

A Study of Regulators for Delivering Gases Containing Low Concentrations of Hydrogen Sulfide



Four regulators have been compared for use with low-level reactive mixtures. It was verified experimentally that a two-stage low-volume regulator made of stainless steel was suitable for use with hydrogen sulfide at a concentration of 100 ppb. This regulator does not require passivation when used with flow rates of at least 100 mL/min. Aluminum and nickel-plated brass regulators of the same design were not suitable. Although a traditional two-stage corrosive service regulator constructed of stainless steel could be used, significant passivation times were required to achieve a comparable steady-state level.

As the requirement for the measurement of low levels of sulfur compounds continues, users must find a reliable way to monitor, control, and regulate these gaseous compounds. Instrument manufacturers have been decreasing the lower level of detection into the low parts-per-billion range, and sulfur-containing standards are now available at concentrations of 50–100 ppb (1). The primary issue now becomes how to regulate and deliver these mixtures to the detector.

The primary function of a regulator is to reduce the pressure of a gas to a lower, safer, and more usable level. An equally important function is providing pressure regulation without altering the composition of the gas by a reaction of the gas with the surface of the regulator. This is especially true for reactive or corrosive gases such as hydrogen sulfide, carbonyl sulfide, and sulfur dioxide. For example, hydrogen sulfide is known to react with copper to form copper sulfide and hydrogen. For a pure hydrogen sulfide-containing gas, a few hundred parts-per-million reacting with and adsorbing onto the internal copper surfaces of the regulator would not be noticeable.

If a regulator made of a copper-containing material were to be used for relatively low concentrations of hydrogen sulfide, much or all of the hydrogen sulfide would react with

the copper surface or adsorb onto other surfaces. As a result, the observed concentration of hydrogen sulfide at the outlet of the regulator would be reduced significantly. This undesirable effect could be avoided partially by the use of materials not containing copper or copper alloys. However, even if copper or copper alloys are avoided, this undesirable effect might still be present if trace amounts of hydrogen sulfide are being used.

Surface area also is an important consideration. To minimize any potential reactions or interactions with the wettable surfaces of the regulator, the residence time of the gas in the regulator must be minimized. It also is recognized that high surface-area materials take longer to dry (2). Residual moisture in the regulator can increase the probability of surface reactions and corrosion (3) and eventual regulator failure. To minimize these reactions, the surface area (volume) must be minimized.

This article focuses on the issue of choosing an appropriate regulator whose materials of construction and design will minimize the loss of low-concentration reactive gas mixtures.

Experimental

A Sievers model 355 sulfur chemiluminescence detector (Ionics Instruments, Boulder, Colorado) that was interfaced to a Varian model 3800 gas chromatograph (Walnut

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Creek, California) was used. The column used was a 30 m × 0.32 mm Varian fused-silica PLOT column. A Silcosteel-coated gas-sampling valve (Restek Corp, Bellefonte, Pennsylvania) was used to introduce the samples into the gas chromatograph. Silcosteel-coated tubing was used for all lines the sample came in contact with, including the 1-mL sample loop. Flow controllers were manufactured by MKS Instruments (model 1479A, Andover, Massachusetts), and mass flow meters were manufactured by Aalborg Instruments and Controls (model GFM171S, Orangeburg, New York).

All calibration standards and gases used in this study were obtained from Air Liquide America L.P. (Santa Fe Springs, California).

Regulator Comparisons

A 198 ppb hydrogen sulfide cylinder was attached to the regulator inlet. The regulator outlet was connected to a stainless steel mass flow controller delivering a constant flow rate directly to the sulfur chemiluminescence detector. The mass flow controller had been in use with hydrogen sulfide for an extended period of time and should therefore exhibit very little or no interaction with hydrogen sulfide because of passivation. A control experiment was performed in which a regulator was not used to determine any reactivity related to the mass flow controller. By examining the difference in signals between the various regulators and the control, the effect of the regulator's materials of construction and wettable surface area could be determined. The corrosive service regulator had some prior service history with hydrogen sulfide, and the nickel-plated brass regulator had been used with an inert gas. A 198 ppb hydrogen sulfide sample in balance nitrogen was used at a flow rate of 20 mL/min for this evaluation. The sample was flowing continually through the regulators and directly into the analyzer.

Effect of Flow Rate

The materials of construction for regulators used in this evaluation are listed in Table I. Regulators A and B were prototypes obtained from Air Liquide America L.P. (Cambridge, Maryland). These are both low-volume (low wettable surface area) regulators having a piston as the first stage and a diaphragm as the second stage. The corrosive service regulator, regulator C, was a conventional two-stage stainless steel corrosive service regulator. Regulator D was a model 1002 Calgaz regulator (Air Liquide America L.P.) similar in design to regulators A and B.

The orifice used for comparison was

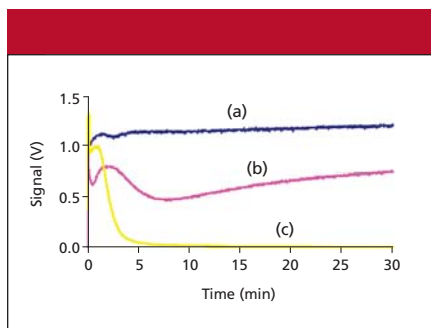


Figure 1: Initial comparative study using 198 ppb hydrogen sulfide in balance nitrogen with (a) a reference value obtained using an orifice, (b) a traditional two-stage corrosive-service regulator, and (c) a low-dead-volume nickel-plated brass regulator.

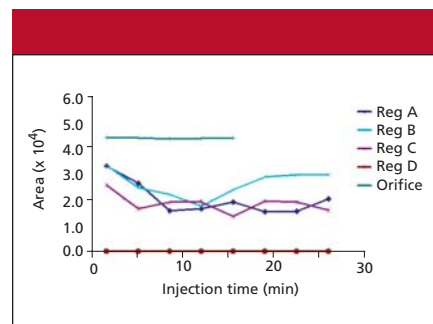


Figure 2: Regulator comparison with 100 ppb hydrogen sulfide flowing at 5 mL/min. Reg A = low-volume two-stage stainless steel regulator, Reg B = low-volume two-stage aluminum regulator, Reg C = conventional two-stage stainless steel high-volume corrosive-service regulator, Reg D = low-volume two-stage nickel-plated brass regulator.

approximately 30 μm and was made from Hastelloy and subsequently coated with Sulfinert™.

At low flow rates, the gas remains in the regulators for a longer period of time, and thus, any type of reactivity between the gas and the regulator materials should be observed more easily. The mass flow controller was placed downstream from the gas chromatograph to accurately control the flow rates at the lower values and to avoid any type of reactivity of the sample with the mass flow controller's materials of construction. In this experiment, the pressure of the sample line was kept constant and the flow rate was changed. By keeping the pressure constant, the amount of gas entering the analyzer essentially was the same even though the flow rates were different. The different flow rates provide different contact times with the regulator and the tubing. The tubing volume was kept to a minimum and the tubing was coated with Sulfinert™, so therefore the main source of reactivity should be the regulators. In this configuration, a direct comparison between the signal from the regulators and the orifice should not be made because of differing pressures present in the sampling loop. The pressure in the sample loop when testing the regulators was 23.4 psia and 14.7 psia when using the orifice. The signal obtained from the orifice should be used as a reference and always should be less than that from the regulators. Regulators A and B were new without any prior service history. Regulator D had been used in inert gas service previously, and regulator C had some prior service history with hydrogen sulfide.

Requirement for Passivation

To assess the effect and requirement for reg-

ulator passivation, new regulators without any prior service history were compared with passivated regulators. The regulators used in the flow evaluation might have experienced some activation or deactivation of their surfaces as a result of this previous history. A new corrosive-service two-stage regulator was used and compared with one that had been in service for more than two years. The regulator first was tested at 5 mL/min and then at 100 mL/min. A similar method was used for comparing the stainless steel low-volume piston regulators.

Results and Discussion

When examining the data, it is important to understand the various sources of error. It is believed that the main source of experimental error in these experiments results from the sulfur chemiluminescence detector (4). The relative standard deviation of successive analyses typically varies within a range of 2–6%. It also has been observed that the system response can drift significantly during the day. Periodic runs of various references were performed to determine if this occurred during the analysis.

There are various characteristics to study when examining the signals from the regulator evaluations. Any decrease in signal levels would suggest some level of reactivity. A linear, exponential, or power increase or decrease would suggest strong reactivity. A logarithmic increase would indicate some type of reactivity but with passivation or loss of reactivity with time (adsorption or reaction until active sites are consumed or filled). An immediate steady-state signal response would indicate either no reactivity or a constant reactivity. One might be able to distinguish between the two steady-state possibili-

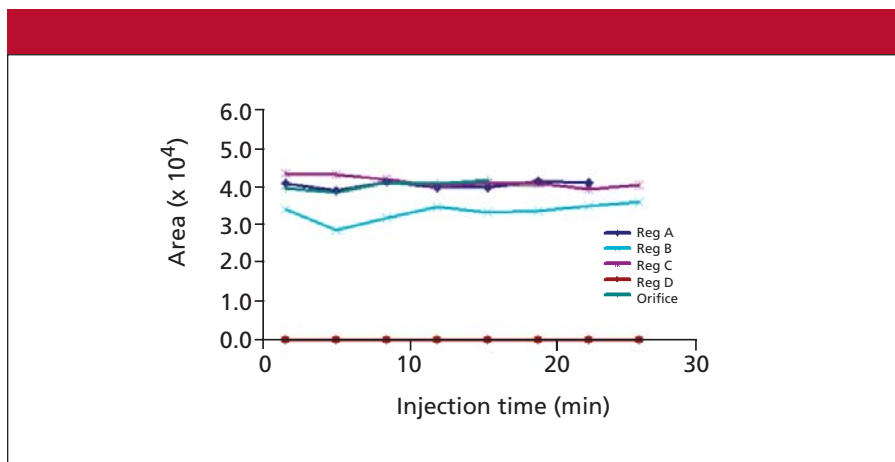


Figure 3: Regulator comparison with 100 ppb hydrogen sulfide flowing at 50 mL/min. Reg A = low-volume two-stage stainless steel regulator, Reg B = low-volume two-stage aluminum regulator, Reg C = conventional two-stage stainless steel high-volume corrosive-service regulator, Reg D = low-volume two-stage nickel-plated brass regulator.

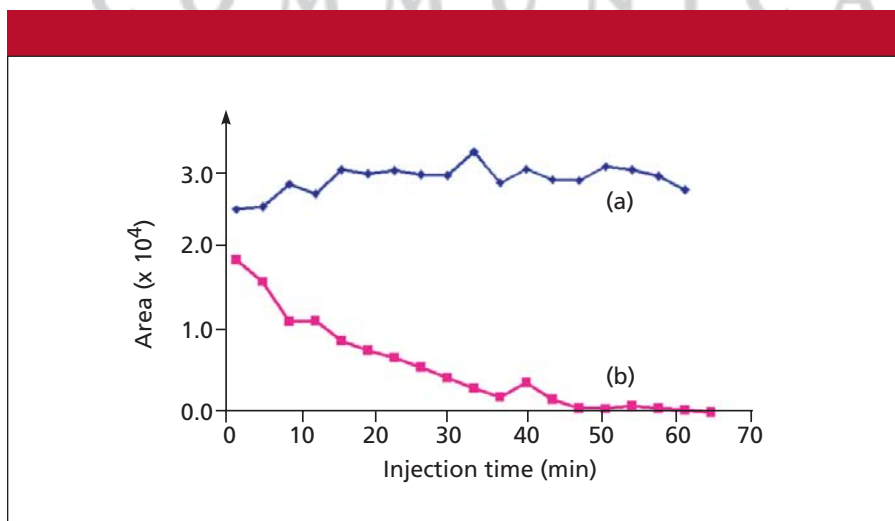


Figure 4: Effect of passivation on traditional two-stage corrosive regulators with a 5-mL/min flow of 100 ppb hydrogen sulfide in balance nitrogen. Shown are results obtained using (a) a fully passivated regulator and (b) a new regulator.

ties by comparing the result with the control experiment, which is assumed to have no reactivity.

Regulator Comparison

The effect of the regulator on the delivery of a 198 ppb hydrogen sulfide balance nitrogen mixture was evaluated by comparing the response through a standard two-stage corrosive-service regulator with a high surface area (regulator C, Table I) with a low-volume regulator that was nickel-plated brass (regulator D, Table I). The reference value for 198 ppb hydrogen sulfide was obtained by removing the regulator. Referring to Figure 1, the addition of the regulator clearly affects the experimental results. As passivation of the gas on the surface approaches completion, the signal is

observed to increase. For the low-volume nickel-plated brass regulator, the signal quickly diminishes as the gas reacts with the regulator surface.

The initial rise in concentration observed with both regulators probably is due to the residence time of the gas in the regulator. When the cylinder is opened, the gas entering the regulator immediately exits and thus has little time to react with the regulator. The gas eluted later appears to have a sufficient residence time to react completely with the regulator materials.

Effect of Flow Rate

If a regulator is truly nonreactive with the sample gas, there should not be any dependence upon the flow rate. That is to say, increasing the contact time of the reactive

gas with the regulator surfaces should have no effect on output concentration. This effect was examined by looking at four flow rates of a standard containing 100 ppb hydrogen sulfide balance nitrogen: 5, 10, 50, and 100 mL/min.

Referring to Figure 2, at a hydrogen sulfide flow rate of 5 mL/min, the stainless steel regulators (regulators A and C) and the aluminum regulator (regulator B) illustrated similar behavior after the first four injections. The behavior is characterized by a significant decay in the initial signal. After four injections, the regulator signals stabilized to varying levels. The nickel-plated brass regulator (regulator D), however, never showed an increase in signal.

As the flow rate of the hydrogen sulfide standard was increased to 10 mL/min, the performance of the regulators improved. The signals were relatively steady although the steady-state values were significantly lower than the control. The aluminum regulator still showed a decrease as a function of time and the nickel-plated brass regulator showed no signal. At a standard flow of 50 mL/min (Figure 3) and 100 mL/min, both stainless steel regulators behaved similarly. The signals were similar to that of the orifice and invariant in time. The aluminum regulator yielded a slightly lower signal level at 50 mL/min and a comparable signal level at 100 mL/min. As before, the nickel-plated brass regulator yielded no signal at all.

It is a general trend for the regulators to give a more stable result with the higher flow rates. There does not appear to be a significant difference in the repeatability of the data obtained from the regulators when flow rates are in excess of 50 mL/min. However, it appears that the magnitude of the signal for the aluminum regulator at 50 mL/min is less than the signals for the stainless steel regulators.

The Requirement for Regulator Passivation

A comparison of the behavior of regulators in previous service (passivated) with new regulators (without previous use) was made. The previous service regulators had been passivated and utilized. The regulators were tested at two flow rates with 100 ppb hydrogen sulfide: 5 mL/min and 100 mL/min. The effect of the 5-mL/min flow rate can be observed in Figure 4 for both the new and passivated conventional two-stage regulators. While the regulator that was previously passivated shows a fairly constant response, the signal observed from the new regulator quickly decays. Subsequently, the new regu-

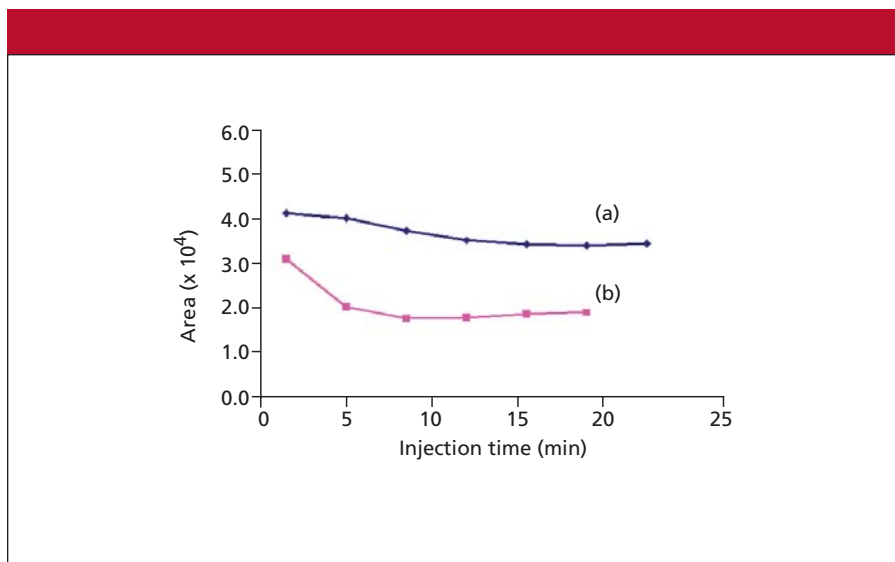


Figure 5: Effect of passivation on a stainless steel low dead volume regulators with a 5-mL/min flow of 100 ppb hydrogen sulfide in balance nitrogen. Shown are results obtained using (a) a fully passivated regulator and (b) a new regulator.

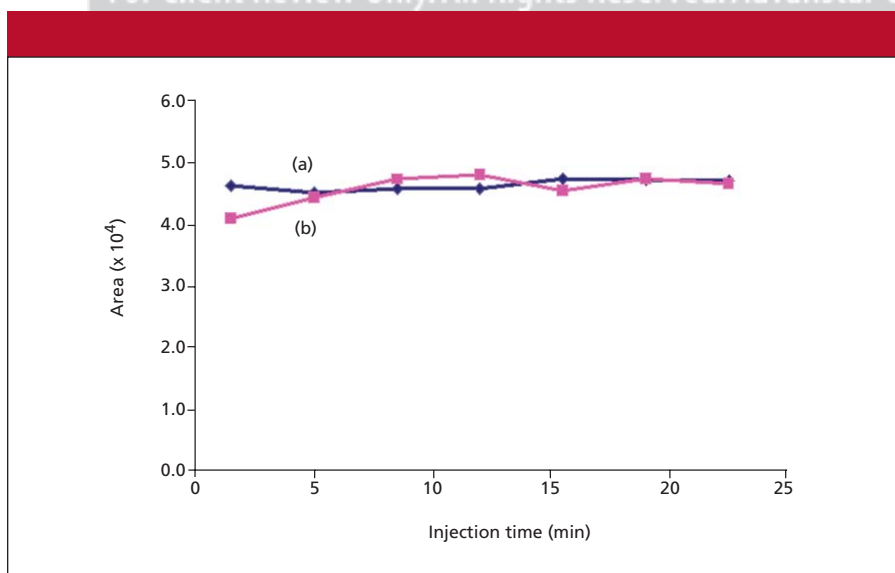


Figure 6: Effect of passivation on a stainless steel low dead volume regulators with a 100-mL/min flow of 100 ppb hydrogen sulfide in balance nitrogen. Shown are results obtained using (a) a fully passivated regulator and (b) a new regulator.

Table I: Description and materials of construction of evaluated regulators

Regulator Part	Reg A	Reg B	Reg C	Reg D
Body	SS 316	Aluminum	316 SS	Ni plated brass
Diaphragm	SS 304	SS 304	SS 316	SS 304
Seat	Teflon, Viton	Teflon, Viton	PTFE	Teflon, Viton
Filter	None	None	316 SS	Brass
Gauge	SS 316	None	3136 SS	Cr plated brass

lator was passivated overnight with 5000 ppm hydrogen sulfide in balance nitrogen. The signal of the 100 ppb hydrogen sulfide standard was monitored subsequently at a flow rate of 100 mL/min. The signal intensity of the previously passivated regulator

yielded a 33% higher signal than that obtained from the partially passivated regulator at 100 mL/min, indicating that surface adsorption and passivation occurs on the surface of the partially passivated regulator.

For the stainless steel low-volume regula-

tor, the difference between a new and passivated regulator was not as significant at 5 mL/min (Figure 5). At the 100-mL/min flow rate of the standard (Figure 6), there was no observable difference between the passivated regulator and a second new regulator without previous service. This probably was a result of the smaller wettable surface area of the piston-style regulator compared with the traditional two-stage corrosive-type regulator.

Conclusion

Materials of construction and wettable surface area of regulators play important roles for use in low-level corrosive-reactive gas service. Nickel-plated brass regulators never should be used for parts-per-billion level mixtures of hydrogen sulfide. The major advantage that the low-volume two-stage regulator (5) has when compared with the conventional large-volume, two-stage, corrosive-service regulator is that no passivation is necessary before use. This is expected to decrease the time required for analysis and calibration.

The excellent performance of this regulator is due not only to the materials of construction but also to the decreased residence time of the gas in the regulator. This lower residence time minimizes contact of the gas with the regulator's wettable surface areas, thereby decreasing the probability of any surface reactions. This will provide better reproducibility of data because of the greatly diminished surface reactions.

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