Challenge
Precise and long-term stable detection of chlorine (TX) impurities in the ultra-trace range, complete digestion of highly volatile hydrocarbons at different pressures and aggregation states

Solution
Matrix-optimized sample dosing for controlled combustion combined with efficient gas purification for maximum transfer yield and most sensitive detection

Intended audience
Polymer industry, chemical industry, refineries, contract labs

Determination of Total Chloride in LPG and Gaseous Hydrocarbons by Microcoulometry in Accordance with UOP 910

Introduction

Monitoring chlorine as an undesired element is important in many points in the value chain of a refinery or petrochemical complex. This starts with the desalination of crude oil, where chlorine (Cl) contents can be high, to industrial intermediates and consumer products, where this element should not even be detectable. As chlorine quantities decrease during processing, the requirements for fast and reliable trace determination increase in inverse proportion. The presence of chlorine traces poses serious dangers for refinery parts like hydro or catalytic cracking units. If not removed, the Cl compounds can cause massive damages by fouling and corrosion processes but also by catalyst poisoning and shortage of its economic life. The formation of undesired chlorinated hydrocarbons as byproducts is an additional risk.
Not only in the common liquid streams, but also in gaseous and LPG streams used in this process, the total organic halogen (TX) content must be monitored for a full assessment and prevention of risks for the process and derivation of maintenance tasks for the Cl guard systems (HCl / RCl* removal by absorbers). For liquid matrices versatile regulations exist to support the analyst, such as ASTM D4929, ASTM D5808, EPA 9076, or UOP 779, but these cannot be used for gaseous matrices. Here, often gas test tubes (e.g., Dräger) are in use, they enable easy and quick onsite checks by a simple color indication. They are well suited for middle to higher chlorine contaminations, but less reliable for high purity streams. If precise quantification of trace and especially ultra-trace contents in gas and LPG samples is crucial, combustion elemental analysis coupled with coulometric detection of the chlorine, as described in UOP 910, is the best option.
The multi EA 5100 is such an analysis system. It is applicable for precise Cl determination in gaseous and under pressure liquefied (LPG) samples in accordance with this standard. Besides this, also liquid and solid samples can be processed with the same analyzer, when adding suited sample supply systems.

* hydrogen chloride gas and organic chlorine compounds

Materials and Methods

Samples and reagents

- Different gaseous and liquefied pressurized hydrocarbons (e.g., propylene)
- Calibration gas standard (c_{Cl} 3.84 µg/L), Air Liquide*

Sample preparation

The samples are highly volatile gaseous materials or liquefied pressurized gases. To prevent system damages due to possible solids particles accompanying the sample (rust from pipes and tubes or other undesired or interfering components), it is always recommended to filter the gas or LPG material before entering the analyzer. Thanks to the protective filter integrated in the used gas sampling system, the samples could be analyzed directly without a manual treatment step.

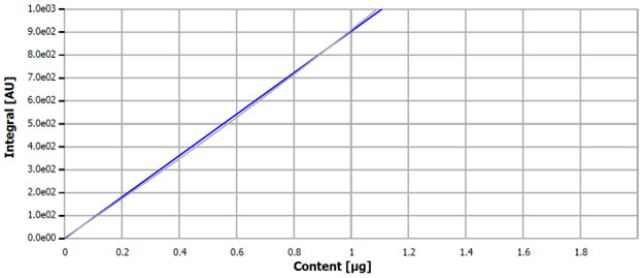
Calibration

The system was calibrated before analysis. Calibration was carried out by utilization of a gaseous standard based on dichloromethane in methane, with a Cl concentration of 3.84 µg/L. Different injection volumes in the range of 5 to 100 mL were applied. Figure 1 depicts a typical calibration curve and the performance parameters for the ultra-trace range.

Table 1: Process parameters multi EA 5100

Parameter	Chlorine
Standard concentration	3.84 µg/L
Volume range	5–100 mL
Detection limit	1.02 ng
Linearity	Linear
Correlation coefficient	0.99995

Table 2: Example Cl calibration curve

Chlorine


Instrumentation

For all analyses of gases and liquefied pressurized gas (LPG), a multi EA 5100 combustion elemental analyzer was used in vertical operation mode. This ensures sharp peak modulation and thereby reduction of baseline effects on the quantification of element traces in the sub-ppm level. Equipped with matrix-optimized sample supply systems, gaseous samples can be analyzed safely with high precision, no matter if under ambient pressure, highly pressurized, or even liquefied under pressure (LPG). In general, dedicated dosing systems are used for gases and LPG samples to better meet the specific requirements of each matrix type and pressure. Combined systems, ensuring the separation of gas and LPG branch to prevent cross contaminations, can also be used. This is especially recommended for low sample numbers, simple sample matrices, and concentrations in the mid to upper ppm level.

For the measurements carried out in this application note, specific dosing systems have been used. For gaseous samples (pressurized and non-pressurized) the GSS module with adapter box was used. The non-pressurized gases (e.g., in Tedlar bags) were introduced directly, pressurized gases (e.g., in Swagelok cylinders) were automatically expanded via an adapter box before dosing. For LPG samples the LPG module was used. The sample aliquot to be dosed was taken out of the liquid phase, preventing sample changes and adsorption loss, which often occurs when sample aliquots are taken out of the evaporated material.

The GSS and the LPG module allow variable injection volumes. In addition, a purge gas stream ensures a fast and quantitative transfer of all sample components into the combustion tube. There the sample digestion is carried out by efficient catalyst-free high temperature combustion in a quartz tube. The process is split into two phases. First, evaporation of light components and pyrolysis of the heavier ones takes place within an inert argon atmosphere. In the second phase the system switches completely to oxygen and if present, remaining components are combusted quantitatively. The implemented Auto-Protection System guarantees highest operational safety, it can trap particles and aerosols while condensation is prevented, thus complete transfer of the formed HCl gas into the “high sensitive” cell is assured. Afterwards the determination of the chlorine content is carried out by means of a micro-coulometric titration. The Cl detection unit enables a limit of detection as low as 10 ng Cl absolute.

* alternatively calibration can be carried out by utilization of liquids standards, e.g., 402-889.071 kit calibration solutions 0.1-10 mg/L chlorine, Analytik Jena

Method parameters

Samples were analyzed using a standard library method. Table 3 summarizes the parameter settings for sample introduction and combustion process. For samples an injection volumes of 20 and 100 mL for gases and 50 µL for LPG were used.

Table 3: Process parameters multi EA 5100

Parameter	Specification
Operation mode	Vertical
Furnace temperature	1,050 °C
2nd combustion	60 s
Ar flow (1st phase)	100 mL/min
O_2 main flow	200 mL/min
O_2 flow (2nd phase)	100 mL/min
Purge gas (Ar)	50–60 mL/min
Injection volume (LPG)	10–50 µL
Injection volume (GSS)	20–100 mL
Injection speed (GSS)	30 mL/min

Evaluation parameters

Table 4 summarizes the parameter settings for the detection.

Table 4: Detection parameters ("high sensitive" Cl option)

Parameter	Specification
Cell temperature	22 °C
Titration delay	1
Max. integration time	350 s
Threshold	300 cts
Threshold value	10 cts
Baseline/drift correction	Automatic

Results and Discussion

Measurement results for samples and the standard gas are summarized in Table 5. The results are average values calculated on basis of three replicate analyses. Deviations of the results are very good for the measurement of chlorine contents in the trace range. Typical measuring curves for samples and standards are shown in Figures 1–6.

Table 5: Results for Cl determination for different gaseous samples and standard material

Sample	Volume	c_{Cl} (TX)	SD
Methane	20 mL	4.04 µg/L	± 0.22 µg/L
Natural gas	20 mL	3.59 µg/L	± 0.20 µg/L
Butane/butene mix	20 mL	1.93 µg/L	± 0.06 µg/L
Ethylene	100 mL	0.68 µg/L	± 0.11 µg/L
LPG (propylene)	50 µL	0.60 mg/L	< 0.01 mg/L
Standard gas (nominal value 3.84 µg/L Cl)	20 mL	3.96 µg/L	± 0.04 µg/L

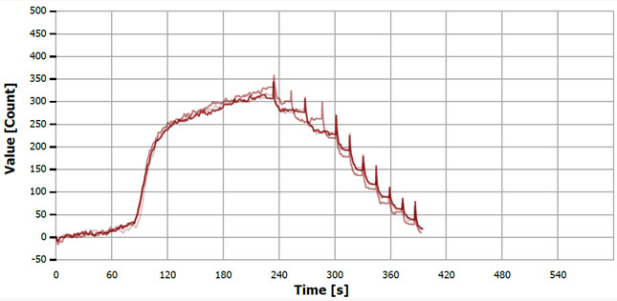


Figure 1: Measuring curve for sample "methane"

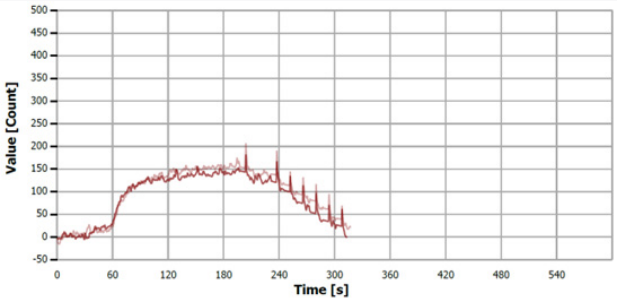


Figure 2: Measuring curve for sample "natural gas"

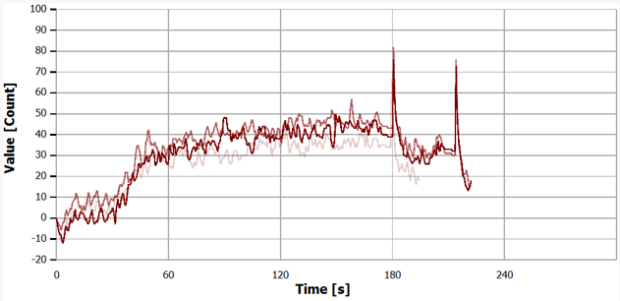


Figure 3: Measuring curve for sample "butane/butene mix"

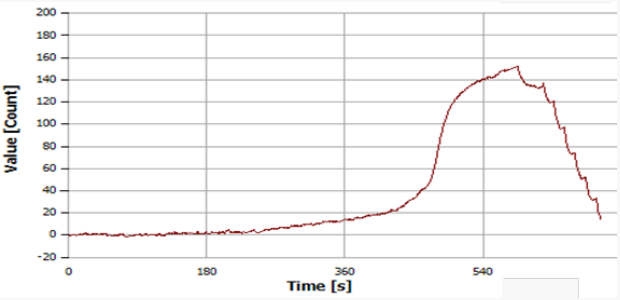


Figure 4: Measuring curve for sample "ethylene"

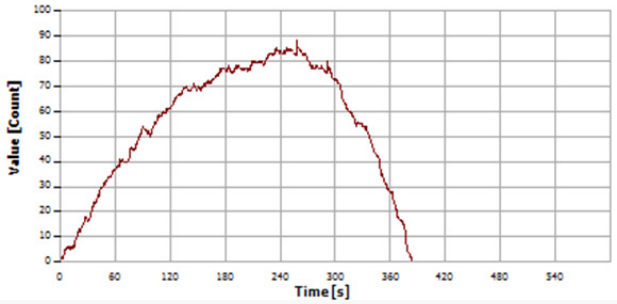


Figure 5: Measuring curve for sample "LPG (propylene)"

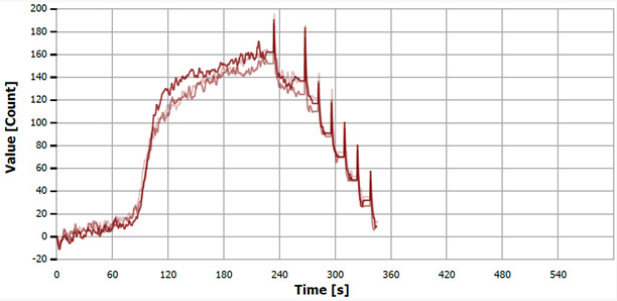


Figure 5: Measuring curve for "gas standard 3.84 µg/L Cl"

Conclusion

The multi EA 5100 and its matrix-optimized gas sampling systems are perfectly suited for the determination of chlorine in various gaseous and liquefied pressurized samples independent of their pressure. The integrated high-performance drier and heated auto protection system ensure that even the tiniest chlorine traces arrive quickly in the coulometric detection system.
The high sensitivity of its sensor electrode and the wide linearity of the coulometer allow for reliable results in the ultra-trace range. If necessary, the sample volumes can be adapted flexibly to allow most sensitive quantification (up to 100 mL for gaseous samples, up to 50 µL for LPG samples). For higher concentrations the sample volumes can be reduced to safe analysis time, thus ensuring a higher sample throughput at lower consumption. This and the low maintenance requirement and quick readiness for operation make the used system well suited for applications in research and development, quality control, and process monitoring, independant if for routine labs or shift operation.

Figure 7: multi EA 5100 with gas sampling system

Recommended device configuration

Table 6: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 5100	450-300.011	multi EA 5100 – combustion elemental analyzer for sulfur, nitrogen, chlorine, and carbon analysis in solids, liquids, and gases
Cl module basic	450-300.023	Extension for chlorine determination with coulometric titration
Extension kit Cl high sensitive	450-300.024	Extension of Cl module for the determination of very low chlorine contents
LPG module 2.0	450-900.465	Sample introduction system for liquefied pressurized gases (LPG)
Gas sampling system - GSS	450-126.420	Sample introduction system for gaseous samples
GSS adapter box	450-007.531	For introduction of pressurized gases up to 200 bar
multiWin software	450-011.803	Operation and data evaluation software for multi EA 5100

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