

FROM: Jeff Coburn, RTI
TO: Docket
SUBJECT: Information on Chloride Trap Control Device Received from
ExxonMobil
DATE: October 31, 2002

- (1) Analytic Techniques Available Within SYNETIX for the Measurement of Chloride in Gas
- (2) Chloride Guard Monitoring
- (3) Cl analysis
- (4) Viso Hot Flue
- (5) Chloride Trap Data



ANALYTICAL TECHNIQUES AVAILABLE WITHIN SYNETIX FOR THE MEASUREMENT OF CHLORIDE IN GAS, LIQUID AND SOLID SAMPLES.

The analytical techniques commonly used in Synetix Billingham are described.

1 : CORNING 926 CHLORIDE ANALYSER.

Principle : coulometric titration
formation of silver chloride (precipitate) allowing to regain initial potential.



Samples : solid and possibly liquid (ideal for chloride loading on discharged absorbent).

Range : percent level only.

Sample prep : grinding of the sample, dissolve 1g in 25ml of 50%v/v Nitric Acid, boil for an hour, cool down and dilute to 250ml with water.

2 : DRÄGER TUBE

Principle : The tube contains two layers : a white pre-layer and a blue indicating layer. When air or gas sample are sucked through the tube, the indicating layer changes colour to yellow in the presence of hydrochloric acid.

$\text{HCl} + \text{bromophenol blue} \rightarrow \text{yellow reaction product.}$

Sample : gas only.

Range : two different tubes : 1 to 10ppm and 50 to 5000ppm.

Cost : £26 for 10 tubes.
£56 for pump.

Sample prep : none.



3 : HALL DETECTOR FROM VARIAN.

Principle : The Hall electrolytic conductivity detector (Hall detector) used in gas chromatography is a highly sensitive detector ordinarily configured to detect exclusively compounds containing one of the following :

Halogens

Sulphur

Nitrogen

The operation of the detector in connection with chloride containing compounds is as follows. The sample from the column of the gas chromatograph enters the reactor, a Nickel tube heated to some 850°C. A reaction between the chlorinated compound and the hydrogen reaction gas is catalysed by the Nickel tube with the result that most of the chloride exits the tube in the form of HCl. In the cell the gas is brought into contact with n-propanol solvent in which the HCl dissolves, increasing the conductivity of the solvent. The gas exits down the centre of the cell while the solvent clings to the walls and is thus introduced into the conductivity measuring cell. A slug of chlorinated compound in the carrier thus produces an electrical peak at the detector output which may be observed on a chart recording or converted to a numeric area value by an integrator.

Sample : Gas or liquids. Samples containing high levels of hydrocarbons can damage the reaction tube and therefore reduce its lifetime. Very successful techniques for the determination of organochlorides. The determination of HCl is made a lot more difficult not to say impossible due to the chromatographic part of it (ie : suitable column).

Range : ppm levels.

Sample prep : None

Cost : Varian stopped supplying this type of Detector last year.



4 : EUROGLAS CHLORIDE ANALYSER ECS1600.

Principle : The measurement process consists of four components :

a : The introduction of the substance to be analysed (sample) into the furnace.

burnt Liquid Module : The sample is injected with a syringe (automated injection at variable speed) and then carried by a flow of argon into the furnace and in oxygen.

Solid Module : For sample with boiling temperatures above 450°C.

Gas module : Introduction of gas sample with pressure from atmospheric up to 20 Bars.

b : The incineration of the sample in the furnace, thus releasing hydrogen chloride.

chloride. The The furnace is divided into two temperature zones. Each zone can be individually adjusted to all temperatures up to 1250°C. In principle the incineration process will give rise to CO₂, water and hydrogen incineration gases arrive in the scrubber via the outlet. The scrubber is filled with concentrated sulphuric acid. Water and any other unwanted components are left behind in the scrubber.

c : Coulometric titration :

The hydrogen chloride dissolve in the liquid of the titration cell. Coulometric titration takes place automatically using silver/silver chloride reaction.

d : Presentation and processing of the data.

software. The The operator can communicate with the ECS 1600 by means of a monitor and a keyboard. The course of the titration can be followed on the monitor. The data is processed with the help of the special Euroglas results are reported by means of the printer built into the ECS 1600.

Sample : gas, liquid and solid with minimum sample preparation.

Range : ppm to ppb levels. Total chloride determination and possibility of differentiating HCl from organochloride.

Cost : £35k

Analysis Time : between 3 and 10 minutes.

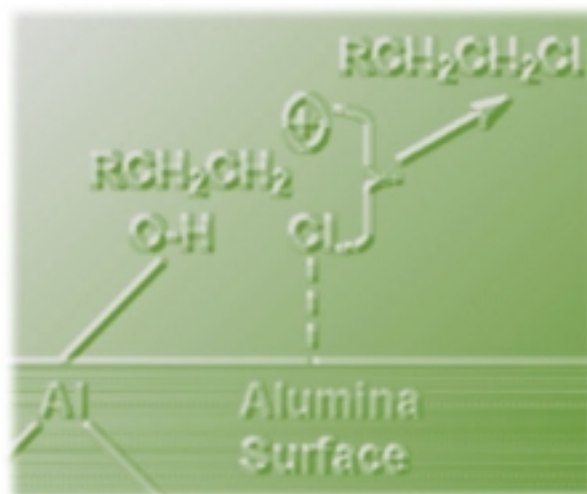
Also potential to carry out sulphur determination using a different titration cell (iodine titration).

N.B. All these techniques cover the determination of HCl and organochloride but do not include Chlorine Cl₂ .

On-Site Chloride Guard Monitoring Program

Synetix has licensed and developed new technology that can quantitatively measure both HCl and organic chlorides (RCI) in the gas inlet and outlet of chloride guard beds. The measurement equipment is ready for use in the field to deliver feedback on the chloride levels present within minutes.

Using technology similar to HCl 'sniffer' tubes, the gas sample can be withdrawn at any convenient point on either side of the chloride guard. The technique measures both the HCl quantity and also the organic chloride level, which is not detected by traditional tubes.



The technology can be accessed in two ways:

- 1) A Synetix representative can visit the site to take measurements and collect operating data. This can be done at a frequency appropriate to the projected bed-life to monitor performance and assess remaining capacity. It can also be done on a one-off basis to check guard integrity or trouble-shoot problems.
- 2) The technique and equipment for initial testing, together with methodology, can be made available upon purchase of **PURASPEC** 2200 series absorbents for chloride removal.

The need for effective chloride removal

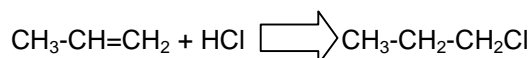
When chloride leaves the Catalytic Reformer plant, it commonly leads to two problems. Firstly, where water is present, vigorous corrosion occurs. Secondly, HCl will combine with any NH_3 present leading to precipitation of ammonium chloride. These usually lead to production restrictions or downtime. Organic chloride itself does not react the same way, but it will readily decompose at higher temperatures giving HCl. Therefore it is important to ensure that all chloride species are removed and that this can be measured.

In summary, the chloride guard monitoring programme provides the following benefits for customers:

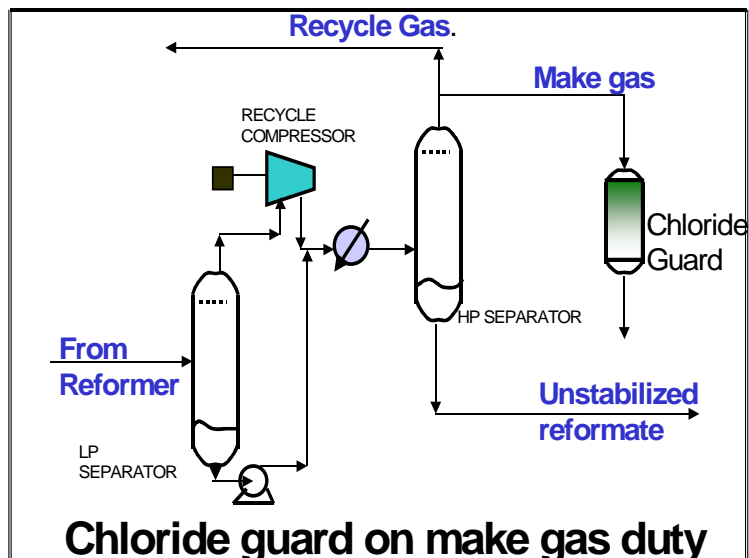
- Quantitative analysis of chlorides inlet the bed resulting in accurate prediction of bed life.
- Analyses of HCl and organic chlorides exiting the bed which monitors bed performance.
- Detection of organic chlorides slipping from the bed prior to corrosion or fouling problems in downstream equipment

Why and where does organic chloride form ?

It is recognised that recombination of HCl and low levels of olefins can occur across acidic, catalytic surface sites. These acidic sites can also facilitate undesirable reactions forming green oils. The problems are generally more acute with CCRs than Semi-Regen Reformers as the levels of HCl and olefins are higher.



The use of chemical absorbents, such as **PURASPEC 2250/55**, rather than more traditional aluminas, reduce the surface acidity and formation potential.



What is the experience with the measuring technique ?

The following examples illustrate the successful use of the method:

- 1) One refinery engineer uses the technique to monitor the performance of their CCR make gas chloride guard. His experience is that, when he detects organic chloride (RCI) slip, there will be fouling on local HDS units due to ammonium chloride formation, if the chloride guard is not changed out. When using standard HCl 'sniffer' tubes, fouling had occurred before detecting any chloride breakthrough.
- 2) A refiner operates a lead-lag make gas chloride guard on a CCR. He suspected chloride slip and a survey was requested. A level of 1.5-2 ppm chloride (all HCl) was detected at the lead bed inlet, with the result being the same with this technique and a standard HCl 'sniffer' tube. However, while the standard tube found no slip after the beds, this technique measured 1 ppm RCI slip leaving the lead bed and 0.6 ppm RCI leaving the lag bed and passing on to downstream equipment. This data decided the refiner to expedite replacing the absorbent.

For more information about Syntex range of catalysts and associated Services please contact your Syntex representative or visit our website at www.syntex.com



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Notes on Chloride Analysis

- A) The chloride content of gaseous and liquid samples can be determined within Synetix using the Euroglas ECS 1600 equipment. This equipment is based around a coulometric titration cell with a sample furnace to convert all the halogens present in the sample to the hydrogen halide. The equipment is usable over the range of 0.1 to 1000mg chloride per litre of sample but the range can be extended by suitable dilution of more concentrated samples.

Partial speciation of the chlorides present within liquid samples can also be achieved using pre-treatment prior to analysis using the ECS 1600. The main types of pre-treatment are intended for determination of the organo-chloride content and involve adsorption (onto activated charcoal), extraction (usually ethanolic) or inert gas purging. Operating ranges are quoted as 0.1 to 1000mg / L for extraction and 10 to 1000µg / L for adsorption and purging.

- B) Organo-chlorides in liquid or gaseous samples can also be speciated using gas chromatography, with a halogen specific detector. Qualitative / quantitative analysis is carried out by comparison with available standards. Typically, detection limits are in low ppm levels but this is compound dependant and can be optimised to detect to sub ppm levels.

Alternative techniques:

- 1) The total Cl level is measured in a similar way using incineration followed by micro coulometric titration (limit of detection quoted as > 1ppmw). The inorganic Cl is then determined separately using an extraction with pure water followed by ion chromatography (limit of detection quoted as >0.2ppmw)
- 2 A liquid hydrocarbon sample is combusted in an O₂/H₂ flame to produce HCl. This is then absorbed into an aqueous solution of NaOH. Mercury thiocyanite and ammonium iron sulfate are then added and the sample placed in a quartz cell. The level of chloride is then determined by absorptiometric analysis. This technique is used for Cl in the range 1-1000ppm.
- 3 There are several commercial suppliers of gas detection tubes that cover a wide range of HCl concentrations. Some have sub ppm minimum detection levels but the % error levels can be high. Other species present in the gas feeds can cause interference in the analysis.



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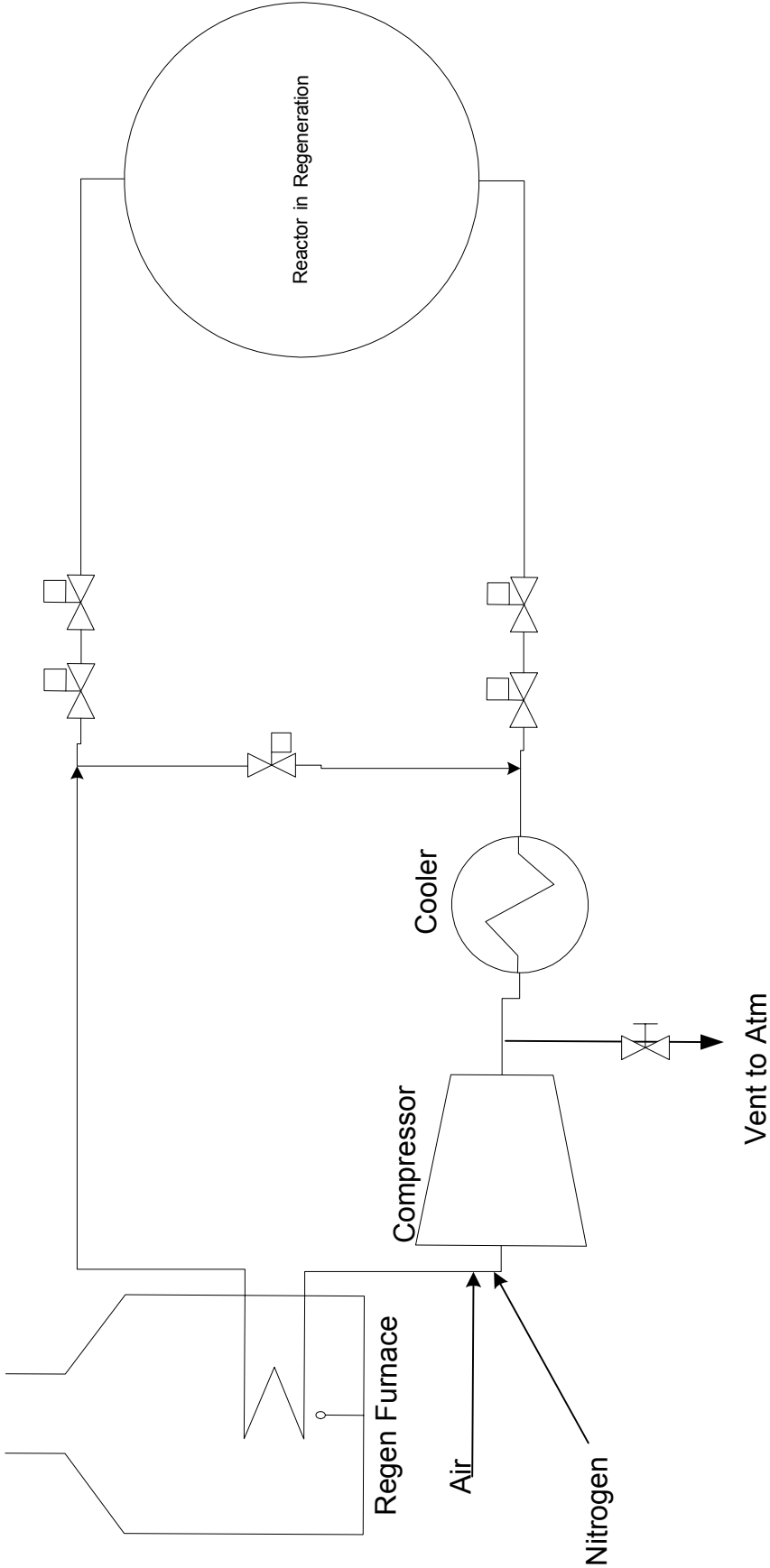
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Typical Cyclic Powerformer Hot Flue Gas
Regeneration System



Date	Header	HCI			
	Inlet	Top	Middle	Bottom	Outlet
16-Jun-01	285	200	0	0	0
28-Jun-01	350	200	0	0	0
22-Jul-01		110	0	0	0
26-Jul-01	200	200	0	0	0
8-Aug-01	100	100	0	0	0
23-Aug-01	150	90	0	0	0
27-Aug-01	200	200	0	0	0
30-Aug-01	200	180	0	0	0
2-Sep-01	120	100	0	0	0
8-Sep-01	140	120	0	0	0
14-Sep-01	200	60	0	0	0
20-Sep-01	50	50	0	0	0
26-Sep-01	300	50	0	0	0
29-Sep-01	140	120	0	0	0
30-Sep-01	100	50	0	0	0
7-Oct-01	50	50	35	0	0
12-Oct-01	100	50	0	0	0
30-Oct-01	100	90	0	0	0
2-Nov-01	100	100	0	0	0
16-Nov-01	300	50	0	0	0
20-Nov-01	130	100	0	0	0
7-Dec-01	250	75	0	0	0
11-Dec-01	100	40	0	0	0
23-Dec-01	50	50	0	0	0
26-Dec-01	290	95	0	0	0
12-Jan-02	40	40	0	0	0
20-Jan-02	200	200	0	0	0
17-Feb-02	80	80	0	0	0
20-Feb-02	300	40	0	0	0
6-Mar-02	150	40	0	0	0
24-Mar-02	150	50	0	0	0
27-Mar-02	200	200	0	0	0
31-Mar-02	150	0	0	0	0
4-Apr-02	190	170	80	0	0
8-Apr-02	190	40	60	0	0
13-Apr-02	100	25	25	0	0
15-Apr-02	160	80	70	0	0
18-Apr-02	280	0	0	0	0
22-Apr-02	40	20	0	0	0
29-Apr-02	400	0	0	0	0
2-May-02	380	0	0	0	0
9-May-02	200	0	50	0	0
13-May-02	50	0	0	0	0
19-May-02	25	15	20	25	0
23-May-02	300	0	30	0	0
26-May-02	400	0	10	0	0
31-May-02	50	0	0	0	0
19-Jun-02	30	30	0	0	0
22-Jun-02		200	0	0	0
29-Jun-02	50	0	20	0	0

Date	Header	HCI			
	Inlet	Top	Middle	Bottom	Outlet
4-Jul-02	80	0	0	0	0
14-Jul-02	0	0	0	0	0
19-Jul-02	350	250	0	0	0
24-Jul-02	30	50	0	0	0
25-Jul-02	25	0	0	0	0
3-Aug-02	70	50	0	0	0
4-Aug-02	60	50	0	0	0
10-Aug-02	300	250	0	0	0
14-Aug-02	85	75	55	0	0
17-Aug-02	60	90	0	0	0
23-Aug-02	100	0	0	0	0
14-Sep-02	70	50	25	0	0
18-Sep-02	25	0	0	0	0
07-Oct-02	70	50	25	0	0
11-Oct-02	0	0	0	0	0
16-Oct-02	0	0	0	0	0
19-Oct-02	0	0	0	0	0
10-Nov-02	150		0	0	0
17-Nov-02	250	0	0	0	0
21-Nov-02	50	50	0	0	0
24-Nov-02	0	0	0	0	0
25-Nov-02	150		0	0	0
31-Dec-02	400	0	0	0	0
04-Jan-03	380	0	0	0	0
05-Mar-03	180	0	0	0	0
11-Apr-03	200	0	0	0	0
14-Apr-03	300	0	0	0	0
21-Apr-03	300	0	0	0	0
11-May-03	250	0	0	0	0
14-May-03	300	0	0	0	0
29-May-03	160	0	0	0	0
04-Jun-03	180	0	0	0	0
09-Jun-03	200	80	0	0	0
21-Jun-03	160	0	30	0	0
27-Jun-03	300	0	0	100	0
30-Jun-03	0	0	0	0	0
16-Jul-03	450	45	50	100	0
18-Jul-03	180	0	40	0	0
20-Jul-03	110	40	40	0	0
21-Jul-03	100	40	40	0	0
25-Jul-03	100	60	30	0	0
27-Jul-03	150	10	0	100	0