On evaporation kinetics of multicomponent aerosols: Characteristic times and implications for volatility measurements.

Andrey Khlystov [*]

Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512

March 15, 2024

This manuscript has been submitted to Aerosol Science and Technology but has not been peer-reviewed yet. Subsequent versions of this manuscript could have slightly different content. If accepted, the final version of the manuscript will be available via the DOI link on this page.

Abstract

This paper presents a theoretical analysis of the evaporation of individual compounds from an aerosol in vapor-free conditions, demonstrating that the evaporation of mixture components is interconnected via the ratio of their characteristic times. These characteristic times are proportional to the square of the initial particle diameter and inversely proportional to the compound saturation vapor concentration (SVC). A single ordinary differential equation (ODE) can adequately describe the behavior of all mixture components. It is shown that the time needed to evaporate a specific compound fraction is primarily controlled by the compound's characteristic time, with lesser influences from compound abundance in the mixture and the amount of less volatile material. Consequently, the relative abundance of indi-

---

[*] E-mail: `andrey.khlystov@dri.edu`; Corresponding author

vidual compounds has a minor effect on evaporation. Compounds evaporate in the reverse order of their SVC, with the time required to evaporate 50% of their original mass being roughly half of their characteristic time. The reduction in ODEs provides significant computational benefits. Additional simplifications are derived that further accelerate calculations by two orders of magnitude while maintaining accuracy. The theory can guide experimental design for aerosol volatility measurements and demonstrate that a unique volatility basis set (VBS) can be fit to experimental data if the number of observations equals at least the number of volatility bins minus one. However, assumptions regarding parameters used for VBS fitting can result in ambiguity in the derived VBS, making it essential to use the same parameters for modeling evaporation as those used to derive the VBS from experimental data.

1 Introduction

Understanding evaporation kinetics of individual compounds from droplets of mixed substances is required for a range of applications spanning atmospheric chemistry, spray drying, fuel delivery for combustion, and drug delivery using aerosolized formulations (Martin et al., 2005; Sazhin, 2017; Tikkanen et al., 2019). The complexity of aerosol gas-particle interactions is especially apparent in the case of atmospheric aerosols that are composed of thousands of compounds, for the majority of which the thermodynamic properties are unknown (Bilde et al., 2014). The volatility properties of a compound play a central role in controlling its atmospheric fate and lifetime, as its physical state – condensed or in gaseous form – determines the kind of reactions it can undergo as well as their rates (Seinfeld and Pandis, 2006; George et al., 2015; Shrivastava et al., 2017; Carlton et al., 2020). The volatility basis set (VBS) is widely used to simplify the complexity of aerosol mixtures and make volatility-related calculations computationally feasible. The VBS representation has been implemented in several atmospheric chemical transport models (Lane et al., 2008; Murphy and Pandis, 2009; Ahmadov et al., 2012; Jo et al., 2013; Koo et al., 2014). In the VBS representation, a complex mixture is simplified to a set of surrogate compounds whose volatilities differ by an order of magnitude (Donahue et al., 2006). Compounds comprising the aerosol mixture, as well as their surrogate representation in the VBS, are assumed to form a quasi-ideal mixture that behaves according to the absorptive partitioning theory (Pankow, 1994).

Due to the large variety of mixtures (and the corresponding VBS) that can be encountered in real life applications, predictions of evaporation of individual compounds from a mixture has mostly relied on numerically solving a set of ordinary differential equations (ODE) that describe evaporation rate of a compound based on its molar fraction in the mixture (Seinfeld and Pandis, 2006). Likewise, experimental methods for derivation of the VBS rely on numerical modeling to fit the changes in particle size or mass of individual compounds or their broad groups measured in a thermodenuder (TD) (Cappa, 2010; Fuentes and McFiggans, 2012; Riipinen et al., 2010; Saha et al., 2017) or a single particle levitation apparatus (Krieger et al., 2012; Cai et al., 2015; Kohli and Davies, 2021). In addition to being computationally demanding for large datasets, the numerical modeling was reported to produce solutions that strongly depend on the assumed thermodynamic and kinetic properties of compounds in the mixture, such as their enthalpy of vaporization or the accommodation/evaporation coefficients, that are generally not known *a priori* (Cappa and Jimenez, 2010). The measurement noise could also lead to large uncertainties in the derived VBS (Karnezi et al., 2014).

The variability of VBS that can be encountered in the atmosphere and other applications combined with the non-transparent nature of numerical solutions of ODE describing aerosol evaporation make it difficult to gain insight into the relative importance of different factors that control aerosol evaporation. For example, it would be helpful to estimate evaporation times for individual (real or surrogate) compounds from an arbitrary mixture given the compound thermodynamic properties and the particle size. Such estimates could help derive parameterizations to implement the kinetic aspects of gas-particle exchange in atmospheric chemical transport models. They can also inform the experimental design for measurements of aerosol volatility. For example, they can help estimate the evaporation time and/or temperature range needed to cover a certain range of aerosol volatility. A better understanding of individual compound evaporation would also allow answering questions, such as whether there is a unique solution to the observed particle size changes as a function of time or temperature in the absence of any experimental noise, or whether VBS derived using a set of assumed parameters (e.g., the enthalpy of vaporization and evaporation coefficient) can be used with another set of such parameters.

In this paper, a theoretical analysis of evaporation of individual compounds from an aerosol particle in vapor-free conditions is presented to assess the effect of mixture composition on compound evaporation times. Implications for aerosol volatility measurements and the feasibility of obtaining a unique VBS fit into experimental data are also discussed.

2 Theory

2.1 Evaporation of a multicomponent particle

Let us consider a particle composed of an ideal liquid mixture of volatile compounds with the initial mass fractions $f_i = m_{i,0}/m_{t,0}$, where $m_{i,0}$ is the initial mass of compound i and $m_{t,0}$ is the total mass of the particle equal to the sum of individual compounds in the mixture. If compound saturation concentrations (C_i) are separated by orders of magnitude, then the set of f_i represents the volatility basis set. In the following analysis, however, such a separation of C_i values is not required, and the mixture could be composed of an arbitrary set of compounds with an arbitrary set of C_i. It is assumed that there are no inter-particle transfer limitations, such as those found in solid or highly viscous particles (Li and Shiraiwa, 2019). Such an assumption holds well for most conditions encountered in the lower troposphere (Reid et al., 2018). All components of the mixture are assumed to have the same molecular weight (M), density (ρ), surface tension, and evaporation coefficients (α); these assumptions are common in experimental studies of aerosol volatility (Cappa, 2010; Fuentes and McFiggans, 2012; Riipinen et al., 2010; Saha et al., 2017). Evaporation is assumed to occur in a vapor-free environment, i.e., where the gas phase concentration of any component at any time is zero. This assumption represents scenarios in which gas phase components are constantly removed or where the initial aerosol concentration is negligible relative to the equilibrium vapor concentration of individual components. The first scenario is representative of studies using a diffusion denuder that constantly strips gas phase components or where a particle is levitated in a stream of vapor-free gas. The second scenario represents cases where aerosol is strongly diluted or strongly heated, especially when the initial aerosol concentration is small, such as in TD measurements. Surface temperature reduction due to latent heat loss and the Stephan flow are also neglected, which generally holds for ambient temperatures and/or compounds of atmospheric aerosol relevance (Widmann and Davis, 1997; Saleh et al., 2011).

As the particle evaporates, its mass as well as that of the individual compounds decreases. Let us denote the mass fraction remaining (MFR) of a compound i as $x_i = m_i/m_{i,0}$, where m_i is the mass of compound i at any moment in time. Likewise, let us define the MFR of the total mixture as z (a different symbol is used to avoid confusion with the MFR of individual compounds). It can be easily shown that the MFR of the total mixture can be represented as:

$$z = \sum_i f_i x_i \tag{1}$$

Assuming a spherical particle, the MFR of the total mass can be used to calculate the particle diameter $d = d_0 z^{1/3}$, where d_0 is the initial particle diameter.

The mass evaporation rate of component i in the transition regime is described by the following equation (Seinfeld and Pandis, 2006):

$$\frac{\mathrm{d}m_i}{\mathrm{d}t} = -2\pi D_i d C_i F(d) K(d) \frac{m_i}{m_t}, \tag{2}$$

where D_i is the gas phase diffusion coefficient of the compound, C_i is its saturation vapor concentration (SVC), $F(d)$ is the Fuchs-Sutugin correction and $K(d)$ is the Kelvin correction (Seinfeld and Pandis, 2006). It is proportional to the compound molar fraction in the mixture, which is equal, under the assumption of identical molecular weights, to the ratio of its mass, m_i, and the total particle mass, m_t. Since the particle diameter is a function of the total particle mass m_t and thus z (see above), we can rewrite Eq.2 as:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = -\tau_i^{-1} F(z) K(z) \frac{x_i}{z^{2/3}}, \tag{3}$$

or:

$$\frac{\mathrm{d}\log(x_i)}{\mathrm{d}t} = -\frac{F(z)K(z)}{\tau_i z^{2/3}}, \tag{4}$$

where τ_i is the characteristic time for compound i:

$$\tau_i = \frac{\rho d_0^2}{12 D_i C_i}. \tag{5}$$

From Equation 4 it follows that the MFR change rates of any two compounds i and j in an evaporating particle relate to each other according to the following relationship:

$$\frac{\mathrm{d}\log(x_i)}{\mathrm{d}t} = a_{i,j}\frac{\mathrm{d}\log(x_j)}{\mathrm{d}t}, \tag{6}$$

where

$$a_{i,j} = \frac{\tau_j}{\tau_i}. \tag{7}$$

Since all compounds start evaporation with MFR = 1, it follows from Equation 6 that at any time the MFR of any two compounds in the mixture relate to each other according to the following relationship:

$$x_i = x_j^{a_{i,j}}. \tag{8}$$

This, in turn, means that the MFR of the total mixture can be expressed via the MFR of any individual component in the mixture:

$$z = \sum_j f_j x_i^{a_{j,i}}. \tag{9}$$

In other words, the behavior of the whole mixture, as well as any of its compounds, can be known from the behavior of any of its components. If the initial particle composition (f_i) and the compound properties (τ_i) are known, one does not need to solve a system of N (the number of compounds in the mixture) ordinary differential equations (ODE), as solving one differential equation (Eq.3 with z expressed via Eq.9) corresponding to one of the compounds is sufficient. Once the behavior of one of the compounds is known, the total MFR (and thus the particle size) can be determined using Eq.9 and the MFR of any other mixture component calculated using Eq.8.

2.2 The effect of VBS shape on evaporation kinetics

2.2.1 Continuum regime

Let us consider evaporation in the continuum regime with negligible Kelvin effect, i.e., when $F = K = 1$. By combining Eq.4 and Eq.9, and expressing it via x_i instead of its logarithm, we get:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = -\tau_i^{-1}\left(\sum_j f_j x_i^{a_{j,i}-1}\right)^{-2/3} x_i^{1/3}. \tag{10}$$

By integrating the above equation, we obtain:

$$\int_{x_i(t)}^{1} \left(\sum_j f_j x_i^{a_{j,i}-1} \right)^{2/3} x_i^{-1/3} \mathrm{d}x_i = t_i^*, \tag{11}$$

where $t_i^* = t/\tau_i$ is the effective time for compound i. This expression can be numerically integrated to find the time necessary to reach a certain $x_i(t)$, such as the point of half evaporation ($x_i(t) = 0.5$).

Let us now consider the expression inside the brackets under the integral on the left hand side of Equation 11. By introducing a variable $n = j - i$, the sum in the brackets becomes:

$$\sum_j f_j x_i^{a_{j,i}-1} = \sum_{n=-i}^{N-i} f_{n+i} x_i^{a_n - 1}, \tag{12}$$

where N is the number of compounds in the mixture.

In the VBS scheme, SVC of compounds in a mixture are separated by an order of magnitude. For such a ten-fold spacing in SVC, $a_n = 10^n$ (see Eq.7). This means that for $n < 1$ (i.e., for compounds with SVC lower than that of the compound under consideration), $x_i^{a_n-1}$ quickly approaches x_i^{-1}, while for positive n, it quickly reaches 0, because by definition $x_i \leq 1$. For $n = 0$, $x_i^{a_n-1} = 1$. Thus, the sum in Eq.12 can be approximated as:

$$\sum_{n=-i}^{N-i} f_{n+i} x_i^{a_n-1} \approx f_i + x_i^{-1} \sum_{j<i} f_j = f_i \left(1 + x_i^{-1} b_i\right), \tag{13}$$

where

$$b_i = \frac{\sum_{j<i} f_j}{f_i}, \tag{14}$$

which is the ratio of compound's initial mass to that of all compounds in lower volatility bins.

Equation 11 can then be rewritten as:

$$f_i^{2/3} \int_{x_i(t)}^{1} \frac{(x + b_i)^{2/3}}{x} \mathrm{d}x \approx t_i^*. \tag{15}$$

This expression shows that the evaporation of each component in the mixture is influenced by the initial ratio of its mass to that of the material found in the lower volatility bins, as well as its initial mass fraction in the mixture.

Let us now consider a few limiting scenarios. For the bin with the lowest volatility, where $b_i = 0$, or for the bins for which the amount of material in the lower volatility bins is negligibly small, the above expression reduces to:

$$1.5 f_i^{2/3}(1 - x_i^{2/3}) \approx t_i^*. \tag{16}$$

Thus, the evaporation of the least volatile bin in any mixture can be approximated by the evaporation of a pure compound, but corrected for its mass fraction in the VBS (i.e., $f_i^{2/3}$). This expression is also valid for any other bins that have much more material than all the lower volatility bins combined.

Another limiting case arises when the bin contains very little material relative to the lower volatility bins, i.e., when $b_i \gg 1$. In this case, Equation 15 reduces to:

$$-\left(\sum_{n<i} f_n\right)^{2/3} \log(x_i) \approx t_i^*. \tag{17}$$

This equation is similar to that describing evaporation of a volatile compound from a non-volatile matrix.

It should be noted that Equation 15 has an analytical solution. The value of the integral on the left-hand side of the equation can be calculated from its indefinite form:

$$\begin{aligned}\int \frac{(x+b_i)^{2/3}}{x}\mathrm{d}x = {} & -0.5\ b_i^{2/3}\log(x) \\ & + 1.5\left(b_i^{2/3}\log\left((b_i+x)^{1/3} - b_i^{1/3}\right) + (b_i+x)^{2/3}\right) \\ & + \sqrt{3}\arctan\left(\frac{2(1+x/b_i)^{1/3}+1}{\sqrt{3}}\right).\end{aligned} \tag{18}$$

Equations 16, 17, and 18 can be used for quick estimation of the time needed to evaporate a certain fraction of material in each volatility bin, with Eq.18 giving the best approximation.

2.2.2 Free molecular regime

In the free molecular regime, the expression describing evaporation rate of compound i in vapor-free condition is (Seinfeld and Pandis, 2006):

$$\frac{\mathrm{d}m_i}{\mathrm{d}t} = -\frac{\overline{c_i}}{4}\pi\alpha_i d^2 C_i \frac{m_i}{m_t}, \tag{19}$$

where α_i is the accommodation coefficient and $\overline{c_i}$ is the mean molecular velocity of the evaporating species:

$$\overline{c_i} = \sqrt{\frac{8\,R\,T}{\pi\,M_i}}, \tag{20}$$

in which R is the universal gas constant, T is the temperature, and M_i is the molar weight of the compound.

By introducing a characteristic time for the free molecular regime

$$\tau_{if} = \frac{2\,\rho\,d_0}{3\,\overline{c_i}\,\alpha_i C_i}, \tag{21}$$

Equation 19 can be rewritten as:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = -\tau_{if}^{-1}\left(\sum_j f_j x_i^{a_{j,i}-1}\right)^{-1/3} x_i{}^{2/3} \tag{22}$$

This expression is similar to that for the continuum regime (Eq.10), and the same steps taken in Section 2.2.1 can be repeated to arrive at the following exact and approximate equations:

$$\int_{x_i(t)}^{1}\left(\sum_j f_j x_i^{a_{j,i}-1}\right)^{1/3} x_i^{-2/3}\mathrm{d}x_i = t_i^*, \tag{23}$$

$$f_i^{1/3}\int_{x_i(t)}^{1}\frac{(x+b_i)^{1/3}}{x}\mathrm{d}x \approx t_i^*. \tag{24}$$

An analytical solution for the indefinite form of the integral in Equation 24 is:

$$\begin{aligned}\int \frac{(x+b_i)^{1/3}}{x}\mathrm{d}x =& -0.5\ b_i^{1/3}\log\left(b_i^{2/3}+(b_i(b_i+x))^{1/3}+(b_i+x)^{2/3}\right)\\ &+3\,(b_i+x)^{1/3}\\ &+b_i^{1/3}\log\left((b_i+x)^{1/3}-b_i^{1/3}\right)\\ &-\sqrt{3}\ b_i^{1/3}\arctan\left(\frac{2(1+x/b_i)^{1/3}+1}{\sqrt{3}}\right).\end{aligned} \tag{25}$$

When the bin contains much less material than the lower volatility bins (i.e., $b_i \gg x_i$), the approximate expression is:

$$-\left(\sum_{n<i} f_n\right)^{1/3}\log(x_i)\approx t_i^*. \tag{26}$$

For the lowest volatility bin or when $b_i \ll x_i$, the approximate expression is:

$$3\,f_i^{1/3}(1-x_i^{1/3})\approx t_i^*. \tag{27}$$

2.2.3 Transition regime

For the transition regime, Equation 11 will include Fuchs-Sutugin, F, and Kelvin, K, corrections:

$$\int_{x_i(t)}^{1}\left(\sum_j f_j x_i^{a_{j,i}-1}\right)^{2/3}(F\,K)^{-1}x_i^{-1/3}\mathrm{d}x_i = t_i^*. \tag{28}$$

A simplification using b_i is also applicable in this case, resulting in the following equation:

$$f_i^{2/3}\int_{x_i(t)}^{1}\frac{(x+b_i)^{2/3}}{x\,F\,K}\mathrm{d}x \approx t_i^*. \tag{29}$$

The above expressions can be used to find the time needed to reach a certain MFR ($x_i(t)$) for any compound in the mixture. Given the complex nature of the Fuchs-Sutugin and Kelvin corrections, it is not practical to search for an analytical solution for the above equation. One can still estimate the time needed to reach a certain MFR using equations for the continuum and the free molecular regimes, as the transition regime is bounded by them.

3 Discussion

3.1 Computational implications

The analysis provided in the preceding sections demonstrates that evaporation of a chemical mixture in an aerosol can be modeled using a single ordinary differential equation that describes the evaporation of one of the compounds in the mixture. This significantly simplifies and speeds up numerical modeling of aerosol evaporation. It is important to note that Equations 11, 23, and 28 are applicable to any mixture of compounds and are not limited to the VBS representation, where the volatility bins are spaced by a factor of 10. When using the VBS representation, calculations can be further simplified by taking into account the contribution of different volatility bins in the VBS representation (such as Equations 15, 23, and 29). For the continuum and free molecular regimes, integration can be avoided altogether as analytical solutions are available (Equations 18 and 25).

The approximate solutions provide very good accuracy, especially for the mid-range volatility bins and larger MFR. Figure 1 shows a summary of errors in the effective time for a middle bin of an 11-bin VBS for evaporation in the continuum regime calculated using the simplified formula. The errors were calculated using 1000 randomly generated VBS. The errors are very small, less than 5% for the effective time to evaporate half of the compound. Even for MFR of 90%, the errors are below 20%. Simplified calculations for the most volatile bin show errors of less than 2% for 90% MFR and below. For the least volatile bin, the errors are larger, with the simplification overestimating the effective time to reach 50% MFR by about 10% on average. The good accuracy and computational advantages of the approximate solutions make them very attractive for applications where extensive computations are required. For example, calculations using Equations18 and 15 implemented in Python are approximately 230 and 120 times faster than those done using Equation 11.

3.2 The effect of the VBS shape on evaporation time

We can use the simplified analysis provided in Sections 2.2.1 and 2.2.2 to gain insight into how the VBS shape, i.e., the distribution of material over individual bins, affects the evaporation kinetics of individual volatility bins.

Let us use the continuum regime as an example. Due to the similarity of the functions describing the effective time required to evaporate a certain fraction of the bin material (Eq.11, 23, and 28), the main conclusions will also hold for the free molecular and transition regimes. Let us use the simplification of reducing the number of bins to just two – the bin under consideration and a combined bin containing all lower volatility bins (Eq.13). Under this simplification, the effective time to reach certain x_i (Eq.15) depends only on the fraction of the material in a bin (f_i) being considered and the ratio of the material in the lower volatility bins to the mass in that bin (b_i). It should be noted that the evaporation of bins with different volatility will depend on these parameters in exactly the same way; the only thing that will change is the effective time that depends on their SVC via their characteristic time.

To demonstrate how the evaporation time of a certain bin depends on the amount of material in it and lower volatility bins, let us consider the effective time needed to evaporate half of the bin's material, $t^*_{0.5}$. Figure 2 shows $t^*_{0.5}$ as a function of f_i and b_i. The f_i and b_i combinations used in the figure were constructed with mass fractions ranging from 0 to 1 in 0.004 increments. One value was assigned to the bin to be considered and the other to the total of all lower-volatility bins. From these two numbers b_i was calculated, which then was used to calculate a characteristic time using Equation 15. The number of all possible combinations is $250 \times 250 = 62,500$. However, the mass fraction of the lower volatility bins cannot exceed $1 - f_i$, resulting in two times less points, i.e., 31,250.

$t^*_{0.5}$ shows a steady increase with increasing either f_i or b_i. Bins with small f_i and small b_i show short effective times. Such situations (both f_i and b_i small) are possible only when most of the initial particle mass is evaporated. The maximum possible effective time is $\log(2) = 0.693$ that corresponds to evaporation of the most volatile bin that contains a negligible amount of material relative to the material in the lower volatility bins (Eq.17). Another limiting case is where the VBS is dominated by one component, i.e., when the aerosol is essentially composed of a pure material. In this case the effective time to evaporate half of the material is 0.555 (Eq.16).

Another important observation is that $t^*_{0.5}$, as well as the effective times required to reach other MFR, do not vary significantly for most combinations of f_i and b_i. Figure 3 shows a summary of the effective times needed to reach MFR of 10%, 50%, and 90%. The data set was derived in the same way as described for Figure 2. The mean and median values of $t^*_{0.5}$ are 0.469 and 0.491, respectively, the standard deviation is 0.125, and the interquartile range is 0.390–0.564. Most of the possible f_i and b_i combinations have $t^*_{0.5}$ within 25% of the mean. The lowest possible effective time is approaching zero, which happens if the initial mass fraction of the evaporating bin is close to zero (Eq.15, 17) and if, at the same time, b_i is also close to zero (Fig.2). Thus, large deviations from the mean are possible only when most of the particle mass has evaporated. For $t^*_{0.5}$ to be 10 times lower than the mean, the bin should contain no more than 2.5% of the total mass and the lower volatility bins significantly less than that.

The analysis for the free molecular regime produces very similar results. The mean and median values of $t^*_{0.5}$ are 0.563 and 0.583, respectively, the standard deviation is 0.084, and the interquartile range is 0.520–0.625. If one neglects the Kelvin effect, $t^*_{0.5}$ in the transition regime will have values between those for the free molecular and the continuum regimes, i.e., around 0.5. The Kelvin effect will shift these values lower, especially for the situations where the initial diameter is small (below 100 nm) and/or when most of the particle mass is evaporated, resulting in small particle diameters where the Kelvin effect is most pronounced. For the exact values, Equation 28 should be used.

In summary, the VBS shape has a relatively minor effect on the evaporation times of individual compounds in the mixture. This follows from the above discussion and Eq.8 that stipulates that at no time can a compound evaporate more than a compound with a higher volatility. It follows then that individual compounds evaporate in the order of their characteristic times, i.e., in reverse order of their SVC, with their $t^*_{0.5}$ being approximately half of their characteristic times.

3.3 Implications for volatility measurements

The above discussion has several implications for the measurements of aerosol volatility distributions. First, it shows that a VBS can be derived from measurements of one of the mixture components with known thermodynamic properties. Using such data and Equation 8, the MFR of other compounds in the mixture can be calculated, from which the original VBS can be reconstructed. The equations derived in the previous sections can also be used to estimate the low and high volatilities that can be measured using a given measurement configuration, as discussed below.

Let us first consider particle levitation techniques. In such measurements, the measurement time will determine the range of volatilities that can be determined. Likewise, the time resolution of the measurements will determine what volatilities can be resolved. Both the range and the resolution will also depend on the precision of the size or mass measurements. Suppose we are working with a single component aerosol. If we are to detect a 1% change in particle mass, the compound should have the effective time of 0.01 or less (Eq.16). For the initial diameter of 10 μm and a measurement duration of one hour (and assuming the unit density and the diffusion coefficient of 0.05 cm^2/s), this means that the compound SVC needs to be 4.6 μg/m^3 or higher to be detectable with this mass resolution and measurement duration. A 10 times less volatile compound will require a 10 times longer measurement time. It should be noted that the effective times are proportional to $f_i^{2/3}$, which means that less abundant compounds will require a higher volatility to be detected. For example, a compound whose initial mass fraction is 10% would need to be about 5 times more volatile than the above estimate. Likewise, the first measurement time will determine the highest volatility that can be resolved.

In thermodenuder measurements, the effective time of different compounds changes mostly due to changes in compound SVC with the TD temperature, with a relatively small contribution of changes in the TD residence time due to changing temperature of the measurements. Therefore, the analysis presented in this paper is also applicable to TD measurements. For example, we can estimate the minimum volatility that can be detected for a given residence time, enthalpy of vaporization, and mass accuracy. Let us assume a 20 s residence time, 1% mass accuracy, 300 nm initial diameter, enthalpy of vaporization of 100 kJ/mol, a unit density, diffusion coefficient of 0.05 cm^2/s, and the maximum measurement temperature of 200°C. The 1% mass accuracy requires an effective time of 0.01. This translates to the minimum SVC of 3.75 μg/m^3 at the maximum TD temperature. Using the Clausius-Clapeyron relationship, this translates to the SVP at 25°C of 2×10^{-6} μg/m^3. It should be noted that a mass resolution of 1% for TDMA measurements is rather ambitious. A more realistic estimate is about 10% (assuming the common size resolution of such measurements being 64 size bins per decade of size, which results in a volume or mass resolution of $10^{3/64} - 1 = 0.11$). This would require a minimum characteristic time of approximately 0.1, resulting in the minimum SVC to be 10 times higher than the previous estimate. The highest volatility that can be resolved will depend on the lowest temperature that is measured. For example, if the first temperature point is 5°C above the reference temperature, the effective time of 0.1 would translate to SVC of about 2 μg/m^3 at 25°C. Bins with the higher volatility will evolve within this temperature bin and would be difficult to resolve.

Likewise, a minimum temperature step can be estimated that is required to achieve the common VBS resolution of a factor of 10 in volatility. Such a temperature step is approximately equal to $\log(10)\, RT^2/\Delta H$, where R is the universal gas constant, T is the temperature of the measurements, and ΔH is the enthalpy of vaporization. For 100°C and $\Delta H = 100$ kJ/mol, such a step is 26.6°C. For 25°C, the step is 17°C. A higher enthalpy of vaporization will require a proportionally smaller temperature step. Increasing the flow through the TD will result in lower effective times, thus shifting the measurement range to higher volatilities.

The theory and calculations presented here also confirm, at least to a large degree, the approach proposed to calibrate TD measurements using pure compound aerosols with known volatility properties (Faulhaber et al., 2009). In this approach, the temperature at which half of the pure compound aerosol is evaporated is used to translate the TD temperature to the SVC coordinates. The amount of material evaporated as a function of temperature is thus converted to a VBS (mass vs. SVC). Such an approach, however, is biased, because the effective time of pure compound aerosols tends to be higher than that of compounds in mixtures. For a pure component aerosol, Equation 16 can be used with $f_i = 1$ resulting in a $t*_{0.5}$ of 0.55. The random simulations discussed above have median values of about 0.49. This calibration approach thus underestimates the volatility of compounds in a mixture by about 10%, though the deviations could be larger for individual bins, depending on their f_i and b_i.

3.4 Uniqueness of VBS fit into experimental data

One of the common tasks in aerosol volatility studies is the derivation of a VBS from a set of experimental data, such as those obtained through particle levitation techniques or TD measurements. The goal is to find a VBS that best reproduces the observed changes in particle size or mass over time or with temperature. This is achieved by numerically modeling evaporation using equations like Equation 2. An important question arises: for a given set of observations, does a unique solution exist, or could multiple VBS configurations fit the same data?

Setting aside, for the moment, the influence of assumed values for the accommodation coefficient and other relevant parameters, as well as the impact of experimental uncertainties, let us explore the possibility of identifying a unique solution using the analysis presented above. Assume there are K observations to be fitted with a VBS comprising N components or volatility bins. The total number of unknowns is $K+N$: N initial mass fractions f_i in the VBS to be determined, and K MFR values x_i for one of the compounds at each observation point. The MFRs of the other compounds are not independent variables and can be calculated using Equation 8. Conversely, there are $2K+1$ equations: K equations for the K time or temperature points (e.g., Equation 28), K equations linking the measured MFR to the MFR of the selected compound (Equation 9), and an additional equation constraining the VBS such that $\sum f_i = 1$. Thus, the system is determined when $N+K = 1+2K$, meaning the minimum number of observations required to uniquely fit an N-bin VBS is $N-1$.

In practical applications, factors discussed in Section 3.3 should be considered. For example, the measurement duration and/or temperature will determine the range of volatilities that can be resolved. Likewise, the time or temperature resolution will determine the volatility resolution. Provided the measurements sample the proper characteristic times, a unique solution for the VBS should be obtained. Another complication is that the number of compounds or volatility bins are often not known *a priori*. If the time or temperature resolution is high, more volatility bins can be resolved. A solution obtained for a given resolution will reproduce the observations at that resolution.

Since in most practical applications at least one of the necessary parameters needs to be assumed, this necessarily leads to ambiguity in the derived VBS. As the evaporation of a compound is controlled by its characteristic time, a change in any of the parameters in Equation 5 or 21 will result in a proportional change in the derived VBS. For example, in the free molecular regime, a VBS derived with the accommodation coefficient of 1 will be shifted by one bin towards lower volatilities relative to a VBS that is derived from the same data using the accommodation coefficient of 0.1. In TD measurements, a change in the assumed enthalpy of vaporization will result in both shifting of the VBS along the volatility coordinate and its distortion (getting wider or narrow). It should be kept in mind that the derived VBS will reproduce aerosol evaporation as long as the parameters used for their derivation are used to model evaporation of that aerosol. Therefore, care should be taken in modeling studies to use the same parameters as were used to derive the VBS from experimental data. If there is a need to use a different set of parameters, the VBS needs to be recalculated using the new parameter set.

4 Conclusions

The theoretical analysis presented in this paper demonstrates that the time evolution of the mass fraction remaining (MFR) of individual compounds in an evaporating aerosolized mixture can be described by a single ordinary differential equation (ODE) describing the evaporation of one of the mixture constituents. This is possible due to the interdependence of MFRs of different compounds in the mixture via the ratio of their characteristic times, such that if at any given time the MFR of one of the compounds is known, the MFR of other mixture components can be calculated.

The time required to reach a certain MFR for any compound in the mixture is controlled mostly by the compound's characteristic time, which is proportional to the square of the initial diameter of the evaporating particle and the inverse of the compound saturation vapor concentration (SVC). In addition to the characteristic time, the timing of individual compound evaporation depends, to a lesser degree, on the compound abundance in the mixture and its ratio to the amount of material in the mixture that has lower SVC.

The shape of the volatility basis set (VBS), i.e., the relative abundance of individual compounds in the mixture, has a relatively small effect on evaporation of individual compounds. Individual compounds evaporate in the reverse order of their SVC, with the time required to evaporate 50% of their original mass being approximately half of their characteristic time.

The reduction in the number of ODEs needed to solve mixture evaporation offers significant computational advantages. Additional simplifications were derived that can speed up calculations by two orders of magnitude relative to the exact single ODE solution, while still providing good accuracy.

The theory presented in this paper can be used to inform the experimental design for the experimental determination of volatility properties of aerosols. The derived formulas can be used to estimate the volatility range of the measurements as well as their resolution.

A unique VBS fit to an experimental dataset can be obtained if the number of observations is equal to or greater than the number of volatility bins minus one. However, the uniqueness of the solution can be influenced by measurement duration, temperature, time or temperature resolution, and the number of volatility bins, which are often not known *a priori*.

Assumptions made regarding parameters such as the accommodation coefficient and enthalpy of vaporization can lead to ambiguity in the derived VBS. Therefore, it is crucial to use the same parameters for modeling evaporation as those used to derive the VBS from experimental data. If a different set of parameters is required, the VBS needs to be recalculated for the new parameter set.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grants No. AGS-0955845, AGS-1760328, and OIA-2148788.

Disclosure Statement

The author declares no conflicts of interest.

ORCID

Andrey Khlystov: 0000-0001-9606-3919

References

Ahmadov, R., McKeen, S., Robinson, A., Bahreini, R., Middlebrook, A., De Gouw, J., Meagher, J., Hsie, E.-Y., Edgerton, E., Shaw, S., et al.: A volatility basis set model for summertime secondary organic aerosols over the eastern United States in 2006, Journal of Geophysical Research: Atmospheres, 117, 2012.

Bilde, M., Barsanti, K., Booth, M., Cappa, C., Donahue, N., McFiggans, G., Krieger, U., Marcolli, C., Topping, D., Ziemann, P., Barley, M., Clegg, S., Dennis-Smither, B., Emanuelson, E., Hallquist, M., Hallquist, A., Khlystov, A., Kulmala, M., Mogensen, D., Percival, C., Pope, F., Reid, J., Ribeiro da Silva, M., Rosenoern, T., Salo, K., Soonsin, V., Yli-Juuti, T., Prisle, N., Pagels, J., Rarey, J., Zardini, A., and Riipinen, I.: Saturation vapor pressures and transition enthalpies of low volatility organic molecules of atmospheric relevance: from dicarboxylic acids to complex mixtures., Chemical Reviews, Under review, 2014.

Cai, C., Stewart, D. J., Reid, J. P., Zhang, Y.-h., Ohm, P., Dutcher, C. S., and Clegg, S. L.: Organic component vapor pressures and hygroscopicities of aqueous aerosol measured by optical tweezers, The Journal of Physical Chemistry A, 119, 704–718, 2015.

Cappa, C.: A model of aerosol evaporation kinetics in thermodenuders, Atmospheric Measurement Techniques, 3, 579–592, 2010.

Cappa, C. and Jimenez, J.: Quantitative estimates of the volatility of ambient organic aerosol, Atmospheric Chemistry and Physics, 10, 5409–5424, 2010.

Carlton, A. G., Christiansen, A. E., Flesch, M. M., Hennigan, C. J., and Sareen, N.: Multiphase atmospheric chemistry in liquid water: impacts and controllability of organic aerosol, Accounts of Chemical Research, 53, 1715–1723, 2020.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environmental Science & Technology, 40, 2635–2643, 2006.

Faulhaber, A., Thomas, B., Jimenez, J., Jayne, J., Worsnop, D., and Ziemann, P.: Characterization of thermodenuder – particle beam mass spectrometer system for the study of organic aerosol volatility and composition, Atmospheric Measurement Techniques, 2, 15–31, 2009.

Fuentes, E. and McFiggans, G.: A modeling approach to evaluate the uncertainty in estimating the evaporation behaviour and volatility of organic aerosols, Atmospheric Measurement Techniques, 5, 735–757, 2012.

George, C., Ammann, M., D'Anna, B., Donaldson, D., and Nizkorodov, S. A.: Heterogeneous photochemistry in the atmosphere, Chemical reviews, 115, 4218–4258, 2015.

Jo, D., Park, R., Kim, M., and Spracklen, D.: Effects of chemical aging on global secondary organic aerosol using the volatility basis set approach, Atmospheric Environment, 81, 230–244, 2013.

Karnezi, E., Riipinen, I., and Pandis, S.: Measuring the atmospheric organic aerosol volatility distribution: a theoretical analysis, Atmospheric Measurement Techniques, 7, 2953–2965, 2014.

Kohli, R. K. and Davies, J. F.: Measuring the chemical evolution of levitated particles: a study on the evaporation of multicomponent organic aerosol, Analytical Chemistry, 93, 12 472–12 479, 2021.

Koo, B., Knipping, E., and Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, Atmospheric Environment, 95, 158–164, 2014.

Krieger, U. K., Marcolli, C., and Reid, J. P.: Exploring the complexity of aerosol particle properties and processes using single particle techniques, Chemical Society Reviews, 41, 6631–6662, 2012.

Lane, T. E., Donahue, N. M., and Pandis, S. N.: Simulating secondary organic aerosol formation using the volatility basis-set approach in a chemical transport model, Atmospheric Environment, 42, 7439–7451, 2008.

Li, Y. and Shiraiwa, M.: Timescales of secondary organic aerosols to reach equilibrium at various temperatures and relative humidities, Atmospheric Chemistry and Physics, 19, 5959–5971, 2019.

Martin, A. R., Kwok, D. Y., and Finlay, W. H.: Investigating the evaporation of metered-dose inhaler formulations in humid air: single droplet experiments, Journal of aerosol medicine, 18, 218–224, 2005.

Murphy, B. N. and Pandis, S. N.: Simulating the formation of semivolatile primary and secondary organic aerosol in a regional chemical transport model, Environmental science & technology, 43, 4722–4728, 2009.

Pankow, J. F.: An Absorption-Model Of Gas-Particle Partitioning Of Organic-Compounds In The Atmosphere, Atmospheric Environment, 28, 185–188, 1994.

Reid, J. P., Bertram, A. K., Topping, D. O., Laskin, A., Martin, S. T., Petters, M. D., Pope, F. D., and Rovelli, G.: The viscosity of atmospherically relevant organic particles, Nature communications, 9, 1–14, 2018.

Riipinen, I., Pierce, J., Donahue, N., and Pandis, S.: Equilibration time scales of organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics, Atmospheric Environment, 44, 597–607, 2010.

Saha, P. K., Khlystov, A., Yahya, K., Zhang, Y., Xu, L., Ng, N. L., and Grieshop, A. P.: Quantifying the volatility of organic aerosol in the southeastern US, Atmospheric Chemistry and Physics, 17, 501–520, 2017.

Saleh, R., Shihadeh, A., and Khlystov, A.: On transport phenomena and equilibration time scales in thermodenuders, Atmospheric Measurement Techniques Discussions, 1, 571–581, 2011.

Sazhin, S. S.: Modelling of fuel droplet heating and evaporation: Recent results and unsolved problems, Fuel, 196, 69–101, 2017.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, 2006.

Shrivastava, M., Cappa, C. D., Fan, J., Goldstein, A. H., Guenther, A. B., Jimenez, J. L., Kuang, C., Laskin, A., Martin, S. T., Ng, N. L., et al.: Recent advances in understanding secondary organic aerosol: Implications for global climate forcing, Reviews of Geophysics, 55, 509–559, 2017.

Tikkanen, O.-P., Hämäläinen, V., Rovelli, G., Lipponen, A., Shiraiwa, M., Reid, J. P., Lehtinen, K. E., and Yli-Juuti, T.: Optimization of process models for determining volatility distribution and viscosity of organic aerosols from isothermal particle evaporation data, Atmospheric Chemistry and Physics, 19, 9333–9350, 2019.

Widmann, J. F. and Davis, E. J.: Evaporation of Multicomponent Droplets, Aerosol Science and Technology, 27, 243–254, https://doi.org/10.1080/02786829708965470, 1997.

Figure captions

Figure 1: Errors in the simplified effective time calculations for a middle bin of an 11-bin VBS in the continuum regime. 1000 randomly generated VBS were used for calculations.

Figure 2: The effective time needed to evaporate half of the material in a bin as a function of the mass fraction in that bin and the mass fraction of material in all bins with a lower volatility.

Figure 3: Effective times (t/τ_i) needed to reach mass fraction remaining of 10%, 50%, and 90%.

Figures

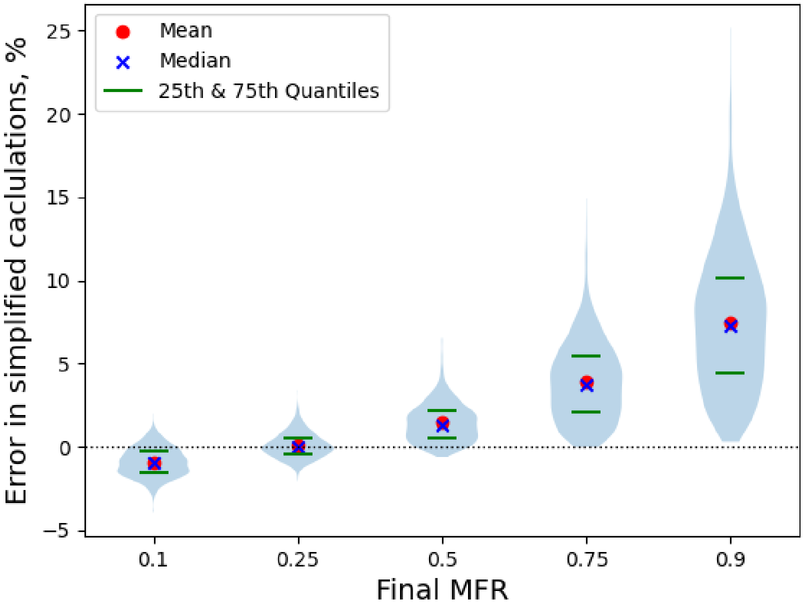

Figure 1: Errors in the simplified effective time calculations for a middle bin of an 11-bin VBS in the continuum regime. 1000 randomly generated VBS were used for calculations.

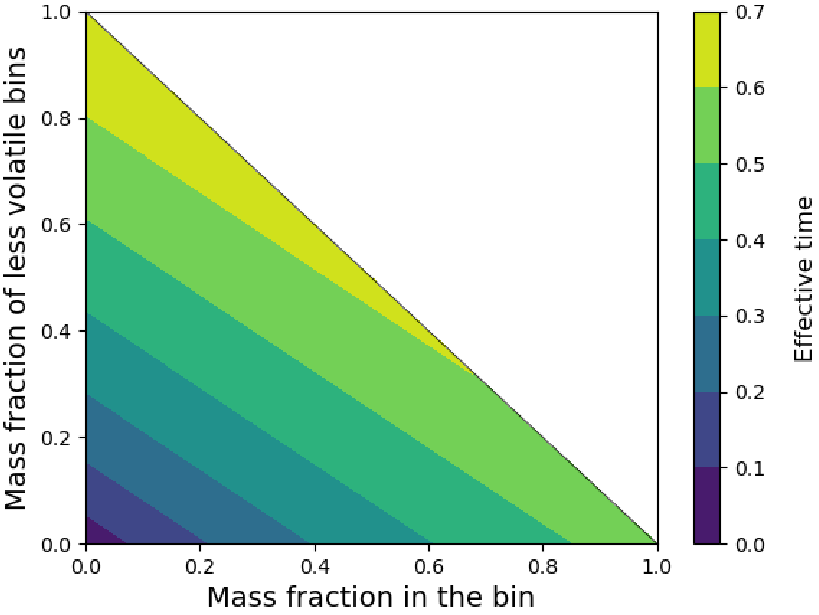

Figure 2: The effective time needed to evaporate half of the material in a bin as a function of the mass fraction in that bin and the mass fraction of material in all bins with a lower volatility.

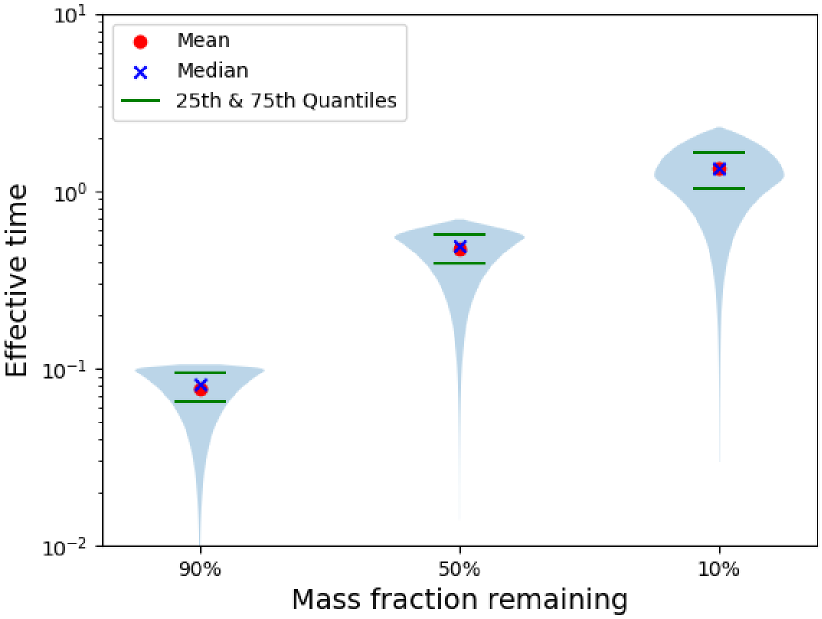

Figure 3: Effective times (t/τ_i) needed to reach mass fraction remaining of 10%, 50%, and 90%.