

SHELL INTERNATIONAL CHEMICALS B.V.
AMSTERDAM - THE NETHERLANDS

SHELL EO/EG PROCESS MEMORANDUM 108

SUBJECT : PROCESS ANALYSERS

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INTRODUCTION

The object of this document is to review the preferred analysis methods and the minimum requirements for the quality measuring instruments.

On-line stream analysers to monitor feed stock impurities and composition of feed and product streams are necessary for an economic and safe operation of the process.

Moreover, a number of on-line analysers in areas outside the EO reactor are mentioned.



TABLE OF CONTENTS

1	STREAM ANALYSIS REQUIREMENTS.....	3
1.1	EO reactor feed and product streams	3
1.2	Ethylene and methane feed streams	4
1.3	Recycle gas stream	4
1.4	Residual absorber overhead	4
1.5	Liquid streams	4
2	PROCESS ANALYSER SPECIFICATIONS.....	6
2.1	Process gas chromatographs.....	6
2.2	Mass spectrometer	6
2.3	Oxygen analysers	8
2.4	Infrared absorption analysers.....	9
2.4.1	Reactor feed gas, ethylene contents	9
2.4.2	Reactor feed / product gas, carbon monoxide	9
2.5	Chlorides analyser.....	9
2.6	EO analysers	10
2.7	Total sulphur analyser.....	11



1 STREAM ANALYSIS REQUIREMENTS

1.1 EO reactor feed and product streams

A single on-line process gas chromatograph (GC) is required to analyse feed and product gases for ethylene, ethane, methane, nitrogen, carbon dioxide and oxygen plus argon. The analysis for these components is required in the flammability determinations at the reactor inlet and outlet and for monitoring changes in CO₂ concentration. It is not necessary for the process chromatograph to split argon and oxygen into two separate peaks since separate oxygen analysers are provided. When calculating the oxygen and argon concentration from the combined peak area, it is important to note that the two components have different response factors. For this reason, the response factor of the combined oxygen/argon peak will vary depending on the ratio of the two components.

A separate, on-line process GC is required to determine EO in the common reactor product stream, thus providing enough analytical data for calculation of the reactor system selectivity.

In addition to the analysis of ethylene in the common reactor feed as by the on-line GC, a separate ethylene analyser is required for ethylene feed rate control. This analyser shall give a continuous recording on the ethylene concentration and shall be based on the infrared absorption principle.

Fast response on-line oxygen analysers are required in the common reactor feed gas stream (two analysers) and in the reactor product gas stream (one analyser) for continuous monitoring of the oxygen concentration. Each analyser shall be provided with a high alarm and a function analysing fast increases in gas loop oxygen concentration. The analysers will be connected to the PLC to initiate the oxygen shutdown system in case the oxygen concentration might increase above pre-set levels, see process memorandum 111. In addition a deviation alarm between the two reactor inlet oxygen analysers is added to reduce the probability of failure of the shut down system. It is required to have an extra oxygen analyser installed to serve as a common spare.

To enable monitoring of the dedicated reactor product streams and to study the performance of the two reactors separately, one additional oxygen analyser is provided switching between the reactor outlets. The information on the performance of the separate EO reactors, as measured by the oxygen analyser, will be used to, if required, fine-tune the flow through the EO reactors by manually setting the control valves in the dedicated reactor inlets to achieve similar performance of the two reactors. This analyser will not be connected to the oxygen safeguarding system. No fast loop is applied for this analyser; maximum residence time is 3 minutes.

A chlorides analyser is required to determine the following chlorinated hydrocarbons: ethylchloride, vinylchloride, methylchloride, ethylene dichloride and preferably allylchloride in the common feed to the EO reactors for calculation of the I-factor.

For the detection of the on-set of a runaway reaction, it is required to have a carbon monoxide analyser on the common reactor product gas stream. It is also recommended to apply an analyser on the common reactor feed to detect pre-ignition.



The analysers should be of the infrared absorption type.

1.2 Ethylene and methane feed streams

On-line continuous monitoring of both the ethylene and methane feedstocks for total sulphur is recommended to safeguard the catalyst. One analyser can be used to analyse the ethylene and methane feeds one after another. A stream selector system shall send either a methane or an ethylene sample to the analyser.

1.3 Recycle gas stream

In order to have a measure for the performance of the EO absorber, it is required to have an on-line process GC at the recycle gas outlet from the EO absorber to measure the EO concentration. The analyser alternately switches between the EO absorber overhead and the residual absorber overhead.

1.4 Residual absorber overhead

In order to have a measure for the performance of the residual absorber, it is required to have an on-line process GC at the overhead gas outlet from the residual absorber to measure the EO concentration. The analyser alternately switches between the EO absorber overhead and the residual absorber.

1.5 Liquid streams

On-line analysers are required for the following liquid streams:

1. pH and conductivity of bleed from HP steam drum to MP steam drum
2. Conductivity of condensate from CO₂ stripper overhead knock out drum
3. Conductivity of liquid from water knock out drum
4. Density of CO₂ stripper bottoms
5. pH of quench bleed stripper bottoms
6. pH of quench bleed flasher bottoms
7. pH of lean absorbent
8. pH of glycol bleed flasher bottoms
9. pH of LE column bottoms
10. Density of aqueous EO to glycol unit feed pump (see Figure 1)
11. Composition of MEG, DEG and TEG
12. UV of MEG: 220 nm, 275 nm and 350 nm



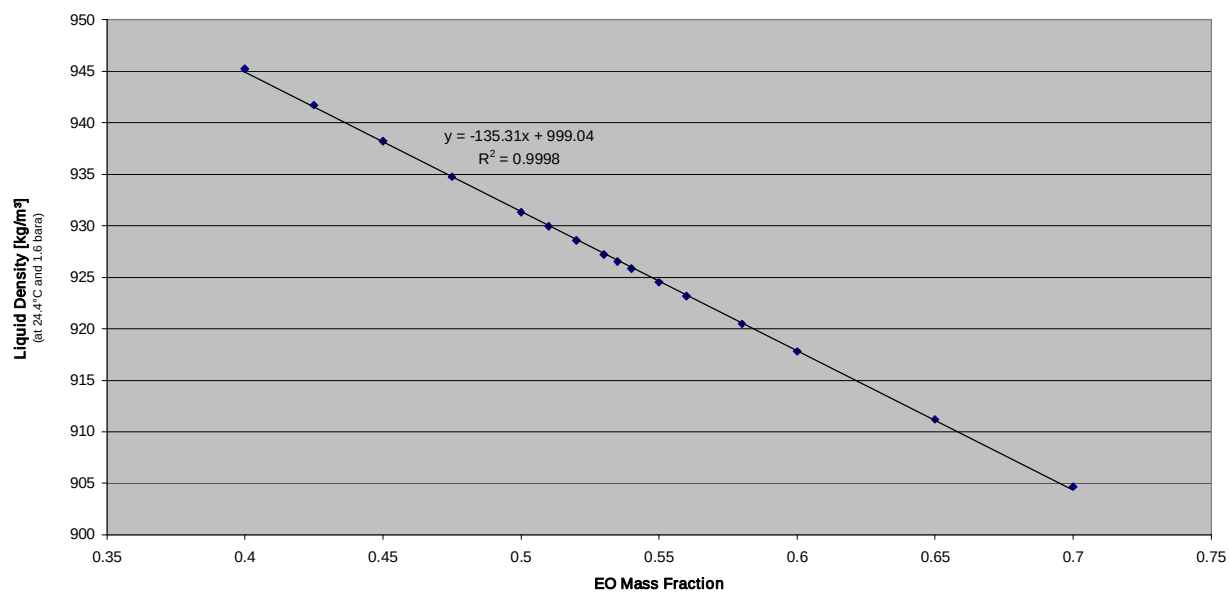


Figure 1 Density of Aqueous EO Solutions



2 PROCESS ANALYSER SPECIFICATIONS

Only the basic specification data for on-line process analysers are provided. For engineering and procurement more detailed specifications will have to be prepared.

In case name and model of a manufacturer are mentioned this indicates that those analysers have been successfully applied.

For a description of the sampling systems, refer to process memorandum 109, which provides a sample flow scheme and other information required for detailed engineering of sampling systems.

For the design and engineering of the sampling systems and analyser facilities, the following vendors are recommended:

Imtech, Tholen, The Netherlands,
tel. +31 166 609609 / fax +31 166 609 600
Controlec Construction, Spijkenisse, The Netherlands,
tel. +31 181 624 666 / fax +31 181 623 087

2.1 Process gas chromatographs

Manufacturers: ABB Process Analytics
Siemens e.g. Siemens MAXUM edition II
Yokogawa

Reactor feed and product gas composition GC. Operating ranges.

<u>Component</u>	<u>Range, % Mole</u>
Nitrogen	0 - 100 note 1)
Argon + Oxygen	0 - 20 note 2)
Carbon dioxide	0 - 10
Ethane	0 - 5
Ethylene	0 - 40
Methane	0 - 70

1) The wide range for nitrogen is required for start-up. After start-up the system should be calibrated for 0 - 5%.

2) May be presented as one peak, representing the sum of Ar+O₂.

2.2 Mass spectrometer

As an alternative to the process gas chromatographs a mass spectrometer could be applied. In order to assure proper, accurate and reliable analytical results for a mass spectrometer qualified and experienced maintenance and calibration technicians are vital and an absolute necessity for success. Experience has shown that during initial



start-up a mass spectrometer technician must be dedicated full time to ensure successful operation of the system.

Experience with mass spectrometers in Shell designed EO/EG plants is limited. Only one plant has been designed with a mass spectrometer and the information from that plant is stated below. Other plants have retrofitted mass spectrometers from other vendors. However, no information on the performance of these analysers is available at the moment.

The mass spectrometer must be connected to analyse the common feed inlet to the reactors as well as the product gas from the reactors. The mass spectrometer comes with a 16 port rotary valve. For the connection to the process refer to the sampling system quality instruments drawings as provided in process memorandum 109. All tubing should be of 1/8" diameter or less in order to keep 'clearing' time to a minimum. Note that the mass spectrometer is not shown in these drawings.

Components to be analysed: CH₄, C₂H₄, C₂H₆, EO, CO₂, N₂, O₂, Ar and H₂O (9 components). Relative accuracy within 0.5 %. Sample time: 0.5 minute per sample, every value updated every 1.5 minutes. As for the analysis of CO, there is no accurate way to measure this using a mass spectrometer due to the base peak being the same as N₂ and the fragment matrix being so similar to CO₂. Therefore a dedicated analyser for the measurement of CO has to be available.

The recommended type is the ABB Questor Mark IV quadra-pole mass spectrometer with its own air conditioner and air filtration system. The mass spectrometer should have 3/4" quadra-poles which are good for mass to charge ratios (m/Z) from 0 to 250. The detector must be a Faraday plate type with a lower detection limit of 10 ppm. The stand alone PC of the unit should be located within a few feet of the mass spectrometer to allow for easy troubleshooting and calibration. The incoming sample is pressure reduced (1.8 bar) and cooled to 20°C and is filtered via 2 micron in-line filters.

Experience shows that 8 separate gas mixtures are needed to do a proper calibration. These calibration gases should be of the highest grade available. The following calibration gases have to be used:

1. Ultra High Purity (UHP) Argon (99.999%)
2. 25% ethylene, balance Argon
3. 10% ethane, balance Argon
4. UHP Methane (99.999%)
5. 10% CO₂, balance Argon
6. 2% EO, balance Argon
7. 25% C₂H₄, 0.1% C₂H₆, 4% N₂, 2.5% CO₂, 2.5% EO, 0.5% Ar, balance CH₄
8. 3.75% O₂, 14% N₂, balance CH₄

Mixture 7 has a 6-12 month shelf life due to the presence of EO. Mixture 8 is a highly explosive mixture that comes at a very low cylinder pressure and does not contain much volume.

The mass spectrometer must be overhauled every 6 months to a year, depending on how clean the process is. This requires a downtime of about 36 hours. Alternate



means of obtaining the analysis data is required during this downtime. A spare parts service agreement for maximum 3 days parts turn-around on non-stock items is advised.

2.3 Oxygen analysers

Manufacturer: Servomex
Model: Servomex series 2200

The recommended oxygen analysers are of the paramagnetic, high-speed type, which directly use the paramagnetic susceptibility of the gas as a measure of the O₂ concentration. Analysers which use the paramagnetic susceptibility in combination with thermal conductivity measurements are not recommended.

The presence of other compounds will affect the outcome of the oxygen analyser. Therefore, in the DCS the indication of the oxygen analyser will have to be compensated for the diamagnetic properties of all components in the gas stream. The direct, uncompensated value will be sent to the oxygen safeguarding system to ensure a fast enough response.

The oxygen analysers must have a live zero to differentiate in case of malfunction between a zero signal and a zero percent oxygen reading. The analyser calibration will be performed with a prepared sample gas that has an oxygen content in the normal range of operation of the analyser. There shall be no range change switches provided as part of the analyser, calibration on air or operation on a higher range is not appropriate. Calibrate the oxygen analysers at different times to prevent common mode failure of all analysers.

Oxygen analysers connected to the oxygen safeguarding system are required for the common reactor feed gas stream (two analysers) and the common reactor outlet gas stream (one analyser) plus an installed spare, switchable to any of these duties. The oxygen shut-down system will be initiated by high oxygen content in either process stream.

Recommended operating range: 0 - 10% mole oxygen. Repeatability within max 1% of full scale.

The common spare analyser must be capable to take over from any of the three oxygen analysers connected to the safeguarding system. The signal from the common spare analyser must be properly connected to the oxygen shut-down logic, depending on whether it is analysing the feed or product. In case one of the three oxygen analysers has been put in maintenance mode and has not been replaced by the common spare analyser, the oxygen shut down system shall be activated. In case the common spare analyser is in take-over mode an alarm should signal. The trip and alarm functions of the oxygen analyser under maintenance shall be taken over by the common spare analyser.

The oxygen analysers shall be provided with:

- instrument failure alarm
- low flow alarm in the sample loop to the analyser



- calibration mode alarm
- barometric pressure compensation (flow cell pressure)

The sampling system has to be designed so that the time lag between the sample leaving the process connection and arriving at the analyser shall be well below 10 seconds. To achieve this, the sample fast loop for the reactor feed and reactor outlet gas analysis shall be returned to the residual EO absorber. The maximum of 10 seconds for the time lag refers only to the sample transport time. The overall lag time is the time elapsed between starting to open the oxygen flow control valve and the appearance of the oxygen on the analyser in the control room. The overall lag, as demonstrated in a plant test, may not exceed 20 seconds. The fast loop of the common reactor feed stream analysers shall be equipped with two low flow trip initiators, arranged in a 1 out of 2 configuration. The fast loop of the common reactor outlet stream analyser shall be equipped with a low flow trip. The low flow trip initiators activate the oxygen shut down system.

An oxygen analyser is required to monitor the dedicated reactor product streams. This analyser will not be connected to the safeguarding system. The recommended operating range is 0 – 10 % mole oxygen. Relative accuracy within 0.5 % max.

2.4 Infrared absorption analysers

Manufacturers: Maihak A.G.
Emerson Process Management
Servomex

2.4.1 Reactor feed gas, ethylene contents

Recommended measuring range: 0 - 50% mole C₂H₄ in the reactor feed gas.
Relative accuracy 1% max. Total response time 60 seconds.

2.4.2 Reactor feed / product gas, carbon monoxide

An IR analyser should be applied to measure the carbon monoxide content in the reactor feed (optional) and the common product stream (required). The recommended measuring range is 0 - 500 ppm mole CO. The instrument should be provided with an adjustable alarm switch to operate at a pre-set CO level. Total response time to be maximum 60 seconds.

2.5 Chlorides analyser

Manufacturers: ABB Process Analytics
Siemens e.g. Siemens MAXUM edition II
Yokogawa
Foxboro

FID type GC to be connected to the common fast loop in the EO reactor inlet. The



following components are to be analysed: ethylchloride, vinylchloride, methylchloride, ethylene dichloride and preferably allylchloride. Relative accuracy within 1.5 %. Total cycle time 20-30 minutes. Measuring range: 0 - 10 ppm mole. Minimum detection 0.3 ppm. Minimum guaranteed repeatability 3%.

2.6 EO analysers

GLC for EO reactor product gas, EO absorber/residual absorber overhead. Relative accuracy to be within 2 %. Total response time to be maximum 5 minutes.

Recommended operating ranges:

- 0 - 5% mole EO in reactor product gas. The sample shall be drawn directly from the hot sample loop and the analyser is to operate at a sufficiently high temperature to prevent any condensation of water and subsequent losses of EO.
- 0 - 200 ppm mole EO in the EO absorber overhead. The analyser alternately switches between the EO absorber overhead and the residual absorber overhead.
- 0 – 1000 ppm in the residual absorber overhead.
- 0 – 10 ppm in the vent absorber overhead.

EO in the loop gas can be analysed by a mass spectrometer, if present.



2.7 Total sulphur analyser

The recommended method is to apply an analyser where all sulphur components are converted into H_2S in a micro hydrogenation converter. The detection of the sulphur can be done by either flame photometric detection or by colorimetry, measuring the colour density resulting from formation of lead sulphide on an impregnated tape. The range should be 0 to 1 ppm total sulphur in ethylene or methane combined. If sulphur content in the separate methane feed is much higher (beyond range of analyser), a separate lab analyser should be provided. The accuracy of the on-line analyser should not be compromised, as a good sulphur content estimate is required for the ethylene feed.

Manufacturers: ABB Process Analytics
 Model: ABB vista 2000
 Houston - Atlas, Inc.
 Model: VII Series
 DelMar
 Model: TG series

