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Using Axial Dispersion Residence Time Distributions**

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Measurement Timestamps for Venus Mass Spectrometer Using Axial Dispersion Residence Time Distributions

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Precision atmospheric measurements from the Deep Atmosphere Venus Investigation of Noble gases, Chemistry, and Imaging (DAVINCI) mission will be used to describe columnar chemical variations for a broad range of atomic masses, relative abundances of trace species, and isotope ratios of noble gases. The Gas Processing System (GPS) in DAVINCI's Venus Mass Spectrometer (VMS) is responsible for transferring and enriching gases delivered to the Quadrupole Mass Spectrometer (QMS) at the heart of VMS. Flow simulations were performed with simplified computational and analytical models to inform trade studies and examine the nuances of timestamping samples admitted into the QMS. We evaluate the statistical latency of samples in relation to the altitudes from which they would be retrieved. Samples are considered concomitant when the residence time of aged atmosphere is minimized and can be mapped to a corresponding altitude range. By computing the fraction of "acceptably" aged fluid parcels, preliminary results indicate that the GPS could operate at 95% measurement concomitance with altitude, on average. The method applies to laminar pipe flow without convective mixing, diffusion, or secondary friction losses. For continuous sampling, targeting a high level of concomitance alleviates some aspects of data uncertainty including altitude (i.e., temporal) smearing.

I. Introduction

A. Mission context and instrument overview

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NASA's Pioneer Venus descent probe and USSR's Venera and Vega programs encompass the only atmospheric campaigns to Venus. Combined, these missions provide some characterization of the planet's chemical composition but lack robust data for the deep atmosphere and heavy noble gases [1,2]. The next *in situ* probe to Venus is NASA's Deep Atmosphere Venus Investigation of Noble gases, Chemistry, and Imaging (DAVINCI) mission. Its advance suite of instruments will make the finest resolution measurements ever, spanning the entire atmospheric column. The Venus Mass Spectrometer (VMS) is one of these instruments that utilizes a Gas Processing System (GPS) and heritage Quadrupole Mass Spectrometer (QMS) from the Sample Analysis at Mars (SAM) [3] instrument. These components will help collect and measure the homospheric isotope ratios of noble gases, characterize the relative abundances of key reactive species, and perform a general census of mass spectra through the duration of DAVINCI's descent [4].

Components in the GPS (see Fig. 1 and Fig. 2) consist of: inlet assemblies that include Puncture Valves (PVs) that maintain the inlet lines at high vacuum prior to entry, microvalves, high-conductance valves, heated gas transfer lines, particle filters, exhaust and bypass volumes, a Wide-Range turbomolecular Pump (WRP), a chemical getter coupled to the QMS, a Gas Enrichment System (GES), and carefully sized flow restrictors. Specifically, the GES serially removes dominant gases via scrubbers, getters, and the Noble Gas Trap (NGT) to enrich fractions of targeted trace species for QMS measurements. The first stage is comprised of a scrubber to remove CO₂ and improve the N₂ signal.

Simultaneously, a Thermo-Electric Cooler (TEC) helps to establish appropriate temperatures on the NGT cold trap to condense Kr and Xe. When the valve to the NGT is closed, a getter is exposed to the volume to sorb reactive species, thereby enabling scans of light noble gases, Ne and Ar. Later, the cold trap is heated to release condensed species, primarily heavy noble gases, Kr and Xe. In addition, getters are used to sorb reactive gases from the NGT headspace.

The GPS participates in each of the VMS science modes. For VMS, science commences at the top of the upper cloud layer that enshrouds the planet. In this region, at nearly 60 km altitude, the pressure is approximately 0.25 bar, and the temperature is 270 Kelvin [5, 6, 7]. When DAVINCI reaches the surface, it will be subjected to environmental state conditions of 90 bar and 730 K. This range of atmospheric conditions (i.e., from the top of the cloud columns to surface level) presents an opportunity for exercising clever design and operations schemes for the GPS. The GPS must also maintain the QMS sensor at required vacuum levels when the ion source is activated to collect enough trace noble gases for enrichment and detection, as well as continuously provide fresh samples at targeted intervals for analysis by the QMS. To accomplish these objectives, the atmospheric sampling is segregated into the upper and lower atmosphere regions. Inlet 1 and its downstream GPS architecture are used for the upper atmosphere ingest, and Inlet 3 for the

lower atmosphere. To move fluid through the system, evacuated tanks are initially under vacuum upon atmospheric entry, and are used to maintain a pressure differential for passive pumping.

B. Gas residence time and concomitance

Each sampling interval admitted to the QMS should be mapped to precisely one altitude interval. To achieve this concomitance, the samples need to be fresh and exhibit no “memory effects” of previous sampling. However, because 1) the length of the gas transfer path is not negligible, 2) the viscous boundary in laminar pipe flow [8, 9] retards velocities near pipe walls, and 3) stagnant or recirculation regions, such as Dean vortices [10] impede downstream advancement, gases propagate through system at different rates. Consequently, any infinitesimally thin cross section of gas within the pipe will contain fluid that represents an aggregate of different time histories. This aggregation can be statistically portrayed by an age, or Residence Time Distribution (RTD). The modern concept of RTDs was described by Danckwerts [11] to evaluate the retention of individual fluid molecules, particles, or parcels that enter a volumetric domain. Deriving an RTD differs from a conventional control volume analysis since in the former, each fluid element is timestamped, from entry to exit, through the control volume (and therefore “tracked”), while the latter is an element-agnostic application of mass conservation (where all elements inside the control volume are indistinguishable).

The RTD for laminar pipe flow without diffusion only comprises of axial dispersion [12]. Qualitatively, axial dispersion flow physics is characterized by the no-slip boundary condition that produces a parabolic profile, resulting in a stratified composition of “old” and “new” gas in a cross section of a pipe (see Fig. 3). In continuous sampling applications, a new slug of gas cannot fully displace an old slug [13]. Additionally, depending on the plumbing material, some metals could selectively interact with atmospheric gases, which may then desorb into the freestream flow at some later time [14]; water is a notable example [15]. However, adsorption and desorption physics is not within scope of this paper. The effects of thermal convection induced by heated pipe walls may further affect diffusion and mixing [16, 17] but was also not considered.

In this paper, we present the current state of concomitant gas flow modeling within the VMS GPS. We describe the role of pipe geometries, fluid properties, and science drivers in the system design. While there are several operational modes pertinent to the GPS, this paper focuses on two sampling modes: 1) upper atmosphere (UA) Direct Mode ingest, and 2) gas phase and supercritical phase lower atmosphere (LA) Direct Mode ingest. Direct Mode refers to sample acquisition from atmosphere and direct delivery to the QMS without chemical processing. Specifically, this

paper describes how the GPS may be designed to negotiate science-driven requirements to obtain fresh samples at prescribed measurement intervals. The complexities of timestamping (or altitude stamping) are discussed under the assumption of laminar pipe flow. We demonstrate the use of flow parameters to quantify the temporal signature of the composition reported by the QMS in the context of the altitude from which a sample is retrieved.

II. Methods

The work represented in this paper assumes a simplified model for the GPS network. A numerical approach is applied, which can be extended to more complex pipe networks, if necessary. Additionally, for a simple straight pipe, time-averaged flow conditions were used to analytically derive ballpark RTDs and compliance for sampling concomitance. Together, this paper demonstrates that the numerical technique is consistent with analytical flow physics. However, for analyses that do not comprise of time-averaged conditions, a straightforward analytical calculation could be complex (requiring simultaneous solutions for mass, energy, and momentum equations), and therefore, it may be more favorable to pursue a numerical approach through a commercial solver.

Numerical flow simulations were performed using the Gas Models library in Matlab Simscape 5.4, which leverages the Simulink environment (R2022b). Mass and energy conservation equations were enforced for all fluid elements used in the Simscape model. Convective heat transfer and momentum balance (including viscous friction losses) were applied only to elements with outlets (e.g., pipes) and not to constant volume elements with no outlets (e.g., chambers). All flow is subsonic and is choked when the velocity reaches the local speed of sound.

Simscape permits thermodynamic effects to be computed with either ideal gas, semiperfect, or real gas properties. In our analysis, a single component composition of CO₂ was assumed. For the upper atmosphere sample region, an ideal gas formulation was implemented since the range of pressure and temperatures is not extreme enough to deviate from ideal. However, a compressibility factor of 0.997 was prescribed, corresponding to atmospheric conditions of approximately 0.5 bar and 300 K during the GES ingest. For the lower atmosphere sampling region, ideal gas properties were also used for simplicity, although real gas properties may be more suitable in a higher-fidelity simulation. Both gas phase CO₂ (gCO₂) and supercritical CO₂ (sCO₂) properties were derived from NIST REFERENCE Fluid Thermodynamic and Transport PROPERTIES (REFPROP) Database, version 10 [18]. The Equation of State (EoS) employed by REFPROP for CO₂ is based on the Helmholtz free energy model from Span-Wagner [19]. The Span-Wagner EoS shows generally good agreement with empirical results for sCO₂ [20].

A. Modeling assumptions

The input Venusian pressure and temperature profile for the GPS domain was derived from Monte Carlo analysis of descent trajectories using the Venus Global Reference Atmospheric Model (GRAM) 2005 model [21]. This model draws from the Venus International Reference Atmosphere (VIRA) that was developed from Pioneer Venus data. To ensure that the inlet orifices have access to samples commensurate with the Venus environment at altitude, the orifice was assumed to be positioned outside of the descent sphere boundary layer. Flow perturbations from other probe structures was assumed to have been mitigated.

Additionally, the dynamic pressure resulting from the descent sphere moving through the atmosphere was not incorporated into the model. Through the descent, the dynamic pressure into the inlet orifice is estimated as typically less than 1% of the static pressure and is, therefore, not a substantial contribution toward the total pressure. Gas flowing into the QMS through the capillary leaks was assumed to be very low and negligible compared to the bulk flow. The capillary leaks draw from the bulk flow in the plumbing that connects the inlets to the bypass volumes, essentially “sipping” gas from this flow. The bypass volumes serve as a passive pump to move fresh atmosphere through the system so that by the end of the descent, the QMS scans will have profiled the full atmospheric column. When the bypass volumes equilibrate with the system, it is said to have reached its capacity.

B. Simscape model elements

A simplified model of the flow path for the two sampling regions is shown in Fig. 4. The simplified model provides an approximation for the expected GPS flow characteristics. Figure 3 illustrates the configuration for both the UA and LA, but each has different geometries for the configuration elements (see Table 1 for nominal values).

Specifically, for UA sampling, atmosphere enters through Inlet 1, puncture valve PV1, and valve V1. From V1, the plumbing splits into three paths. If V8 is assumed to be closed, then the bulk flow passes through V15 into Inlet 1 Bypass since the capillary leak CL1 significantly restricts the flow in pipe P7 relative to P5. Moreover, Fig. 1 diagram is not to scale, and restrictor R1 and P5 are very long compared to other elements in this flow path. Thus, the UA system was simplified as a two-element model, flanked by an infinite pressure reservoir that represents Venus atmosphere and a constant volume chamber that represents the bypass volume.

Similarly, for LA sampling, atmosphere enters through Inlet 3, PV3, and V4. The bulk flow passes into Inlet 3 Bypass since CL2 significantly restricts the flow in P8 relative to P9. Moreover, Fig. 1 diagram is not to scale and, R3 and R5 are long compared to other elements. Thus, the LA system was modeled using the same elements as the UA.

C. Concomitance requirements

A combination of DAVINCI's descent rate through the atmosphere (quickest clip is assumed to be 50 m/s) and the quickest expected QMS scan time (preliminarily defined by 1 point per mass in vector mode with 20 ms integration time) was used to select a turnover rate, or volume exchange rate, for all components in a flow path. The result was a target rate of greater than 2 volumes/s during UA sampling and 4 volumes/s during LA sampling. For a pipe of constant cross-section, a minimum of 2 volumes/s (as an example) translates to a required flow of at least 2 m/s.

Knudsen numbers within pipelines are $\ll 1$ for both UA and LA regions, so the flow is well within the continuum regime. With an average Reynolds number of approximately $Re=750$ for the LA GPS configuration (and similar for UA), we expect laminar flow and a parabolic Hagen-Poiseuille velocity profile. Thus, it is assessed that the core of laminar flow through the pipe contains the freshest fraction of sample, and the edges of the flow toward the wall contain the oldest.

With a well-designed GPS configuration, it's evident that the core will satisfy the flow rate needed to achieve what we have generally defined as a volume exchange (or turnover) rate requirement. At some radial distance away from the center of the pipe, the velocity is too slow to represent a composition concomitant with altitude. A critical velocity for this cutoff can be defined – to elaborate, the 2 volume/s target requires flow speed equivalent to two pipe lengths per second. We therefore evaluate an acceptable load into the QMS by examining the fraction of pipe cross-section that meets or exceeds the required flow speed. The resulting concomitant fraction is based on the GPS configuration, geometries, and pipe conductance. It also assumes that the capillary leaks sip from a well-mixed region that integrates gas from the entire cross section of pipe.

D. Analytical verification of the RTD

For laminar pipe flow with no diffusion and only axial dispersion, the streamlines are collimated and colinear with the long axis of the pipe. Under this assumption, the RTD can be derived directly from the Hagen-Poiseuille velocity profile. For fully developed flow past entrance length (L_e) for a straight pipe of length L and radius R , consider a region of interest spanning between x_1 and x_2 downstream from L_e . As shown in Fig. 5, a given pressure drop ΔP across L drives the flow, and the velocity distribution, u varies as a function of the radial distance r from the pipe centerline such that,

$$u(r) = \frac{dx}{dt} = \frac{1}{4\mu} \frac{\partial P}{\partial x} (R^2 - r^2) \quad (1)$$

Rearranging and solving for time yields,

$$dt(r, x) = \frac{4\mu L}{\Delta P} \frac{x_2 - x_1}{R^2 - r^2} \quad (2)$$

$$\int_0^t dt(r, x) = \frac{4\mu L}{\Delta P} \frac{x_2 - x_1}{R^2 - r^2} \quad (3)$$

$$t(r, x) = \frac{4\mu L}{\Delta P} \frac{x_2 - x_1}{R^2 - r^2} \quad (4)$$

III. Results

A. Simulation results

Initial estimates for pipe dimensions in the GPS were based on reasonable values. A parametric sweep of pipe geometries was performed to confirm the nominal selection of dimensions, which are listed in Table 1. Pressure profiles for the UA and LA, using Table 1 parameters in the simplified model, are shown in Fig. 6. Expectedly, as gas propagates through the GPS (from Venus atmosphere, to pipe 1, then pipe 2, and finally terminating the bypass tanks), the pressure drops due to friction and volume expansion. Both BP1 and BP3 volume pressures approach the average pressure of the pipes that feed into the bypass tanks themselves.

This reduction in the pressure gradient reduces flow. Notably in the UA inlet 1 flow path, the flow rates peak before dropping slightly. Such an amelioration in flow is a result of the BP1 volume approaching “capacity”, indicating the onset of pressure equilibration in the tank with the rest of the system, and ultimately, with Venusian atmosphere. Flow rates reach zero when the bypass volume loses its ability to passively pump.

The fully developed laminar velocity profile for UA and LA pipe 2 is depicted in Fig. 7. Pipe lengths throughout the GPS are on the order of hundreds of millimeters. The hydrodynamic entrance lengths are on the order of a few millimeters. Thus, the parabolic profile represents the vast majority of the pipe 2 flow characteristics, even with potential bends to accommodate routing. Using the velocity profiles and the pressure gradients established in pipe 2, a concomitant fraction based on the respective turnover requirements was calculated. The average concomitant fraction, was 95.3% in the UA and 96.5% in the LA, yielding an average chemical signal-to-background of 20. Here,

we loosely define the background as the fraction of composition that is non-compliant, lingering, or residual. Based on this preliminary work, the GPS is expected to satisfy performance expectations for DAVINCI science.

B. Analytical results

For demonstrative purposes, the time-averaged pressure drop from upper atmosphere simulations was used in Eq. (4) to generate an RTD as a function of radial distance from the pipe center (Fig. 8a). As expected, the residence time increases to infinity when $r=R$. To evaluate the fraction of the RTD that meets the upper atmosphere sampling target of 2 volumes/s (i.e., 0.5 s/length), the RTD was discretized monotonically and converted into a probability distribution of residence times (Fig. 8b). Approximately 97% of particles meet the 0.5 s/length turnover requirement, which matches closely with the numerical determination of 95% concomitance.

IV. Conclusion

When a fluidic system cannot clean its sampling interfaces between analysis points (e.g., with a high temperature bakeout, fluid purge, etc.), the resulting measurement will retain memory from previous samples. This is especially true for continuous sampling applications needed for high resolution profiling. Motivated by this, we used flow simulations to determine a concomitant fraction that describes the temporal signatures of samples delivered to an analyzer. In turn, these signatures can aid with profile construction in processed data products. Moreover, the laminar flow framework underpinning this approach may provide a lower bound for the altitude concomitance metric since diffusion and thermal-fluid convection were not considered. However, head losses were also not considered. A model incorporating losses from flow separated regions may cut into built-in conservatism by contributing ancillary memory effects due to retention in pipe bends, dead zones, and hydraulic diameter changes.

Measurements that baseline the concomitant fraction, as described in this paper, will require a sufficiently long sampling window. Additionally, it will require admittance of a fully mixed sample into the analyzer so that an integrated cross section of gas in the pipe can be assumed. Mixing can be achieved by creating turbulence at the location of a capillary leak into the QMS, for example. Another approach includes sampling at sufficiently long distances downstream from the pipe inlet to allow adequate time for diffusive mixing, and also specifically by Taylor-Aris dispersion (see Fig. 9) [22]. Diffusive mixing via Taylor-Aris dispersion can radially flatten the age profile, potentially homogenizing the age distribution in a cross section of pipe. One caveat to diffusive mixing is that it requires sufficiently long distances from the inlet, which adds burden to spaceflight systems and may not be practical

1
2
3 for VMS. Another caveat is that it could broaden the axial variation in age to the point where a volume element may
4 no longer be sufficiently homogeneous to approximate as a single concomitant timepoint. Accordingly, one can
5 imagine that if the QMS sampling window approaches the targeted temporal resolution of the measurement profile,
6 axial variations in age may need to be factored. It is worth clarifying – generally, mixing does not increase
7 concomitance. It merely attempts to achieve radial homogeneity, so that our definition of concomitance can be utilized.

8
9 This study has established a threshold criterion to describe concomitant samples, where prior to mixing, the core
10 of laminar pipe flow may be compliant, and the outer region may not. However, sample acquisition in continuous flow
11 applications comprises of complex temporal effects (especially when including non-straight pipes), exhibiting
12 nonlinear and heterogenous gradations in sampling latency. The first particle from a sample that reaches the analyzer,
13 presumably at peak velocity propelled by Hagen-Poiseuille flow, is the concomitant reference. This implies that every
14 other particle from a cross section of sample is not synchronous with the origin and has a unique timestamp relative
15 to the reference particle. Rather than a concomitant fraction that effectively rejects the non-compliant portion of a
16 sample, an improved representation may attempt to reconcile the contribution of all components in a sample, perhaps
17 by a statistical description for its age.

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36 pressure and temperature profiles.

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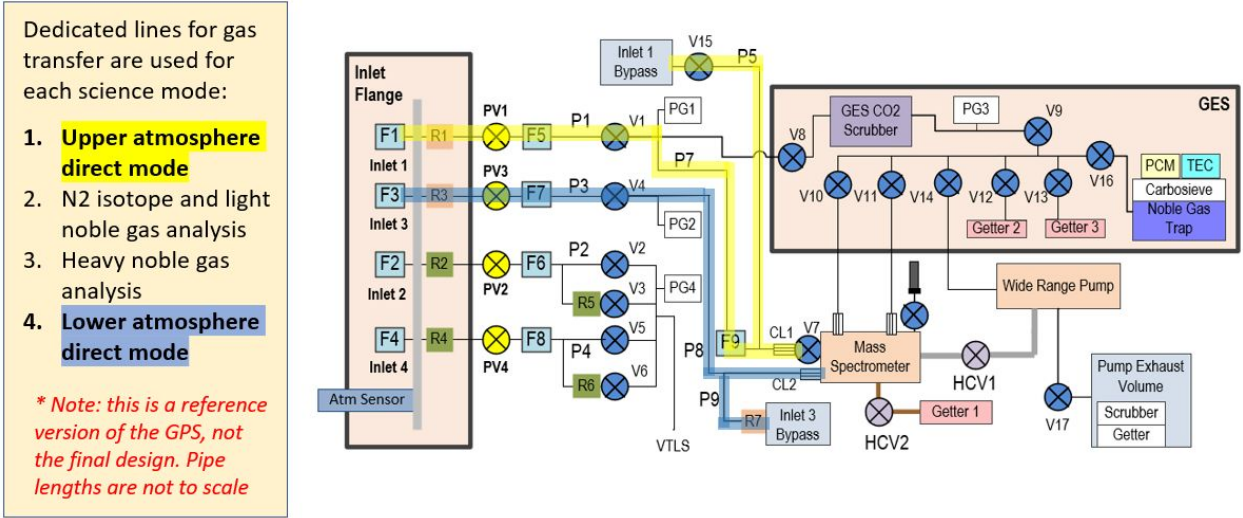


Fig. 1 VMS GPS flow diagram (preliminary design)

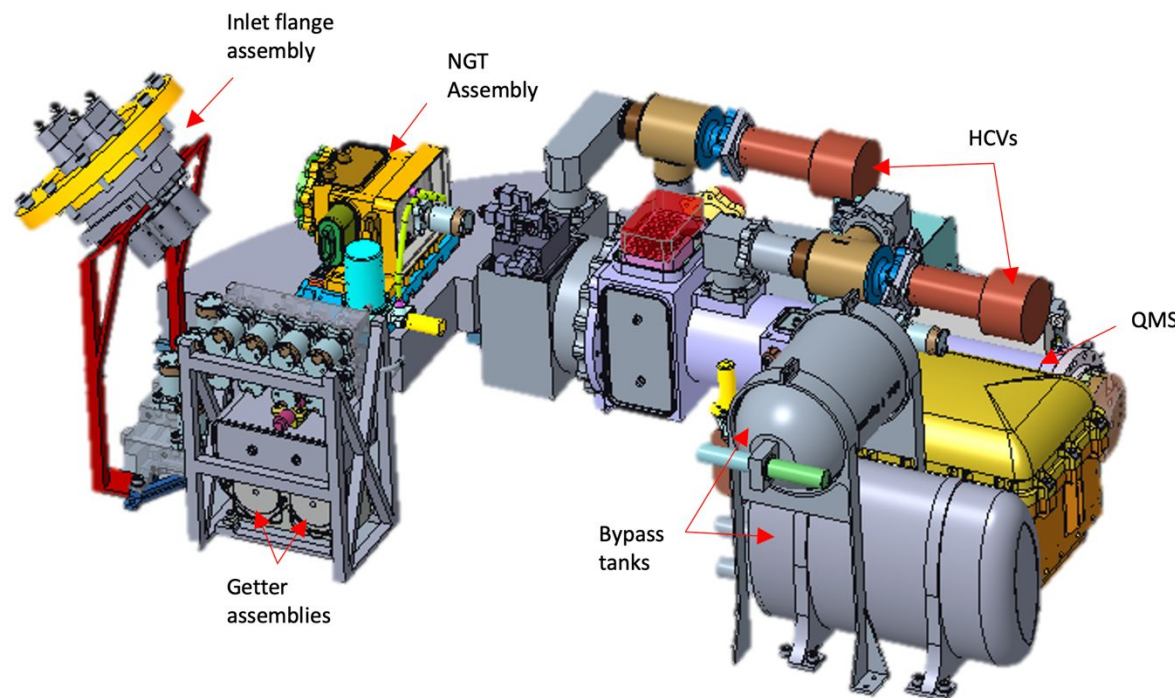


Fig. 2 VMS GPS CAD model overview (preliminary design)

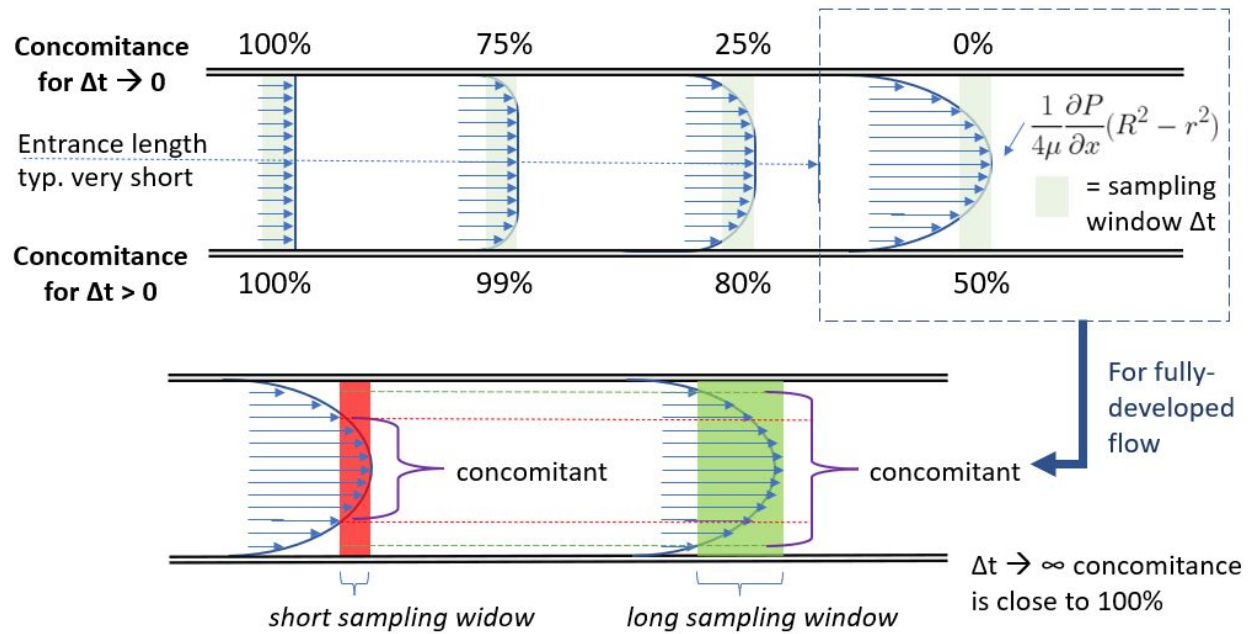


Fig. 3 Laminar flow concomitance

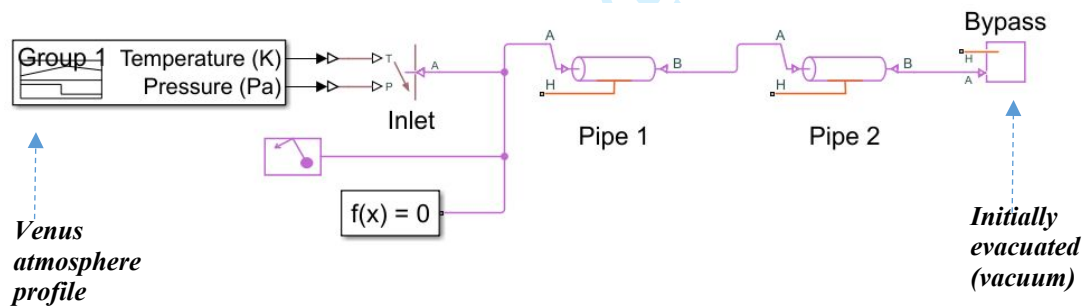


Fig. 4 Simscape simplified model diagram for both UA and LA

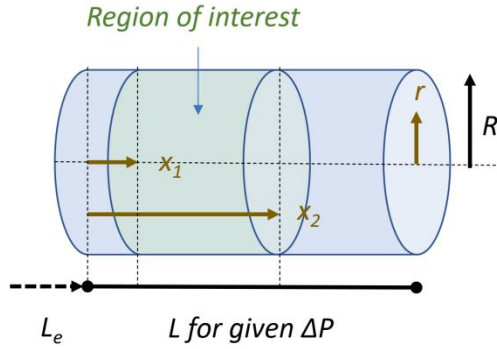


Fig. 5 Simplified pipe model for computing fully-developed laminar flow RTD

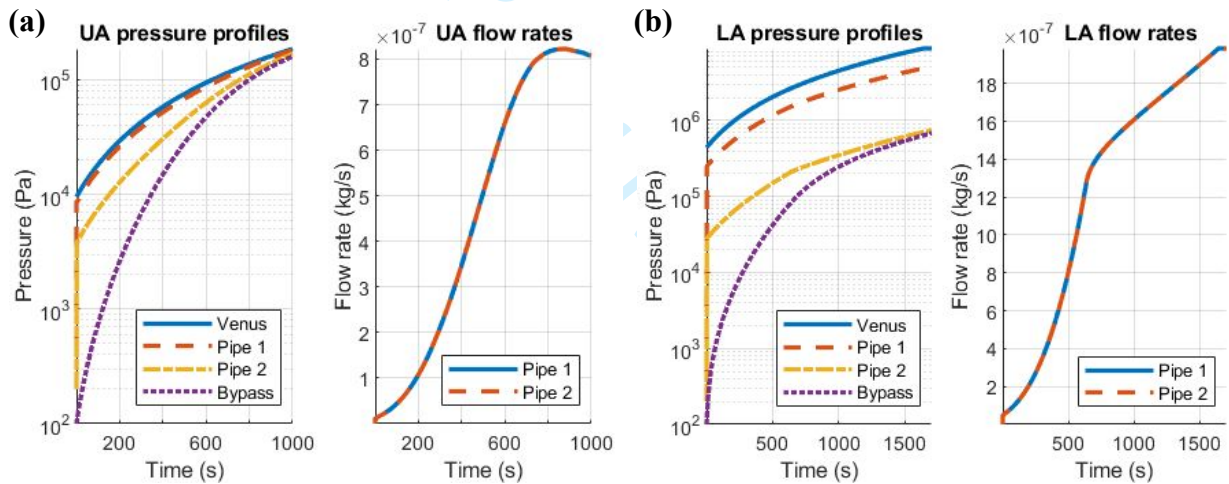


Fig. 6 Pressure and flow rate profiles for (a) the UA and (b) the LA

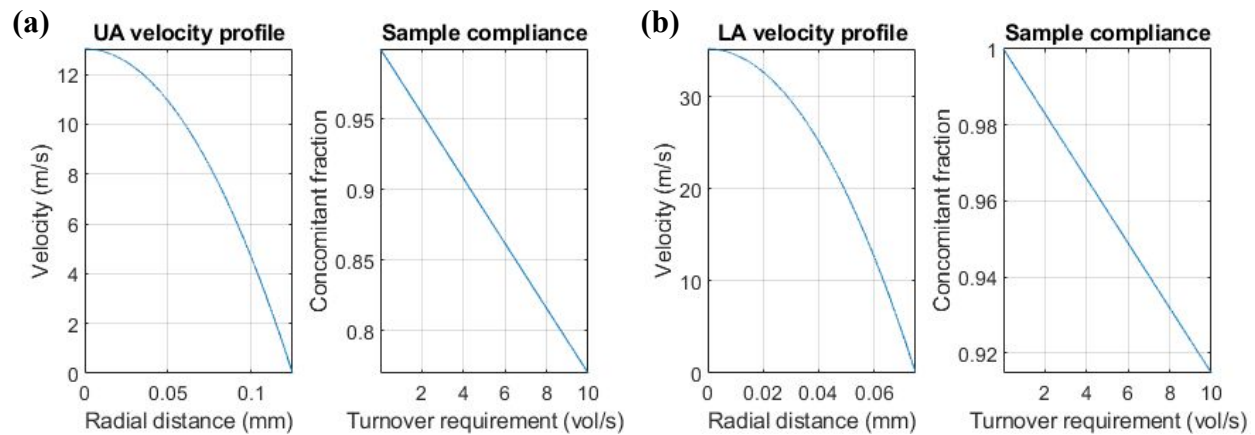


Fig. 7 Velocity profiles in pipe 2 and concomitant fraction averages for (a) the UA and (b) the LA

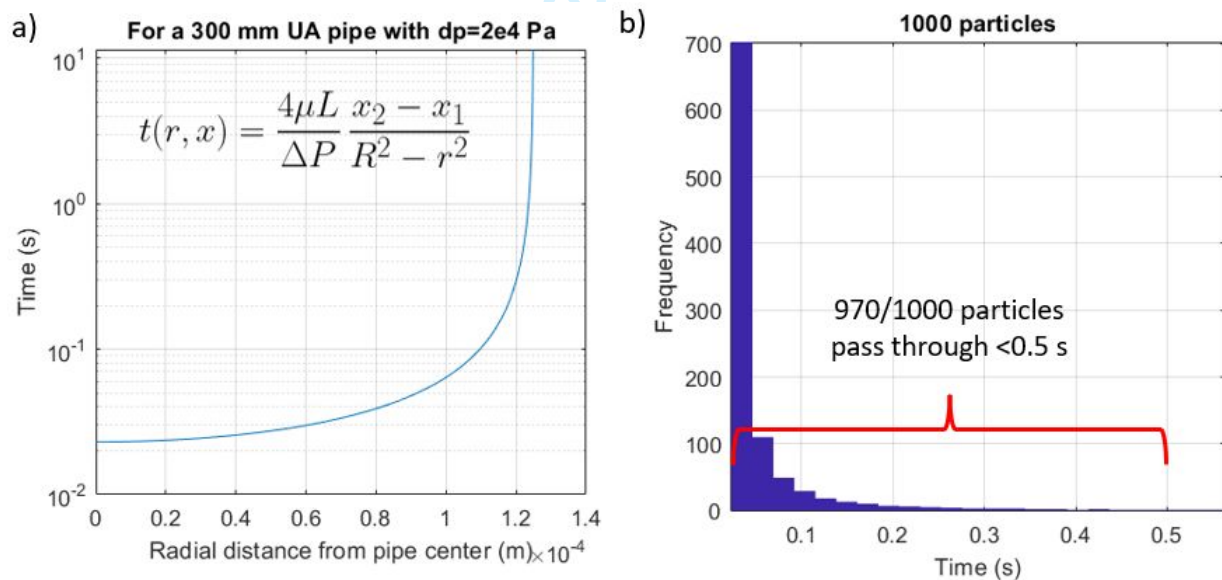


Fig. 8 (a) RTD for time-averaged pressure drop in the UA and (b) probability distribution of residence times

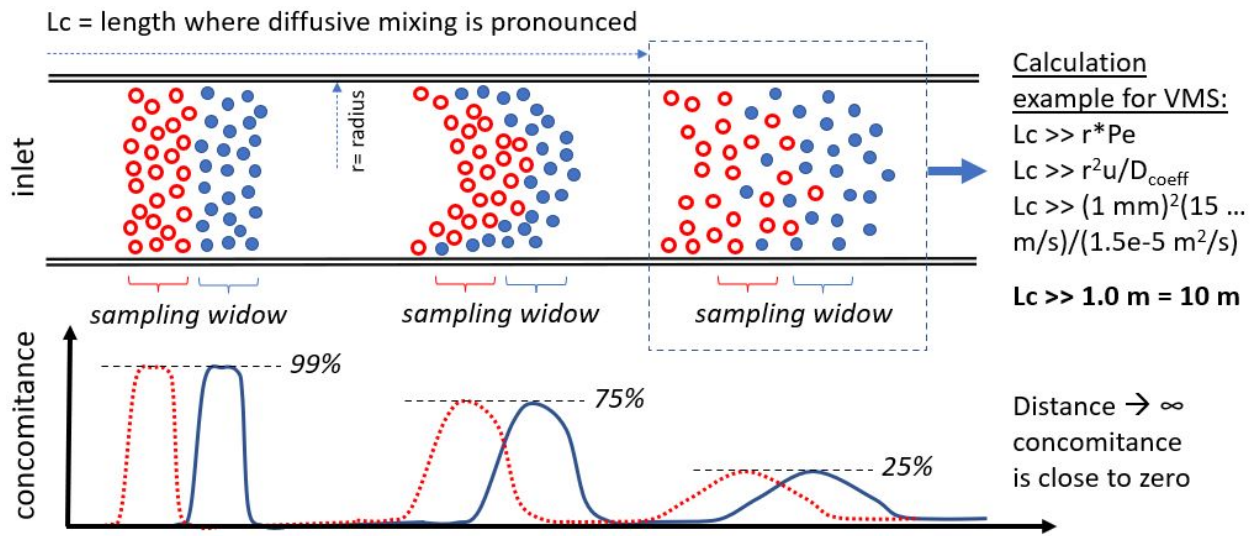


Fig. 9 Taylor-Aris dispersion and measurement concomitance

Table 1 Nominal values for numerical and analytical flow simulations

Sampling region	Pipe 1	Pipe 2	Bypass volume	Gas model
Upper atmosphere	ID = 0.25 mm, L = 200 mm	ID = 0.25 mm, L = 300 mm	BP1 = 250 cc	Ideal gas, Z= 0.997
Lower atmosphere	ID = 0.055 mm, L = 356 mm	ID = 0.15 mm, L = 300 mm	BP3 = 500 cc	Ideal gas, Z= 0.997