

The detection of Total Organic Chloride and/or Hydrogen Chloride

Utilizing A Dry Colorimetric Detector

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Halogenated hydrocarbons and hydro halogenated compounds are found in a wide variety of chemical, petrochemical and refinery processes. Interest in detecting the total of these types of compounds arises in monitoring ambient air for leaks, spills or personnel protection and in monitoring feed stocks for the purpose of catalyst protection. 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. The corroded pipeline or vessel is always a safety concern. With proper sample conditioning the analyser can determine the organic chlorides or hydrochloric acid (HCL) content in gases and volatile liquid hydrocarbon streams. This paper describes the use of, on-line or in lab analysers based on the dry colorimetric technique, in performing these measurements. This technique is shown to have distinct advantages over traditional competing techniques like Microcoulometry and Wickbold.

2. Significance and the need to monitor Total Organic Chlorides and/or HCL

2.1 Petrochemical Plants and Plant Safety:

- The presence of organically bound chlorides and/or HCl in hydrocarbon process streams can prove harmful to equipment and reactions in process involving hydrocarbons.
- Organic chloride species are potentially damaging to refinery processes. Hydrochloric acid can be produced in hydro treating or reforming reactors and this acid accumulates in condensing regions of the refinery. Maximum chloride levels are often specified for process streams and for hydrocarbon products.
- High corrosion due to hydrochloric acid may eventually lead to safety concerns as the vessels weaken
- Feed stock quality assessment of ethylene and propylene used in manufacture of polyethylene or polypropylene.
- Total Chlorides in mix butylenes

2.2 Compliance with government regulations.

- Increasing regulatory pressure has produced great interest in monitoring for hydrogen chloride (HCl) and chlorine (Cl₂) in stacks and from other sources. Measurement of these gases have important process control implications as well.
- Gases from landfill sites that are used to produce electricity or heat must be monitored for Total Halogen content.
- Halogenated acids or gases produced by medical incinerators must be monitored.

3. Test methods:

Traditional spectroscopic methods like Schöniger and Wickbold methodologies have been used in the detection of total organic chlorides. These classical methods have not always been found to be satisfactory. These methods were replaced by microcoulometry detection technique in the eighties. Microcoulometry was suitable only for the laboratory analysers and it was not practical for coupling with on-line analysers. Even for the laboratory applications, the microcoulometry detector has now been replaced by the dry colorimetric detector. The microcoulometry detector requires frequent cleaning of the cell, changing of the chemicals in the cell and then the safe disposal of these chemicals. On the other hand, the dry colorimetric detector does not require the use of wet chemicals and is simple to use.

The microcoulometry detector is not easily adaptable to on-line applications. So for most of on-line applications, Dry Colorimetric Detector (DCD) is used.

C.I. Analytics analysers for the detection of organic chlorides,

follow ASTM D with one exception, The detector used is the DCD. The key advantages of using a DCD are the ease of use, the sensitivity and the fact that there is no need to clean the cell or exchange the solutions. Using the modified ASTM D 5808, sample introduction, conversion of organically bound chlorides to HCl is as the same described in the ASTM D 5908, with one definite improvement, the detection technique.

4. Dry Colorimetric Detector

4.1 Introduction

Classical Colorimetry utilizes an impinger to collect gas in a liquid medium. Chemical reagents are then added to the medium to cause it to change colour in proportion to the concentration of gas present. The resulting colour 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 as gas collecting and analyzing 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 colour in proportion to the amount of gas: the higher the target gas concentration, the darker the stain that will appear. The change in colour, 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.

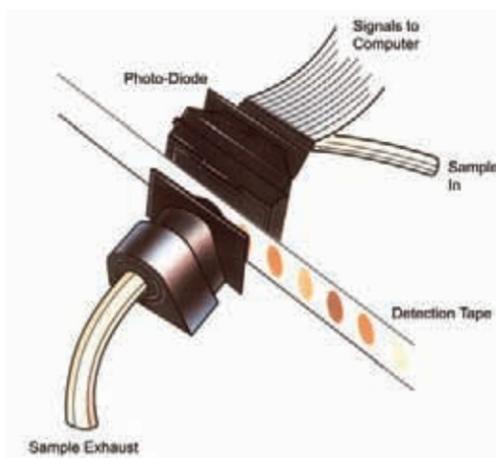


Figure 1: Modern Dry Colorimetric Detection: The C.I. Analytics System

4.2 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 analyzer'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.



Figure 2: Inside of the optics block

The use of this spectrophotometric technique, in combination with micro-processor/ computer control, provides excellent accuracy, repeatability, and detect-ability of low ppb (parts-per-billion) concentrations.

4.3 Accuracy of Dry Colorimetry for HCl Detection.

C.I. Analytics has developed a special formula that is deposited on the filter tape. This tape will respond only to HCl. Figure 3 below shows 'stains' developed when testing for total chlorides in propylene sample.

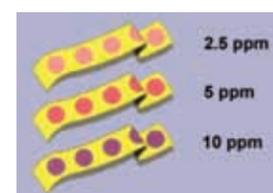


Figure 3: 'HCl' stains on specially formulated SensiTape.

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 analytical methods. Both laboratory and field tests have verified that analysers using Dry Colorimetry give data in agreement with standard reference methods, as typified by the examples in Table 1.

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

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

To detect	Calculated Concentration of Blends	Concentration as Determined by (ASTM D 5808)	CI Analyzer Super C (Modified ASTM D 5808)
		Microcoulometry Detector	Dry Colorimetric Detector
Total	2 PPM	1.1 PPM	1.8 PPM
Chlorides	20 PPM	11 PPM	19 PPM
	200 PPM	110 PPM	122 PPM
Comments	Analysis time	15 minutes per analysis, plus cell clean up time, change chemicals time.	Less than 5 minutes per analysis. No chemicals to change

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

5. Organic Chlorides Analyser: Theory of Operation

5.1 Sample Introduction:

The gas sample under pressure or LPG sample is introduced by using the LPG Station. The LPG station has a fully automated gas or liquid sampling valve that is supplied with the analyser. For LPG samples, the LPG station offers the following features:

- a) Optimal conversion from liquid to gaseous phase by accurate control of vaporization temperature.
- b) High reproducibility
- c) Full control over gas and LPG sample introduction.
- d) Easy switching between the two loops.

Liquid samples may be introduced using the fully automated liquid sampling valve for on line applications. For applications in the laboratory, liquid samples are introduced using optional constant rate syringe injector or auto-injector.

5.2 Conversions in the Pyrolyser

The sample is introduced into a gas stream, at a controlled rate, and carried into a high temperature furnace (1000°C) where an excess of oxygen or air is added.

Pyrolysis converts all organically bound chlorides into organic material in the sample to carbon dioxide and water, while organic chlorides in the sample are converted to HCl. For some applications, the reactor gas used for conversions is hydrogen instead of air or oxygen. The reductive pyrolysis also results in the conversion of organically bound chlorides to HCl. When reductive pyrolysis is used, there is no water formed in the pyrolyser. That is why, reductive pyrolysis is used where ever possible.

5.3 The detection of HCl

The HCl formed in the reactor reacts with the chemicals on the SensiTape, and 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 analogue signal. This signal is converted to a digital format, matched to the gas response curve stored in the analyzer's permanent memory, and displayed/ documented as the actual concentration value.

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

The on-line analyzer has a built in, accurate, gas blend generator. The blends are generated using this built in gas blend generator. One can perform routine calibrations based on time, daily, weekly, monthly or every six months. Please see Figure 4 and 5.

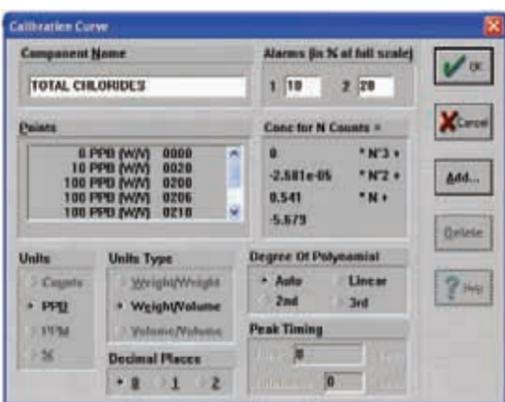


Figure 4: Calibration curves are simple to create chlorides

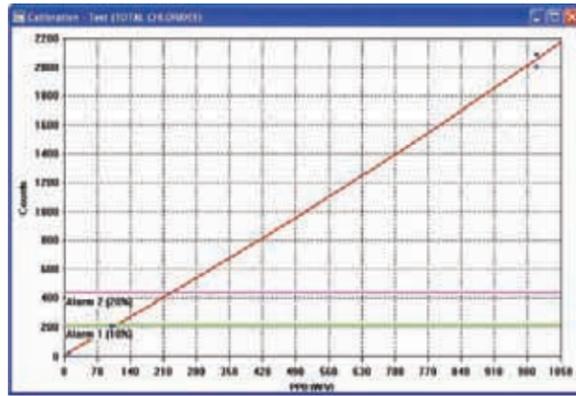


Figure 5: Calibration Curve Total chlorides (ppb) in Ethylene

5.5. Stream Selection Software

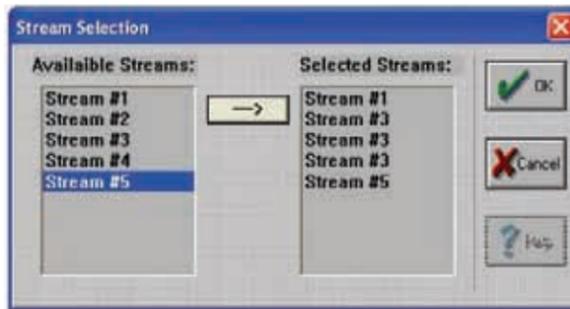


Figure 6: Stream selection Simply select and click

5.6 Key Benefits of Dry Colorimetry for HCL/Total Chlorides Detection in gas and LPG samples:

It has been established that low-level HCl or Total chlorides analysis is of crucial importance for those involved in high-purity monomer production. C. I. Analytics' analyzers operating on Dry Colorimetry that are designed for low-level HCl analysis, offer producers the following key benefits:

- The HCl detection tape reacts instantly to the HCl for fast results that are visible due to the color reaction. For example, it takes less than 60 seconds 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. The HCl must be identified in process streams at ppb or ppm levels for subsequent removal.
- 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.
- Total Chlorides result is obtained.
- No need for GC columns or GC specialists.
- There is no Ethylene interference
- unmatched accuracy at ppb levels
- simple to use by non-technical staff:
- o clear, unambiguous results that require little interpretation: if the instrument operates with a complete computer and proprietary software, the "Peak", as it elutes, can be displayed on the screen, and a numerical concentration value can be viewed
- laboratory or on-line use, depending upon instrument area classification



Figure 7: C.I. Analytics' superC for use in Laboratory (Reactor Option required for Total Chlorides Application is not shown above)

On-line Applications.

A: Case Study: The on line detection of and HCL in high purity ethylene and propylene streams:

Ethylene is pumped through HCl scrubber beds. Parallel scrubbers may be in place so that the flow can be re-routed to an alternate scrubber when HCl breakthrough occurs. A sample is drawn from the post-scrubber flow where the HCl measurement is made. When the HCl concentration approaches the alarm level (200 ppb) ethylene flow is diverted to the alternate scrubber. In this way, the HCl concentration should never exceed 200 ppb, and the process flow does not need to be shut down for replacement of the scrubber beds.

Polyethylene manufacturers (end users of ethylene) may utilize systems such as the Model 8510 or Model 7510 as an incoming ethylene quality measurement tool as well Take as a case study the detection of one impurity: HCl in Ethylene.

B. Case Study: The on line detection of Total organically bound chlorides and HCl in high purity ethylene and propylene streams.

Many plants around the world have Model 9600P and Model 9700P installed for the detection of Total Chlorides at low PPB levels in Ethylene and propylene streams. The analyzer has a built in dual stream selection capability.

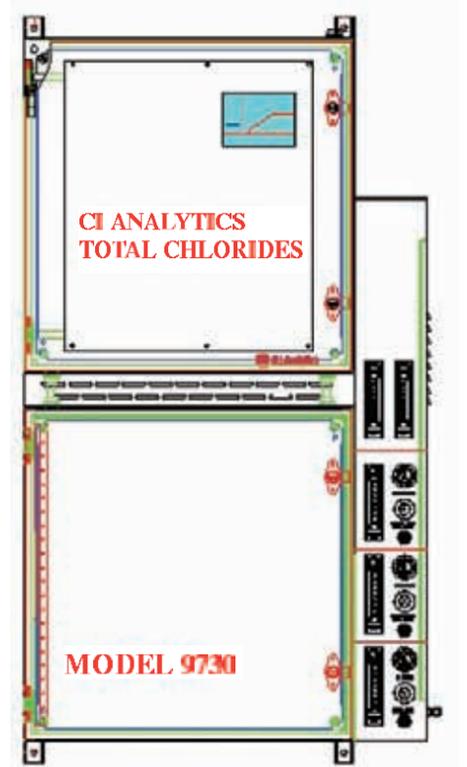


Figure 9: C.I. Analytics' Model 9730 ON-Line Process Gas Analyser for Monitoring of Total Chlorides

The sample is first mixed with hydrogen in the pre heater and then passed via the pyrolyser. The excess hydrogen and high temperature converts all organically bound chlorides to HCL and this is detected by the Dry Colorimetric Detector. The alarm level is usually set at 100 ppb.

Tape conditioning time is user selectable. At the start of the tape conditioning run, the sample stream is switched over and this allows time for purging the sample lines.

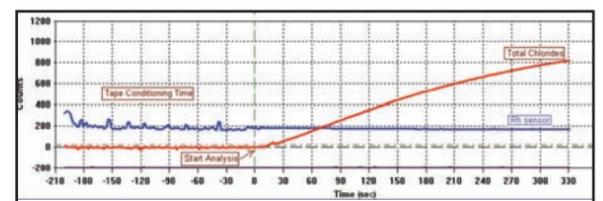


Figure 10: Run in progress Main Screen

C. Lab application: The detection of total organically bound chlorides and HCl in high purity ethylene and propylene samples.

The sample is taken in a dry Teflon lined sample cylinder in accordance with ASTM procedures to take representative sample. The presence of water in the sample or the sample cylinder may lead to lower results, as HCl is easily removed by water droplets.

Conclusion

Low ppb level HCl and /or Total chlorides analysis, is increasingly crucial to ensure the accurate monitoring of total organic chlorides and thus reduce corrosion, avoid catalyst poisoning and meet product quality specifications. The on-line HCl analyzer or Total Chlorides manufactured by C.I. Analytics offers a unique system which allows the process or Q.C. engineer to have real time concentration data, rather than having to wait an extended period of time for laboratory results. The Model 8510 or Model 9730 provides a cost-effective means of continually determining ethylene quality. Payback is short, due to decreased reprocessing time and maximized product output.