

## **DETERMINATION OF HYDROGEN SULFIDE AND TOTAL SULFUR IN NATURAL GAS**

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Hydrogen Sulfide, ( $H_2S$ ) found in natural gas and crude oil, was formed when animal and vegetable matter decayed in the absence of oxygen. Although we generally give credit to the dinosaurs for the oldest and largest sources, we are still generating this dangerous and unstable compound today in landfill, waste water treatment and as a byproduct in chemical and petrochemical processes. The need to detect, quantify and control Hydrogen Sulfide was met in the early 1970's when an industrious group in Houston Texas created the first commercial Hydrogen Sulfide Analyzer. The detection and analysis of Hydrogen Sulfide left the lab and became a valuable field instrument. Their methodology was simply a roll of paper tape, impregnated with a solution of Lead Acetate ( $C_4H_6O_4Pb$ ) and Acetic Acid ( $CH_3COOH$ ). The paper tape was humidified by bubbling the sample gas through a solution of 5% Acetic Acid (95% distilled water), and then directing the gas to a detector block that allowed a very small aperture to expose the tape to any Hydrogen Sulfide that might be present in the gas stream. The Hydrogen Sulfide with the Lead Acetate to form a dark stain of Lead Sulfide ( $PbS$ ). The challenge was to determine exactly how to calculate the darkness of the stain in relation to the concentration of Hydrogen Sulfide present in the gas sample.

### **Note:**

Hydrogen Sulfide is very unstable and will absorb into almost any material, especially water. If the bubbler were filled with pure water, the Hydrogen Sulfide would absorb into the water, creating its own scrubber. As the bubbler solution becomes saturated with Hydrogen Sulfide, the analyzer will indicate a higher level of the compound, making the results unpredictable. The use of 5% Acetic Acid creates a buffer zone that permits the humidification of the Hydrogen Sulfide without losing any of it to the bubbler.

These early analyzers used an incandescent bulb to illuminate the paper surface, and a magnetic drive moved the paper tape slowly across the aperture. Lots of moving parts, and unpredictable chemical reactions caused by the hot incandescent bulb, made the accuracy and dependability of these early analyzers difficult. In spite of the initial problems with Lead Acetate Tape Analyzers for Hydrogen Sulfide, the need to protect the workers from this deadly gas and the process equipment from its highly corrosive nature quickly made this technology the most dominant and successful means of meeting safety and health requirements in the natural gas industry.

Throughout the 1970's, 1980's, 1990's, the technology was tweaked and improved by replacing the bubbler with a more advanced humidifier, that maintained the amount of humidification, regardless of the fluid level of the Acetic Acid solution. High bubbler levels caused liquid carryover and wet or broken tape. The incandescent bulb was replaced with a light emitting diode (LED) to eliminate the heat issues (converting Methyl Mercaptan to  $H_2S$ ) and unpredictable longevity and output of the bulb. The most significant improvement was the development of a "rate of change" program that measured the staining or darkening of the tape in split-seconds, as it was actually happening. With this advance, the detectable range of the paper tape analyzer grew from 0-10 part per million (ppm) to 50 parts per billion (ppb) to

100%. The industry now had an analyzer that could offer repeatability, zero drift, and an interference-free analysis. The advances in control outputs (analog and digital) meant that Gas Control in far away locations could watch, control and manipulate the process in real time. By the end of 2001, there were more than 2,000 of the lead acetate paper tape analyzers in operation in North America alone.

### **The Addition of Total Sulfur Analysis:**

The need to determine the total concentration of sulfur compounds, including sulfur-based odorants is accomplished very simply by subjecting the sample gas to a "furnace" or "pyrolyzer" and introducing Hydrogen to the sample stream. In this Hydrogen rich and heated environment, the Sulfurs are converted to Hydrogen Sulfide. The standard Lead Acetate Paper Tape can then provide Total Sulfur detection down to less than 50 PPB (parts per billion).

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### The Disadvantages:

Every man made creation has its' limits and shortcomings. The Lead Acetate Tape Analyzer is no exception:

### The Bubbler/Humidifier:

The bubbler/humidifier solution is basically vinegar, but with a major difference. Most sources of water contain minerals that can taint or skew the results, since Hydrogen Sulfide will react with them. Distilled water from stainless steel distillers can also provide contaminants that will alter the final H<sub>2</sub>S reading. To provide the required humidification, without impacting the accuracy of the analyzer, the water must be distilled in glass-lined vessels, and then stored in lab grade glass containers. Once the bubbler/ humidifier is filled with the proper amount of 5% Acetic Acid solution, the temperature inside the analyzer cabinet must be kept above freezing by an electric or catalytic heater.

### The Dilution System:

Most analyzers during the 1970-1990 period, required that the sample gas be diluted beyond 50 ppm concentration. The reaction of the Lead Acetate with the Hydrogen Sulfide would accelerate the staining of the paper to a point where the analyzer could not accurately record and display the results. By diluting the sample stream (50% H<sub>2</sub>S/50% Methane or instrument air) the analyzer could handle higher concentrations of the gas. The dilution process required valves and regulators that could cycle swiftly, and repeatedly without failure, which added complexity and cost to the analyzer.

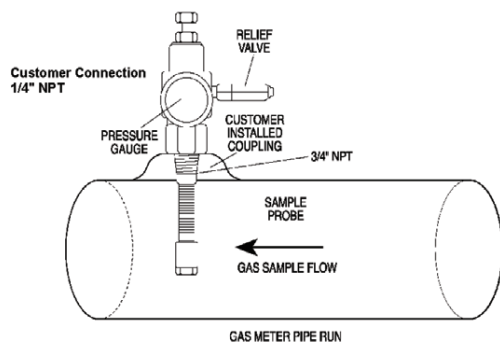
### Lead Acetate Tape:

The paper tape (60% cotton) is saturated with the Lead Acetate crystals by pulling the tape through a bath and then a series of heaters to dry the tape prior to spooling on a cardboard hub. Sealed in a Mylar envelope, the tape can easily offer a five year shelf life. As mentioned above, the Lead Acetate Tape will have dots of Lead Sulfide when exposed to the sample stream. The used or discarded tape will then contain a mixture of both Lead Acetate and

Lead Sulfide, which must be handled with care. The spent or used tape will not leach into the ground water in its' present state, but the EPA requires that the waste be treated as hazardous waste and disposed of accordingly, to avoid exposure by handling or breathing the -dust from the Lead Acetate/Lead Sulfide saturated paper.

### Gas Sample Preparation:

As with any analytical equipment, the Lead Acetate Tape Analyzer requires an adequately prepared sample, free of water or contaminants, and transported to the analyzer in a predictable manner (.4 scfh) for the analyzer to have a stable baseline. Sample probes, inserted to the center of the pipe or meter run will provide the most accurate and contaminant-free sample. Care must be taken to keep any component in the sampling system from leaching out the Hydrogen Sulfide from the gas sample stream, thus causing low or inaccurate readings. Brass, carbon steel, aluminum, most plastics, Tygon tubing, gum rubber and most gasket materials will absorb the unstable gas. Stainless steel and teflon offer the best combination.



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### The Significance of the Change to Silver Tape:

Remember the bubbler?.....the scrubber, dilution system, heater....and the hazardous waste issues?

The Silver Nitrate impregnated paper tape does not have any of these components or concerns. The analyzer will operate from -SOC to +SOC without temperature controls, as well as without humidification or dilution. Also, the Silver Nitrate is EPA classified as non-hazardous and can be handled and disposed of as you would common household waste. The interferent-free analysis is identical to Lead Acetate, but the actual footprint of the unit is significantly smaller (8X18X18 inches vs 14X30X50 inches) as shown below.

0-50ppm Hydrogen Sulfide Analyzer, (Lead Acetate Tape)  
Fiberglass or steel cabinet circa 1990



(14"X30"X50" Cabinet)

0-50 ppm Hydrogen Sulfide Analyzer, (Silver Nitrate Tape)  
Stainless steel cabinet circa 2013



(8"X18"X18" Cabinet)

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### **Conclusion:**

The technology that began in a small South Texas shop in the early 1970's has been tweaked, modified and updated throughout its' 40+ years to become the most reliable and dominant method of detecting and analyzing Hydrogen Sulfide worldwide. The recent (2010) introduction of Silver Nitrate Tape for H<sub>2</sub>S and Total Sulphur analysis will surely carry the technology forward indefinitely.



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