

# Use of Process Analytics in Aromatics (BTX and phenol) production plants

## Case Study · August 2008

Aromatics are planar, cyclic compounds with conjugated double bonds, consisting of the elements carbon and hydrogen. Aromatics are important intermediates and used as starting materials for a wide range of products. Aromatics are derived from crude oil and, in small quantities, from coal.

Siemens Sensors and Communication, a leader in process analytics, has proven worldwide its competence to plan, engineer, manufacture, implement and service analyzer systems for use in aromatics producing plants

Process automation equipment including gas chromatographs and other process analyzers contribute essentially to control and optimize these processes.

## Chemical Industry

**SIEMENS**

# Aromatics

## BTX and phenols

### Aromatics, phenols

Aromatics, so called because of their distinctive perfumed smell, are hydrocarbons that consist exclusively of the elements carbon and hydrogen. The basic aromatics are benzene, toluene and the xylenes (BTX). In chemical industry, the BTX aromatics - largely produced from petroleum - are highly important. They help to fulfill human needs in many areas, such as health, hygiene, housing and food. Examples are pharmaceuticals (Aspirin, Penicillin), packaging materials, clothes, car tires, sport articles, CDs etc.

Phenols are a class of aromatical compounds consisting of a hydroxyl group (-OH) attached to an aromatic hydrocarbon group. The simplest of the class is phenol ( $C_6H_5OH$ ). It is a flammable, colorless or white solid with a strong sweet odor. It is usually sold and used as a liquid, because it dissolves fairly well in water.

The largest market for phenol is in the production of Bisphenol A (BPA), which is manufactured from phenol and acetone. BPA is, in turn, used to manufacture polycarbonate and epoxy resins. Both polycarbonate and epoxy resins are used in many industries and in countless items like CDs or circuit boards or fibre glass. Several routes exist for the production of phenol. Today, the oxidation of Cumene (produced from benzene) is by far the most common route.

Process analyzers, mainly process gas chromatographs, are standard in phenol production plants. They deliver key data to process and product quality control and plant asset management.

Siemens Sensors and Communication provides efficient analyzers, analyzer systems, expertise and solutions to this tasks.

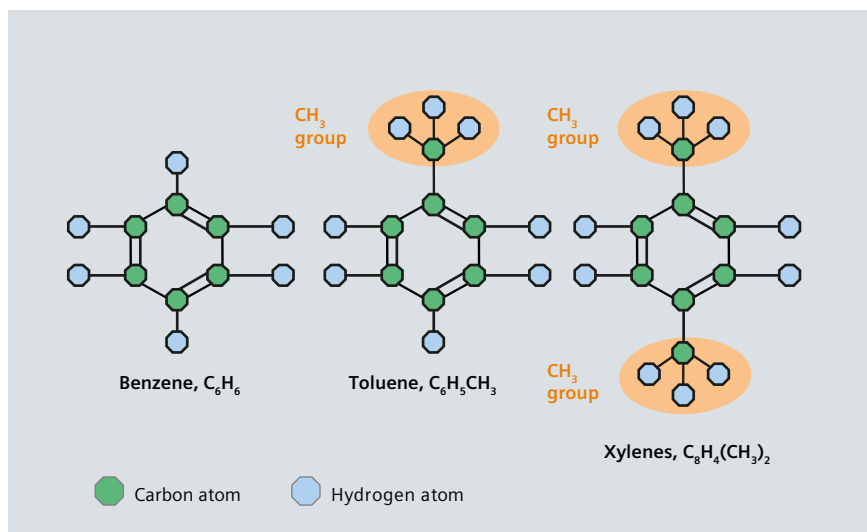


Fig. 1 The main aromatics: Benzene, Toluene, and Xylene(s)

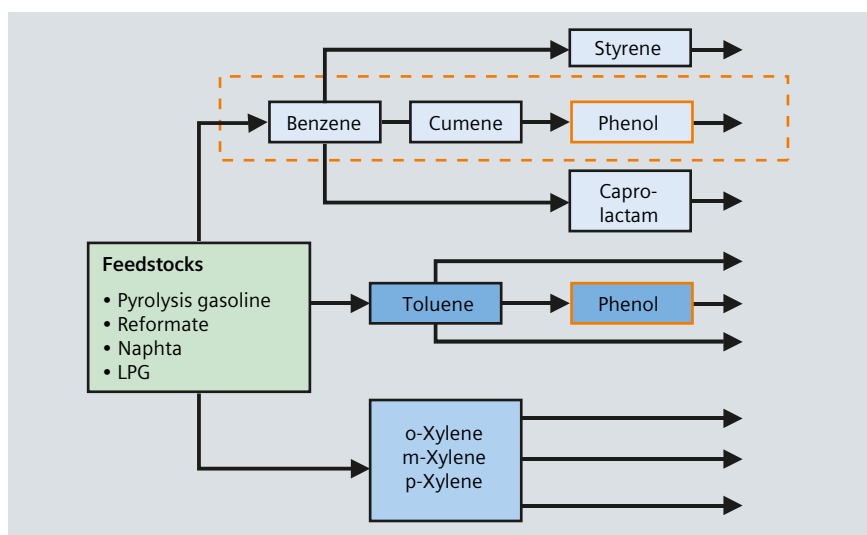


Fig. 2 Production routes of aromatics

## Aromatics

Aromatics, so called because of their distinctive perfumed smell, are hydrocarbons that consist exclusively of the elements carbon and hydrogen. The main aromatics are benzene, toluene and different xylenes, in short BTX. Toluene and the xylenes are derived from benzene by replacing one or two hydrogen atoms by a CH<sub>3</sub> group (fig. 1). The phenols belong to the group of aromatics.

In the chemical industry, aromatics rank amongst the most important intermediate products with a wide range of applications. Aromatics are produced from reformat, pyrolysis gasoline, naphtha, and LPG.

While reformat is the major source of aromatics in most of the world, pyrolysis gasoline is also a significant source of aromatics. Both reformat and pyrolysis gasoline are mixtures of aromatic and aliphatic hydrocarbons, with the proportions of each and the composition of the aromatic portion varying according to the processing conditions during their production.

They differ, however, in the following important respects:

- *Pyrolysis gasoline* is a by-product from olefins manufacture and its yield and composition are determined primarily by conditions fixed by the needs of the olefins producer.
- *Reformat* on the other hand is produced deliberately from naphtha and, within the technical limits available, its production and composition can be set by the needs of the aromatics producer.

In general, pyrolysis gasoline tends to be richer in total BTX than reformat, although an overlap occurs under extreme conditions. The processes applied for the extraction and subsequent separation of the aromatics contained in the two feedstocks are considerably influenced by this difference in composition, with pygas treatment geared primarily to benzene recovery and reformat treatment geared to the extraction of the whole BTX, with particular emphasis on xylenes.



Fig. 3 Phenol production site INEOS Gladbeck, Germany

## Feed materials

■ **Pyrolysis gasoline**  
is the aromatics-rich naphtha-range stream produced in sizeable quantities by an ethylene plant when it cracks butane, naphtha, or gasoil. Pygas resembles reformat. It can serve as a high-octane blendstock for motor gasoline or as a feedstock for an aromatics extraction unit.

■ **Reformat**  
are high-octane liquid products gained from petroleum refinery typically having low octane ratings, through the process of catalytic reforming.

■ **Naphtha**  
is a group of various liquid hydrocarbon intermediate refined products of varying boiling point ranges from 20 to 75 °C which may be derived from oil or from coal tar, and perhaps other primary sources.

■ **LPG**  
(Liquefied petroleum gas) is a mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles. LPG is manufactured during the refining of crude oil, or extracted from oil or gas streams as they emerge from the ground. At normal temperatures and pressures, LPG will evaporate.



# Production of aromatics (BTX)

## Process analytics in BTX units

### Fractionation of aromatics

#### Aromatics Fractionation Units

(also called BTX units) are used to separate a mixture of aromatics into pure Benzene, Toluene, and mixed Xylenes. The resulting BTX product streams are either processed by a chemical unit within the refinery itself or sold for processing in other plants. The feedstock is typically the reformate from a catalytic reforming unit (reformer).

### BTX production

The typical reformate feed stock stream is rich in aromatics with impurities of light paraffins and light naphthenes (P&N), which are predominantly separated in the dehexanizer. In the benzene column, the benzene and the remaining impurities go overhead while the toluene, mixed xylenes, ethyl benzene, and C9+ aromatics go out the bottom. The overhead enters an absorber/stripper unit to purify the benzene. The remaining P&N enters the benzene recovery column, where any remaining benzene is stripped out before the impurities are sent on to further processing.

The bottoms of the benzene column enters an absorber/stripper unit to remove any remaining P&N impurities. The overhead passes to the toluene recovery column where toluene is stripped out before the impurities are sent onto further processing. The purified stream enters the toluene column to separate the toluene.

Note: *Different* solvent extraction processes may be used from plant to plant.

### Process analytics in BTX units

In BTX units, process gas chromatographs are used to

- ensure product purity and
- minimize loss of product.

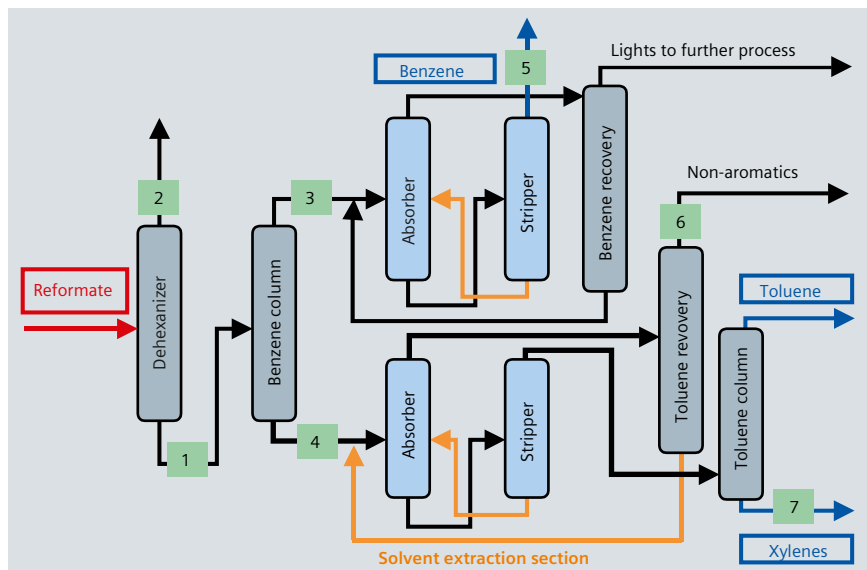


Fig. 4 BTX separation from reformate

Sampling point	Sampling stream	Measuring task	Meas. components [%]	Siemens Analyzer
1	Dehexanizer bottoms	Minimize impurities before getting to the products stream	MCP, Benzene	MAXUM
2	Dehexanizer overhead	Reduce benzene loss	Benzene	MAXUM
3	Benzene column overhead	<ul style="list-style-type: none"> <li>■ Minimize toluene overhead loss</li> <li>■ Minimize impurities reaching benzene product</li> </ul>	MCH, Toluene, Benzene	MAXUM
4	Benzene column bottoms	<ul style="list-style-type: none"> <li>■ Minimize benzene loss to toluene stream</li> <li>■ Minimize impurities from toluene product stream</li> </ul>	Benzene, Toluene	MAXUM
5	Benzene product	Reduce impurities	MCP, MCH Toluene (ppm)	MAXUM
6	Non-aromatics	Reduce toluene loss	Toluene	MAXUM
7	Mixed xylenes	Reduce toluene loss	Toluene	MAXUM

Table 1 Analysis measuring tasks, related to fig. 4  
MCP: Methylcyclopentane, MCH: Methylcyclohexane

Special attention should be paid to the analyzer configuration because many of the compounds are very difficult to properly separate and analyze. High temperature ovens and high efficiency separation technology (capillary columns) support short analysis times. The Siemens MAXUM II Process Gas Chro-

matograph offers all features and technologies to perfectly solve this application. Today the oxydation of cumene (Hock process) is by far the dominant synthetic route to phenol.

Table 1 informs about the various analysis measuring tasks.

# Production of phenol

## Process analytics in the Cumene route

Cumene (produced from benzene and propene) is at first oxidized with oxygen to cumene hydroperoxide (CHP). CHP is then cleaved to phenol and acetone by using a strong mineral acid as catalyst. Beside phenol also acetone is received as by-product. Cumene is the most important feedstock for the production of phenol. Starting with benzene and propene, the cumene route includes several steps:

- **Production of cumene** (Isopropylbenzene) via alkylation of benzene with propylene.
- **Oxidation of cumene** to cumene hydroperoxid, CHP. This reaction is usually carried out in a series of reactors at temperatures of 90 - 130 °C and pressures of 1-10 at. Fresh and recycled cumene is fed, together with oxygen from air. Careful control of acidity levels, temperature and pressure are vital as at higher temperatures, the hydroperoxide is unstable and can decompose violently. The CHP concentration is then increased by vacuum distillation to 65-90 %. The off-gas is purified by condensation and adsorption.
- **Cleavage** Based on an ionic mechanism, in the cleavage section CHP is reacting to acetone and phenol in presence of a sulfuric acid as catalyst. The first leavage reactor operates at 40-80 °C, the second above 100 °C. The product is cooled and neutralized using sodium phenolate (NaPh).
- The organic phase from the cleavage reaction, consisting of phenol, acetone, cumene, AMS, water, and byproducts, is sent to the **distillation section** for separation into acetone, phenol, tar, and crude AMS. The aqueous phase is sent to wastewater treatment.

**Alternatives** for coproduct-free phenol production routes are known (toluene route) or under design, e.g. the direct oxidation of benzene to phenol.

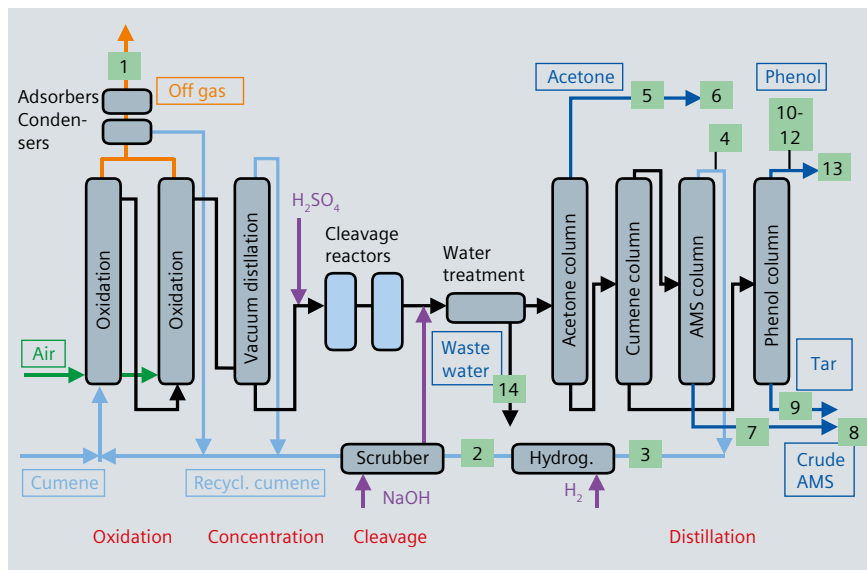


Fig. 5 Phenol production from cumene, flow diagram (AMS: a-methylstyrene)

Sampling point	Sampling stream	Measuring task (compounds)	Measur. range	Measuring task	Siemens Analyzer
1	Off-gas after activated carbon adsorbers	Total hydrocarbons	Acc. to regulations	Emission control	FIDAMAT
2	Cumene after hydrogenation reactor	Ketones, aromatic hydrocarbons, aromatic olefines, phenol, hydrogenation products of aromatics	ppm/% level	Hydrogenation control	MAXUM
3	Cumene before hydrogenation reactor				
5	Acetone column head	Alcohols, aldehydes, ketones, aromatics, condensation products of acetone, e.g. di-acetone alcohol	ppm/% level	Control of by-products	MAXUM PTGC
6	Pure Acetone		ppm level	Product quality control	
4	Head product AMS column	Aromatic hydrocarbons, aromatic olefines, phenol	ppm/% level	Control of by-products	MAXUM
7	AMS column bottom		ppm/% level	Control of by-products	
8	Pure AMS		ppm level	Product quality control	
9	Phenol column bottom tar	Phenol, aromatic ketones, aromatic high boiling constituents	% level		MAXUM PTGC
10	Phenol column head after various purification steps	Ketones, aromatic hydrocarbons, aromatic olefines, phenol, phenolic constituents (e.g. kresols), heterocyclic constituents (e.g. furanes)	ppm/% level	Control of by-products	MAXUM PTGC
11	Pure phenol		ppm level	Product quality control	
12					
13					
14	Wastewater treatment drum	Total Organic Carbon	Acc. to regulations	Wastewater control	TOC

Table 2 Sampling points, measuring tasks and analyzers, correlated to fig. 5

# MAXUM Process GC

## The solution provider for process analysis in phenol plants

### General objectives

In phenol plants, process gas chromatographs are by far the most important process analyzers. They deliver detailed data from the process and enable the control system to continuously optimize the process. The main objectives are

- to optimize and control plant operation for best efficiency and product quality (e. g. impurities in pure phenol < 100 ppm) by continuous monitoring of the process streams composition
- continuous control of by-products to minimize expensive treatment steps such as distillation or ion exchange,
- online product purity control to avoid expenses for a process monitoring laboratory analysis.

### MAXUM II controls process conditions

Product quality of a phenol plant strongly depends on parameters such as

- process stream composition,
- reaction temperatures,
- separation performance, etc.

For process profitability and product quality, a phenol plant must be operated as close as possible to the particular optimal process parameters. This also provides maximum throughput and minimized production costs.

Gas chromatography can support this objective essentially.

### Flashheater injection module

This injection module is specially adapted to vaporize high boiling liquid samples, such as phenols, AMS, fatty alcohols, or glycols. The flashheater combines the design requirements of a liquid injection valve for process use with the performance of a laboratory injector. Optimal and ultra-fast vaporizing is guaranteed by the design of the

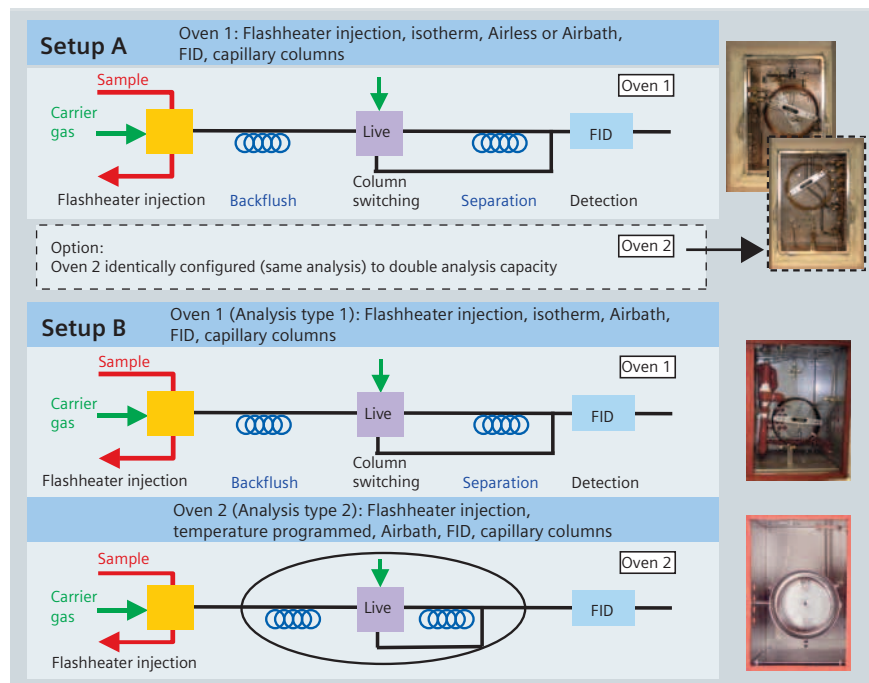


Fig. 6 MAXUM II: Dual oven concept with Airless (A) and Airbath (B) configuration

plunger inside of the injector. No peak tailing effects are occurring.

The plunger is directly heated (appr. 1 000 Amps) with a temperature rise of about 250 °C/min. Heating time is adaptable to the properties of the sample. The control unit also manages a time delay of appr. 0.2 s between moving the plunger into the vaporizer chamber and start of heating.

### Outstanding features

The Siemens MAXUM edition II (fig. 11) represents the top technology with outstanding features resulting in a high versatility to solve demanding application tasks with best possible analytical results at lowest costs. Selected features especially for sophisticated applications, such as in phenol plants, are:

- Multiple analytical tools such as injectors, ovens, detectors or columns to adapt the hardware perfectly to the analytical needs

- Single and independent dual oven concept (fig. 6) for minimizing the number of analyzers
- Temperature programmed oven option to optimize separation and analysis time for high boiling and complex mixtures
- Airless oven to reduce utility costs
- Flashheater injection module (fig. 7) to optimize the evaporation of high boiling liquid samples and to provide lowest detection limits < 1 ppm.
- Valveless column switching to reduce maintenance

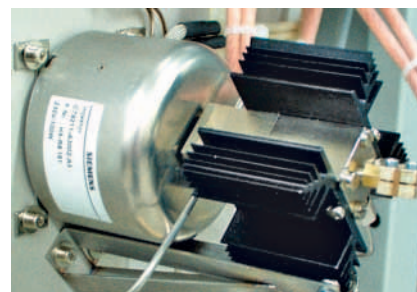


Fig. 7 Flashheater injection module

# 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 & 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. 8-10)
- process gas chromatographs (fig. 11-12)
- 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. 9 Series 6 gas analyzer (field design)



Fig. 10 LDS 6 in-situ laser gas analyzer



Fig. 11 MAXUM edition II Process GC



Fig. 12 MicroSAM Process GC

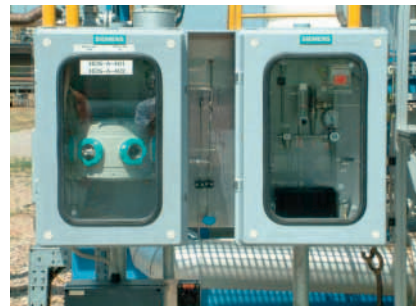


Fig. 13 SITRANS CV Natural Gas Analyzer

# 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 analyser 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 corrosion-proof 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<sub>2</sub> technology to measure smallest oxygen concentrations in pure gas applications.

#### 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.

#### 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.

### In-situ Continuous Gas Analyzers (CGA)

#### LDS 6

LDS 6 is a high-performance in-situ process gas analyser. 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

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 analyser cabinets or for installation in analyser 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. 15 Analyzer house (shelter)

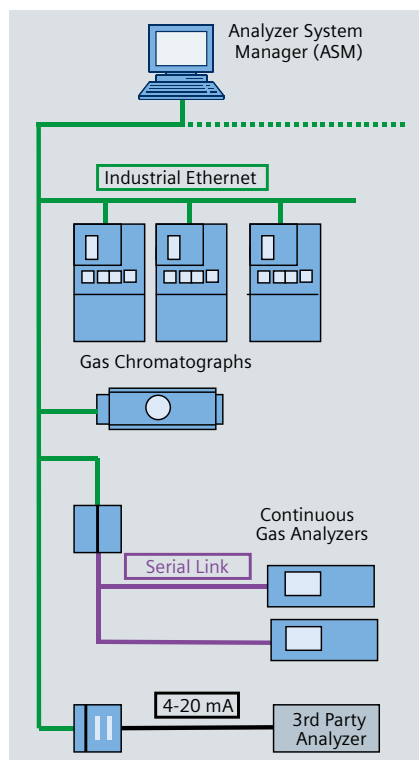


Fig. 14 Communication technologies

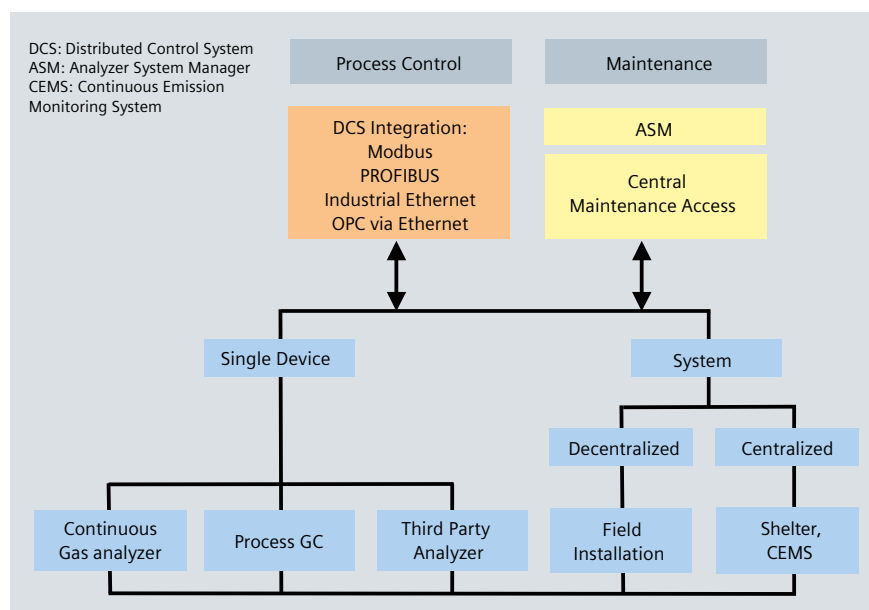


Fig. 16 Networking for DCS integration and maintenance support

## 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 analysers or systems from a maintenance station to ensure correct and reliable operation including preventive or predictive maintenance (fig. 14).

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

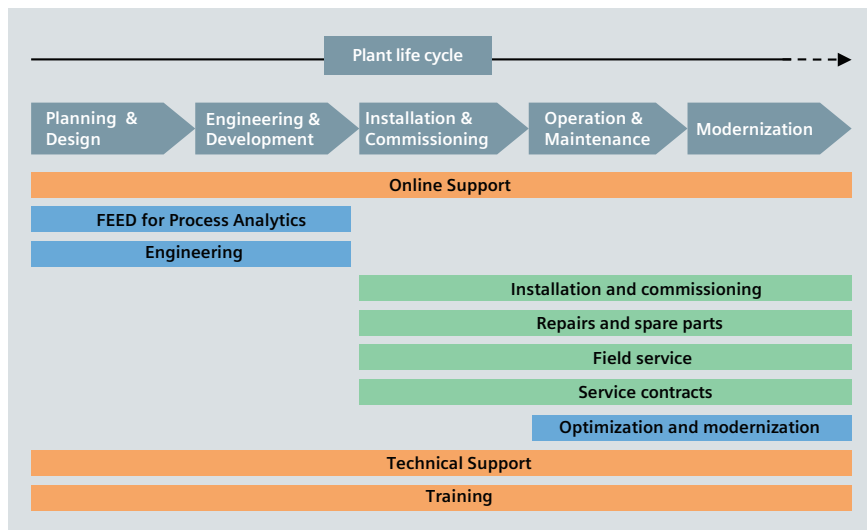


Fig. 17 Portfolio of services provided by Siemens Process Analytics

## 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 analysing 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.

## Siemens Process Analytics - Answers for industry



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