



Total Sulphur and Total Chlorides in Gas and Liquefied Petroleum Gas (LPG) Samples

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Over the last decade, the importance of detecting sulphur and chlorides in gas and LPG products has increased dramatically. This is likely related to the necessity of complying with increasingly stringent government regulations, protecting expensive catalysts, and ensuring product quality. Reasons for detection and control of sulphur and chlorides in different process streams have existed for the last fifteen years, but detection limits have been reduced dramatically in recent times. For example, in order to protect expensive, sulphur-intolerant catalysts, the production feed for polypropylene or polyethylene must be monitored for sulphur and chloride content. The sulphur and chloride analyser used in this application must now have the ability to detect sulphur and chlorides from 1 parts per billion to 10 parts per million.

It is known that the corrosion in a refinery has a significant impact on the profit and safety of the plant. Both sulphur and chlorides play a big role in corrosion related problems. The corroded pipeline or vessel is always a safety concern.

Organically bound chlorides form hydrochloric acid in the process lines. Hydrochloric acid, present as impurity, is the main cause of corrosion of pipelines, vessels and valves.

This paper describes and evaluates one laboratory analyser that can detect both Total Sulphur and Total Chlorides with high levels of accuracy, speed and high degree of automation. The detection of Total Chlorides using titration technique is maintenance intensive. There is a weekly requirement to clean the electrodes and change the solutions. Now there is an option in the market.

Until recently, two separate analysers were required to measure Total Sulphur and Total Chlorides in LPG samples. Some vendors offer the detection of 'chlorides by titration' as an expensive option for the Total Sulphur Analyser. Now, one analyser can perform both these detections from low ppb levels to high ppm levels. This is the Dry Colorimetric Detector for dual detection.

Dry Colorimetric Detector

Introduction

Classical colorimetry utilises an impinger to collect gas in a liquid medium. Chemical reagents are then added to the medium to cause it to change color in proportion to the concentration of gas present. The resulting color change is measured by a laboratory spectrophotometer and compared to known standards.

Ultra-sensitive "tape" detectors are also colorimetric based, but these are dry reaction substrates that serve

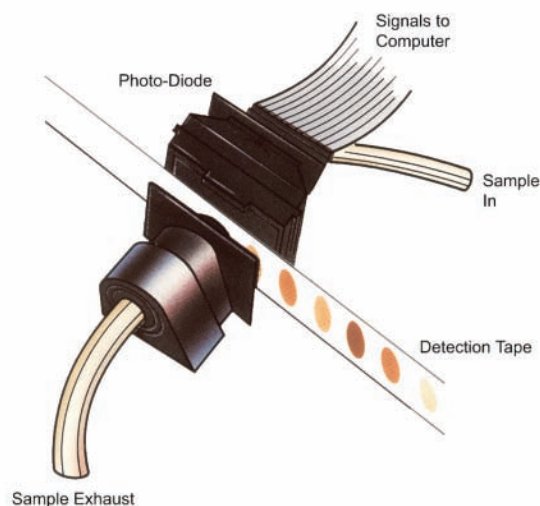


Figure 1 : C.I. Analytics Dry Colorimetric Detection System

as gas collecting and analysing media. Individually formulated for a specific gas or family of gases, each detection tape is a non-toxic, proprietary chemical reagent system. When exposed to a target gas, the tape will change color in proportion to the amount of gas: the higher the target gas concentration, the darker the stain that will appear.

The change in color, or stain, on the tape is read by a photo-optical system in the analysis instrument, and the intensity of this stain is then compared to a standard response curve preprogrammed into the instrument's data system.

The Dry Colorimetric Detector: Analytical Technique

During operation, the detection tape is incremented through a sampling "window" where it is exposed to a metered sample stream. If the target gas is present, a stain proportional to the concentration develops. Simultaneously, a beam of light is reflected off the exposed portion of the tape and the intensity of this light is measured continually. As the amount of reflected light decreases due to stain development, the reduction is sensed by a photocell detector as an analog signal. This signal is converted to a digital format, matched to the gas response curve stored in the analyser's permanent memory, and displayed/ documented as the actual concentration value. All of these functions are microprocessor controlled and, in the best cases, carried out by a complete computer.

The use of this spectro-photometric technique, combined with micro-processor and computer control, provides excellent accuracy, repeatability, and sensitivity at low ppb (parts-per-billion) concentrations.

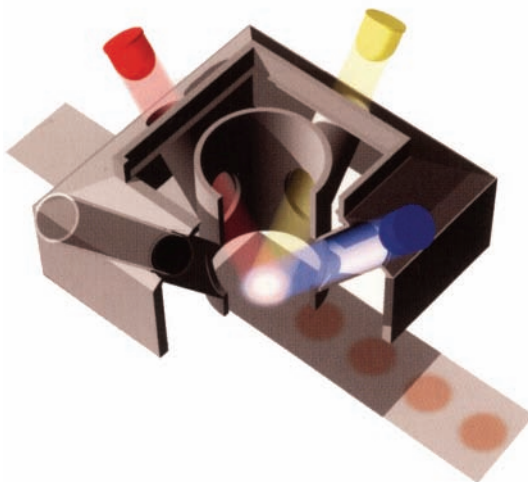


Figure 2 : Inside the Optics Block

Accuracy of Dry Colorimetry for HCl Detection

C.I. Analytics has a Sensi-Tape that specifically responds to Mineral Acids like HCl. Figure 3 below shows 'stains' developed when testing for Total Chlorides in propylene sample. The dry colorimetric detection technique, as outlined above, gives accurate and extremely precise results. Factory calibration of instruments and the detection tape is referenced against NIOSH approved and analytical methods. Both laboratory and field tests have verified that analysers using the Dry Colorimetric method give data in agreement with standard reference methods, as typified by the examples in Table 1.

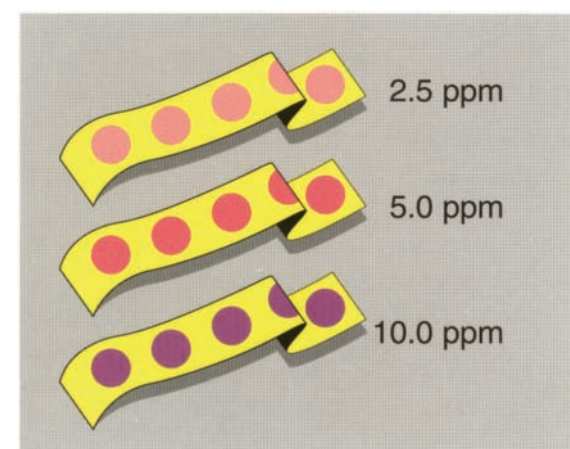


Figure 3 : Typical HCl Stains on Mineral Acid Sensi-Tape

Gas	Concentration as Determined by Standard NIOSH Methods (ppb)	Analyser Reading (ppb)
HCl	200	210
	40	42
	500	504

Table 1 : Dry Colorimetric Results as Compared to Those of NIOSH Standard Method

To Detect	Calculated Concentration of Blends (ppm)	Concentration as Determined by Microcoulometric Detector (ASTM D 5808)	C.I. Analytics Dry Colorimetric Detector
Total Chlorides	2	1.1	1.8
	20	11	19
	200	110	122
Comments		15 minutes per analysis, plus the time to clean-up the cell and change the chemicals	Less than 5 minutes per analysis. No chemicals to change

Table 2 : Dry Colorimetric Results as Compared to other Standard Methods

Accuracy of Dry Colorimetric Detector for Total Sulphur Detection

The most commonly used technique to detect sulphur compounds in petroleum samples is based on a Dry Colorimetric Detector, commonly known as "tape" technology. In this method, organically bound sulphur compounds are first converted to H_2S . The H_2S formed reacts with the moist paper tape impregnated with lead acetate. A sensitive photo-sensor quantifies the change in color of the tape as H_2S passes by the tape and forms black lead acetate.

This detection method is used extensively in the industry for many reasons. First, it is specific to H_2S and according to the claim in ASTM 4045, there are no known interferences. Second, the Dry Colorimetric Detector is extremely sensitive due to the fact that the tape acts as a trap. This is especially true for analysers where the sample passes through the sensitive tape, as opposed to the sample passing by the side of the tape. As more sample passes through the tape, more H_2S molecules are trapped. The "Trap and Release" methods for low level detection are well known. This is on the top of the list. With the Dry Colorimetric detector, the tape is the trap.

One concern with the Dry Colorimetric Detector is with the disposal of lead acetate tape. The actual amount of lead acetate used in this method is so small that the EPA allows the tape to be disposed of like any other paper.

The Dry Colorimetric method has been adapted to gas, LPG and Solid samples. UOP Method 799-08 presents a related technique to quantify Total Chlorides in liquid hydrocarbon samples.

The Conversion and detection principles

Accurate measurement, especially at low ppb levels cannot be made if the flow path of the sample system is not fully inert, or if the vaporisation technique is not configured correctly. When the LPG sample contains heavier sulphur or chloride compounds, the possibility increases that some portion of the compounds will not be measured.

The three most important parameters to detect low ppb levels of sulphur and chlorides are:

1. Sample Introduction, using totally inert sample introduction system
2. High temperature furnace, with precision temperature and flow control controllers
3. Use a trapping technique: the sample must pass through the tape, not just by the side of it.

When selecting an analyser, the first parameter to consider is the sampling system. For low-range sulphur and chlorides detection, the sampling system should offer the following features:

- Optimal conversion from liquid to gaseous phase by accurate control of vaporisation temperature.
- High reproducibility by using gas or liquid sampling valves. If gas valves are used, samples may be injected at atmospheric pressure or under constant pressure.
- Full control over gas and LPG sample introduction, preferably using mass-flow controllers.
- Easy switching between the sample loops for optimum low / high detection range. One can make a selection from the control software to increase the sample size without the need to physically change the loop size.

The next parameter is the need to convert the organically bound sulphur or organically bound chlorides to H_2S or HCl for the detection by H_2S or HCl-specific sensi tape. There are two ways to convert organically bound sulphur to H_2S .

The first technique (ASTM 4045) uses reductive pyrolysis where the organically-bound sulphur is mixed with excess of hydrogen and passed through a high temperature furnace held at $1200^\circ C$. The sulphur combines with hydrogen to form H_2S while the hydrocarbons are reduced to methane gas.

The sensi-tape in the Dry Colorimetric Detector measures the H_2S .

The second technique for this conversion requires, first, oxidative pyrolysis, and then, reductive pyrolysis (based on ASTM 6313). This technique is used to solve the coking problem. In the first reaction zone, the sample containing sulphur compounds and hydrocarbons is blended with air at $1200^\circ C$. The sulphur compounds are oxidised to SO_2 and SO_3 , the hydrocarbons to CO_2 and H_2O . In a second high-temperature zone, a flow stream of hydrogen further reduces the sulphur oxides to H_2S . The water and carbon dioxide formed as combustion by-products interfere with the tape detector and must be removed. Dry Colorimetric technique's strength is that it is based on simple chemistry, and there are no known interferences. Other detection techniques like chemiluminescence and pulsed UV fluorescence detectors suffer from interference from hydrocarbons, requiring GC separations and/or an extremely efficient high temperature reactor to make clean combustion.

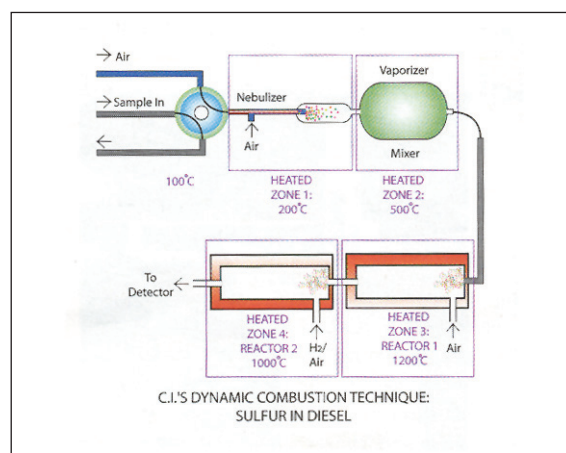


Figure 4 : C.I. Analytics Dynamic Combustion Technique

Detection of Total Sulphur and Total Chlorides in Natural Gas

A fuel-cell manufacturing company previously tried Pulsed FPD and then Chemiluminescence for the detection of less than 100 ppb level of sulphur in natural gas. Both detectors failed to perform. Then this company borrowed Model 9600L from C.I. Analytics. Shortly after, this company purchased the analyser for the following reasons:

1. The low ppb level detection was simple and easy using Dry Colorimetric Detector. The sample introduction was fully automated. There was no need to get the chemist involved. The analysis was done by the pilot plant operators.
2. Six streams were connected to the automated stream selection valve controlled by CiSmart Software. Now all six streams could be analysed around the clock. The data is automatically stored with date and time stamp. This data can be viewed any time.
3. Auto calibration feature allowed time-based calibration validations.
4. Additional impurities, Total Chlorides in Natural Gas could be monitored by just changing the sensi-tape and loading a different method in the CiSmart software.

Detection of Total Sulphur and Total Chlorides in Ethylene and Propylene

To date, the best known technique to detect sulphur compounds like COS at 1 ppb in a Propylene sample is still the Dry Colorimetric Detector. The sample is passed through the tape as opposed to the sample just passing by the tape. This allows the "tape" to act as a H_2S trap (collector). As sample size is increased, so is the amount of the converted H_2S . When sample amount of 300 CC of propylene is passed through the tape, one can get full scale response for 1 ppb level of COS in the sample. In comparison, all other techniques struggle to give 20-50 ppb level results as their signal at that level of detection is lost in the noise. The ability of the tape to trap H_2S and allow use of very large sample amounts is unique in the industry.

Furthermore, recent advances in the detector

technology (Optics Block) have contributed to bring the detection to PPT levels. As the color of the stain varies depending on the sensi-tape model that is used, C.I. Analytics' new optics block brings Dry Colorimetric technology to the next level. During calibration, analysts have the capability to dynamically adjust themselves to maximum sensitivity.

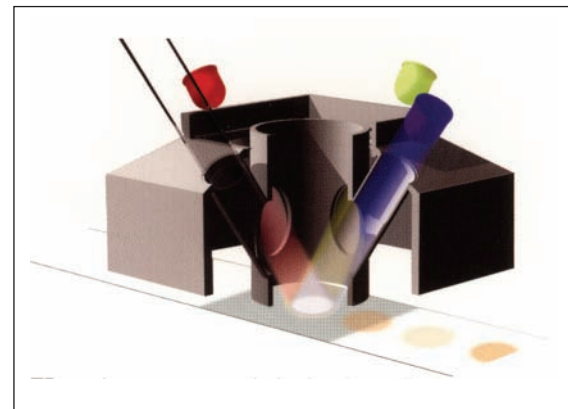


Figure 5 : C.I. Analytics New Optics Block

Analyser Calibration and Data Validation, with built in gas blend generator

Laboratory analysers like the Model 9600L or process analyser of the 9700 Series can be fitted with a built-in Model 960AMF Calibration gas Generator. With the 960AMF, the operator can perform routine calibration checks and develop new calibration curves. There is no more need to purchase expensive sulphur or chloride blends. The 960AMF is also available as a stand-alone, portable unit.

Key Benefits of the Dry Colorimetric Detector with Gas and LPG samples

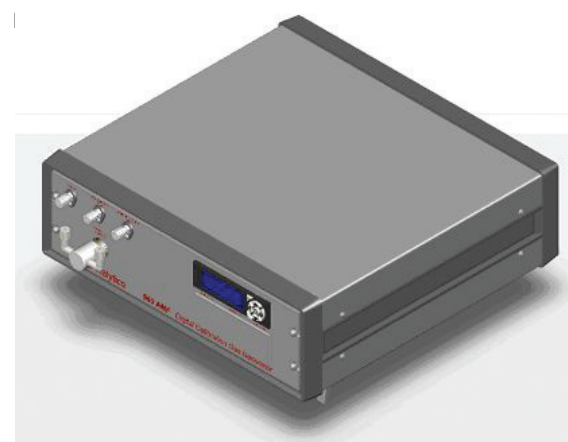


Figure 6 : Model 960AMF Calibration Blend Generator

Chlorides analysis is of crucial importance for high-purity monomer producers. This is why C.I. Analytics' Laboratory and on-line analysers operate on Dry Colorimetry and are designed for low-level analysis. This technology offers the following key benefits:

- The HCl/ H_2S detection tape reacts instantly to the HCl or H_2S , for fast results that are visible due to the color reaction. For example, it takes less than 5 minutes to detect and measure ppb levels of HCl, without use of any GC columns.
- Dry colorimetric detection is very sensitive, allowing for low-level analysis of organic chlorides as HCl and organically bound sulphur as H_2S . The HCl and H_2S must be identified in process streams at ppb or ppm levels for subsequent removal. This dry colorimetry method still provides unmatched accuracy at ppb levels.
- Dry Colorimetry is also very specific to the gas that the detection tape is designed to measure. It will not react to other substances (solvents, hydrocarbons, etc.) often found in process streams or other samples. As a result, expensive downtime due to false alarms is virtually eliminated.
- Laboratory or on-line use in general purpose or ATEX classified areas.
- Total Chlorides using titration technique is maintenance intensive. There is a weekly requirement to clean the electrodes and change the solutions. No such maintenance with the tape method.



Figure 7 :
Model 9730 On-Line
Total Sulphur / Chlorides
Analyser (9700 Series)

- There is no Ethylene interference.
- Simple to use by non-technical staff: clear, unambiguous results that require little interpretation. The instrument operates with a complete Windows-based computer running the CiSmart software suite. The operator can monitor the analysis progress and critical operating conditions directly on the screen.

Conclusion

Very low sulphur or chlorides detection in LPG samples is increasingly crucial to ensure the accurate monitoring of total organic sulphur or chlorides and thus reduce corrosion, avoid catalyst poisoning and meet product

quality specifications. One analyser with the LPG sample introduction system and a calibration gas generator offers new cost effective solution to the monitoring needs.

For laboratory applications, Model 9600L Total Sulphur / Chlorides analyser, paired with the 960AMF Calibration Gas Generator offers a cost-effective solution to monitor impurities in Gas, Liquid, LPG and Solid samples. For On-Line or Process applications, the state-of-the-art Model 9730 with the built-in 960AMF calibrator provide the best solution.

All C.I. Analytics analysers can be adapted to your specific analytical needs. Payback is realised quickly due to decreased reprocessing time and maximised product output.

EDXRF Spectrometer Keeps you Ahead of New Fuel Regulations

With regulations on acceptable levels of sulphur in diesel fuels tightening all around the world, the need for analysis systems that offer maximum sensitivity and extremely low limits of detection has never been greater. PANalytical's (The Netherlands) compact EDXRF spectrometer - MiniPal 4 Sulfur - is designed to deliver best in class performance, keeping you ahead of these new standards. MiniPal 4 Sulfur delivers improved sensitivity, excellent resolution and lower limits of detection, down to 1 ppm. The system's best in class performance results from: a 15 kV silver anode tube that avoids overlap with sulphur signals, and a new silicon drift detector. Powerful system software and Automatic Program Selection (APS), which automatically selects the most appropriate calibration relative to the sulphur content of an unknown sample, makes MiniPal 4 Sulfur easy to use, even for inexperienced users.

The instrument is ideal for quality control and ensuring compliance with the increasing demands of international regulations. All relevant ASTM, ISO, DIN and EPA analysis protocols are supported.

European Union (EU) countries face the introduction of the new Euro V regulations, with its 10 ppm limit on sulphur in ultra low sulphur diesel (ULSD), in January 2009. Through a series of incentives and local initiatives, many EU countries are already in line with the standard. In the US, the EPA (Environmental Protection Agency) has mandated the reduction of sulphur content in ULSD to 15 ppm. All highway diesels must meet this standard by December 2010. In Asia, many national environmental bodies, those in Taiwan and Singapore for example, have adopted the current Euro IV standard and look set to move to the tougher Euro V in due course.

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Accurate, Cost-Effective Solution to Meet New Sulphur Emission Regulations

Thermo Fisher Scientific Inc. (USA) have announced a more compact and cost-efficient solution for refineries and related facilities seeking to meet the new U.S. Environmental Protection Agency's (EPA) sulphur emission regulations. Originally introduced as a two-analyser system, the Thermo Scientific SOLA II Flare™ has been redesigned as a single analyser system for continuous monitoring of sulphur emissions. It offers a dynamic measurement range of 10 ppm to 95 percent of volume, enabling determination of the exact amount of sulphur emitted as well as the duration of the flaring event.

Since the introduction of the SOLA II Flare, Thermo Fisher has installed several two-analyser systems in California refineries to help in compliance with Rule 1118 of the South Coast Air Quality Management District (SCAQMD). The redesigned single-analyser system has a much smaller footprint, requires less maintenance and uses less utility and carrier gases. Collectively these new features lower operating and maintenance costs and minimise overall expense.

"We are committed to developing products that help our customers comply with government regulations as well as provide a significant return on investment," said Mike Landers, refining sales manager at Thermo Fisher Scientific. "The SOLA II Flare is based on our highly successful SOLA II technology platform and is an all-encompassing solution for reliable 24-7 online sulphur measurement. It provides our customers with an accurate, dynamic system that ensures they will have the measuring range necessary to comply with current, as well as future, EPA regulations."

Thermo Fisher and Mangan Inc., a systems integrator with extensive experience in environmental monitoring of flares, have partnered to provide refineries with a complete, turnkey flare emission monitoring solution. After collaborating with Thermo Fisher Scientific following the SCAQMD ruling, Mangan gained an understanding of how to seamlessly integrate the SOLA II Flare into existing plant infrastructures to expedite start-ups and minimise potential downtime.

"Up to this point, refineries often reported sulphur emission estimates or averages during a flaring event without having real data to substantiate them," said Amin Solehjou, managing director at Mangan. "After our work with Thermo Fisher in California, we realised that the online monitoring of the SOLA II Flare enabled actual sulphur quantities to be recorded, even at very low levels. We trust its performance and believe it is the right analyser for customers who need reliable, real-time measurements."

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