis of individual beam particles.

II. Size Separation of Beam Particles and Molecules

Small particles or molecules can be distribution measured by means of a size sorting technique called inertial or collimation separation. On the basis of their measured data of the geometrical properties of aerosol beams, Israel and Friedlander (4) proposed "the possibility of aerodynamically focusing particles of a selected size range in a polydisperse aerosol". The present author has independently developed a similar method for extracting particles and also large molecules of selected size from a particle beam and estimated the properties of the separation process. These estimates are based on a theoretical investigation of the dynamics of beam particles (2).

The dynamics of beam particles are governed by the particle equation of motion (2)

$$m_p \frac{d\vec{V}_p}{dt} = -f (\vec{V}_p - \vec{V}_g) \quad [1]$$

where m_p is the particle mass, $\vec{V}_p$ and $\vec{V}_g$ the local particle and gas velocity vectors, t the time and f the particle friction coefficient. For small particles or for sufficiently dilute suspending gas (i.e., for low particle Reynolds number)

$$\alpha = f/m_p = 9\mu\sigma/(2 a^2 \rho_p C_s) \quad [2]$$

where μ is the suspending gas viscosity, σ the particle shape factor, a the equivalent volume sphere radius of the particle, ρ_p the particle mass density and

$$C_s = C \lambda/a \quad [3]$$

where C is a constant and λ the local gas mean-free-path.

Equation [1] is written in dimensionless form by expressing $|\vec{V}_p|$ and $|\vec{V}_g|$ in multiples of a characteristic system velocity, such as $\bar{c}_0$ the mean thermal velocity of the suspending gas molecules in their stagnation state, by expressing t in multiples of a characteristic system time, namely $D^*/\bar{c}_0$ where D^* is the flow diameter of the nozzle or orifice. The dimensionless equation thus becomes

$$\frac{d\vec{V}_p}{dt} = -\alpha D^*/\bar{c}_0 (\vec{V}_p - \vec{V}_g). \quad [4]$$

For isentropic flow (2)

$$\alpha D^*/\bar{c}_0 = 4.491 \frac{D_p \rho_0 \sigma}{D_p \rho_p C} \left[1 + (\gamma-1) M^2/2 \right]^{-\frac{\gamma+1}{2\gamma-2}} \quad [5]$$

where $D_p = 2a$, ρ_0 is the stagnation state mass density of the suspending gas, γ the specific heat ratio of the suspending gas and M the local Mach number determined by γ and the nozzle or orifice geometry. Hereafter the term nozzle shall refer to either a nozzle or orifice.

Equations [4] and [5] demonstrate that small particles having the same dimensionless size β defined by

$$\beta = \frac{D_p \rho_p C}{D^* \rho_0 \sigma}, \quad [6]$$

obtain identical dynamics. Thus, the trajectory of a beam particle depends on the nozzle geometry, γ and β and on the initial particle location in the flow field.

An identical procedure is used to demonstrate the same result for the case when the beam particles are relatively heavy gas molecules, using in this case a different expression for the friction coefficient (5). The dynamics of these beam particles also depend only on nozzle geometry, γ and the appropriate β and on the initial molecule location in the flow field.

Upon penetrating into the vacuum chamber a distance of several nozzle diameters beyond the nozzle exit, the beam particles have obtained their final (terminal) trajectory. That is, the suspending gas has become so dilute it no longer exerts significant influence on the particle motion and the beam particles continue on straight line trajectories already established at this location. Let θ denote the angle between this terminal particle trajectory and the beam axis. Then

$$\tan \theta = V_r/V_x \quad [7]$$

where V_r and V_x are the terminal velocity components of the particle in the radial and axial directions. Moreover, to adequate approximation at sufficiently large x ,

$$r = x \tan \theta. \quad [8]$$

Figure 1 shows the somewhat idealized results of many calculations of $\tan \theta$ for $\gamma = 1.4$ and for a conical converging nozzle of 30° total included angle. The parameter $y_e = r_e/D^*$ is the dimensionless radial position in the nozzle exit plane. Negative values of $\tan \theta$ indicate the particle has crossed the beam axis. Thus, the large particles (because of their large inertia) retain some of their inward radial velocity component obtained in the converging nozzle section, cross the beam axis and form a diffuse (wide angle) beam.

At the opposite extreme, small particles (because of their low inertia) lose all their inward radial velocity component before nearing the beam axis and, in fact, obtain an outward radial velocity component from the radial expansion of the suspending gas before it has become too dilute to influence particle motion. Particles of small β thus also form a diffuse beam.

At just the right intermediate value of β , 9.70 for the present example, the beam particles just lose their radial velocity component upon reaching the beam axis. A beam of these particles is not diffuse but highly concentrated. If such a beam is directed at a small collimating hole of radius r_h and separation from the nozzle exit L_h such that

$$\tan \theta_h = r_h/L_h, \quad [9]$$

particles for which $\beta = 9.70$ will be transmitted through the hole with ~100 percent efficiency while particles increasingly larger and smaller will be transmitted with increasingly poorer efficiency.

Numerous numerical trajectory calculations indicate that, to adequate first approximation, the terminal particle trajectories are described by

$$\tan \theta = y_e A(\beta) \quad [10]$$

where the function $A(\beta)$, shown in Figure 2, has been extracted from the data of Figure 1 for the system specified. Expressions [9] and [10] can be combined to define the condition for particle transmission through the collimating hole, namely,

$$\tan \theta < \tan \theta_h \quad \text{or} \quad y_e < \frac{r_h}{L_h A(\beta)}. \quad [11]$$

This limiting condition (upper limit of integration over y_e), together with the assumptions of uniform gas flow and particle concentration across the nozzle exit plane, gives the particle transmission efficiency through the collimating hole

$$T(\beta) = \frac{4 \tan^2 \theta_h}{A^2(\beta)} \quad \text{or} \quad 1.0, \quad [12]$$

whichever is less.

Because particles of any β will penetrate the collimating hole if they are sufficiently near the nozzle axis, the transmission function [12] has long "tails" at high and low β values, as illustrated in Figure 3. These tails can be removed, sharply enhancing the resolving power of the collimation separator, by introducing a core flow Q_c of particle free suspending gas.

To further enhance resolving power, complications due to boundary layer effects can also be reduced or removed by introducing an outer sheath flow of particle free suspending gas such that the sample flow Q_s is contained in an annular cross-section surrounded by the core flow Q_c on the inside and the sheath flow $Q_o - Q_s - Q_c$ on the outside, where Q_o is the total flow through the nozzle. Performing the integration with the same assumptions as before, but now incorporating the proper lower and upper limits of integration, the transmission efficiency function becomes

$$T(\beta) = \frac{4 \tan^2 \theta_h / A^2(\beta) - Q_c / Q_o}{Q_s / Q_o} \quad [13]$$

subject to the restriction $0 \leq T(\beta) \leq 1.0$. This function is illustrated in Figure 3 for the case when $\theta_h = 1.0^\circ$ and $Q_{sc} = Q_s + Q_c = 0.36 Q_o$. Of course, in the special case when $Q_s = Q_o$, [13] reduces to [12]. Thus, the transmission function [12] is similar (but not identical) to the case $Q_s / Q_o = 1.0$ in Figure 3 (because of the denominator Q_s / Q_o in [13] which does not occur in the simpler expression [12]).

Size resolution can also be enhanced by placing two collimating holes in series. The collection efficiency $C(\beta)$ for the capture of beam particles in the chamber between the inlet and outlet collimating holes will be given by the difference between the two appropriate transmission efficiency functions [13]. That is,

$$C(\beta) = T(\beta)_{in} - T(\beta)_{out}. \quad [14]$$

The form of $C(\beta)$ is illustrated in Figure 4. Two transmission peaks are always present for such a system. However, the β location of both peaks can be selected so that interference effects are minimized.

We are currently investigating in our laboratory the use of these and similar schemes in collimation spectroscopy measurements of suspended particulate and molecular species and in isotope separations. Although we have not yet obtained experimental data, the data of other workers (6) is suggestive of the effects predicted here.

Although the peak of the transmission function occurs at a fixed value of β , the collimation separation process is readily used to isolate particles or molecules of selected size or weight. As indicated by [6], this is accomplished by adjusting ρ_0 (source density of the suspending gas) or D^* (orifice diameter) so that β obtains the proper value for the selected particle size. In fact, in one apparatus in the author's laboratory the sample is contained in a closed sphere. As the sample pumps out through the nozzle, the aerosol beam collimation (ABC) spectrometer slowly scans particle size from large to small, according to [6]. The various composition scans, obtained by mass spectroscopy at several particle sizes since the composition scan is rapid compared to the size scan, thus represent the average composition distributions for all particles within those size ranges.

III. Composition Analysis of Beam Particles

The second particle beam method considered herein is one that seems capable of explicit, on-line, molecular composition measurement of individual beam particles or, by multiscan summation, of composition distribution measurement of a size-separated sample. The basic processes comprising this method consist of three:

1. Intercepting the particle beam with a focused electron or laser beam of sufficient energy density to vaporize the non-molecular beam particles and to ionize the molecules, all within a short path length (namely, the thickness of the focused electron or laser beam).
2. Extracting (accelerating) these ions by use of a suitable electromagnetic field followed by drifting them across a region so that ions of different charge to mass ratio are separated.
3. Detecting and counting the arrival of ions at the multiplier located at the end of the drift region so that the distribution of ions over arrival time is obtained.

This technique is thus a direct application of time-of-flight mass spectroscopy, the novel feature introduced here being the method of sample introduction and ion generation which, since the ions are all generated in a very brief time interval, is well suited to the TOF technique. Moreover, since ions of opposite charge are extracted in opposite directions, it is a simple matter to measure both positive and negative ions. Indeed, for the case of vaporization by electron beam bombardment, the detection of scattered and secondary electrons which have low energy (<50 eV) can serve both as a

time reference by which the ion mass to charge ratio m/q of all other species is determined and as a trigger signal for obtaining multiscan summations and for temporarily turning off system components (such as the electron beam) to prevent coincidence errors and minimize the background noise signal. The higher energy electrons not scattered from the electron beam are not significantly deflected in the extracting field. For the case of vaporization by laser radiation either emitted electrons or the scattered light signal can serve as the time reference and trigger signal.

The feasibility of this technique is controlled by the feasibility of several processes operating in combination, namely, the vaporization of particles in an intense electron or laser beam, the ionization of these molecules and, finally, the ion dynamics in the ionizer-extractor-detector system.

The present author (7) has calculated the extent to which small beam particles are vaporized in electron beams of moderate energy (≤ 5 keV) and found that submicron water droplets and even water droplets of several μm diameter are fully evaporated in passing through a focused electron beam of ~ 1 keV energy. To fully evaporate larger droplets high intensity beams of energy > 2 keV are required. Indeed, the calculations suggest the possibility of probing the composition of surface layers of variable depth by size sorting the beam particles and regulating the electron beam energy and intensity. Heating of the beam particles will also have to be controlled to prevent pyrolysis of organic species.

The ionization of molecules by electron impact is a classic problem that has been studied by many investigators. The reviews of Massey and Burhop (8)

and of Pichanick (9) are useful overviews, the former comprising a fundamental treatment of the basic physical processes and the latter providing descriptions of several types of detector systems and their principles of operation. The available data indicate that only a fraction of the molecules evaporated from a beam particle will be ionized by electron impact over the short path length available. The fraction ionized will depend on the electron energy, current density, path length through the electron beam and the molecular species. Although additional experimental data is needed, the available data suggest a signal will be obtained which can be used to infer composition information about the particle. For very small beam particles, multiscan summation may be required to obtain adequate signal levels.

The feasibility question thus focuses on the ion dynamics. In order to be useful, the system must be capable of resolving single amu mass differences over an adequate mass range, from one up to several hundred. Several factors combine in their influence on the ion dynamics to impose a limit on the resolution of single m/q signal peaks by causing the peaks to broaden so that neighboring peaks overlap. These factors include

- (1) variation in initial (thermal) velocity of the ion;
- (2) variation in location (in the extraction field) of ionization;
- (3) variation in the instant of ionization;
- (4) variation in ion path length to the detector; and
- (5) variations due to space charge effects.

In the simple analysis of the ion dynamics that follows, only the first three factors are considered. As the influence of the others can be removed or diminished by good system design, the first three factors seem to impose the basic limitations of the method.

The motion of an ion in an electrostatic field is governed by the equation of motion

$$m \frac{d^2x}{dt^2} = -qE \quad [15]$$

where m is the ion mass (kg), x the displacement (m) in the direction of the electrostatic field E (volts/m), t the time (sec) and q the ion charge (coulombs) which may be positive or negative. For convenience, the ion mass will later be expressed as a dimensionless mass number $n = m/m_0$, where $m_0 = 1.660 \times 10^{-27}$ kg = 1 atomic mass unit (amu).

A single integration of [15] for the case when E is constant gives the ion velocity

$$v = -\frac{qE}{m} (t-t_0) + v_0 \quad [16]$$

where v_0 is the ion velocity at time t_0 . A second integration gives the ion location

$$x = -\frac{qE}{2m} (t-t_0)^2 + v_0 (t-t_0) + x_0 \quad [17]$$

where x_0 is the ion location at time t_0 . Solution of the quadratic expression [17] gives

$$t-t_0 = \frac{v_0 \pm [v_0^2 - 2qE\Delta x/m]^{1/2}}{qE/m} \quad [18]$$

where $\Delta x = x - x_0$. We thus obtain for $\Delta x = 0$

$$t - t_0 = \frac{m}{qE} (v_0 \pm |v_0|) = 0 \quad \text{or} \quad \frac{2mv_0}{qE},$$

the latter condition only having physical meaning when $t - t_0$ is positive. If we restrict our consideration to the time range

$$t - t_0 \geq 0 \quad \text{or} \quad \frac{2mv_0}{qE},$$

whichever is greater, then the plus sign is correct in [18] and the ion arrival time at x is given by

$$t = t_0 + \left[\frac{m^2 v_0^2}{q^2 E^2} - \frac{2m(x - x_0)}{qE} \right]^{1/2} + \frac{mv_0}{qE}. \quad [19]$$

For the time range specified, $2m(x - x_0)/(qE) \leq 0$. We see from [19] how variations in t_0 , v_0 and x_0 act to broaden a signal peak. For example, as the initial ion velocity v_0 varies from $-v_0$ to v_0 , the ion arrival time at x changes by the increment $2mv_0/(qE)$.

Consider now the case where the ion is extracted (accelerated) by the constant electrostatic field E acting over the distance $x_1 - x_0$ and then drifts at constant velocity (from [16] and [19])

$$v_1 = -\frac{qE}{m} \left[\frac{m^2 v_0^2}{q^2 E^2} - \frac{2m(x_1 - x_0)}{qE} \right]^{1/2} \quad [20]$$

through a field-free drift region of length L . The ion drift time over this length is L/v_1 so that the ion arrival time at the detector located at the end of the drift region is

$$t = t_0 + \frac{mv_0}{qE} + \left[\frac{m^2 v_0^2}{q^2 E^2} - \frac{2m(x_1 - x_0)}{qE} \right]^{1/2} - \frac{mL}{qE} \left[\frac{m^2 v_0^2}{q^2 E^2} - \frac{2m(x_1 - x_0)}{qE} \right]^{-1/2}. \quad [21]$$

The total variation in ion arrival time due to variations in t_0 , v_0 and x_0 is

$$\Delta t \cong \frac{\partial t}{\partial t_0} \Delta t_0 + \frac{\partial t}{\partial v_0} \Delta v_0 + \frac{\partial t}{\partial x_0} \Delta x_0 \quad [22]$$

where the partial derivatives are easily obtained from [21]. Evaluating these partial derivatives at the central point $t_0 = v_0 = x_0 = 0$, [22] becomes

$$\Delta t = \left| \Delta t_0 \right| + \left| \frac{m}{qE} \Delta v_0 \right| + \left| \frac{m}{qE} \left[-\frac{2mx_1}{qE} \right]^{-1/2} \left(1 - \frac{L}{2x_1} \right) \Delta x_0 \right|. \quad [23]$$

The two Δx_0 terms have opposite sign because a shorter acceleration distance x_1 results in a shorter transit time for the first portion of the ion trajectory but also in a lower ion velocity v_1 and hence a longer transit time over the remaining portion. Since variations in t_0 , v_0 and x_0 cause a cumulative spreading of the signal peak, the breadth Δt of this peak is calculated by summing the absolute value of each term as shown in [23].

The quantity Δt_0 is estimated to be the residence time of the beam particle in the electron or laser beam, either of which can be focused down to a few μm thickness. If Δy represents this thickness, D_p the diameter of the beam particle and V_p the velocity component of the beam particle normal to the axis plane of the sheet ionizing beam, then

$$\Delta t_0 = (\Delta y + D_p) / V_p.$$

Extensive calculated values of V_p are given in (2) for particles suspended in air. Typical values for spheres of specific gravity = 1.0 range between ~100 and ~500 m/sec as particle diameter ranges from ~10 to ~.01 μm . A representative maximum value of Δt_0 is, therefore,

$$\Delta t_0 = 10^{-7} \text{ sec.}$$

An estimate of Δv_0 is obtained by use of the Maxwell velocity distribution. The fraction of a sample of molecules of mass m at absolute temperature T having velocity component in the x direction between $-v$ and v is

$$F = 2 \left[\frac{m}{2\pi kT} \right]^{1/2} \int_{v=0}^v \exp \left(-\frac{mv^2}{2kT} \right) dv.$$

By a simple transformation of variables

$$F = \text{erf.} \left(\left[\frac{mv^2}{2kT} \right]^{1/2} \right).$$

Since the error function reaches a value of 0.9953 when its argument reaches 2.00, we obtain the result that 99.53 percent (essentially all) the sample molecules have their thermal velocity component within the range $-|v_0| \leq v \leq |v_0|$ where v_0 is defined by

$$\left[\frac{mv_0^2}{2kT} \right]^{1/2} = 2.00$$

Thus, $v_0 = \pm \sqrt{8kT/m}$ and

$$\Delta v_0 = \sqrt{32kT/m}. \quad [24]$$

To complete the estimate of Δv_0 we lack only the surface temperature T of the evaporating particle. In the absence of specific data, an assumed value of $T = 1000$ K will be used. Analytical estimates of T would not be difficult but are beyond the scope of this initial study.

The influence of Δx_0 can be controlled by system design. As a particle evaporates in a high current density electron beam or an intense laser beam, many of the evaporating molecules will be ionized before traveling too far from the particle. However, some will travel relatively large distances before ionizing and some will leave the ionizing beam without being ionized at all. To insure that ionization occurs only in a small region Δx_0 , the ions can be extracted in the direction normal to the planar axis of the thin sheet ionizing beam. Then it is assured that ionization occurs only within a small range of x . In this case Δx_0 is the ionizing beam thickness, of the order of $10 \mu\text{m}$. This design may also have significant advantage in minimizing the influence of space charge effects.

If the ions are extracted parallel to the ionizing beam axis, the uncertainty Δx_0 is equal to the height of the ionizing beam of the order of 1 mm. Nevertheless, the influence of Δx_0 may still be removed if $L = 2x_1$. However, as we shall see below, this design condition seems neither necessary nor desirable.

A useful quantity in evaluating the resolving power is the relative signal peak width $\Delta t/\bar{t}$. Combination of [21], [23] and [24] gives

$$\bar{t} = \left[-\frac{2mx_1}{qE} \right]^{1/2} (1 + L/2x_1) \quad [25]$$

$$\Delta t/\bar{t} = \left| \Delta t_0/\bar{t} \right| + \left| \frac{\left[\frac{16 kT}{-qEx_1} \right]^{1/2}}{1 + L/2x_1} \right| + \left| \frac{\Delta x_0}{2x_1} \frac{L-2x_1}{L+2x_1} \right|. \quad [26]$$

A necessary and sufficient condition for the resolution of individual signal peaks is the condition that the relative peak separation is greater than the relative peak width. The relative peak separation is

$$\frac{1}{\bar{t}} \frac{\partial \bar{t}}{\partial m} \Delta m = (2n)^{-1} \quad [27]$$

where n is the ion mass number expressed in amu and $\Delta m = 1$ amu. The useful mass range of an instrument, therefore, comprises the ion mass range defined by

$$Q = (2n)^{-1} - \frac{\Delta t}{\bar{t}} > 0. \quad [28]$$

This function is illustrated in Fig. 5 which shows that resolution improves (Q increases) as n decreases.

The limit of the useful mass range is defined by $Q = 0$. This limit is readily calculated by use of [26] which gives

$$Q = (2n)^{-1} - |An^{-1/2}| - |B| - |C| = 0 \quad [29]$$

where

$$A = \Delta t_0 (|q/2m_0|)^{1/2} \phi^{1/2} x_1^{-1} (R+1)^{-1} \quad [30a]$$

$$B = (|16kT/q|)^{1/2} \phi^{-1/2} (R+1)^{-1} \quad [30b]$$

$$C = (\Delta x_0 / 2x_1) (R-1) / (R+1) \quad [30c]$$

$$R = L/2x_1.$$

The single admissible root of the quadratic expression [29] is

$$n_0 = \frac{A^2 + B + C - A\sqrt{A^2 + 2(B+C)}}{2(B+C)^2} \quad [31]$$

The useful mass range thus extends from zero to n_0 .

To determine the parameters x_1 and ϕ which maximize (or minimize) n_0 we require

$$\frac{\partial n_0}{\partial x_1} = \frac{\partial n_0}{\partial A} \frac{\partial A}{\partial x_1} + \frac{\partial n_0}{\partial B} \left\{ \frac{\partial B}{\partial x_1} + \frac{\partial C}{\partial x_1} \right\} = 0$$

$$\frac{\partial n_0}{\partial \phi} = \frac{\partial n_0}{\partial A} \frac{\partial A}{\partial \phi} + \frac{\partial n_0}{\partial B} \left\{ \frac{\partial B}{\partial \phi} + \frac{\partial C}{\partial \phi} \right\} = 0,$$

since

$$\frac{\partial n_0}{\partial B} = \frac{\partial n_0}{\partial C}.$$

Although these equations and [30] are too complex to be solved for simple analytical expressions for the optimum values of x_1 and ϕ , they do provide a useful result since they require

$$-\frac{\frac{\partial n_0}{\partial A}}{\frac{\partial n_0}{\partial B}} = \frac{\frac{\partial B}{\partial x_1} + \frac{\partial C}{\partial x_1}}{\frac{\partial A}{\partial x_1}} = \frac{\frac{\partial B}{\partial \phi} + \frac{\partial C}{\partial \phi}}{\frac{\partial A}{\partial \phi}} .$$

That is, if this last expression relating x_1 and ϕ is satisfied, then whenever the system is optimized with respect to x_1 it is also optimized with respect to ϕ , and vice versa. The optimization process is thus reduced from two dimensions to one. Calculating the partial derivatives from [30] the optimization condition becomes

$$\phi = (16kT/|q|) \left\{ \frac{R-1}{R^2 + 2R - 1} \right\}^2 \left\{ \frac{\Delta x_0}{2x_1} \right\}^{-2} . \quad [32]$$

When $T = 1000$ K the first factor obtains the value 1.37868 V.

The design expressions [31] and [32] were used to calculate the useful mass range n_0 . Example results are shown in Tables I, II and III. The data of Table I demonstrate that n_0 is indeed maximized (instead of minimized) with respect to variation in ϕ by use of [32]. The first ϕ column values of Table I were calculated by [32] and the corresponding maximum n_0 exceeds the maximum n_0 values for slightly smaller and larger ϕ values shown in the other columns.

The data of Table II show the dependence of the maximum n_0 and the corresponding x_1 and ϕ values on L , Δx_0 and Δt_0 . For example, as Δt_0 is reduced, which could be readily accomplished by accelerating the beam

particles in a helium or hydrogen jet instead of an air jet or analyzing only the smaller beam particles so that terminal particle velocity is higher in either case or by turning the ionizing beam on for only the desired interval, the usable mass range is significantly extended. An additional benefit of turning the ionizing beam on for the desired interval, used together with multi-scan summation, is the ability to measure the composition of molecular species present in the beam.

The data of Table III show that the system design for which $L=2x_1$ is not suitable. In this case, even when the usable mass range obtains its maximum value

$$n_0^* = (2B)^{-1}$$

at $x_1 \gg \infty$, the values of n_0^* are too small.

In conclusion, the simple analysis described and the resulting calculated values of usable mass range suggest this second particle beam method for explicit composition analysis of individual beam particles is indeed feasible and promising. Although many details must still be considered, the usable mass ranges calculated here may be conservative as at least some of the assumed values used in the calculations were conservative. Further study of this method is proceeding in the author's laboratory.

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References

1. Dahneke, B., Aerosol Beams, Chapter 9 in Recent Developments in Aerosol Science, (D. T. Shaw, ed.), John Wiley, New York, 1978.
2. Dahneke, B. E. and Cheng, Y. S., J. Aerosol Sci. 10, 257 (1979).
3. U.S. Patent 3,854,321.
4. Israel, G. W. and Friedlander, S. K., J. Coll. and Interface Sci. 24, 330 (1967).
5. Schwartz, M. and Andres, R., J. Aerosol Sci. 7, 281 (1976).
6. Dun, H., Mattes, B. and Stevenson, D., Chemical Physics 38, 161 (1979).
7. Dahneke, B., in Environmental Pollutants - Detection and Measurement, (T. Toribara, J. Coleman, B. Dahneke and I. Feldman, eds.), Plenum Press, New York, 1978.
8. Massey, H. S. W. and Burhop, E. H. S., Electronic and Ionic Impact Phenomena, Oxford, 1952.
9. Pichanick, F. M. J., in Atomic Sources and Detectors. (V. Hughes and H. Schultz, eds.), Academic Press, 1967.

Table I. Calculated values of the useful mass range n_0 for $\Delta t_0 = 100$ nsec, $\Delta x_0 = 10$ μ m and $L = 1.0$ m.

x_1 , m	ϕ , V	n_0 , amu	ϕ , V	n_0 , amu	ϕ , V	n_0 , amu
.002	3.446	95.0	90.0	119.8	100.0	118.5
.003	17.239	130.4	90.0	143.8	100.0	142.7
.004	53.84	150.4	90.0	152.9	100.0	152.5
.0045	85.73	153.8	90.0	153.937	100.0	153.9
.00456	90.33	153.953	90.0	153.946*	100.0	153.973
.0046	93.50	154.000	90.0	153.940	100.0	153.995
.00464	96.75	154.020*	90.0	153.925	100.0	154.009
.00468	100.08	154.013	90.0	153.901	100.0	154.013*
.0047	101.78	153.999	90.0	153.885	100.0	154.012
.0048	110.59	153.833	90.0	153.777	100.0	153.974
.005	129.90	153.019	90.0	153.4	100.0	153.7
.006	266.21	140.6	90.0	149.4	100.0	150.4
.007	487.43	119.0	90.0	143.3	100.0	144.7
.008	821.85	94.7	90.0	136.4	100.0	138.2
.009	1301.2	72.6	90.0	129.5	100.0	131.5
.010	1960.2	54.6	90.0	122.7	100.0	125.0

*maximum value of n_0 .

Table II. Maximum useful mass range n_0^* calculated for various system parameter values.

L, m	Δx_0 , μm	Δt_0 , nsec	x_1^* , m	ϕ^* , V	n_0^* , amu
1.0	10	100	.0046	93.50	154.0
1.0	10	20	.0090	1301.1	297.2
1.0	5	100	.0030	68.96	202.2
1.0	5	20	.0059	996.8	388.3
2.0	10	100	.0081	226.2	267.6
2.0	10	20	.0156	2977.7	515.5
2.0	5	100	.0053	168.6	351.6
2.0	5	20	.0102	2247.1	674.5
5.0	10	100	.0167	659.5	555.9
5.0	10	20	.0323	8894.9	1068.5
5.0	5	100	.0110	503.3	730.9
5.0	5	20	.0211	6652.6	1400.2

*At maximum n_0 .

Table III. Calculated values of the usable mass range n_0 in amu for the case $L = 2x_1$.

Δt_0 , nsec	x_1 , m	$\phi=10^2$ V	$\phi=10^3$ V	$\phi=10^4$ V
100	0.001	0.021	0.0021	0.00015
100	0.002	0.081	0.0083	0.00083
100	0.005	0.46	0.052	0.0052
100	0.01	1.43	0.20	0.021
100	0.02	3.21	0.78	0.083
100	0.05	5.69	3.82	0.51
100	0.1	6.96	9.09	1.98
100	0.2	7.70	15.3	6.99
100	0.5	8.18	21.5	25.5
100	1.0	8.35	24.0	45.3
100	2.0	8.43	25.4	61.9
100	5.0	8.48	26.3	74.9
100	$\geq \infty$	8.52	26.9	85.2
20	0.001	0.46	0.052	0.0052
20	0.002	1.43	0.20	0.021
20	0.005	3.86	1.18	0.13
20	0.01	5.69	3.82	0.51
20	0.02	6.96	9.09	1.98
20	0.05	7.85	17.1	10.1
20	0.1	8.18	21.5	25.5
20	0.2	8.35	24.0	45.3
20	0.5	8.45	25.7	65.9
20	1.0	8.48	26.3	74.9
20	2.0	8.50	26.6	79.9
20	5.0	8.51	26.8	83.0
20	$\geq \infty$	8.52	26.9	85.2

Figure Captions.

1. Inclination of particle trajectory to beam axis versus dimensionless particle size β for various dimensionless locations in the jet.
2. The function $A(\beta)$ versus β for converging nozzles of various total included angle 2ϕ .
3. Transmission efficiency $T(\beta)$ versus dimensionless particle size β .
The sample flow Q_s is contained between a central core flow Q_c and an outer sheath flow $Q_o - Q_s - Q_c$ of particle free suspending gas. The total nozzle flow is Q_o and $Q_{sc} = Q_s + Q_c$. For these data, the value $Q_{sc} = 0.36 Q_o$ was used.
4. An illustration of the high resolution obtainable by differential collimation separation. Assumed values were $Q_c/Q_o = 0.70$, $Q_s/Q_o = 0.20$, $\theta_{h1} = 1.20^\circ$, $\theta_{h2} = 1.00^\circ$, $\gamma = 1.40$ and $2\phi = 30^\circ$.
5. The form of the resolution function $Q(n)$.

Figure 1. Inclination of particle trajectory to beam axis versus dimensionless particle size β for various dimensionless locations in the jet.

Figure 2. The function $A(\beta)$ versus β for converging nozzles of various total included angle 2ϕ .

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Figure 4. An illustration of the high resolution obtainable by differential collimation separation. Assumed values were $Q_c/Q_0 = 0.70$, $Q_s/Q_0 = 0.20$, $\theta_{h1} = 1.20^\circ$, $\theta_{h2} = 1.00^\circ$, $\gamma = 1.40$ and $2\phi = 30^\circ$.

Figure 5. The form of the resolution function $Q(n)$.