

MASS TRANSPORT IN SAMPLE TRANSPORT LINES ADSORPTION DESORPTION EFFECTS AND THEIR INFLUENCE ON PROCESS ANALYTICAL MEASUREMENTS

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ABSTRACT

The majority of low level concentration measurements, whether for process control, product quality monitoring, or emissions monitoring, are based on extractive analysis of a gas or liquid sample. Often the chemical species to be measured are reactive, and the physical distance between the sample point and the analyzer shelter is significant. In such cases, the ability of the sample system to reliably transport the species of interest in a timely manner is critical to such measurements.

Improper design of the system to meet such requirements results in unnecessary lag time and slow responding systems or makes accurate process gas analysis impossible. To properly employ extractive analytical systems, factors such as response lag and sample loss due to adsorption and chemical reactions on the surfaces of the flow path must be considered and addressed. The theoretical and practical analysis of such factors and design guidelines will be presented.

INTRODUCTION

Increasingly, whether for emissions monitoring or process control, there is a trend towards making process analytical measurements at lower and lower concentrations. The inherent value of accurate and timely measurements may be very high; as such process measurements are often used to protect upstream catalyst beds, expensive reciprocating equipment, or high value products. In all such cases, it is imperative that a representative sample be delivered to the analyzer.

As the concentration of the analyte gas decreases, it becomes increasingly difficult to transport the sample to the analyzer without relevant losses in the sample system. The sample line often represents the largest available surface area for gases to adsorb and desorb in the flow path, and thus is a critical element in ensuring a representative sample is delivered to the analyzers. While there has been an increasing focus on the importance of sample transport¹ there is little data and less understanding in the industry of the properties and processes that affect mass transport in sample lines. Where data does exist, it is often only at one set of conditions, such as temperature, pressure and sample line length, and it has not been clear how to extrapolate such data to other cases.

The chemistry of the sample line surface is of paramount importance in determining the adsorption / desorption characteristics and rates. Pressure affects molecule density and linear flow rates through the line, and thus affects the kinetics in a number of ways. Temperature can greatly affect desorption rates. All of these parameters are discussed, and included in a physio-chemical model of the mass transport in sample lines. Efforts have been made to clearly explain the physical affects which are taken into account, and the model has been implemented in a spreadsheet.

SURFACE EFFECTS

The chemical and structural characteristics of a sample transport tube determine to a large extent how the tube and the sample it is transporting will react. The chemical composition of the metal obviously affects corrosion rates, and it should be equally apparent that changes in the chemical composition will affect the type of chemical reactions and the binding energy of adsorbed molecules on the tube surface of a given metallurgy. The surface roughness of the tube walls greatly affects the surface area available for the reaction to occur on – smooth mirror like surfaces offering substantially less surface as compared to rough walls. Various surface treatments affecting the surface chemistry or roughness or both are used to prepare stainless steel tubes for use in sample transport.

The interior surface of a stainless steel tube can be of variable quality and composition and is dependent on the initial material quality, fabrication methods and post fabrication–processing. The most widely specified material for instrument sample lines and gas distribution applications is 316L stainless steel². This 316L stainless is able to form a stable and protective oxide layer primarily due to the presence of more than 16% chromium and the formation of stable and inert chromium oxide (Cr_2O_3) on the surface³. Despite this fact, there is significant iron content in such tubing, and typical chromium to iron ratios are less than 1.5:1. Indeed, many “as-manufactured” tubes will have free iron on the surfaces, which is highly reactive. The presence of free iron is often determined through the use of ASTM A380 “Ferroxyl Test for Free Iron”. The iron surface and iron oxides are readily attacked, and provide pathways for both corrosion and increased surface activity under harsh conditions⁴. Furthermore, the iron oxides provide active adsorption sites which strongly absorb species such as water⁵ and hydrogen sulfide⁶.

To address such issues, as-manufactured tubing is often subjected to post-treatment in an effort to improve the performance of tubing in real-world applications. Such post-treatment may include:

- A) Chemical passivation,
- B) Electropolishing, and/or
- C) Coating.

Chemical cleaning and passivation treatments on stainless steel tubing are an important aspect in preparation of these surfaces for use in critical environments and applications⁷. The surface to be passivated must be clean and oil free⁸. Passivation is the removal of exogenous iron or iron compounds from the surface of stainless steel by means of a chemical dissolution, most typically by a treatment with a dilute nitric or citric acid solution that will remove the surface contamination, remove iron, enhance the chromium to iron ratio, but will not significantly affect the stainless steel itself. Furthermore, the chemical passivation oxidizes the surface and the ratio of chromium oxide to iron oxide increases even more dramatically. In addition, the acid will tend to attack high points and sharp peaks more quickly than smooth portions of the tube. As a result, chemical passivation of the tube also reduces the surface roughness. Note that surface roughness is most commonly expressed in terms of Ra, which is a measure of the mean deviation from the centerline or average height expressed in micro-inches.

Electropolishing is often performed on as-manufactured tubing of the highest quality. Such tubing meets strict compositional guidelines and starts with a nominal surface roughness of 20 Ra. The process uses a mixed acid solution as the electrolyte - and a cathode is drawn through the inside of the tube. The tube becomes the anode, so it preferentially dissolves free iron, removing metal from the peaks.⁹

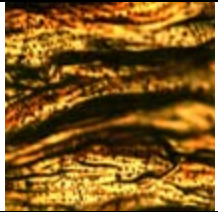
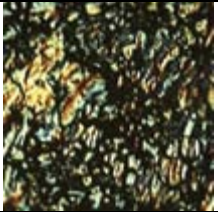
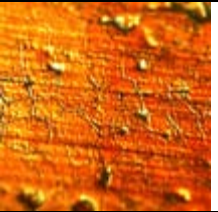
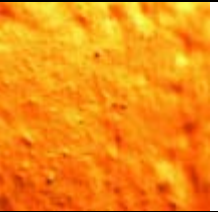
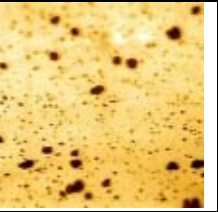
Electropolishing further increases the chromium to iron (Cr/Fe) ratio on the surface and oxidizes the chromium to greatly enhance the chromium oxide to iron oxide (CrOx/FeOx) ratio, and reducing the reactivity of the surface. The process reduces the surface roughness, resulting in a mirror polished surface with much less surface area exposed for molecular reactions to occur. In addition to appearance, electropolished tubing has five primary advantages¹⁴:

- 1) Extremely smooth surface, which minimizes adherence of particles and adsorption of gases or liquids,
- 2) Removal of all oils and iron from the surface,
- 3) Increased chromium to iron ratio which improves corrosion resistance and reduces chemical activity,
- 4) Creation of a passive chromium oxide layer that is free of iron contamination,
- 5) Improved mechanical property performance through minimization of surface stresses.

In addition, to electropolishing, it is possible to preserve, protect and enhance the performance of stainless steel tubing by adding an inert coating. In particular, it has been demonstrated a mechanically robust and long-lasting coating can be produced through the deposition of an amorphous silicon layer onto, and into, the steel surface via a chemical deposition process¹⁰ at 400°C. The process can be further enhanced to improve surface inertness and reduce moisture hold-up¹¹. The initial surface roughness of the electropolished tubing is approximately 7-10 micro-inches, to which a 5 micron coating of amorphous silicon is deposited and further chemically treated to increase inertness and hydrophobicity.

Typical micrographs of stainless steel tubing that has been subjected to various surface treatments are shown in Table I. In general, the surface roughness decreases dramatically as one looks from left to right in the table. The passivation and electropolishing processes eliminate free iron and greatly increase the chromium to iron ratio at the surface. Note that the electropolishing process can reduce the surface area available for chemical reaction by as much as an order of magnitude¹⁴. The coating processes (SilcoTech®) provide a stable, inert passivation layer with no exposed metal oxides. This important modification to the surface chemistry does not necessarily reduce the rate at which molecules adsorb, but greatly reduces the energy with which they bind to the surface and thus the molecules desorb easily and remain primarily in the gas phase.

TABLE I. TYPICAL SURFACE MICROSCOPIC IMAGES OF STEEL TUBING

Conventional 316 SS	SilcoSteel on Conventional	Chemically Passivated	Electropolish	Electropolished And Sulfinitert
				

CHROMATOGRAPHIC ANALOGY

It is useful to compare the transport of analyte molecules of interest in an extractive analyzer installation, (or the transport of gases in a gas distribution network) to the events that occur in a gas chromatograph which employs a capillary column. In a gas chromatographic, a small sample of analyte is injected and transported along capillary column by the inert carrier gas. Capillary columns may have typical dimensions of 0.1 mm internal diameter and 10 meter length. Thus, the line length to ID ratio is about 10,000 to 1. In an analyzer installation, we transport analyte molecules of interest (e.g. H₂S) in an “inert” carrier gas (e.g. methane) along a sample line with typical dimensions of 0.18 inch id and 150ft lengths, giving a length to ID ratio of 10,000 to 1 ! As gas is transported down the column (sample line) – it is adsorbed and desorbed from the stationary phase (wall) and the appearance of the gas at the end of the column (sample line) at some time which is significantly delayed from the time the carrier gas first exits.

This analogy is useful – in that it allows those familiar with chromatography to directly apply their intuitive understanding of that field to sample lines and mass transport. Common rules of thumb apply – for example – a rough dirty surface in a column will lead to peak tailing or no peak at all (the effect of using standard drawn stainless tubing in some applications). Increasing the temperature of the transport line will increase the response speed – and temperature needs to be tightly controlled. Clean smooth surfaces make for more inert, better responding columns (i.e. electropolishing). For the best response, a chemical inert coating should be applied to the column (amorphous silicon coatings).

ADSORPTION, DESORPTION AND MASS TRANSPORT

The surface of stainless steel tubing is a mixture of oxides of the various compounds that make up the steel. For simplicity, we will consider it a mixture of two types of sites, surface sites that won't absorb an analyte of interest, and surface sites that will. In Figure 2, we depict sites that are able to adsorb a molecule of water as brown iron oxide lattice structures, and sites that will not adsorb a water molecule as green chromium oxide lattice structures. This is an artistic representation and in fact water can potentially adsorb on both surfaces. In fact, it has been shown that water adsorbs on at least five different types of sites in stainless steel¹². Equally important, it is the interstitial spaces at grain boundaries which often act as traps for adsorbed species. Although water vapor is depicted as the adsorbed species in Figure 2, the Figure applies equally well to other chemical species.

The rate of adsorption out of the gas phase and onto the surface is proportional to the concentration of adsorbate molecules in the gas phase and the number of free sites on the surface¹³, thereby following Langmuir isotherms and kinetics. It should be immediately apparent that processes such as electropolishing which reduce the amount of surface area (and thus the number of adsorption sites) will reduce the rate at which the adsorbate molecules get adsorbed and the total amount of molecules the tube can adsorb. It is important to also realize that in most cases, the adsorbate can spontaneously be released from the surface as well, with the rate of desorption being proportional to the number of adsorbed molecules. It is the competition between these two processes that determines the maximum amount of adsorbate the tube can hold at equilibrium.

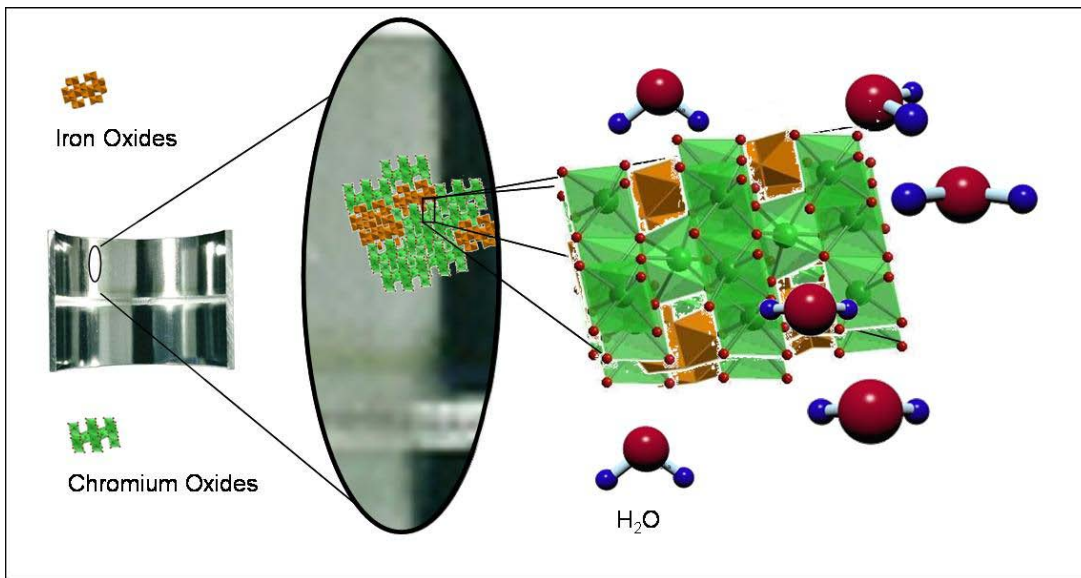


FIGURE 2. WATER ADSORPTION ON STEEL SURFACE

Referring to Figure 3, we can use the representation shown to begin to consider a model for the adsorption / desorption processes, and to further develop that model to provide useful predictions of the mass transport phenomena that occur as a reactive gas flows down a tube. Such systems

are typically solved through partial differential equations, which for this system may be represented as:

$$\underbrace{\frac{\partial \rho \phi}{\partial t}}_{\text{Transient term}} + \underbrace{\nabla \cdot (\rho \vec{u} \phi)}_{\text{Convection term}} = \underbrace{\nabla \cdot (\Gamma \nabla \phi)}_{\text{Diffusion term}} + \underbrace{S_\phi}_{\text{Source term}} \quad (1)$$

However, such representations provide little understanding to the layman and the solution of such equations requires sophisticated numerical analysis packages. Rather than pursue this approach, we propose to solve the mass transport problem using a series of simplified finite difference equations, similar to the approach taken by Air Products¹⁵, and which can then be easily implemented in a spreadsheet such as Microsoft ExcelTM.

The sample tube of length L is divided into a large number of individual elements, each of length Δl , internal radius r , surface area, SA ($SA=2\pi r \Delta l$) and volume V ($V= \frac{4\pi r^2 \Delta l}{3}$). The gas is flowing into the tube at flow rate F , so moves down the tube with velocity v , where $v= F/ \pi r^2$. Thus, the gas will pass through the volume element Δl in a time $\Delta t= \Delta l/v$.

The gas concentration flowing into the first volume is the inlet concentration or the concentration with which we are determining the mass transport characteristics, and this gas is allowed to flow into the tube at pressure, P . We will assume that at the flow rates we are working with that P does not change substantially along the length of the tube, and as well that the tube is maintained at some constant temperature, T .

It will be assumed that the tube has some number S_l active sites per square centimeter of linear surface area for adsorption available initially (before any have been occupied by adsorbed molecules), so the total number of sites in a volume element is S_l multiplied by the surface area of the element, SA .



FIGURE 3. MECHANISM AND ELEMENTS OF THE MODEL

The concentration of analyte molecules that exits volume element i of the tube between time t and time $t + \Delta t$ will be given by Equation 2.

$$C_{i+1}(t+\Delta t) = C_i(t) - k_{ads} \cdot C_i(t) \cdot S_i(t) \cdot SA + k_{des} \cdot [S_T - S_i(t)] \cdot SA \quad (2)$$

In Equation 2, $C_i(t)$ represents the concentration of analyte molecules flowing into segment i so the first term represents the inlet concentration. During this time interval, gas phase molecules, $C_i(t)$, react with available surface sites, $S_i(t)$, and get adsorbed with some rate constant k_{ads} . Thus the second term in (2) represents the rate at which molecules are adsorbed out of the gas phase and onto the surface. In the third term, the difference $S_T - S_i(t)$ represents the number of sites which are currently filled with analyte molecules (recall that S_T is the total number of sites that could possibly hold a water molecule with $S_i(t)$ represents the number of free sites available in volume element i at time t).

While Equation 2 gives us a finite difference equation in the gas phase concentrations to work with, a similar equation for the adsorbed phase is needed as well, and is presented in Equation 3.

$$S_i(t+\Delta t) = (S_i(t) - k_{ads} \cdot C_i(t) \cdot S_i(t) + k_{des} \cdot [S_T - S_i(t)]) \cdot SA \quad (3)$$

The rate constant for adsorption, k_{ads} , is typically relatively independent of the tube material and is primarily dependant on collision frequency with the walls. However, how long it stays on the surface is strongly dependant on the surface chemistry. Thus, the rate of adsorption will usually increase with increasing temperature since the kinetic theory of gases predicts collision frequency being proportional to $T^{1/2}$. However, the dominant effect with increasing temperature is a rapid increase in the desorption rate, k_{des} . The desorption rate constant typically follows an Arrhenius behavior, and thus increases exponentially with increasing temperature. This desorption rate is expressed as:

$$k_{des}(T) = A \cdot e^{-\Delta E/RT} \quad (4)$$

ΔE is the activation energy to break the bond of the adsorbed state, R is the Ideal Gas Constant, T is the temperature and A is constant. This provides us some insight into the effects of chemical passivation and chemically treating the tube wall. Such treatments change the surface chemistry and produce a substrate where the adsorbate (such as water) bonds weakly and thus desorbs more easily at a given temperature.

As mentioned previously, rough surfaces have large surface areas per unit length of tube, and thus have larger numbers of free sites, S_T . This increases both the rate of adsorption and the total amount of adsorbate the tube can hold. Surface treatments such as chemical passivation and electropolishing reduce the surface area and thereby the number of free sites. Furthermore, such treatments change the surface chemistry by converting the strongly adsorbing iron oxide rich surface to a weaker adsorbing chromium oxide rich surface. Again, the adsorption rate may be similar, but the retention time or the mean time spent on the surface can be quite different. Weaker adsorption sites have a lower activation energy (see Equation 4) required to break the adsorbate-surface bond, and thereby increases the desorption rate. Similarly, chemical

treatments such as the application of an inert glass-like layer on the surface of the tube further reduce the bond strength and increases desorption.

MODEL IMPLEMENTATION

A complete description of the model implementation will be provided in a subsequent paper. A brief description of the implementation is presented here. In this case, we will consider how the conditions in the first and second segment of the sample line change as a gas is injected. As gas is initially injected into the first segment of the tube, the inlet concentration is C_{inlet} . Consider this first segment of the tube to be a mixing vessel, to which the total number of molecules allowed to enter is $C_{inlet} * F * \Delta t$ where F is the flow rate and Δt is the time interval as defined earlier. Since the gas has just entered the tube, there will be no adsorption sites occupied, so the number of free sites available will be S_I . Similarly there are no adsorbed molecules to desorb yet. So, once time Δt is over, the final concentration in the first segment of tube will be

$$C = C_{inlet} - k_{ads} * C_{inlet} * S_I + k_{des} * (0) \quad (5)$$

And the number of free sites / adsorbed sites in the first segment of tube will be:

$$\text{Free sites after first time interval} \quad S = S_I - k_{ads} * C_{inlet} * S_I \quad (6)$$

$$\text{Adsorbed sites after first time interval} \quad S_{ads} = k_{ads} * C_{inlet} * S_I \quad (7)$$

All other segments of tube may be ignored because no gas has had sufficient time to flow there yet.

In the next time interval, we repeat the calculations, but now for both segment 1 and segment 2 of the tube. The gas flowing into segment 2 has the concentration given as exiting segment 1 in the previous time interval, and we perform the same calculations. The gas flowing into segment 1 is still C_{inlet} , but the adsorption reaction has to take into account the reduced number of sites and desorption from free sites must now be considered. In subsequent time intervals, the same calculations are performed, moving stepwise along the tube length and allowing equilibrium to be achieved at each step, thereby solving the system equations as function of space and time.

These calculations are easily configured in a spreadsheet, use three tables to keep track of the gas phase concentrations, the number of free sites remaining, and the number of full sites. These iterative calculations, while time consuming, allow us to model the propagation of the sample gas down the tube.

RESULTS AND DISCUSSION

Recently, there have been numerous studies on the mass transport of trace species through sample lines of various compositions. Such studies have been performed with analytes such as water vapor¹⁶, hydrogen sulfide¹⁷, and methyl mercaptan¹⁶.

The water vapor data was obtained for nominal concentrations of 1 ppm and using 100 foot sample lines operated at 60 °C. The data clearly shows the effect of changing the material used in

the sample line, with electropolished (EP) and electropolished/Silconert lines (EPS) demonstrating much faster wet-up and dry-down times in the test. It is clear that chemical treatment such as electropolishing or applying amorphous coatings dramatically affects the mass transport characteristics and the suitability of the tube for transporting samples of industrial interest. Example “wet-up” data is presented in Figure 5. In this figure, the concentration of water at the exit of the tube was monitored as a function of time after a step change in water concentration was injected into the tube.

The theoretical model described previously was implemented in Excel[®], and used to simulate the results obtained during empirical testing. The Model results are shown in Figure 6. While the model in its present state does not predict the results obtained empirically with great precision, it definitely identifies the common trends of the data. Further refinement of model parameters is required. Of greater importance, the use of the model now allows us to extrapolate the empirical results obtained. In the model, we can readily change the pressure, flow rate or sample line length and observe the effects on response speed.

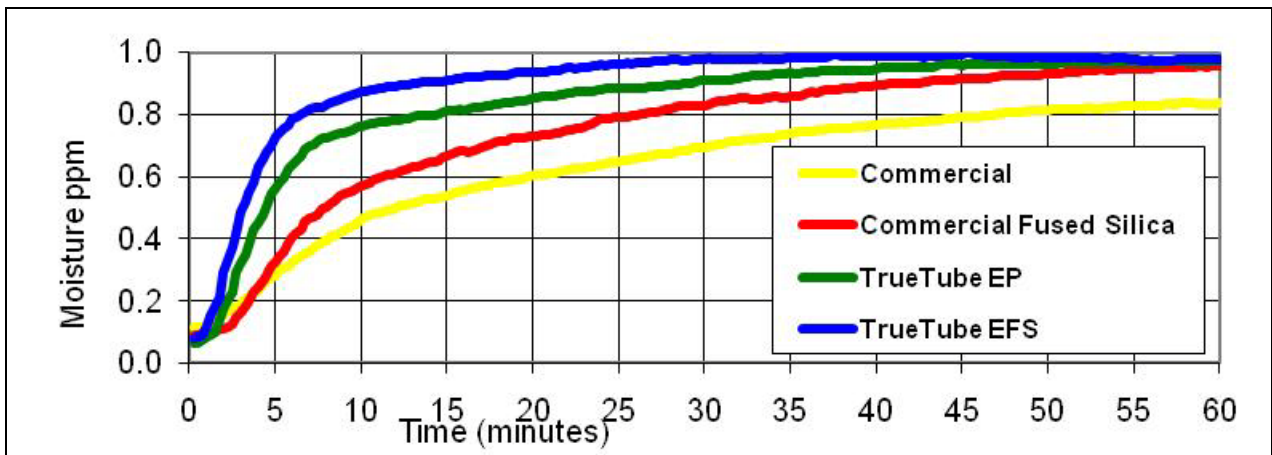


FIGURE 5. “WET-UP” DATA FOR 1 PPM CHALLENGE GAS AT 0.35 SLPM

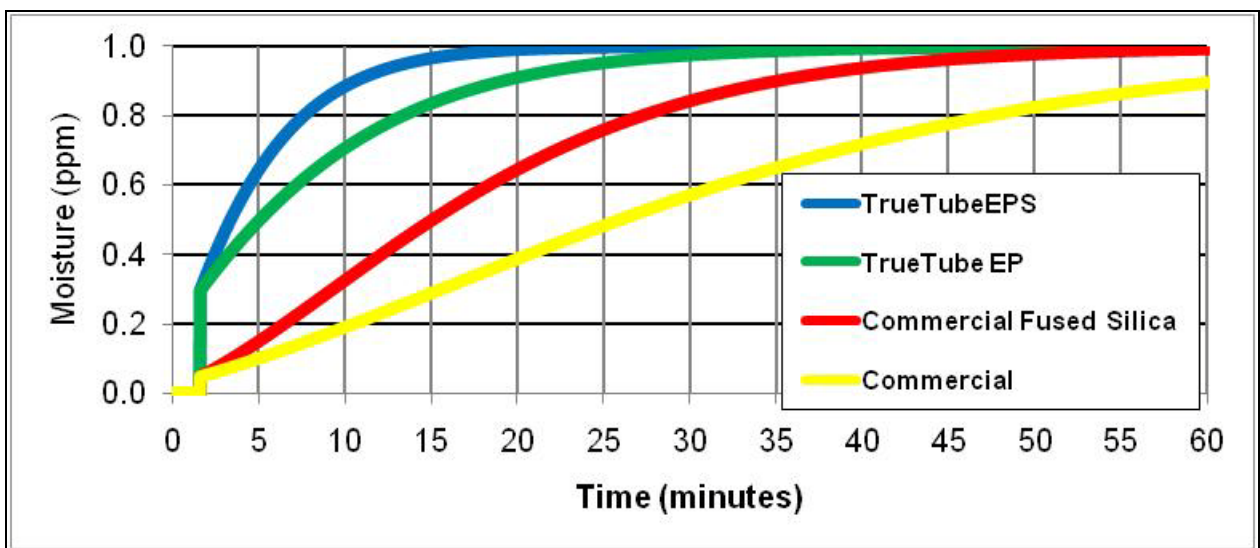


FIGURE 6. “WET-UP” MODEL FOR 1 PPM CHALLENGE GAS AT 0.35 SLPM

Assuming that the model is deemed valid, the use of the model allows us to also extrapolate the data to different inlet concentrations. Such extrapolations are of course extremely useful, as they alleviate the requirement to repeat experiments at a variety of different conditions, and allow for rapid evaluation of alternative solutions.

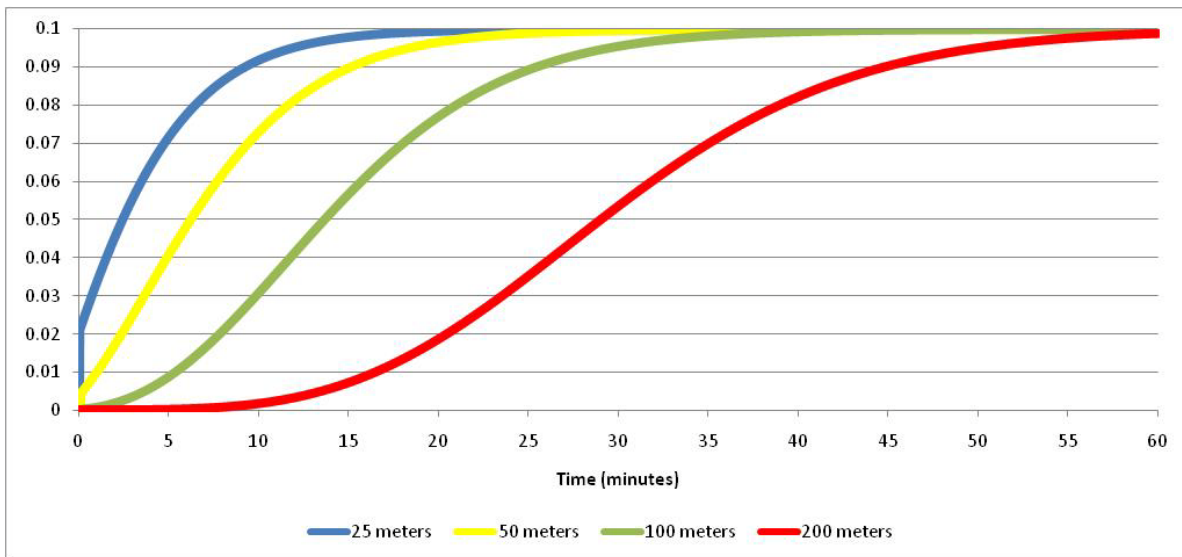


FIGURE 7. RESPONSE TIME TO A 100 PPB “WETUP”

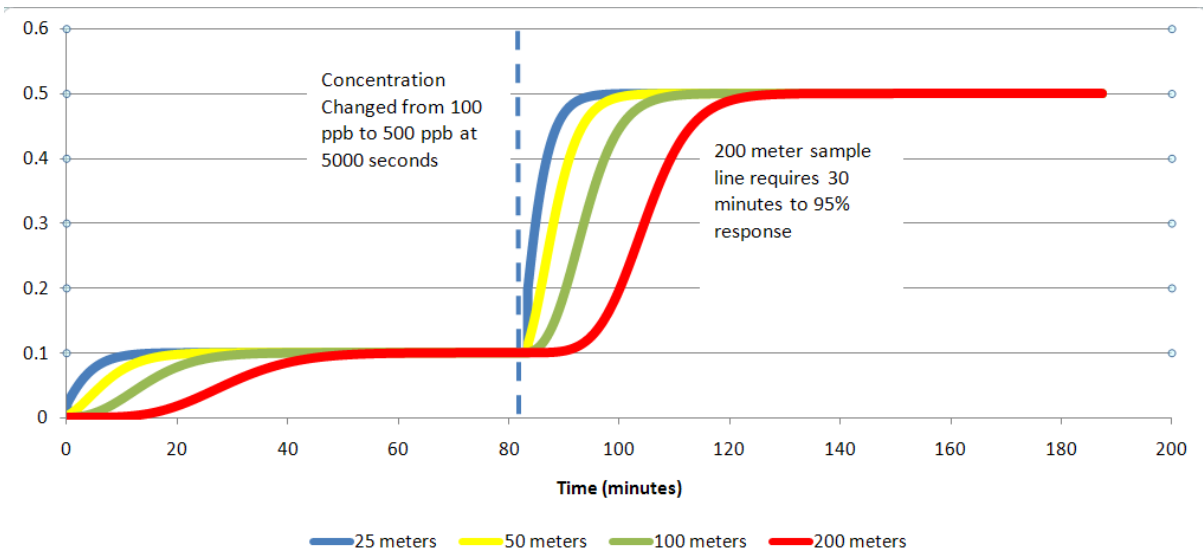


FIGURE 8. RESPONSE TO A +400 PPB STEP CHANGE

The model parameters developed in fitting the above data were applied to two other cases. In Figure 7, the model predictions for the effect of sample line length on the wet-up of an electropolished and SilcoNerted sample line are shown. The same adsorption/ desorption

parameters are used as were used to approximate the 1 ppm data shown previously. The only parameters changed in the model were the line lengths, the flow rate (now 10 slpm) and the inlet concentration (now going from zero to 100 ppb). In Figure 8, we extend the analysis to include an examination of the effect of a step change from 100 ppb to 500 ppb moisture, with other conditions as in Figure 7.

Such experiments would be difficult, expensive and time-consuming to perform in the laboratory. Assuming the model is correct, it shows that a 200 meter EPS sample will equilibrate to a 100 ppb wet-up in one hour and that it will respond to a step change to 500 ppb and achieves equilibrium in under 40 minutes. Both of these results are theoretical and require laboratory confirmation.

SUMMARY AND CONCLUSIONS

Critical factors which affect adsorption and desorption processes in sample lines and gas distribution systems include the surface roughness, surface chemistry, pressure and temperature. The surface chemistry and temperature strongly affect the desorption rate strongly, and therefore impact system response speed. Rather than solve the complex partial differential equations shown previously, a simplified set of finite difference equations has been presented as a means to model the mass transport problem.

Some comparison of the model to empirical data has been performed, and it appears the model is consistent with the general trends seen in empirical results. Additional work is required to address deficiencies in the model (such as the inclusion of only one type of adsorption site), but the model already appears useful as a means of predicting experimental results and allowing for rapid characterization of the effects of changing process variables.

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