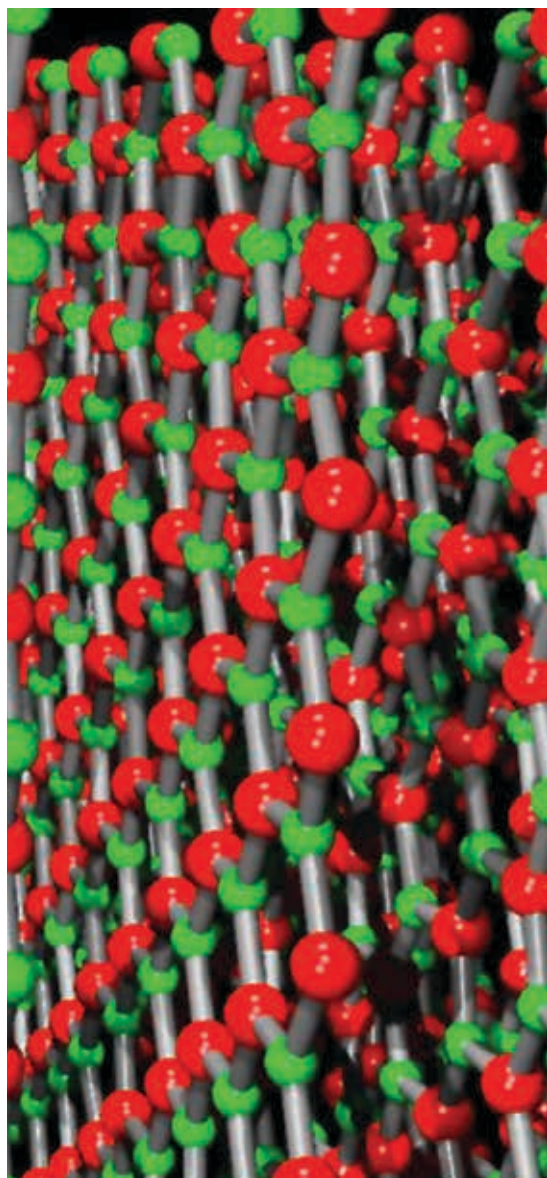


Case Study

Process Analytics in Ethylene Oxide and Ethylene Glycol Plants

Chemical Industry



Perfect solutions from Siemens Process Analytics

Ethylene Oxide (EO)

Ethylene oxide, C_2H_4O , under normal conditions, is a colorless, flammable gas. It is very toxic and carcinogen. Industrial production started in 1925 using the chlorohydrin process and was improved in 1931 by introducing the much more economic direct catalytic oxidation method. Currently, almost all ethylene oxide production plants are based on the direct oxidation process with air or oxygen using a silver based catalyst. CO_2 and water are produced as by-products of the reaction.

Because EO reacts readily with many chemicals, it is one of the most versatile intermediates in the production of several industrial chemicals, the most notable of which is ethylene glycol. It is also used as a sterilant for medical equipment. However, most of it is converted into products such as fibers, foils, bottles, plasticizers, solvents, antifreezes, cosmetics, sport articles, CDs etc.

Ethylene Glycol (EG)

Ethylene glycol ($C_2H_4(OH)_2$) is produced from ethylene oxide through a catalytic reaction with water at higher temperature resulting in a yield of mono-ethylene glycol (MEG), known as glycol, and the by-products di-ethylene glycol (DEG) and tri-ethylene glycol (TEG).

Ethylene glycol is commonly used as an antifreeze agent in automobile cooling systems. It is also used in deicing solutions for aircraft and boats. Other uses include solvents for the paint and plastic industry, and hydraulic brake fluids. In pure form it is a colorless clear liquid with a sweet taste and a slightly syrupy texture. If ingested, ethylene glycol can damage the kidneys, heart and nervous system.

Integrated EO/EG plants

Modern EO/EG plants are highly integrated units where part or all of the EO produced in the EO section can be recovered as glycols, if desired, in the glycol section. Plant integration allows for significant savings in utilities as well for the recovery of all bleed streams as high-grade-products instead of lower grade products in the case of non-integrated plants.

Ethylene Oxide and Ethylene Glycols

Ethylene oxide production

The major production steps of the oxygen-based EO process are:

- Ethylene (acc. to IUPAC: Ethene) and oxygen are mixed with recycle gas and, after adding a moderating substance such as chloro-ethane, fed into a multi-tubular reactor. There, ethylene oxide (EO) is selectively produced utilizing a silver-based catalyst at 200 to 300 °C and 10-20 bar. Along with ethylene oxide (80-85 %), CO₂, H₂O and heat are generated. Reaction heat is recovered by boiling water at elevated pressure on the reactors shellside. It is used at different locations of the plant.
- EO contained in the reactor product gas enters the EO absorber section where EO is scrubbed from the gas by water. The EO-containing water is concentrated by stripping producing crude EO which is suitable for feeding directly to a glycol producing plant. When pure EO is the desired final product, the crude EO is fed to a purification column.
- The cycle gas leaving the absorber is fed to the CO₂ removal section, where CO₂ (a by-product of the EO reaction) is recovered. Some of the CO₂ remains in the cycle gas and returns to the EO reactor.

Process constraints

Various constraints exist regarding safe operation, product quality and plant efficiency in running and optimizing the EO production process:

- Oxygen is required as reactant to run the process and added to the cycle gas. However, at a certain concentration level (known as flammable limit) in the gas mixture, oxygen will cause the danger of a gas explosion. Therefore, the content of oxygen in the cycle gas must be monitored continuously with high accuracy and reliability.
- Methan is able to increase the flammable limit (which is treated as positive effect) and, hence, is added to the cycle gas in the form of natural gas.

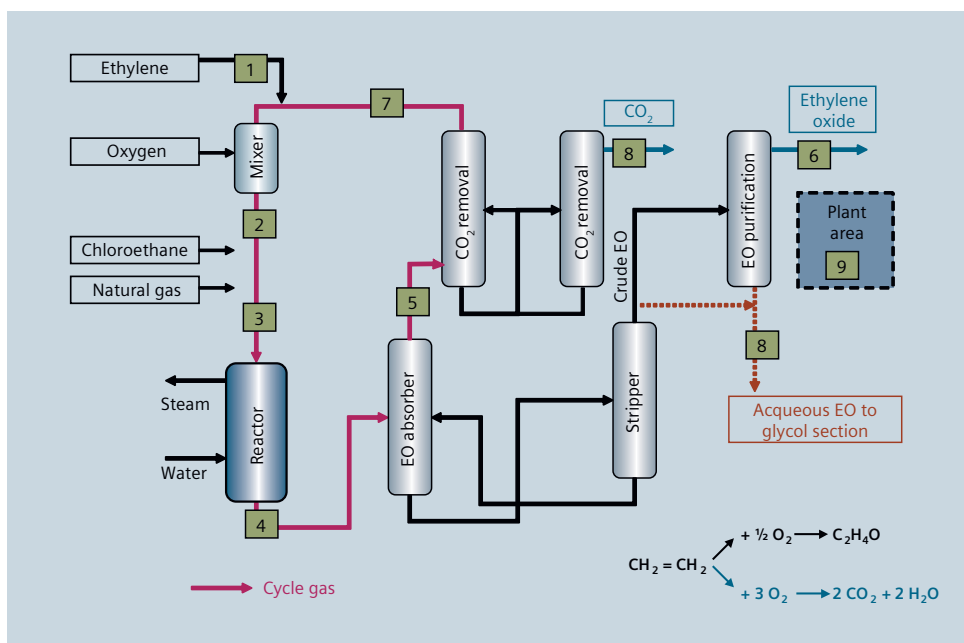


Fig. 1: Ethylene oxide production process with measuring points (see details in table 1)

Natural gas, however, is commonly contaminated with gaseous sulfur compounds that are known as poison to the silver catalysts.

- Catalyst selectivity is an important parameter in EO production and should be as high as possible. Usually, during catalytic processes, other competing reactions can take place, and reactants are converted into undesired products. The ratio between desired products and the undesired products is called catalyst selectivity. Catalyst selectivity is optimized by adding moderating substances such as chloro-ethane.

Control of cycle gas composition

The desired product ethylene oxide represents only a relatively small percentage of the total effluent stream leaving the reactor. The remainder of the reactor effluent comprises several diluents and reaction by-products. The task of the diluents is to prevent the gas mixture to reach unwanted combustibility levels during the reaction. If the flammability limit is reached or exceeded, the complete oxidation of ethylene to

CO₂ and water will occur explosively. Process operation is desired under conditions which will maximize the conversion of ethylene to ethylene oxide yet avoid safety problems. In order to find such an optimum, gases such as nitrogen and methane are fed to the cycle gas and mixed with the reaction by-product carbon dioxide, and argon, which enters as an impurity in the oxygen feed. The goal is to find an optimum mixture which permits operation of the process at maximum concentrations of oxygen and ethylene thus increasing the selectivity of the ethylene present to ethylene oxide and, on the other side prevents from the danger of explosion.

Process analyzer are used to find this optimum mixture and to keep the gas concentrations at the predetermined levels during the process. See table 1 for measuring details.

Ethylene glycol production

The aqueous EO solution from the ethylene oxide production section is sent to the glycol section. There, ethylene glycol (MEG, Monoethylene glycol) is produced from EO by reacting it with water at a 10 to 1 ratio of water to EO. This excess of water helps to reduce by-product formation. Some higher glycols are produced as co-products: diethylene glycol (DEG) and triethylene glycol (TEG). The reactor product is sent to a multi-effect evaporation train for removal of the water from the glycols in three successive stages. The glycols are then sent to the fractionation train where the MEG, DEG and TEG products are recovered and purified.

Final product samples are collected from the overhead or side stream of the purification towers (fractionators). A variety of process analysis is performed, including water content, MEG, DEG or TEG (see table 2). Other measurements are color, acidity, aldehyde impurity content and TOC (fig. 2). The product must meet sales specifications prior to being released for shipment to customers. Otherwise the product is normally reprocessed.

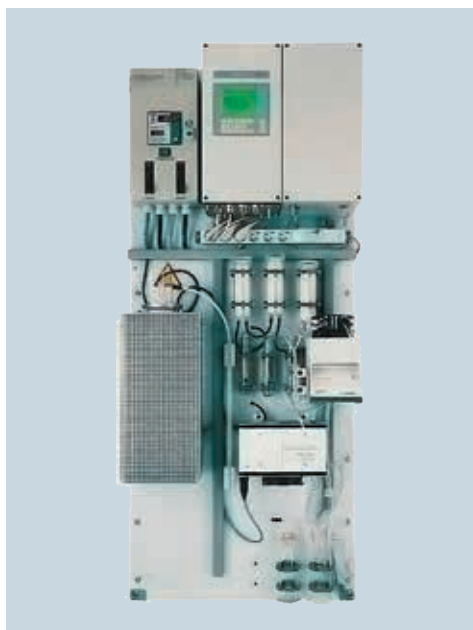


Fig. 2: TOC system (ULTRAMAT 6 based third party analyzer)

Sampling Point Sampling Stream		Measuring Task	Measuring Components	Meas. Range	Siemens Analyzer
1	Ethylene feed	Ethylene purity to avoid catalyst poisoning	C ₂ H ₂ S compounds	%	MAXUM II
2	Cycle gas after mixer	Process control	CO ₂	0 ... 5	MAXUM II
			CH ₄	0 ... 80	
			C ₂ H ₄	0 ... 40	
			C ₂ H ₆	0 ... 2	
			C ₂ H ₄ O	0 ... 3	
			N ₂	0 ... 20	
			Ar/O ₂	0 ... 25	
			H ₂ O	0 ... 3	
			C ₂ H ₄	0 ... 40	ULTRAMAT 6
			CO ₂	0 ... 5	
		Explosion protection (LEL monitoring)	O ₂	0 ... 12	OXYMAT 6 OXYMAT 6 OXYMAT 6
			O ₂	0 ... 12	
			O ₂	0 ... 12	
3	Cycle gas at reactor inlet	Cycle gas composition	CI-HCs CI-Hcs		MAXUM II
4	Cycle gas at reactor outlet	Process control	CO ₂	0 ... 5	MAXUM II
			CH ₄	0 ... 80	
			C ₂ H ₄	0 ... 40	
			C ₂ H ₆	0 ... 2	
			C ₂ H ₄ O	0 ... 3	
			N ₂	0 ... 20	
			Ar/O ₂	0 ... 25	
			H ₂ O	0 ... 3	
		Explosion protection (LEL monitoring)	O ₂	0 ... 12	OXYMAT 6 OXYMAT 6 OXYMAT 6
			O ₂	0 ... 12	
			O ₂	0 ... 12	
5	EO absorber overhead	Cycle gas composition: Process control	C ₂ H ₄ C ₂ H ₆ C ₂ H ₄ O Ar/O ₂ CO ₂ H ₂ O	0 ... 40 0 ... 2 0 ... 0,05 0 ... 30 0 ... 30 0 ... 10	MAXUM II
6	EO product	Product quality	Formaldehyde Acetaldehyde C ₂ H ₄ , CO ₂ , H ₂ O		MAXUM II
7	CO ₂ absorber overhead	Cycle gas composition	C ₂ H ₄ C ₂ H ₆ C ₂ H ₄ O Ar/O ₂ CO ₂ H ₂ O	0 ... 40 0 ... 2 0 ... 0,05 0 ... 30 0 ... 30 0 ... 10	MAXUM II
8	EO to glycol section	Aldehyde content	Aldehyde		TPA
9	Plant area	Waste water monitoring	EO in water TOC		MAXUM II TPA

Table1: Ethylene oxide process, measuring points (TPA: Third Party Analyzer)

Process Gas Chromatography

The MAXUM gas chromatograph fullfills the requirements for glycols quality control perfectly:

- Accurate analysis by optimized injection: Injection module with best evaporation characteristics for high boiling samples (MEG, boiling point 194-205°C, DEG: 242-247°C, TEG: 278°C) avoid discrimination effect or hydration to water.
- Repeatable analysis by interference free separation. Safe separation of trace components is performed by elimination of main components by heart-cut. Used analytical tools: Siemens live switching in combination with capillary columns. Verification of the results by additional control parameter: cut-rest of main component, GC oven and ambient temperature. The excellent measuring stability, caused by the outstanding MAXUM hardware, is evident from fig. 4.
- Extended calibration cycles (typically > 6 weeks) by on-line calibration using closed cylinders. No enrichment with atmospheric moisture occurs in comparison to laboratory calibration principle.
- Inert capillary column systems to analyze traces of formalehydes and other highly reactive components.

High-precision O₂/Ar measurement through combined data processing with OXYMAT analysis results; see next page.

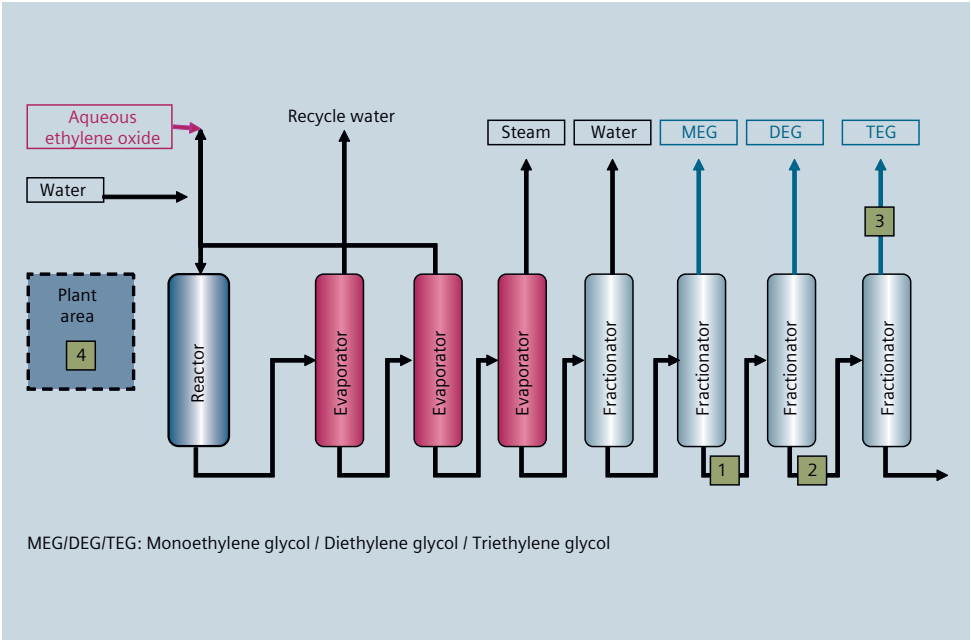


Fig. 3: Ethylene glycols production process

Sampling Point Sampling Stream		Measuring Purpose	Measuring Components	Measuring Ranges	Siemens Analyzer
1	MEG fractionator bottom	Quality control MEG	DEG, TEG Water in MEG	Medium ppm level	MAXUM (Oven 1)
2	DEG fractionator bottom	Quality control DEG	MEG, TEG Water in DEG	Medium ppm level	MAXUM (Oven 2)
3	TEG fractionator overhead	Quality control TEG	DEG, TEG Water in TEG	Medium to high ppm level	MAXUM
4	Plant area	Waste water and condensate monitoring	TOC in water		TPA

Table 2: Ethylene glycols process, measuring points
MEG = Monoethylene glycol DEG = Diethylene glycol TEG = Triethylene glycol
TEEG = Tetraethylene glycol TOC = Total Organic Carbon TPA = Third Party Analyzer

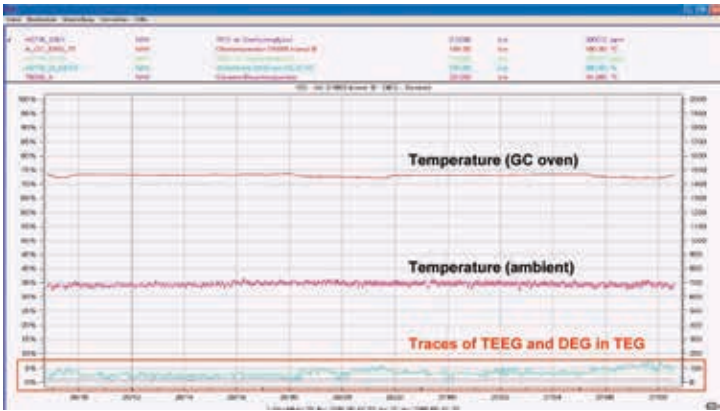


Fig. 4: Stability of MAXUM PGC system



Fig. 5: Ethylene glycol plant (INEOS Worringer, Germany)

OXYMAT 6 Ensures Plant Safety

Composition of the reaction gas

The EO reaction gas is a mixture of combustible, oxidizing and inert gases and made of O_2 and C_2H_4 along with various diluent ingredients. Due to the flammable nature of oxygen, the ethylene production process relies on precise and accurate control of oxygen, and particularly, the "Limiting Oxygen Value" (LOV) or "Maximum Allowable Oxygen Concentration" (MAOC). The LOV is the oxygen concentration at which a combustion reaction will propagate through the ethylene oxide process gas. Hence, using too much oxygen can result in a catastrophic ignition, while using too little will result in poor yield. To control this critical situation independent reactor inlet and outlet oxygen analyzers are used for oxygen monitoring and automatic safety shutdown and isolation of oxygen feeds.

Typically, a certain offset from the LOV is defined (fig. 6) as safety margin. If the inlet oxygen concentration exceeds this LOV offset, the reactor must be shut down immediately to ensure that the safety margin is maintained. The size of the offset depends on the system geometry and other parameters. For example, the shut down could be triggered as the oxygen concentration exceeds LOV-2 vol%. Therefore it is crucial to monitor and control oxygen concentration at the reactor with highest degrees of accuracy and reliability.

Gain in allowable O_2 concentration

The danger of a gas explosion arises as the oxygen concentration comes closer to the LOV value. Considering the standard deviation values of available oxygen analyzers (fig. 6), the analyzer with a lower standard deviation (shown in blue) will allow a higher oxygen concentration and thus a higher process yield than an analyzer with a higher standard deviation (shown in brown).

OXYMAT 6

OXYMAT 6 is well known for its outstanding features in reliability and stability with a very low standard deviation. It is specified by many chemical companies as preferred analyzer for this demanding application. OXYMAT 6 reliably ensures process safety and, at the same time, allows for best possible process yield and cost reduction.

The measuring principle uses two gases: a reference gas, typically nitrogen or air, and the sample gas. The reference gas (shown in green, fig. 7) is introduced into the sample cell through two channels. The reference gas stream on the right-hand side (intensive green) meets the sample gas within the area of a magnetic field.

The oxygen molecules (shown as blue beads) are drawn to the right, generating a pressure to the right reference gas

Flammable limit

Gas mixtures consisting of combustible, oxidizing, and inert gases are only flammable under certain conditions. Flammable limits define the proportion of combustible components in a gas mixture, between which limits this mixture is flammable. The lower flammable limit (LFL) describes the leanest mixture that is still flammable, while the upper flammable limit (UFL) gives the richest flammable mixture. Increasing the fraction of inert gases in a mixture raises the LFL and decreases UFL. Temperature and pressure also influences flammability limits. Higher temperature results in lower LFL and higher UFL, while greater pressure increases both values. The effect of pressure is very small.

channel. Because the two channels are connected, the pressure difference, which is proportional to the oxygen concentration, causes a cross flow, which is converted into an electric signal by a microflow sensor. Through suitable selection of the reference gas the zero point can be elevated physically with elevated oxygen concentration, e.g. 98-100% oxygen for purity monitoring.

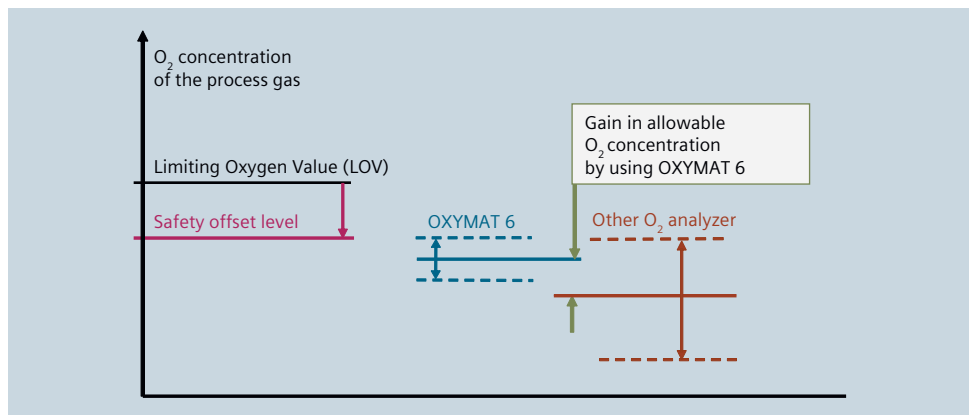


Fig. 6: Gain in allowable oxygen concentration

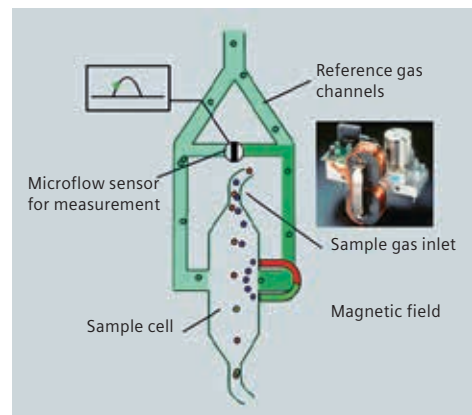


Fig. 7: Measuring principle OXYMAT 6

Siemens Process Analytics at a Glance

Product overview

Siemens Process Analytics is a leading provider of process analyzers and process analysis systems. We offer our global customers the best solutions for their applications based on innovative analysis technologies, customized system engineering, sound knowledge of customer applications and professional support. And with Totally Integrated Automation (TIA). Siemens Process Analytics is your qualified partner for efficient solutions that integrate process analysers into automations systems in the process industry.

From demanding analysis tasks in the chemical, oil and gas and petrochemical industry to combustion control in power plants to emission monitoring at waste incineration plants, the highly accurate and reliable Siemens gas chromatographs and continuous analysers will always do the job.

Siemens Process Analytics offers a wide and innovative portfolio designed to meet all user requirements for comprehensive products and solutions.

Our Products

The product line of Siemens Process Analytics comprises

- extractive and in-situ continuous gas analyzers (fig. 8-11)
- process gas chromatographs (fig. 12-13)
- sampling systems
- auxiliary equipment

Analyzers and chromatographs are available in different versions for rack or field mounting, explosion protection, corrosion resistant etc.

A flexible networking concept allows interfacing to DCS and maintenance stations via 4-20 mA, PROFIBUS, OPC, Modbus or industrial ethernet.



Fig. 8 Series 6 gas analyzer (rack design)



Fig. 12 MAXUM edition II Process GC



Fig. 9 Series 6 gas analyzer (field design)



Fig. 13 MicroSAM Process GC



Fig. 10 LDS 6 in-situ laser gas analyzer



Fig. 14 SITRANS CV Natural Gas Analyzer



Fig. 11 SITRANS SL In-situ laser gas analyser

Product Scope

Siemens Continuous Gas Analyzers and Process Gas Chromatographs

Extractive Continuous Gas Analyzers (CGA)

ULTRAMAT 23

The ULTRAMAT 23 is a cost-effective multicomponent analyzer for the measurement of up to 3 infrared sensitive gases (NDIR principle) plus oxygen (electrochemical cell). The ULTRAMAT 23 is suitable for a wide range of standard applications. Calibration using ambient air eliminates the need of expensive calibration gases.

CALOMAT 6/62

The CALOMAT 6 uses the thermal conductivity detection (TCD) method to measure the concentration of certain process gases, preferably hydrogen. The CALOMAT 62 applies the TCD method as well and is specially designed for use in application with corrosive gases such as chlorine.

OXYMAT 6/61/64

The OXYMAT 6 uses the paramagnetic measuring method and can be used in applications for process control, emission monitoring and quality assurance. Due to its ultrafast response, the OXYMAT 6 is perfect for monitoring safety-relevant plants. The corrosionproof design allows analysis in the presence of highly corrosive gases. The OXYMAT 61 is a low-cost oxygen analyser for standard applications. The OXYMAT 64 is a gas analyzer based on ZrO_2 technology to measure smallest oxygen concentrations in pure gas applications.

FIDAMAT 6

The FIDAMAT 6 measures the total hydrocarbon content in air or even in high boiling gas mixtures. It covers nearly all requirements, from trace hydrocarbon detection in pure gases to measurement of high hydrocarbon concentrations, even in the presence of corrosive gases.

ULTRAMAT 6

The ULTRAMAT 6 uses the NDIR measuring principle and can be used in all applications from emission monitoring to process control even in the presence of highly corrosive gases. ULTRAMAT 6 is able to measure up to 4 infrared sensitive components in a single unit.

ULTRAMAT 6 / OXYMAT 6

Both analyzer benches can be combined in one housing to form a multi-component device for measuring up to two IR components and oxygen.

In-situ Continuous Gas Analyzers (CGA)

LDS 6

LDS 6 is a high-performance in-situ process gas analyzer. The measurement (through the sensor) occurs directly in the process stream, no extractive sample line is required. The central unit is separated from the sensor by using fiber optics. Measurements are carried out in realtime. This enables a pro-active control of dynamic processes and allows fast, cost-saving corrections.

Process Gas Chromatographs (Process GC)

MAXUM edition II

MAXUM edition II is very well suited to be used in rough industrial environments and performs a wide range of duties in the chemical and petrochemical industries and refineries. MAXUM II features e. g. a flexible, energy saving single or dual oven concept, valveless sampling and column switching, and parallel chromatography using multiple single trains as well as a wide range of detectors such as TCD, FID, FPD, PDHID, PDECD and PDPID.

MicroSAM

MicroSAM is a very compact explosion proof micro process chromatograph. Using silicon-based micromechanical components it combines miniaturization with increased performance at the same time. MicroSAM is easy to use and its rugged and small design allows mounting right at the sampling point. MicroSAM features drastically reduced cycle times, provides valveless sample injection and column switching and saves installation, maintenance, and service costs.

SITRANS CV

SITRANS CV is a micro process gas chromatograph especially designed for reliable, exact and fast analysis of natural gas. The rugged and compact design makes SITRANS CV suitable for extreme areas of use, e.g. off-shore exploration or direct mounting on a pipeline. The special software "CV Control" meets the requirements of the natural gas market, e.g. custody transfer.

Siemens Process Analytics – Solutions



Fig. 15 Analyzer house (shelter)

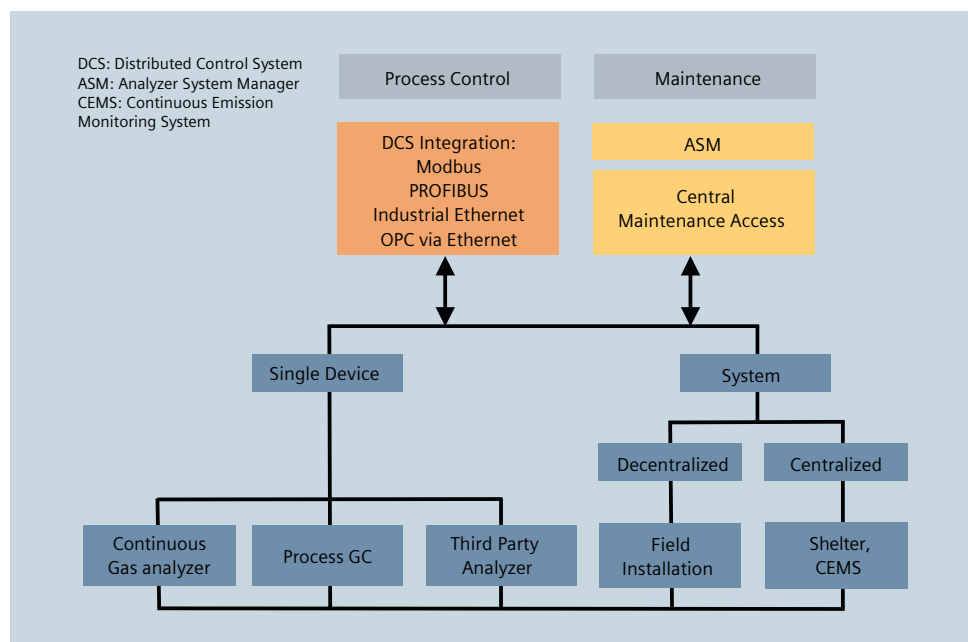


Fig. 16 Networking for DCS integration and maintenance support

Analytical solutions are always driven by the customer's requirements. We offer an integrated design covering all steps from sampling point and sample preparation up to complete analyzer cabinets or for installation in analyzer shelters (fig. 15). This includes also signal processing and communications to the control room and process control system.

We rely on many years of world-wide experience in process automation and engineering and a collection of specialized knowledge in key industries and industrial sectors. We provide Siemens quality from a single source with a function warranty for the entire system.

Read more in chapter "Our services".

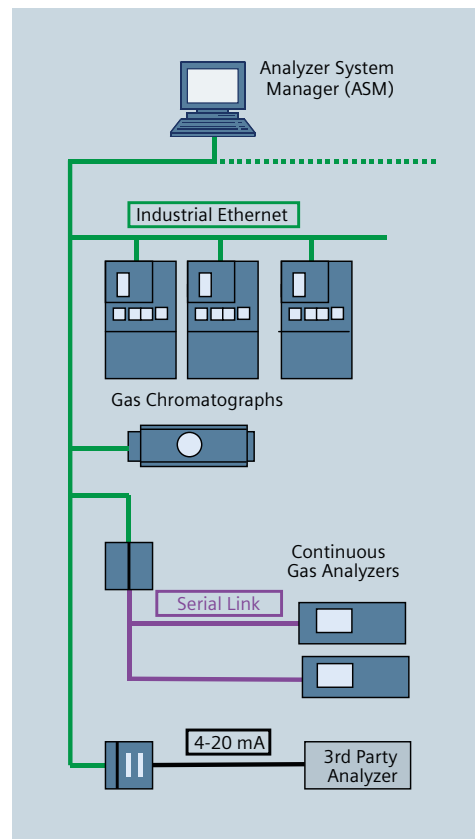


Fig. 17 Communication technologies

Analyzer networking for data communication

Engineering and manufacturing of process analytical solutions increasingly comprises "networking". It is getting a standard requirement in the process industry to connect analyzers and analyzer systems to a communication network to provide for continuous and direct data transfer from and to the analysers. The two objectives are (fig. 16).

- To integrate the analyzer and analyzer systems seamlessly into the PCS / DCS system of the plant and
- To allow direct access to the analyzers or systems from a maintenance station to ensure correct and reliable operation including preventive or predictive maintenance (fig. 17).

Siemens Process Analytics provides networking solutions to meet the demands of both objectives.

Siemens Process Analytics – Our Services

Siemens Process Analytics is your competent and reliable partner worldwide for Service, Support and Consulting.

Our resources for that are

- **Expertise**
As a manufacturer of a broad variety of analyzers, we are very much experienced in engineering and manufacturing of analytical systems and analyzer houses. We are familiar with communication networks, well trained in service and maintenance and familiar with many industrial processes and industries. Thus, Siemens Process Analytics owns a unique blend of overall analytical expertise and experience.
- **Global presence**
With our strategically located centers of competence in Germany, USA, Singapore, Dubai and Shanghai, we are globally present and acquainted with all respective local and regional requirements, codes and standards. All centers are networked together.

Service portfolio

Our wide portfolio of services is segmented into Consulting, Support and Service. It comprises really all measures, actions and advises that may be required by our clients throughout the entire lifecycle of their plant:

- Site survey
- Installation check
- Functionality tests
- Site acceptance test
- Instruction of plant personnel on site
- Preventive maintenance
- On site repair
- Remote fault clearance
- Spare part stock evaluation
- Spare part management
- Professional training center
- Process optimisation
- Internet-based hotline
- FEED for Process Analytics
- Technical consulting

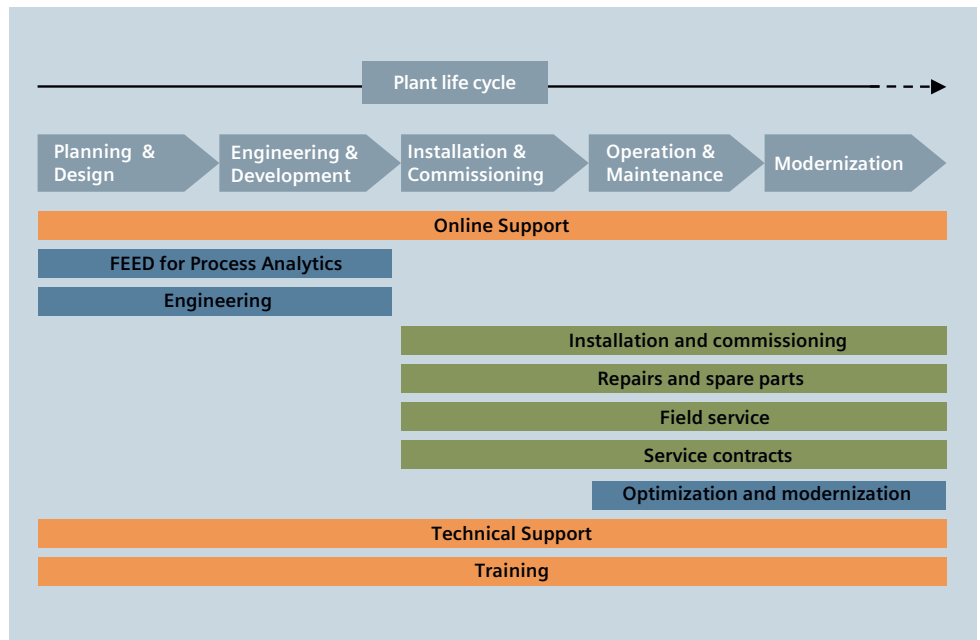


Fig. 18 Portfolio of services provided by Siemens Process Analytics

FEED for Process Analytics

Front End Engineering and Design (FEED for PA) is part of the planning and engineering phase of a plant construction or modification project and is done after conceptual business planning and prior to detail design. During the FEED phase, best opportunities exist for costs and time savings for the project, as during this phase most of the entire costs are defined and changes have least impact to the project. Siemens Process Analytics holds a unique blend of expertise in analytical technologies, applications and in providing complete analytical solutions to many industries.

Based on its expertise in analytical technology, application and engineering, Siemens Process Analytics offer a wide scope of FEED services focused on analyzing principles, sampling technologies, application solutions as well as communication system and given standards (all related to analytics) to support our clients in maximizing performance and efficiency of their projects.

Whether you are plant operators or belong to an EPC Contractor you will benefit in various ways from **FEED for Process Analytics** by Siemens:

- Analytics and industry know how available, right from the beginning of the project
- Superior analyzer system performance with high availability
- Established studies, that lead to realistic investment decisions
- Fast and clear design of the analyzer system specifications, drawings and documentation
- Little project management and coordination effort, due to one responsible contact person and less time involvement
- Additional expertise on demand, without having the costs, the effort and the risks of building up the capacities
- Lowest possible Total Costs of Ownership (TCO) along the lifecycle regarding investment costs, consumptions, utilities supply and maintenance



Notes:

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