

A Comparison of Coatings Used to Enhance the Moisture Performance of Analyzer Flow Paths

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Key Words

Amorphous silicon, amorphous carbosilicon, moisture, adsorption, inert, CEMS, corrosion, sample loss

Abstract

The use of coatings to improve the performance of analyzer flow-paths has grown with increasingly stringent monitoring regulations. This paper will review test data and recommend coating compatibility for moisture and moisture related adsorptive effects in continuous emission monitor (CEM) flow paths. Data will be applicable to equipment used in stack gas monitoring, compliance with Rule 1118 for flare gas emissions, mercury sampling and general data for any components exposed to sulfur and chloride containing streams and environments. Industrial applications benefiting from this study will include stack gas sampling, environmental quality testing, refining streams, oil and gas exploration and transport, or any industry transporting, retaining or testing active or corrosive compounds in continuous emission monitoring systems.

Introduction

Continuous emission monitoring technology has been used to monitor stack emissions in refinery, power and other stationary sources since 1970. Annual costs related to monitoring and control of stationary sources have increased from \$6 billion in 1972 to nearly \$30 billion in 2000.¹ The total number of CEMS increased from approximately 600 systems in 1970 to over 6000 systems by 2005.² Operating costs of CEMS can be high with the cost of analysis for one sample ranging from \$100 for US EPA 29 up to \$430 for EPA 324.³ The risk of costly compliance issues, poor utilization of capital and high sample/analysis costs dictate that sampling and analysis systems perform at peak efficiency and precision. To assure peak performance, analyzers and sample transfer systems must be designed

for optimum sample transfer while minimizing sample loss due to moisture's adsorptive effects. Samples must be handled correctly to ensure they are representative of the actual process emission. The US EPA has identified moisture as one of the major causes of bias effects in CEM systems (Table 1).⁴ Moisture can have both negative adsorptive effects and corrosive effects on sample transfer and analysis. Minimizing moisture and removing entrained moisture is a key factor in maintaining consistent analytical results in CEM systems. Optimizing material compatibility for moisture resistance (hydrophobicity) will reduce sampling failures while improving analytical results. This study compares the hydrophobicity of select, inert materials by tensiometric measuring techniques. Surface energy effects are used to determine water contact angle, or hydrophobicity, of 304 stainless steel, and 304 stainless steel coated with PTFE (Teflon®), amorphous silicon, carbosilicon and various functionalized amorphous and carbosilicon surfaces.

Table 1:
Factors Contributing to Sampling System Problems in Continuous Emission Monitoring Systems⁴

System Problem	Description
Plugging	Particulate matter clogs sampling probe
Scrubbing	Precipitates on probe "scrub" SO ₂ from sample gas
Pressure Effects	Pressure changes affect dilution ratio causing measurement errors
Temperature Effects	Temperature changes affect dilution ratio causing measurement errors
Droplet Scrubbing	Evaporation of droplets in sonic probe can plug probe or cause pre-dilution and inconsistent measurements
Multi-Component Cal Gas Effect	Mixtures of cal gases may alter the expected gas velocity through the sonic orifice, biasing measurements.
Contaminated Dilution Air	Trace amounts of measured gas in dilution air cause errors.
Varying Dilution Air Pressure	Poor quality dilution air regulator adversely affects dilution ratio.
Water Entrainment	Collected liquid can scrub soluble gases, dilute sample gas, or cause leaks through corrosion.
Leaks	In negative pressure system, leaks may dilute sample gas.
Adsorption	Gas adsorbs on walls of tubing causing measurement errors, particularly at low emissions concentrations.
Absorption	Gas is absorbed in moisture condensed in the H₂O conditioning system.
Moisture Monitor Errors	Systematic error in moisture monitor may produce bias.

Continuous emission monitors (Figure 1) often operate in challenging environments and must sample complex and often corrosive or active elements and compounds such as SO₂, NO_x, hydrogen sulfide, mercury and mercury oxides. When combined with moisture, corrosives such as hydrochloric, nitric, sulfuric and other acids are formed. The overall effect of moisture contamination in sampling systems results in significant degradation of sample quality due to:⁴

- Adsorption of active compounds into entrained water
- Dilution of the sample
- Adsorption of soluble gasses into water droplets
- Formation of acids within the sample systems
- Formation of adsorptive rust particles in the sample system.
- Formation of adsorptive particulates within the sample system.

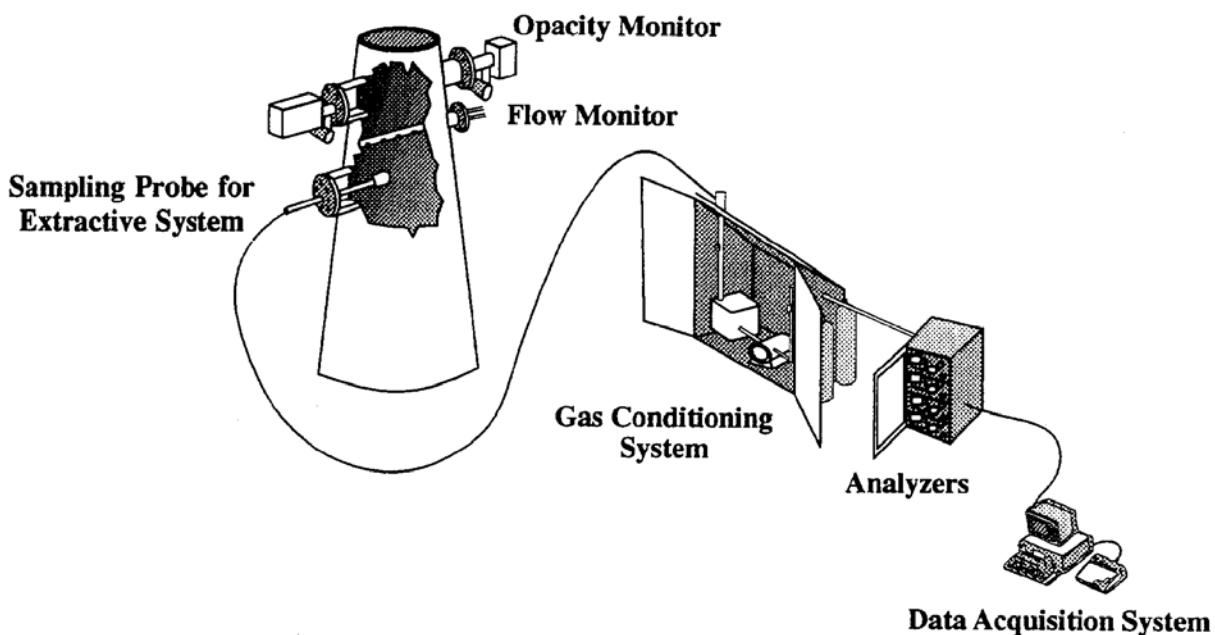


Figure 1: A typical continuous emission monitoring system (CEMS) (U.S. EPA Image)⁴

Good system design, installation practices and maintenance will dramatically improve CEMS performance and avoid sample loss and system failure. Design factors that improve CEMS performance are:

- Heated transfer lines
- Proper sample transfer line installation
- Filtration systems
- Corrosion resistant materials
- Moisture removal/minimization practices such as sloped heat trace transfer lines.
- Flow velocity optimization
- Pressure regulation/management
- Inert coatings

One key factor often overlooked in system design and installation is the selection of proper materials to maximize sample/system compatibility and the minimization of moisture effects in wetted flow paths. As detection limits decrease, the impact of moisture and surface adsorptive effects become dramatic. Selecting and matching compatible surfaces will ensure robust and reliable sample transfer and analysis and will improve system performance when combined with robust system design, installation and maintenance practices.

Previous work, adsorption/desorption moisture effects

Previous studies have shown that moisture's adsorptive effects can be minimized with proper material compatibility. Materials that exhibit high hydrophobicity tend to adsorb less water and will release moisture faster than hydrophilic (wetting) surfaces. Harris, et al. studied moisture adsorption and release times in 1/4in stainless steel tube (Figure 2). The study compared functionalized amorphous silicon surface with electropolished and commercial 316L stainless steel tube 1/4in OD x 100 ft.⁵

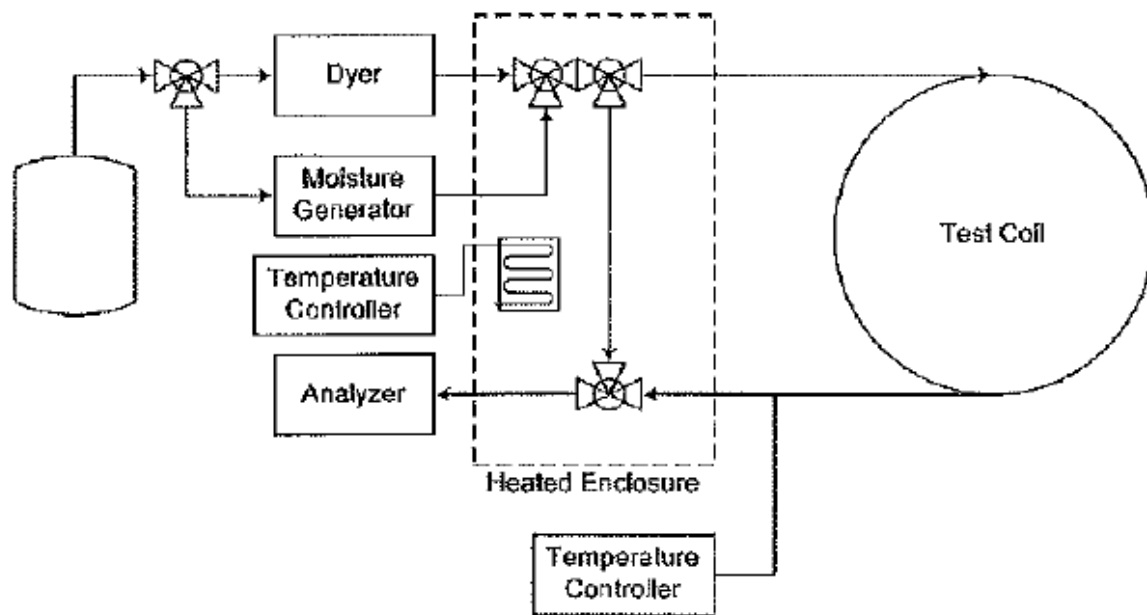


Figure 2: Moisture wet-up and dry-down test configuration. (Courtesy of Haritec Scientific and O'Brien Corp)⁵

Figures 3 & 4 compare 1ppm moisture take up and dry-down of conventional 316SS, electropolished 316SS and functionalized amorphous silicon coated electropolished stainless steel 1/4in tube (0.020in wall) x 100ft (Cardinal UHP St. Louis, MO). Data for wet-up and dry-down experiments, measuring

the relative response time for moisture content change in the 3 tube samples demonstrate a significant reduction in both moisture dry-down and wet-up time in the carbon functionalized amorphous silicon tube versus untreated substrates. The carbon functionalized amorphous silicon surface reached saturation in 30 minutes, vs. 60 minutes for electropolished and 180 minutes for conventional tubing. In a typical CEM system, moisture content in carbon functionalized amorphous silicon surfaces will hold significantly less moisture (Figure 3).

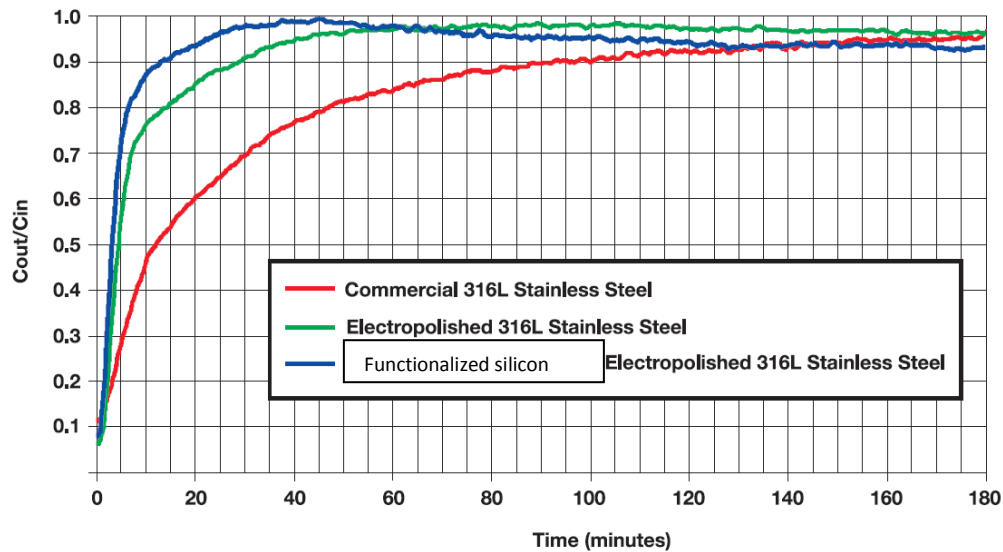


Figure 3: Moisture adsorption rates of 1/4in tubing is dramatically reduce with hydrophobic functionalized amorphous silicon surface.⁵

Moisture dry-down curves for the 3 surfaces show the carbon functionalized amorphous silicon surface achieved complete dry-down in 35 minutes while the electropolished and conventional surfaces required 65 and 175 minutes respectively. CEM systems utilizing the carbon functionalized amorphous silicon surface will release adsorptive and corrosive moisture nearly 50% faster than untreated surfaces (Figure 4)

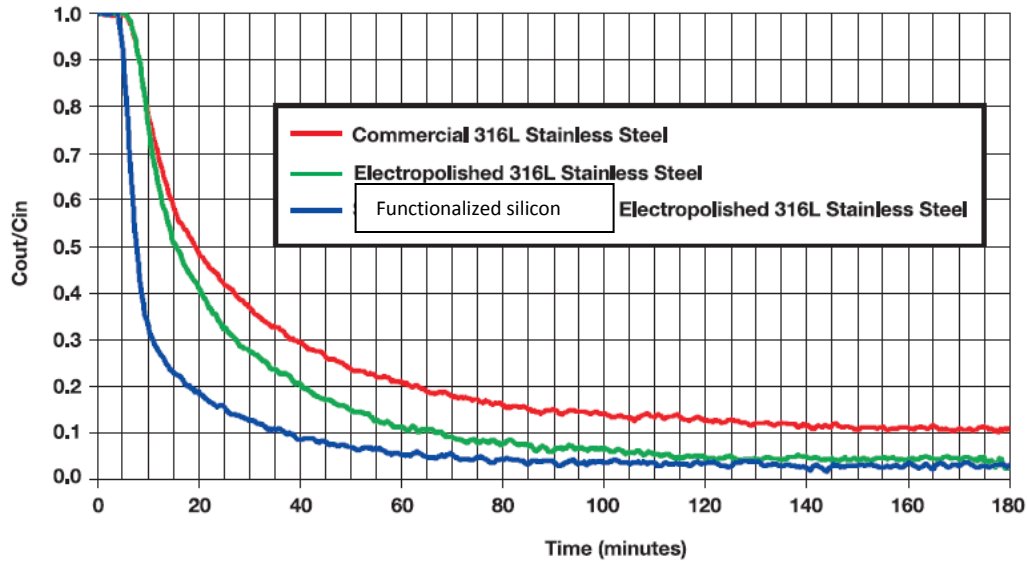
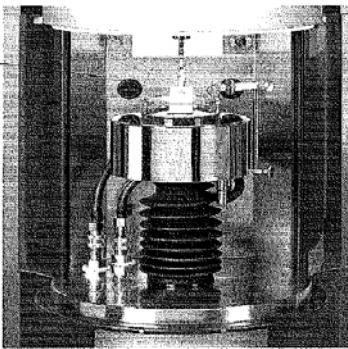


Figure 4: Treated carbon functionalized amorphous silicon surface will release moisture nearly 50% faster than electropolished or conventional stainless steel surfaces.⁵



Experimental

Surface contact angle measurements of 304 stainless steel, PTFE, amorphous silicon, carbosilicon and functionalized silicon plates were determined and compared using a Kruss model K100 tensiometer (Figure 5).⁶

Figure 5: Kruss model K100 tensiometer⁶

The hydrophobicity of a surface can be directly measured with a tensiometer (Figure 5). The molecular composition of a surface directly dictates the hydrophobic nature and therefore the moisture retention or loss performance of a material. A more hydrophobic surface will not adsorb water as easily as a hydrophilic one. And therefore, a hydrophobic surface will release water more readily than a hydrophilic one. A tensiometer can provide powerful data when developing surface chemistry to be applied in low moisture / moisture repellent applications.

The amorphous silicon, carbosilicon and functionalized samples were prepared by coating 304 SS plates with amorphous silicon or carbosilicon by chemical vapor deposition. Additional

functionalization was achieved by bonding hydrocarbons (alkenes) or fluorinated alkenes to the pendent silicon hydrides on the surface (Figure 6). (US patent 6,444,326 and 6,511,760, patent pending).

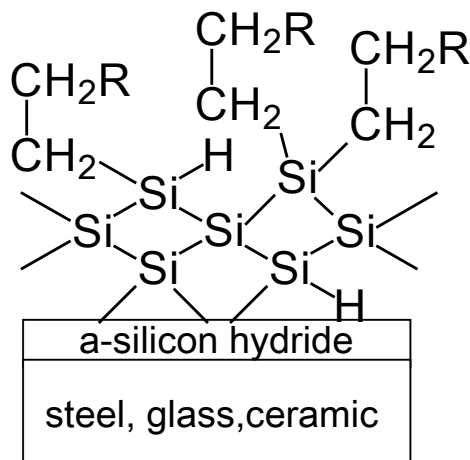


Figure 6: Amorphous silicon is diffused into 304 SS plates by CVD process. Carbon chains (alkenes) or fluorocarbon chains are then bonded to active sites on the amorphous or carbosilicon surface.

Samples were tested in a Kruss model K100 tensiometer using the Kruss liquid plate measurement method. 17 Mohm deionized water (DI water) was used to determine wetting. The Kruss tensiometer DI water container was raised to the test plate/water interface by a lift table. A precision balance then measured the water surface tension force interaction with the plate surface as the plate advanced into and then receded from the DI water (Figure 7).

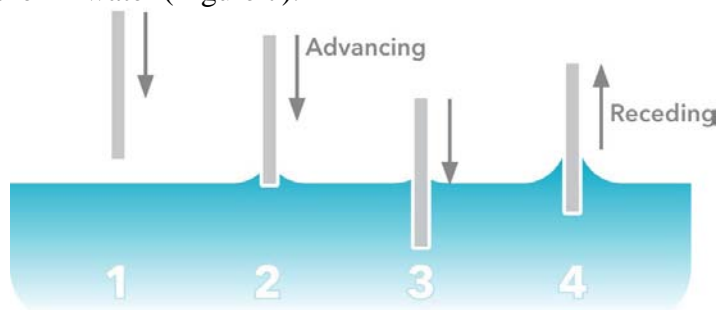


Figure 7: Advancing and receding contact angles are calculated by measuring water/ sample interface force generated when immersing the test plate into DI water. Bolin Scientific image⁷.

As the test plate is advanced into the DI water, liquid surface tension and wetting forces act upon the test plate. Plates that interacted with the DI water wetted and exerted higher force on the plate. Plates that did not interact with the DI water did not wet and consequently, exerted low to negative force (repelling force) on the plate as it was advanced and withdrawn from the DI water (Figure 8).

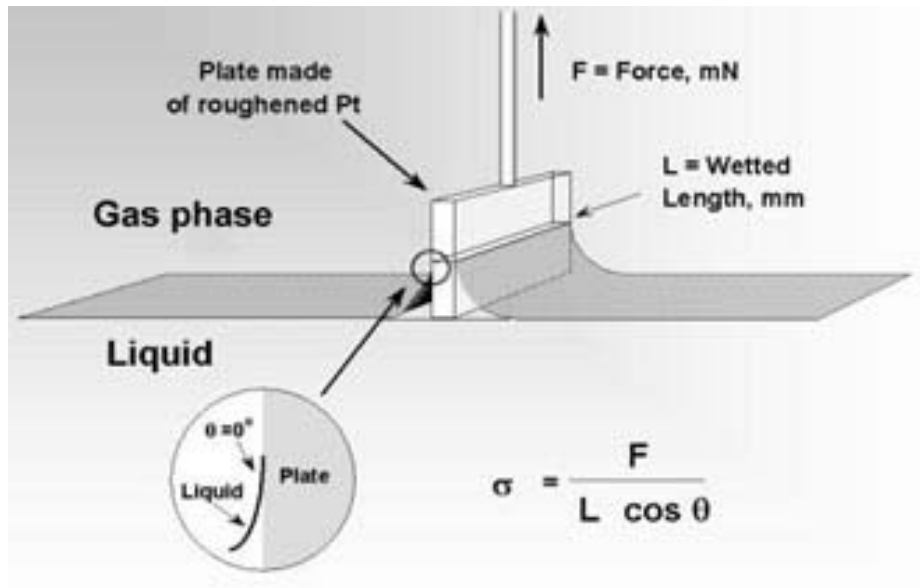


Figure 8: Wetting forces exerted by surface tension on test plates advancing and receding in DI water are used to calculate wetting contact angle. Krüss image.⁶

As the plated is immersed in the DI water media, advancing and receding contact forces were plotted. (Figure 9) Low downward forces or repelling forces are plotted as a negative number. Repelling forces indicate a low wetting, hydrophobic surface. As the plate enters the water, hydrophobic surfaces will repel the water, creating an upward force (shown as a negative number in the plot). Hydrophilic surfaces will create a downward, attractive force (shown as a positive number on the plot), indicating a low contact angle. As the coupon is removed from the water, receding forces pull on the plate, creating a downward force. Hydrophobic surfaces have low to negative receding forces indicating a high contact angle. Contact angles greater than 90 degrees indicate a hydrophobic, non-wetting surface. The advancing force indicates the lowest surface energy of the test surface and the receding force indicates highest surface energy. Advancing/receding hysteresis can be influenced by surface roughness, differences in surface heterogeneity or kinetic factors. The resulting advancing/receding hysteresis plot fully characterizes the test surface.

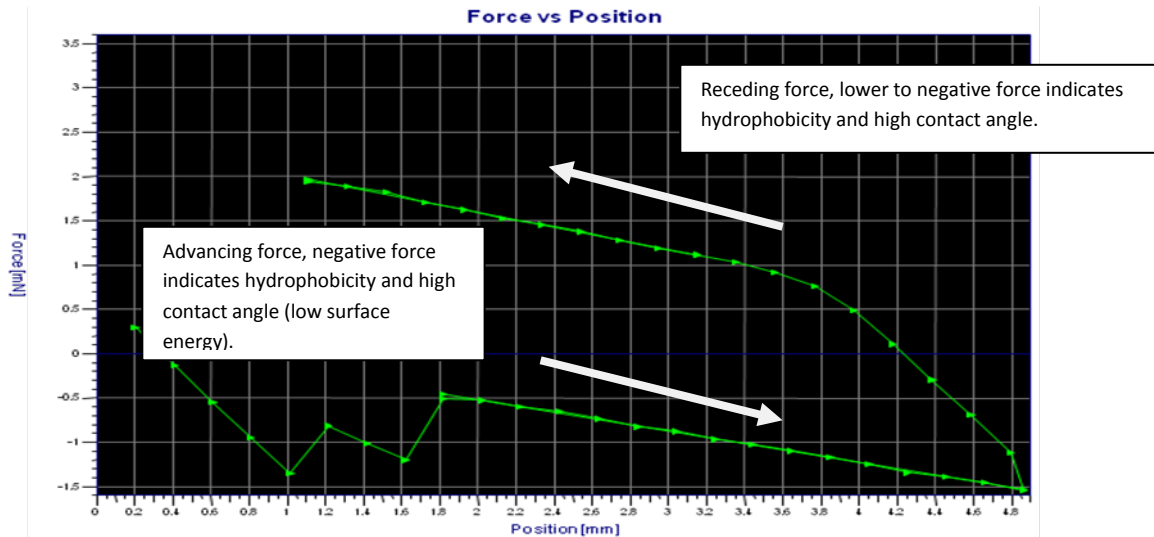


Figure 9: Advancing and receding forces are plotted; negative forces indicate repelling, non-wetting/hydrophobic, surfaces which are ideal for minimizing moisture contamination in CEM systems.

Tensiometric comparison of 304 stainless steel, amorphous silicon and carbon functionalized amorphous silicon advancing and receding force show the 304SS and amorphous silicon surfaces demonstrate high positive force during advancement and receding of the plate (hydrophilic, wetting surface) (Figure 10). The carbon functionalized amorphous silicon plate exhibits relatively low advancing and receding forces (high contact angle) indicating a hydrophobic surface.

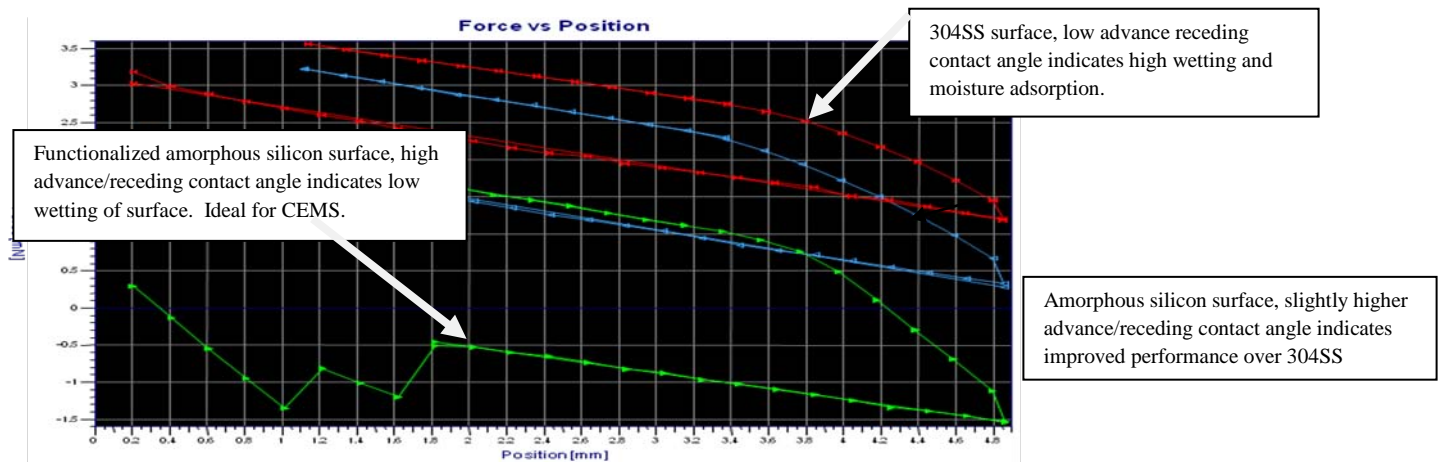


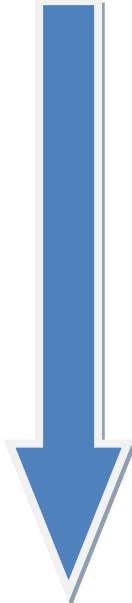
Figure 10: Contact angle comparison of 304SS amorphous and functionalized silicon surfaces.

Results

Table 2 compares tensiometric contact angle data of 304 stainless steel, amorphous silicon, functionalized amorphous silicon, PTFE, carbosilane, and functionalized carbosilane surfaces.

Results show the 304SS surface exhibits a low advancing contact angle of 53 degrees (low hydrophobicity) while PTFE and functionalized carbosilane (F) (fluoro-treated) exhibited the highest advancing contact angle 125 to 131 degrees.

Table 2: Comparison of advancing and receding contact angles in commonly used CEM systems.

Surface	Advancing / Receding Contact Angle	<div style="border: 1px solid black; padding: 5px; display: inline-block;">Increasing hydrophobicity</div> 
304 SS	37.2 / 0.0	
a-Silicon	53.6 / 19.6	
Funct. a-Silicon (HC)	87.3 / 51.5	
Carbosilicon	100.5 / 63.5	
Funct. Carbosilicon (HC)	104.7 / 90.1	
PTFE	125.4 / 84.0	
Funct. Carbosilicon (F)	131.7 / 60.8	

Hydrocarbon functionalized amorphous silicon (HC) demonstrated near hydrophobic (non wetting) performance with an advancing contact angle of 87.3 degrees.

Higher contact angle measurements indicate greater hydrophobicity and consequently greater ability to shed water resistance in analytical systems. Surfaces found to have a high contact angle exhibit lower moisture take-up and faster dry down in continuous emission monitoring systems.

Table 3 summarizes the overall material moisture compatibility of surfaces commonly used sample transport and analysis in continuous emission monitoring systems. The carbosilane and PTFE surfaces exhibited superior non-wetting performance. Functionalized amorphous silicon exhibited significant hydrophobic characteristics with a nearly 90 degree contact angle and a 50% improvement in moisture wet-up and dry down performance when compared to 304 stainless steel. Amorphous silicon exhibited some marginal improvement in moisture performance when compared to 304 SS.

Table 3: Summary of moisture compatibility in continuous emission monitoring systems.

Surface	Moisture Compatibility
a-Silicon	Fair
Funct. a-Silicon (HC)	Good
Carbosilane	Excellent
Funct. Carbosilicon (HC)	Excellent
Funct. Carbosilicon (F)	Excellent
304 SS	Poor
PTFE	Excellent (heat limited)

Conclusion

The low surface energy, hydrophobic, characteristics of functionalized carbosilicon, functionalized amorphous silicon and PTFE materials will enhance continuous emission monitoring system performance by minimizing moisture up-take into the system. Carbosilicon, functionalized carbosilicon, PTFE and functionalized amorphous silicon surfaces exhibit significant moisture minimizing, hydrophobic, performance, however, most grades of PTFE are limited to applications where operating temperatures do not exceed 250C. Amorphous silicon offers some minimal improvement in hydrophobicity. The high moisture take-up of 304SS does not make it a compatible surface for use in sample transfer and analysis of compounds susceptible to moisture adsorption effects in continuous emission monitoring systems.

Proper material selection will improve system performance by minimizing water adsorption and sample loss. Hydrophobic surfaces will reduce corrosion potential in CEM systems and will improve the inertness of the analytical flow path by reducing moisture related adsorptive effects. Compatible hydrophobic surfaces will improve analytical precision and minimize maintenance and retest costs due to corrosion or degradation of sample quality. Material compatibility, along with robust system design

factors should be considered whenever selecting, installing, or maintaining continuous emission monitoring systems.

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