

Improving the speed and accuracy of water vapor and hydrogen sulfide measurements by optimizing the sample transport system.

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ABSTRACT

Natural gas is processed in order to meet customer specifications, such that it may be sold based on energy content. Suppliers and producers whose product does not meet the customer / pipeline specifications are “shut-in” until it can be demonstrated that the product is within specification. With the advent of shale gas production and more complex and diversified streams entering the transportation, there is increased interest and demand for accurate, reliable and timely analysis of gas quality. The validity of such measurements can be strongly impacted by the sample gas transport system, the process by which the gas is removed from the process and move to the analytical systems. For trace components like moisture and hydrogen sulfide, the adsorption and desorption of the analyte from surfaces in the system must be considered. A thorough description of the effects as well as recommendations on system optimization is presented.

INTRODUCTION

The analysis of natural gas has various purposes, from process optimization, to ensuring critical specifications are met during custody transfer, to determination of product value. In each of these cases the accuracy and timeliness of results are of paramount importance. While the response speed of the analytical technique has important implications here, it is well accepted that the design and implementation of the analyzer sample system that often determines the overall performance of the system.

Effective sample conditioning and transport is imperative to providing a representative sample of process fluids to an extractive process analyzer¹. The process of sample conditioning begins at the sample point, where preferably a probe is used to extract a sample of the gas. Frequent sample conditioning operations performed at the probe include filtration for particulate and/ or liquids and may include pressure control. External to the probe there may be additional pressure reduction operations which often must be performed under controlled temperature conditions, flow control and additional filtration. The pre-conditioned sample is then transported to the process analyzer, where additional steps may be taken to remove contaminants which may alter the sample composition or cause problems

with the analysis. Care must be taken to perform each of these operations in an optimized manner if we are to expect a meaningful result from the process analyzers.

Herein, we intend identify key concepts which must be addressed when designing a proper sample system, with an emphasis on one of the least known and considered effects – the adsorption and desorption of analytes in the sample transport tubing and its effect on accuracy and response time.

SAMPLE CONDITIONING

Sample conditioning is the process of extracting a “representative” sample from a process pipe or vessel, making it compatible with the sample transport system, and further treating it such a way as to make it suitable for the analyzer or analytical technique chose. The sample conditioning system is a physical assembly of fluid processing components that ensures that the sample delivered to the analyzer is compatible with its requirements despite any and all process fluctuations. It exists as a physical entity within the much larger environment of the sample handling system, which encompasses to some extent the process itself as well as the sample extraction, transport, conditioning, disposal arrangements and the analyzer itself².

The purpose of the sample conditioning system is to deliver a representative sample to the analyzer for subsequent analysis. In terms of natural gas processing, numerous definitions of representative sample exist³.

From the Gas Processors Association publication GPA 2166-05, "The objective of the listed sampling procedures is to obtain a representative sample of the gas phase portion of the flowing stream under investigation. Any subsequent analysis of the sample regardless of the test is inaccurate unless a representative sample is obtained." And from ISO-10715 a representative sample is, "A sample having the same composition as the material sampled, when the latter is considered as a homogeneous whole." Finally, API 14.1 offers a similar statement in the latest revision, "a representative sample is compositionally identical or as near to identical as possible, to the sample source stream." These standards are the most common and current ones referenced on gas sampling procedures.

The single largest source of error in the analysis of natural gas samples is distortion of the sample composition while extracting, transporting or conditioning the sample for the analyzer⁴. In general, it is assumed that sampling clean dry natural gas which is well above its hydrocarbon dewpoint is simple, while sampling natural gas that is near its dewpoint is much more problematic. This is arguably true for bulk compositional measurements such as hydrocarbon composition and energy content, but may not be true when one considers trace components such as sulfur species and water content. In the latter cases, material compatibilities must be considered carefully and the choices made may significantly affect the analytical results, even for clean dry gas samples.

In evaluating and selecting materials, many guidelines and regulations exist to assist us in matters such as corrosion resistances (NACE), or in regards to elastomer compatibility and seals. Less often addressed

is the subject of adsorption and desorption of trace components in the sample handling system. Adsorption desorption effects are most relevant during the transport and analysis of trace components: at high concentrations the surfaces quickly come to equilibrium and the surface is not able to substantially change the concentration of the gas but at low concentrations the surface may absorb a significant percentage of the component present and may take a long time to come to equilibrium.

In all cases, the delivery of a representative sample begins with extraction of the sample gas from the process, and is followed by the subsequent transport of said gas to the analyzer.

SAMPLE GAS EXTRACTION

All gas samples should be extracted through a sample probe and this component must be considered as the first part of the sample transport system. A commonly applied rule of thumb is that the probe should extend into the central 1/3 of the process pipe, although this decision may be impractical in some cases due to probe resonance effects^{5,6}. Sample probes within a flowing pipeline can vibrate as the gas forms eddy behind the probe. If the probe is too long, the vibration frequency can eventually cause the probe to break.

In extracting the process sample, one must consider whether in-situ filtration and / or in-situ pressure reduction should be applied and the impact of these operations on producing a representative sample. This is well addressed in API 14.1 and has been thoroughly covered by other authors^{7,8}. Filtration to prevent the further transport of particulate and especially liquid droplets should be performed at the probe and at pipeline pressure and temperature. This fact clearly indicates the benefits of in-situ filtration probes in all cases. Changing the temperature or the pressure of the gas before eliminating entrained liquids will always change the gas composition.

In sharp contrast, in-situ pressure regulation should only be employed in cases where it is known sufficient dewpoint margins exist. As a safety margin against uncertainties in predicted hydrocarbon dew points, API Chapter 14.1 recommends that sampling equipment be maintained at least 30°F (17°C) above the predicted hydrocarbon dew point. In situations where the gas is at or near its dewpoint in the pipeline, an in-situ regulator is generally unacceptable as the regulator will be at the same temperature as the pipeline and provide insufficient excess heat energy to prevent condensation occurring during the expansion.

SAMPLE TRANSPORT AND SAMPLE LINES

Specifying the best sample line for a project requires a thorough analysis of the system and requirements. Of particular importance are:

- 1) Species to be analyzed,
- 2) Sample gas composition and dewpoint / phase behaviour,
- 3) Length of the sample line run,

- 4) Operating pressure and temperatures,
- 5) Required gas velocities and response times, and
- 6) Material compatibility.

The bulk composition and phase behavior are required to determine the operating temperature necessary to prevent sample condensation, dewpoint issues. Recall that API 14.1 recommends all equipment be maintained at least 30°F (17°C) above the worst case dewpoint temperature. Assuming that heating is required for the line – there is little benefit in providing only marginal capabilities and thus a larger dewpoint margin is warranted.

The length of the sample run, pressures, temperatures and required response time all play important roles in specifying the tubing diameter and gas flow rates. Care should be taken to also consider the pressure drop during the transport of the gas, although gas phase pressure drops are typically small at the flow rates used for analyzer sample systems.

Materials compatibility can become a critical factor in terms of analytical performance, accuracy and response time. 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. The adsorption desorption process can result in long response times or even completely erroneous values when measuring trace species such as hydrogen sulfide, water vapor or mercaptans.

The surface chemistry of the sample line 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 must be understood to provide physio-chemical model of the mass transport in sample lines.

ADSORPTION DESORPTION EFFECTS

When a sample of gas touches the walls of any tubing or container, some of the molecules stick to the surface. The surface contains a multitude of adsorption sites where the molecules may stick. Imagine a metal surface that has been scrupulously cleaned, and all these active adsorption sites are available. These active sites are surface structures where an uneven distribution of electrons causes negative or positive charges to accumulate⁹. When we allow a gas containing trace amounts of polar molecules such as H₂S or H₂O to contact this surface, the molecules flock to these activate sites. As the number of molecules stuck to the surface increase, fewer sites are available and the rate of adsorption decreases. As well, molecules stuck to the surface occasionally escape (desorb) and come back out into the gas phase. The system reaches equilibrium when the rate of adsorption and the rate of desorption equal each other.

There exists a popular (if ill-conceived) notion that once this effect has occurred the first time, the line has been conditioned or pickled and no more adsorption or desorption will occur. However, this is not

the case. If the concentration of the analyte increases, the rate of adsorption increases and the system must now achieve a new equilibrium. If the concentration of the analyte suddenly drops, then the rate of adsorption decreases but desorption stays the same – and the concentration at the analyzer slowly tails to zero.

Material treatment and coatings can greatly affect the rate of adsorption loss to surfaces. This effect has been extensively demonstrated for sulfur compounds in both static (sample cylinders) and dynamic (sample line) applications. In sample cylinders, complete loss of sulfur species can be seen in a few days for uncoated vessels, but coated vessels can retain sample integrity for days or weeks for some species as depicted in Figure 1.¹⁰ In flowing systems, the adsorption effects substantially delay the appearance of the inlet gas at the exit of the tube as shown in Figure 2¹¹, where the 316L stainless steel line does not come to equilibrium in 15 minutes when challenged with 0.863 ppm H₂S.

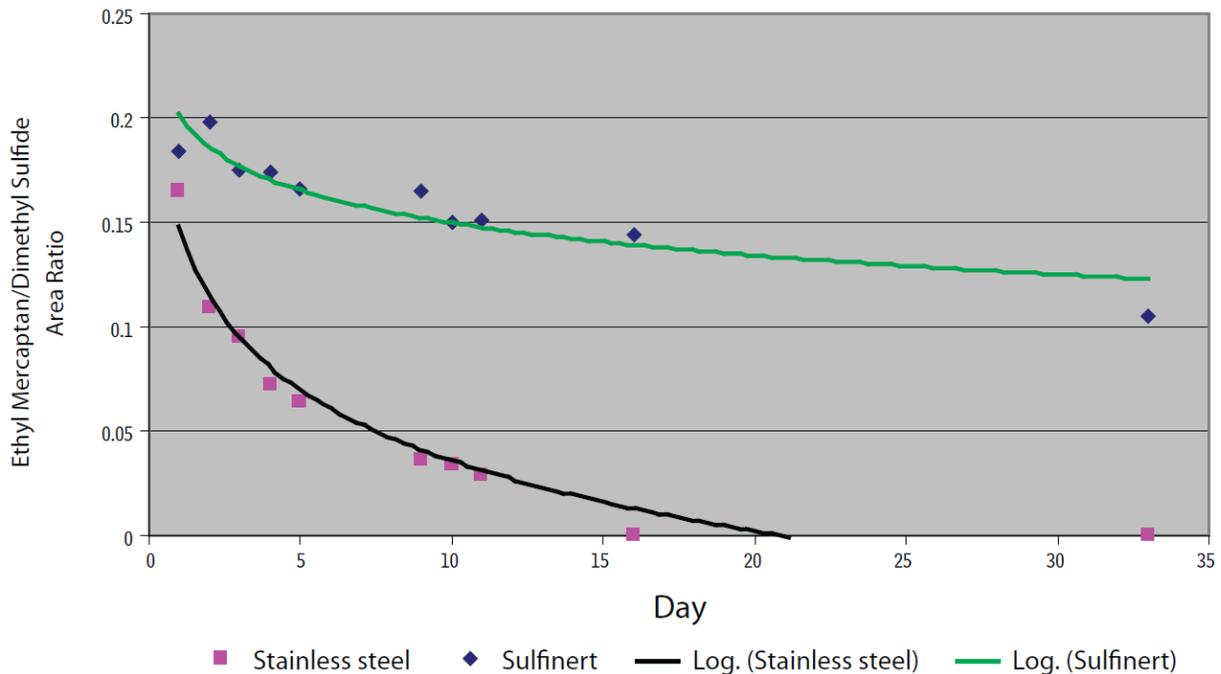


Figure 1 Samples collected in Sulfinert® treated cylinders are significantly more stable than those collected in untreated cylinders. Samples in untreated cylinders quickly lose reactive sulfurs, due to interaction with the stainless steel surface.

Given the obvious and dramatic impact of surface treatments on the adsorption of gases of interest in the natural gas, refining and petrochemical industry, it is important that we understand first what how these treatments affect the surfaces involved and how those effects impact the mass transport. The mass transport properties can be examined in varying degrees of mathematical rigor, and we have chosen to develop a model which encompasses the major effects in evaluating transport along sample tubing.

The model proves useful to evaluate the effects of changing parameters like pressure, temperature, flow rate and tubing diameter on response time in analytical systems.

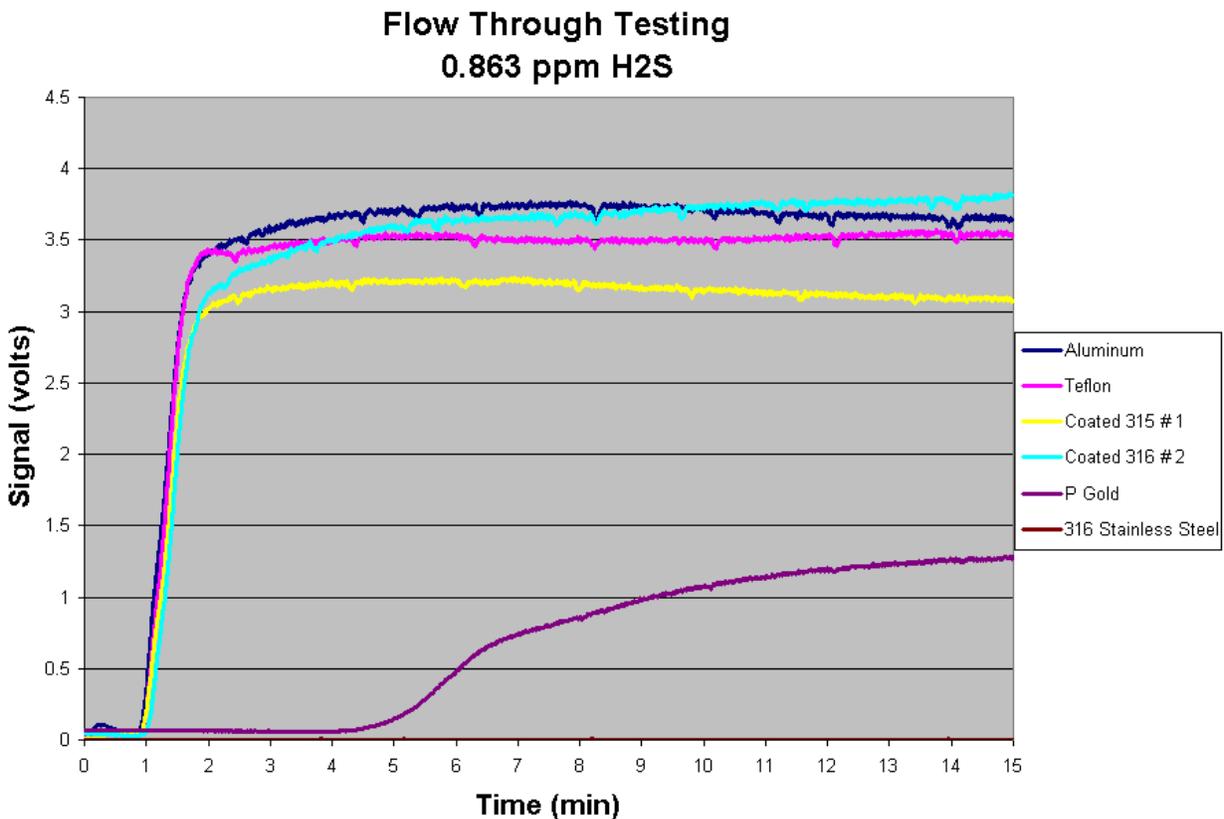


Figure 2 Flowing H₂S in nitrogen sample – 6 foot sample line at a linear velocity of 2 cm/sec.

SURFACE MORPHOLOGY

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 steel¹². 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 surface¹³. 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 conditions¹⁴. Furthermore, the iron oxides provide active adsorption sites which strongly absorb species such as water¹⁵ and hydrogen sulfide¹⁶.

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 applications¹⁷. The surface to be passivated must be clean and oil free¹⁸. 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.¹⁹

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, electro polished tubing has five primary advantages²⁴:

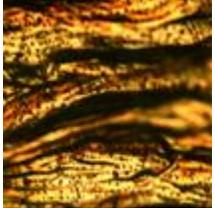
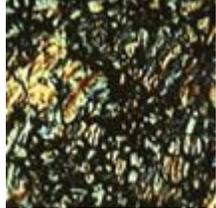
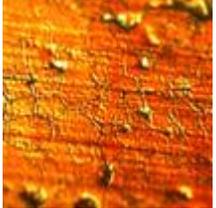
- 1) Extremely smooth surface, which minimizes adherence of particles and adsorption of gases or liquids,
- 2) Removal of all oils and iron from the surface,
- 3) Increased chromium to iron ratio which improves corrosion resistance and reduces chemical activity,

- 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 process²⁰ at 400°C. The process can be further enhanced to improve surface inertness and reduce moisture hold-up²¹. 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 magnitude²⁴. 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 Sulfinert
				

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 absorb 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 steel²². 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 3, 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 surface²³, 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.

Referring to Figure 4, 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:

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

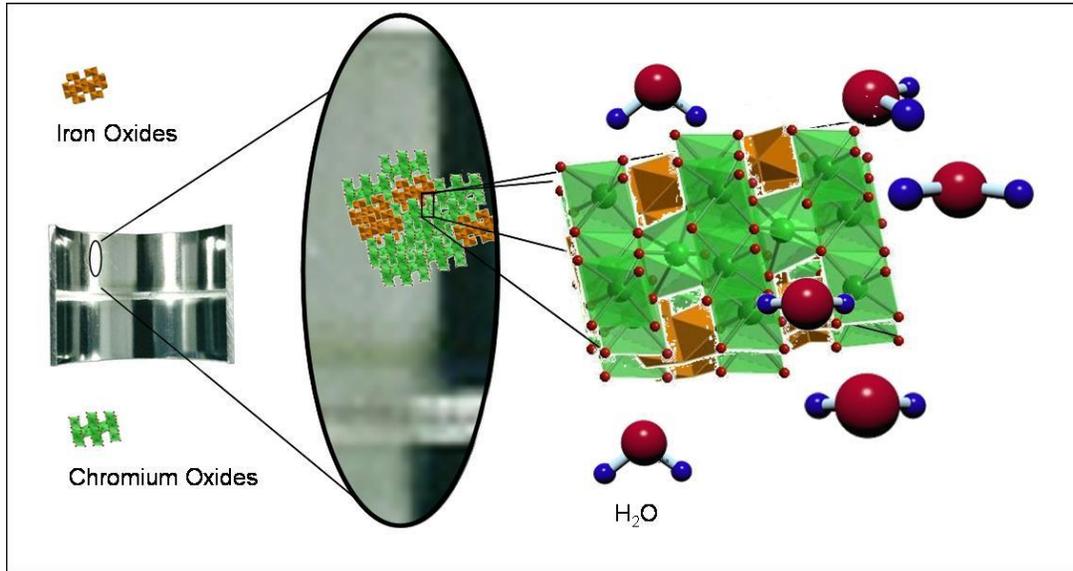


Figure 3. Water adsorption on stainless steel surfaces

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 Products²⁵, 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 ($V=4\pi r^2 \Delta l/3$). 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_i 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_i multiplied by the surface area of the element, SA .

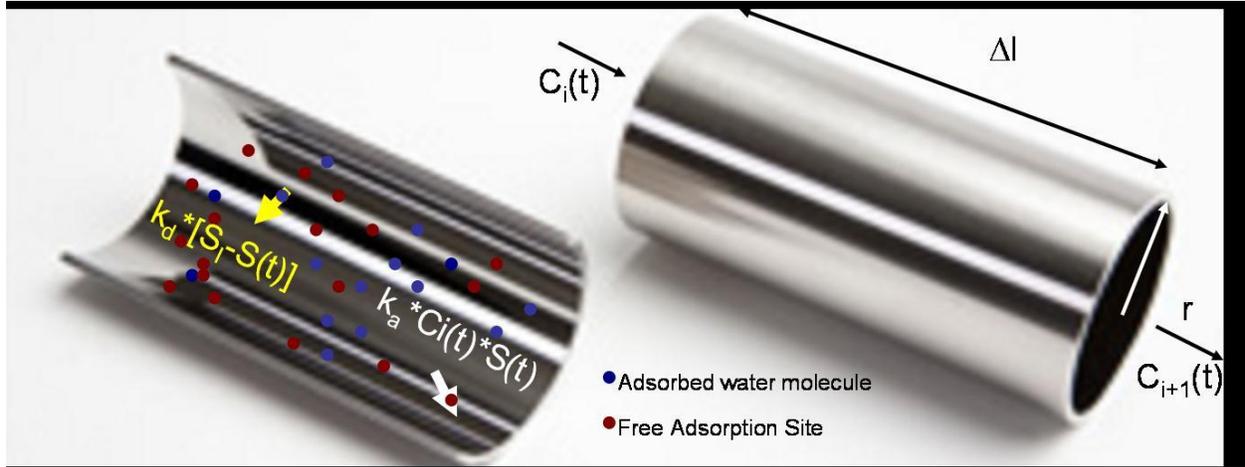


Figure 4. Mechanism and Elements of the Model

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.

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

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 $S_i - S_i(t)$ represents the number of sites which are currently filled with analyte molecules (recall that S_i 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.

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

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 dependent 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_f . 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.

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 vapor²⁶, hydrogen sulfide²⁷, and methyl mercaptan²⁸.

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.

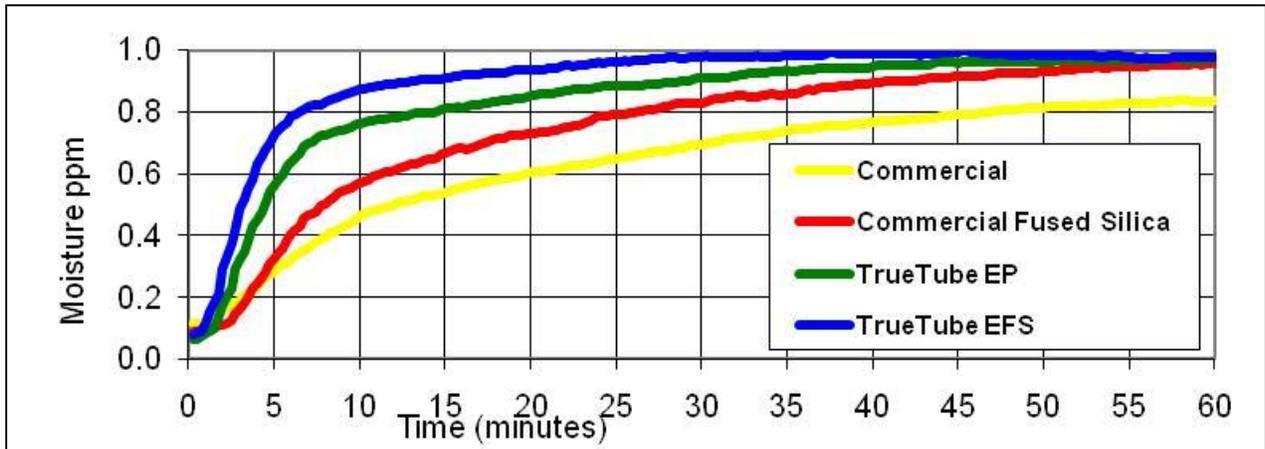


Figure 5. "Wet-up" Data for 1 ppm challenge gas at 0.35 slpm

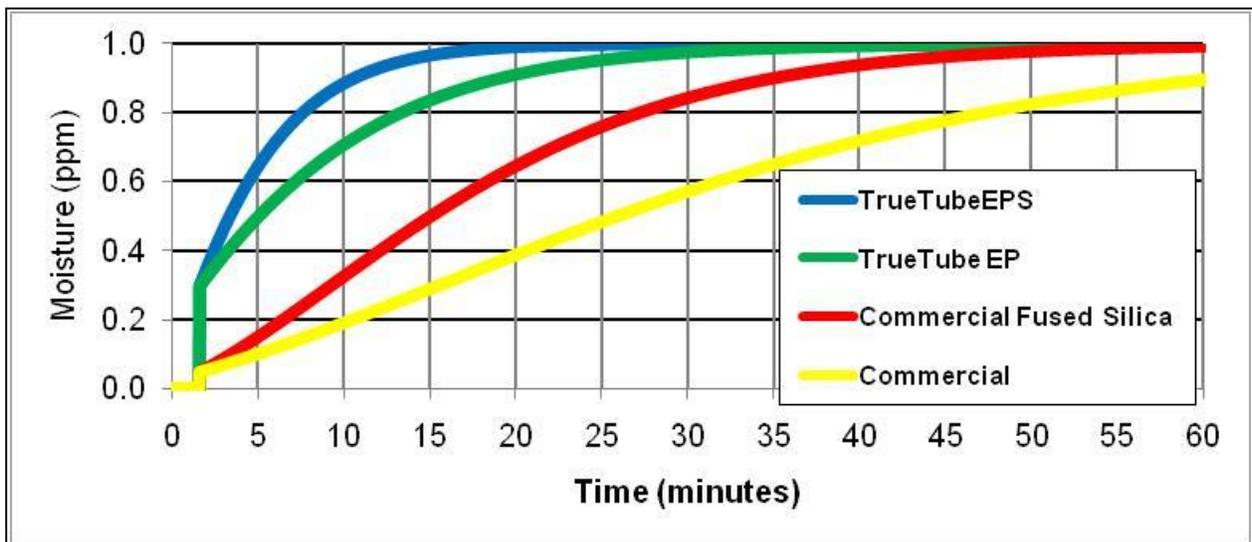


Figure 6. "Wet-up" Model for 1 ppm challenge gas at 0.35 slpm

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.

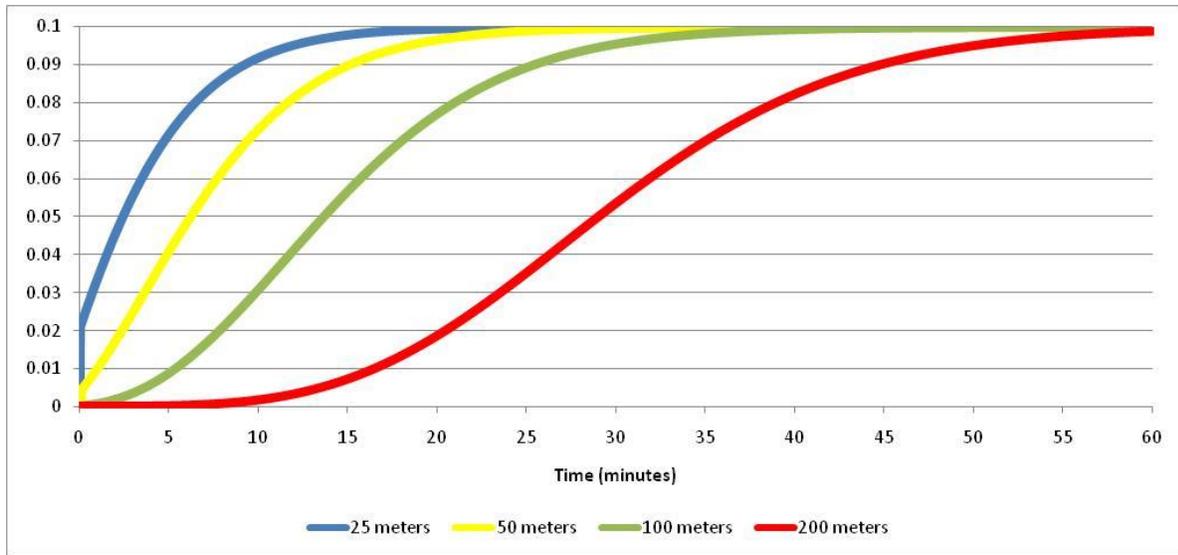


Figure 7. Response TIME to a 100 ppb "wetup"

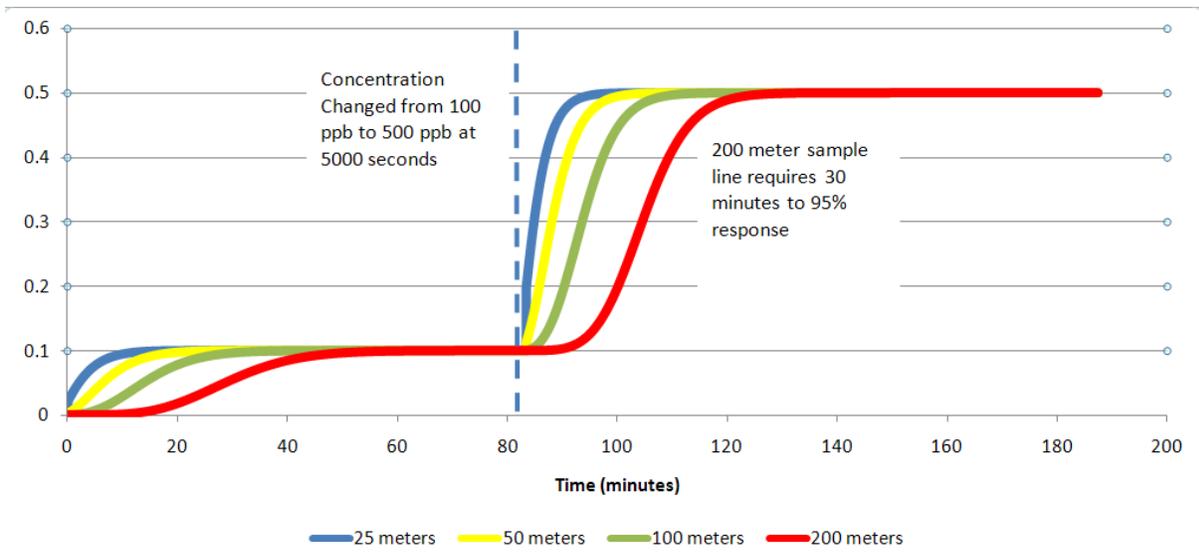


Figure 8. Response to a +400 ppB step change

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.

While the model has been developed based on water vapor adsorption desorption characteristics, the same general trends are seen for trace sulfur species such as H₂S and methyl mercaptan, as well as for species like ammonia.

Testing performed at the Shell Research center demonstrated that conventional stainless steel tubing can adsorb a significant quantity of mercaptans and greatly delay response times in comparison to electropolished and sulfinited tubing²⁸.

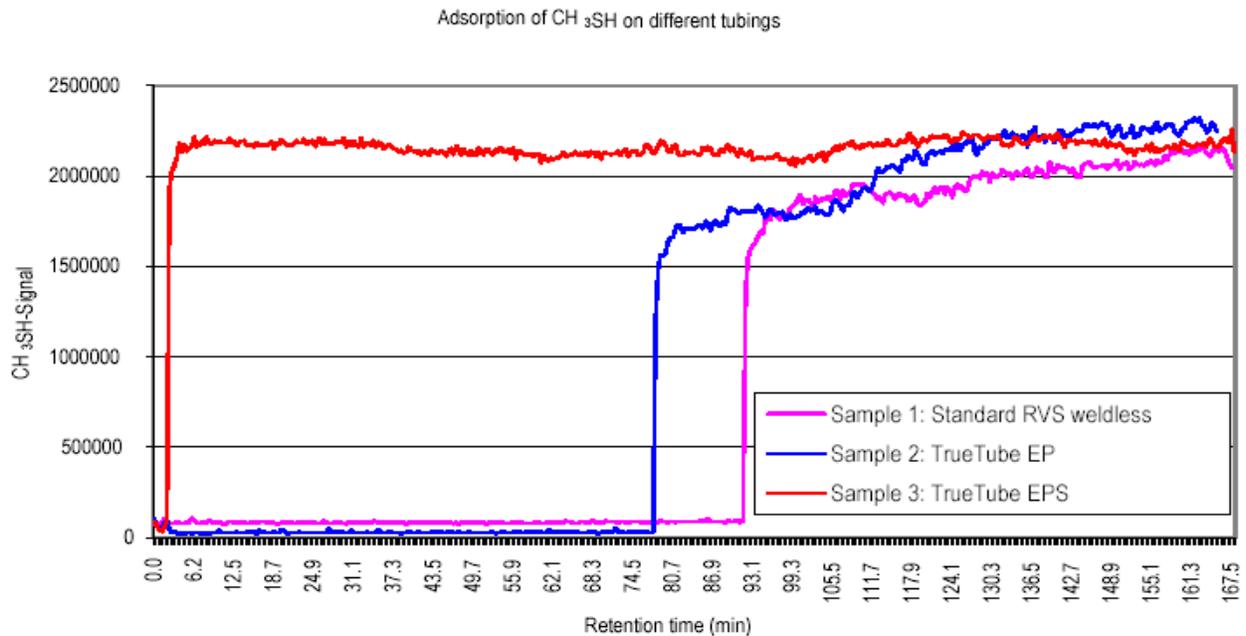


Figure 9. Sulfinitert[®] treated tubing (red) does not adsorb methyl mercaptan (500ppbv), giving accurate results with no delay.

Similar testing was performed to determine impact of sample line materials on response time to changes in H₂S concentrations. Again the trend is clearly seen in that the electropolished and sulfinited sample lines demonstrate faster response speeds and quicker stabilization times as compared to untreated or less treated lines.

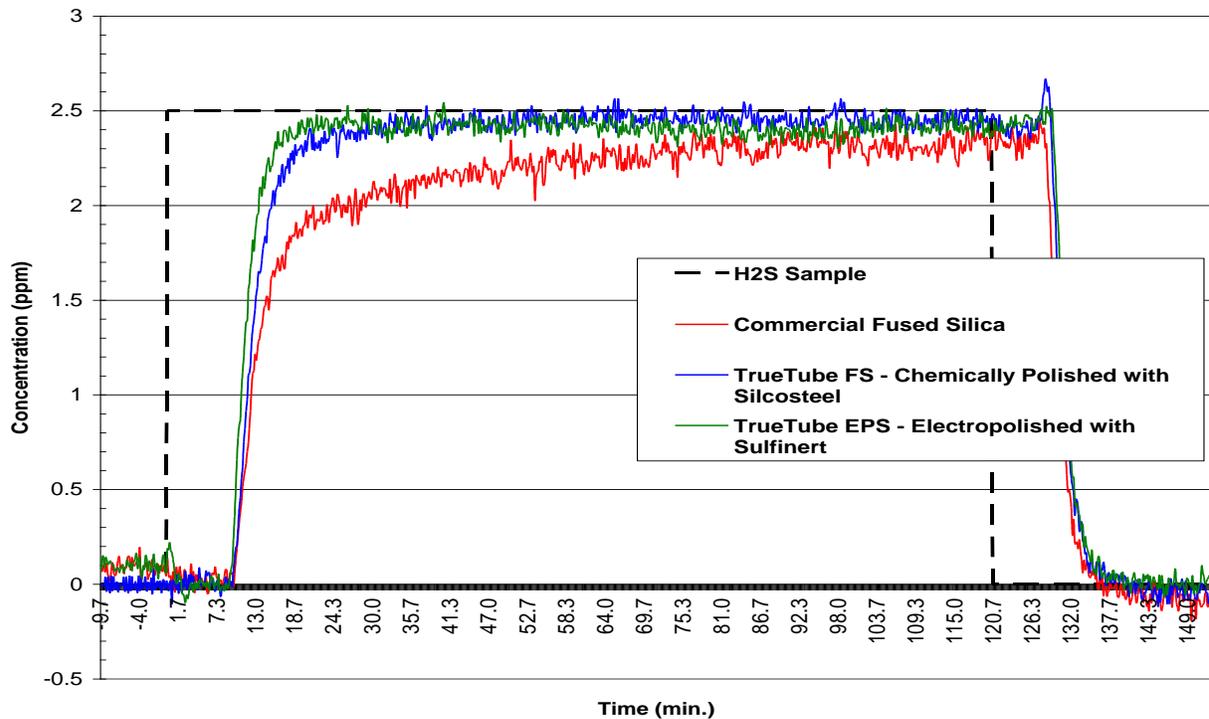


Figure 10. Effects of tubing material of construction on response time.

In a recent paper, Adsorption of dynamically diluted ammonia at part-per-billion to low part-per-million concentrations in dry nitrogen was studied with treated and non-treated stainless steel and polymer test tubes. The treatments included electropolishing and two types of coatings based on amorphous silicon²⁹. In this very thorough work, the authors were able to quantify the number of adsorption sites per square centimeter of tubing surface, which determines the adsorption capacity of the line. The results clearly show that the combination of electro-polishing and sulfinerting the sample lines reduces the adsorption capacity and number of surface sites by more than a factor of 20 relative to a conventional stainless steel line.

Tubing Material	Number of Sites
EP with Sulfinert	4.7×10^{12}
Sulfinert	14.6×10^{12}
EP SS316L	72×10^{12}
SS316L	138×10^{12}

The authors have as yet been unable to find any data on the adsorption desorption characteristics of heavier hydrocarbons (hexanes, heptanes, octanes and nonanes) on stainless steel surfaces. However, given that these species are present in natural gas applications and have bearing on both the energy content and the hydrocarbon dewpoint of the gas, further investigation is warranted.

RECOMMENDATIONS FOR INSTALLATIONS

While it is always difficult to establish installation guidelines that fit every application, the following considerations should be taken when evaluating the design of a sample system, especially when it is to be used for the timely and accurate measurement of trace components.

Sample Line Materials

All the data presented are consistent with the fact that the use of electropolished and sulfinerted sample lines reduces the adsorption of reactive species such as hydrogen sulfide (H_2S), water vapor (H_2O), Mercaptans (CH_3SH) and ammonia (NH_3). While utilization of such materials increases the initial capital cost of an installation, the impact is relatively small in terms of overall project scope. The benefits can be dramatic, such as a 20 fold reduction in surface area for adsorption and dramatically improved response speeds and analytical accuracy.

Heat Tracing

The use of heat traced lines (where possible) is strongly recommended. As shown in Figure 11, the rate of desorption doubles for about every 50 °F the sample line temperature is increased. Increasing the desorption rate reduces the total amount of material the sample line can adsorb at equilibrium and increases the response speed.

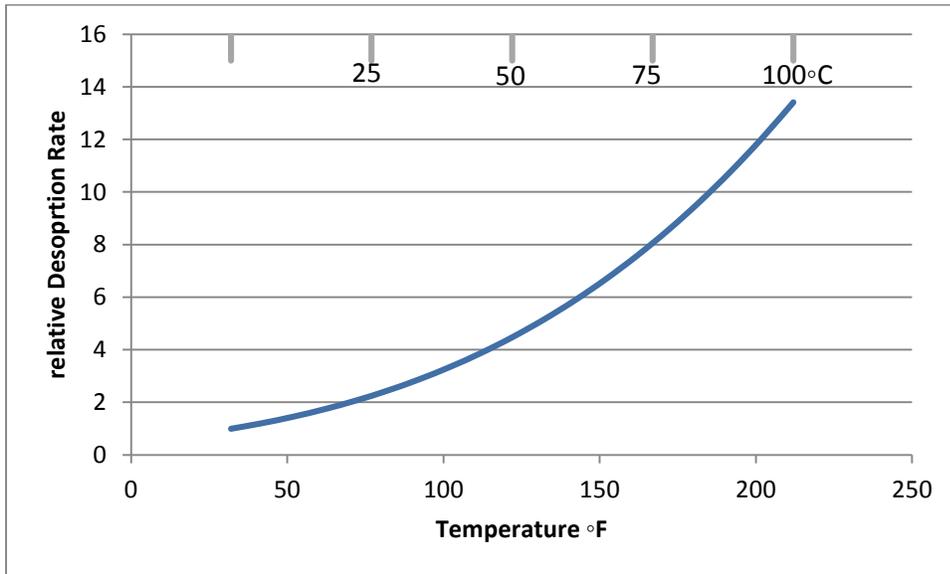


Figure 11. Effect of Temperature on the rate of desorption from surfaces (assumed activation energy of 22 KJ/mole)

An additional benefit is that heat traced lines prevent the daily or diurnal temperature changes which can occur and result in inaccurate readings during the temperature change.

In the event that heat tracing is impossible or impractical, it becomes even more important to consider the effects of sample line materials, lengths and diameters. Materials should definitely be chosen to

minimize adsorption, and it will be beneficial to insulate the line. The insulation will not prevent the line from experiencing temperature changes due to ambient conditions, but will slow down the rate at which those temperature changes occur, allowing more time for equilibration and reducing the large concentration changes which may occur during ambient temperature swings.

Sample Line Lengths

Sample line runs should be made as short as possible. Each time the sample line is doubled, the number of adsorption sites is doubled as well so the system will take longer to come to equilibrium. In addition, if the flow rate remains the same, the residence time in the line doubles (giving the gas more time to react) and the first order lag doubles (the time it would take for the gas to transit the tube even if there was no adsorption).

Sample line diameter

Reducing the sample line diameter has two effects, it increases the gas velocity (for the same flow rate) and it reduces the surface area of the tube. Increasing the gas velocity will result in the gas spending less time in the sample tube and having less time to react. Reducing the surface area reduces the overall number of adsorption sites and thereby also improves response time and system bias due to adsorption. The combination is a very effective means to ensure rapid response. Caution has to be taken however. Narrow bore sample lines (such as 1/8" OD tubing) should only be used on streams which will be clean and free of major particulate or condensable material. Fortunately in natural gas applications this is usually the case. Care must also be taken to ensure that the pressure drop along the length of the line is calculated and is acceptable. Such calculations are presented in Reference 2.

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, 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.

The use of the model results has allowed for some general recommendations in regards to sample line installations.

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