CHARACTERIZING THE PERFORMANCE OF SURFACE MODIFICATIONS THAT ENHANCE SENSITIVITY, RELIABILITY, REPRODUCIBILITY AND ACCURACY OF ANALYTICAL INSTRUMENTS

Gary Barone
SilcoTek Corporation
225 PennTech Dr.
Bellefonte, PA 16823

David Smith
SilcoTek Corporation
225 PennTech Dr.
Bellefonte, PA 16823

Marty Higgins
SilcoTek Corporation
225 PennTech Dr.
Bellefonte, PA 16823

KEYWORDS

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ABSTRACT

Analytical and process testing systems are often constructed of materials such as stainless steel or glass. Materials of component construction can contribute to poor reproducibility and inaccurate analyses. The sources of loss originate from a variety of factors such as chemical species adsorption or surface reaction. The application of an inert, durable coating is critical to eliminate testing system inaccuracies and extend system lifetimes.

INTRODUCTION

Process analyzers used in the refining, petrochemical and off-shore environments are exposed to a variety of potentially damaging compounds. Sulfuric acid, hydrochloric acid, caustic streams and salt-water exposure are all detrimental to non-protected surfaces of all on-line and process monitoring components.

In addition to corrosion resistance, process analyzers in these applications must also maintain chemical inertness for the sampling of adsorptive chemicals such as reduced sulfur compounds.

This paper presents laboratory corrosion and chemical inertness test results for a variety of chemically deposited coatings. Through improvements in chemical composition, the properties of existing and new coatings will be evaluated in environments common to the petrochemical, refining and off-shore industries

DISCUSSION

The analysis of interactions between surfaces with liquids and gases improve the understanding of chemical compatibilities. In order to properly specify a passive surface for an analyzer system the chemical compatibilities of the substrate and any coatings is required. When the analytical system in an aggressive environment or analyzing aggressive compounds, research into physical properties of the surface is required to assure reliable performance. There are many subsystems that must be considered in analytical and sampling systems, demonstrated by a common Continuous Emissions Monitoring System (CEMS) layout(1), Figure 1.

CEMS and on-line monitors are often constructed with stainless steel components as a result of the environments they must occupy. As stainless steel is reactive to active organic compounds, surface coatings are required to render the surface inert. Increasingly, the environments and samples experienced by these systems can physically damage components through erosion, corrosion and exposure to sample streams that are acidic. Examples are off-shore platforms, stack gas streams, flare gas streams, semiconductor etch facilities and many common petrochemical streams containing chlorides.

New technologies of surface coatings are in development that can be used on CEMS and on-line systems to address both the chemical reactivity of the stainless steel and provide physical protection during damaging environmental exposure.

Table I summarizes the physical properties of common coatings used for analytical systems along with some corrosion resistant materials(2).

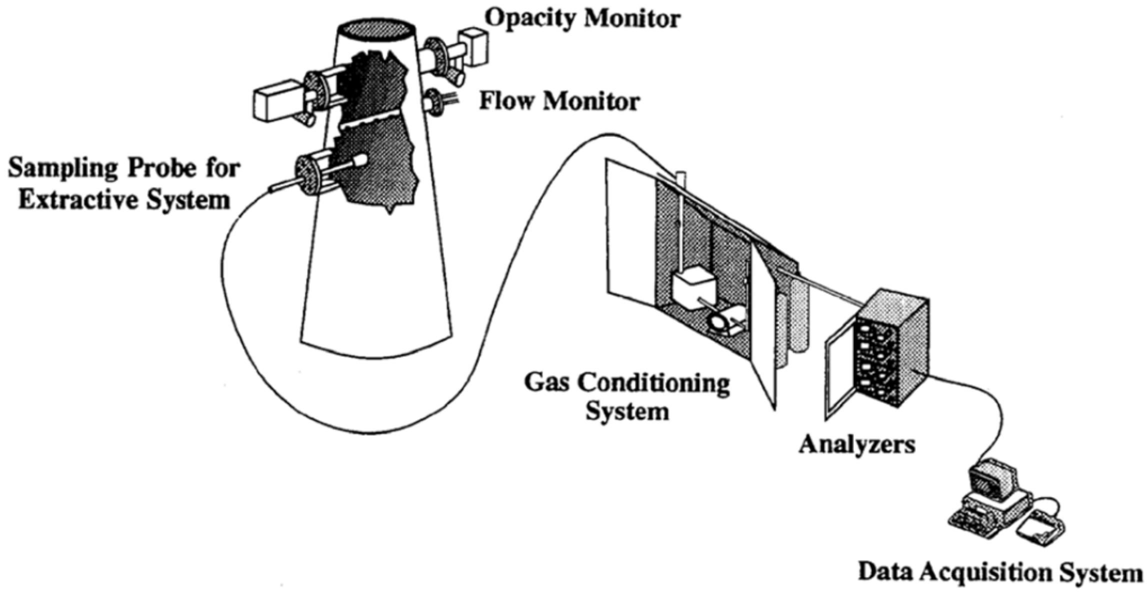

FIGURE 1. TYPICAL CONTINUOUS EMISSION MONITORING SYSTEM

TABLE I. PHYSICAL PROPERTIES OF COATINGS

	MODIFIED SILICON	CARBOXYSILANE	PTFE/PFA
Max Temperature	450ºC	450ºC	260ºC
Min Temperature	-196ºC	-100ºC	-240ºC
Low pH limit	0	0	0
High pH limit	7	14	14
Thickness	0.12um to 0.5um	0.5um to 1.5um	25um
Adhesion	Very Good	Very Good	Poor
Wear resistance	90% of Stainless	2X improvement	10% of SS (est.)
Moisture contact	87°	88-140°	125°
Inertness vs. SS	Very Good	Very Good	Very Good

EXPERIMENTAL

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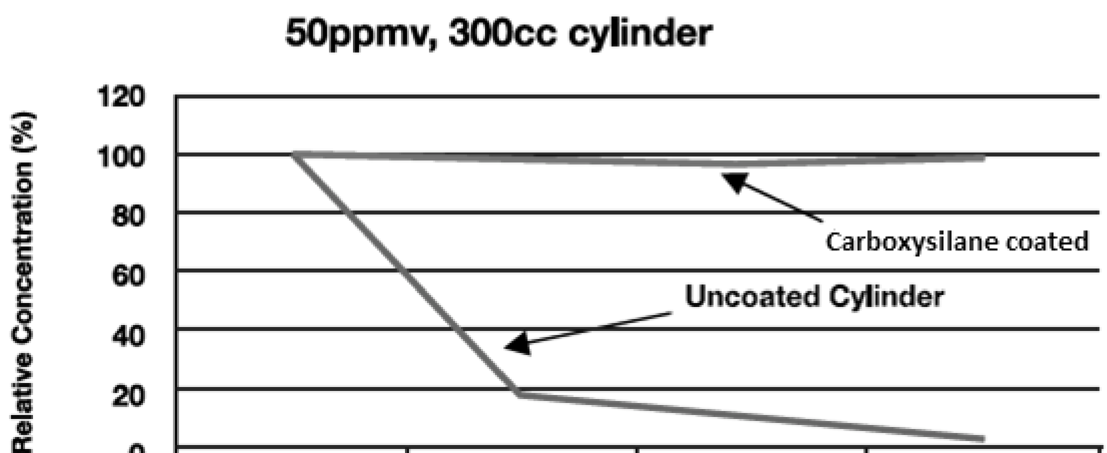
Analytical systems must address the activity of stainless steel components. These components commonly include sampling probes, filtering devices, transfer tubing, connectors, flow cell and flow path components.

The most commonly analyzed class of compounds benefiting from the use of coatings are sulfur containing, most importantly hydrogen sulfide. Sulfur compounds such as hydrogen sulfide, carbonyl sulfide and mercaptans strongly adsorb to the surfaces of stainless steel(3). Using the modified silicon based coatings on analyzers components and flow streams without any concerns for erosion or corrosion produces very reliable, stable and reproducible analytical results(4).



	0:00	25 hours	50 hours	75 hours
Stainless Steel	100	19	10	4
Carboxysilane	100	98	96.6	98.3

FIGURE 2. SULFUR COMPOUNDS AT 50 PARTS-PER-MILLION IN CARBOXYSILANE TREATED STAINLESS STEEL CONTAINERS VERSUS NON-TREATED CYLINDER

In Figure 2 and 3, the degradation of hydrogen sulfide on bare stainless steel is rapid and irreversible: Both at 50ppm and 17bbp levels, H_2S is lost within 24 hours.

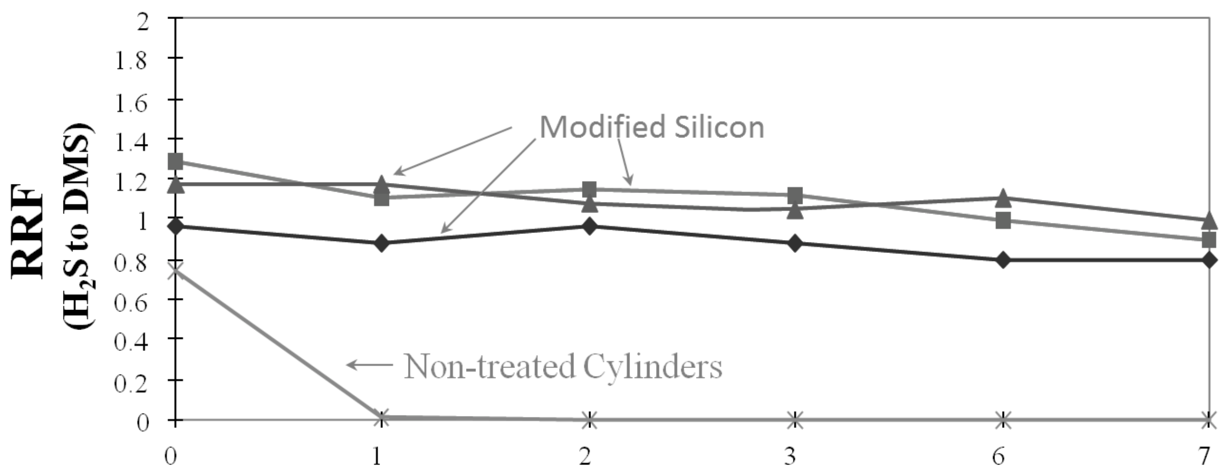


FIGURE 3. SULFUR COMPOUNDS AT 17PPBV IN AMORPHOUS SILICON TREATED STAINLESS STEEL CONTAINERS

Commercially available inert coated components have eliminated the need for traditional flow through passivation techniques for active compounds. Using the flow through passivation method an analyst was required to continuously flow sample or high concentrations of the active compounds to assure all adsorptive sites were occupied. These methods often produced poor reproducibility and could not respond well to changes in sample concentrations as the sample stream concentration would be required to reach equilibrium with the number of surface adsorbed molecules.

Table II contains a list of many common active components and coatings recommended to improve the performance of analytical systems in the given application.

TABLE II. COMPATABILITY OF COMMON COATINGS AND DIFFICULT TO ANALYZE SPECIES

	MODIFIED SILICON	CARBOXYSILANE	PTFE
Sulfurs at ppb levels	X		X
Sulfurs at ppm levels	X	X	X
Moisture	X	X	X
Ammonia(5)	X		X
Mercury(6)	X		X

The effect of moisture on sampling systems can produce poor stability of active compounds. Figure 4 demonstrates the impact of a non-dry, inert sampling cylinder used for storage of hydrogen sulfide. The cylinder in this experiment was simply left open to room air prior to nitrogen purge and fill with hydrogen sulfide containing standard. The moisture containing cylinder demonstrates more loss of hydrogen sulfide then a non-moisture containing cylinders. As a result, a growing request for sample system and analyzer components is reduced hold-up of water. Through reduction of water retention on the surface, analyzer responses after maintenance or water containing "upsets" are minimized and analyzer output data confidence increases.

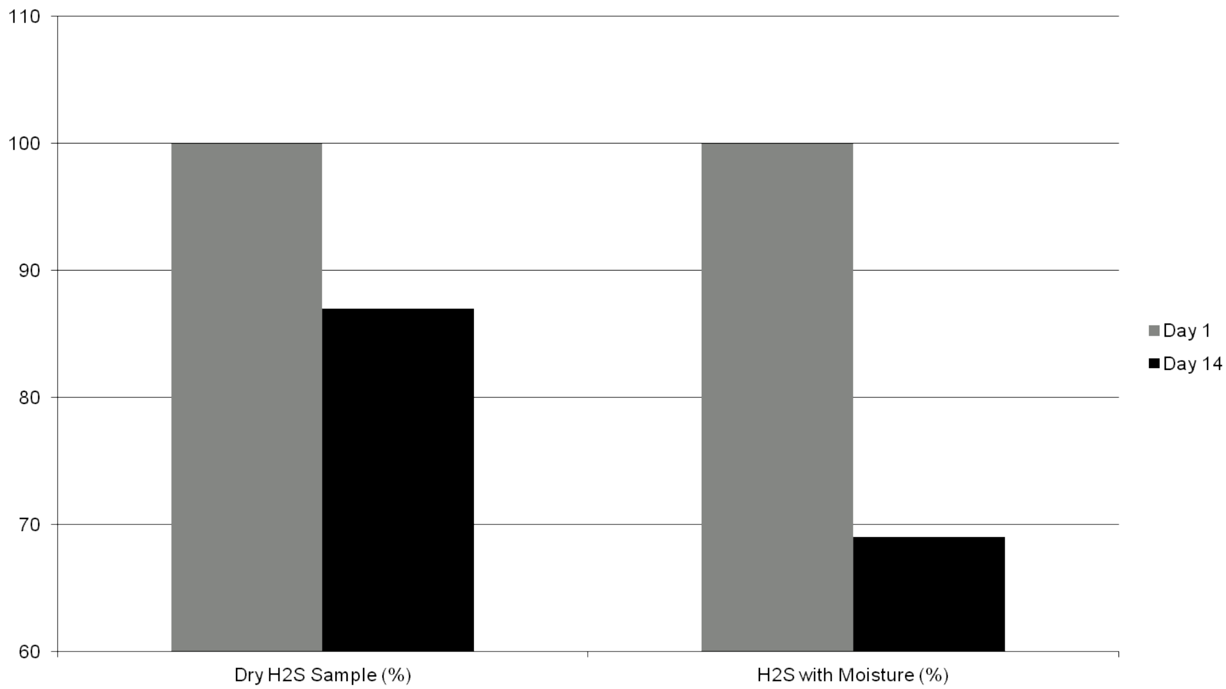


FIGURE 4. HYDROGEN SULFIDE LOSSES DURING SAMPLING WHEN IN CONTACT WITH MOISTURE

A hydrophobic surface will dry quicker and result in an analytical system that is more reliable and reproducible given a larger range of operating conditions. A surface that is hydrophobic is critical in refining and petrochemical applications. Many of the streams are very dry but an upset in process conditions will lead to moisture in the sampling system. This moisture will adversely affect analysis because of the polarity of the water in the system. The faster a system can "dry" of any moisture, the faster the analytical system will begin to generate reliable data.

Table III demonstrates contact angle data for a variety of different surfaces and coatings. Contact angle is the measure of the angle of a drop of water on a surface. A perpendicular measurement would be 90 degree contact angle. The higher the contact angle, the lower the surface energy and the more hydrophobic the surface becomes.

TABLE III. CONTACT ANGLE OF DIFFERENT COATINGS

DI Water	304 SS	Silicon	Modified silicon	Carboxysilane	PTFE
Advancing	36	53.6	87.3	105.5	125.4
Receding	5.3	19.6	51.5	85.3	84

Coatings and alloys are often solutions to systems that are in corrosive environments such as on off-shore platforms or corrosives containing refining and petrochemical streams. As each application in a corrosive environment has a specific given temperature and concentration, it is always recommend to prove out useful life using actual samples of the coating or alloy of choice prior to re-fit of the analytical system.

Table IV provides the results obtained from ASTM G31[7] testing of a variety of acids on bare 316L stainless steel, carboxysilane coated 316L samples and silicon coated 316L samples. The method is an immersion test for 24 hours in a solution at room temperature and pressure. After immersion, differential weighing allows the amount of material loss to be determined. Three samples of each configuration were tested.

TABLE IV. WEIGHT LOSS AFTER 24 HOUR EXPOSURE DURING ASTM G31 TESTING

	316L SS	SILICON COATED	CARBOXYSILANE COATED
24HR; 6N HCl; 22ºC			
MPY (mils-per-year)	114	1.8	2.7
Improvement Factor	---	63	42
24HR; 6N HBr; 22ºC			
MPY (mils-per-year)	3.4	0.5	0.8
Improvement Factor		6.8	4.2
24hr; 5% HF; 22ºC			
MPY (mils-per-year)	120	44.3	80.4
Improvement Factor		2.7	1.5

24HR; 25% H2SO4; 22ºC			
MPY (mils-per-year)	54.6	23.6	5.4
Improvement Factor		2.3	10.1
24HR; CONCENTRATED HNO3; 22ºC			
MPY (mils-per-year)	0.78	0.36	0.1
Improvement Factor		2.2	7.8
24HR; 85% H3PO4; 22ºC			
MPY (mils-per-year)	0.62	0.28	0.08
Improvement Factor		2.2	7.7

Use of inert silicon based coatings for cycling components such as valves results in a system that requires periodic re-coating of the valves. The silicon based coatings have a higher coefficient of friction compared to steel and wear at a faster rate. Development of new analytical system coatings should produce a layer that has a lower coefficient of friction and a slower wear rate compared to stainless steel. Table V summarizes the data obtained from wear studies conducted on both non-treated and treated surfaces. Data was generated to ASTM G133(8) using a pin-on-disk tribometer (Nanovea, Irvin, CA). Results from this experimental method can produce wear behavior and friction coefficients of the plate surface(9). Table VI summarizes the coefficient of friction data.

TABLE V. WEAR PROPERTIES OF COATINGS

PIN ON DISC; 2. Disc; 2.0N	316L STAINLESS STEEL	CARBOXYSILANE COATED 316L STAINLESS STEEL	SILICON COATED 316L STAINLESS STEEL
Wear rate ($x10^{-5} mm^3/N\ m$)	13.810	6.129	2
Improvement Factor over SS	---	2 times	1/3 times

TABLE VI. COEFFICIENT OF FRICTION DATA

	AVG. COEFF. OF FRICTION
Uncoated SS	0.589
Carboxysilane	0.378

CONCLUSIONS

Building on previous study(10) to support the conclusion that coated analytical systems will demonstrate improved reliability, durability while tightening the reproducibility of data generated. With increasing demands on analyzer systems in the field and on processes, new developments are needed to provide equivalent levels of inertness to today's silicon based coatings along with enhanced corrosion protection and resistance to wear. Carboxysilane compounds are demonstrating all of the physical and corrosion improvements while continuing to show improving inertness.

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