TECHNICAL PAPER

Understanding Claus Plant Upsets Using Your Tail Gas Analyzer

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Abstract

The purpose of this technical paper is to afford the reader the understanding of how to use the data produced by an on-line H_2S/SO_2 tail gas analyser for a Claus Sulphur Recovery Unit (SRU) to full advantage in trouble-shooting his plant. The intended audience is process operators/engineers who are involved in the day to day operation of the Claus SRU and the purpose is to train these key personnel in interpreting the data so that it can be used to take appropriate action during process upsets.

It is assumed that the personnel involved in the operation and process optimisation of the Claus SRU already have a sound foundation in the basics of the modified-Claus process and control of that process. There are two technical papers on these subjects, that form part of the five day Sulphur Recovery Seminar on optimising the Claus SRU presented by Global Sulphur Experts Inc. and Western Research. Please refer to these for additional details.

The objective of this paper is to cover the following topics:

- where the tail gas analyser fits in the process
- what the analyser is saying about the process when it is "off-ratio"
- limitations of the tail gas analyser
- secondary sources of information that can be used to confirm the analyser data
- training of non-QMI (analyser) personnel in primary analyser trouble shooting.

The paper is presented in the form of case studies that describe a specific process upset condition and the resulting analyser response. These case studies use actual process data, where it is available, others are historical and are described using empirical results based on experience in over 600 sulphur plant performance tests, as well as input from operating companies.

1.0 Introduction

The H_2S/SO_2 tail gas analyser is an essential element to the operation of any Claus SRU. The primary function of the tail gas analyser is control of the process air to acid gas ratio. This maintains the two primary reactants in the process (H_2S and O_2) in the correct stoichiometry to produce a tail gas with the secondary reactants (H_2S and SO_2) in the well recognised modified-Claus ratio of 2:1, and optimises the formation of product sulphur. This primary function of control, under steady-state conditions, is well understood, but in the case of adverse process conditions, **the output of the analyser is often called into question, when it is, in fact, still giving valid data that can be valuable in trouble-shooting the process.**

It is widely accepted that the tail gas analyser in closed-loop control, can contribute anywhere from **3 to 5 % to the overall recovery efficiency** $(E_R)_{(1)}$ of the plant when compared with a plant on simple feed-forward flow ratio control. This is quite significant in terms of emission control since it can represent a large reduction in SO_2 released to the atmosphere, or alternatively a large change in load for the tail gas clean-up process. In addition, the analyser provides the operator with **valuable information on other operating parameters and process upsets.** For these reasons it is essential that the analyser be in closed-loop control to afford its use to maximum advantage.

Although tail gas analysers have been widely applied to the modified-Claus process for many years, there is sometimes a lack of confidence in the analyser by the operator due mainly to a lack of experience in interpreting the out-put. As a result the analyser is sometimes taken out of closed-loop control, or the results are disregarded altogether. Experience from over 600 installations indicates that this lack of confidence is because the operators do not have a clear understanding of how the analyser responds to certain types of process upset that result in "off ratio", and sometimes extreme, analyser data. Also, as the operators have almost no knowledge of the analyser functionality, they do not have the ability to differentiate between process upsets and a true analyser malfunction.

In summary, the weakest link in the application of any on-line analyser and the control of the process, is most often the interface with the operator. After making a great deal of investment in analysers and training of the analyser personnel, the operators are left to gain their experience over operating time and if the start-up period is problematic, the analyser is never fully accepted. The purpose here, is to give the operators a clear understanding of the analyser response to all process conditions and to foster better communication with the analyser people in terms of feed back and information.

2.0 Case Studies

The following case studies describe some typical process upsets and the expected responses from the tail gas analyser. In addition to the tail gas analyser outputs, other confirming sources of information and process parameters are described. It is assumed that the process and feed conditions are stable before the process upset and the tail gas is "on-ratio".

2.1 Equilibrium Conditions

When the modified-Claus unit is in a steady-state equilibrium condition the H_2S and SO_2 are in the proper ratio of 2:1 in the tail gas. It is important to note that there are normally fluctuations in the order of ± 0.5 to 1.0 % in the "Air Demand" (which is typically on a control scale of -5%...0 ...+5%) due to slight changes in feed composition, flow, temperature and pressure. The time scale of these fluctuation corresponds to the process lag time of the unit, normally in the order of 30 seconds to one minute.

The plant for these case studies is a refinery SRU with two acid gas feeds, one from an amine plant (ARU) running ADIP, and the other from a hydrodesulphurisation (HDS) unit. Additionally there is a sour-water off-gas feed to the SRU. This is a fairly typical refiner SRU arrangement. The ARU and HDS acid gases are in equal quantities.

2.2 Case 1. - Reduction in the ARU Amine Acid Gas Feed

<u>Description of Process Upset</u> - The ARU (ADIP unit) amine acid gas is suddenly reduced to zero. The H_2S concentration in the ARU acid gas is 75% and correspondingly 95% in the second acid gas stream, the HDS (hydrodesulphurisation) acid gas. Although the total acid gas flow rate to the unit is cut in half, the absolute amount of H_2S is only reduced by 44%.

<u>Initial Control Response</u> - The feed forward control system which is linked to flow rate, responds by cutting the air by half, but as this exceeds the requirement there will be an immediate and temporary shortage of combustion air until the tail gas analyser can respond.

<u>Tail Gas Analyzer Response</u> - The H_2S concentration in the tail gas increases and the SO_2 approaches zero. The "Air Demand" signal approaches positive 5% (20 mA), maximum control value to increase the air flow rate.

<u>Confirming Process Indicators</u>

- incinerator temperature increases due to high H_2S
- stack plumes because of increased load of SO_2
- reaction furnace temperature decreases
- stack SO_2 analyser shows increase of SO_2

2.3 Case 2. - Increase in the ARU Amine Acid Gas Feed

<u>Description of Process Upset</u> - Feed increase in the ARU acid gas by 25%. This results in an net increase in total flow of 12.5% and a net increase in H_2S of only 10.5%.

<u>Initial Control Response</u> - The feed forward control system responds by adding air but

this amount is more than is required as the ARU acid gas stream is not as rich as the HDS stream that makes up the balance of the feed.

Tail Gas Analyser Response - The H_2S concentration in the tail gas decreases and the SO_2 increases. The "Air Demand" signal goes from zero to negative 3% (note that this corresponds to the difference between the feed forward control response and the actual amount of required air).

Confirming Process Indicators

- decrease in incinerator temperature (notably incinerator outlet temperature and bed ΔT)
- decrease in unit efficiency (increase in SO_2 as indicated by stack SO_2 emission analyser)
- increase in reaction furnace temperature
- possible pluming

2.4.1 Case 3. - Loss of the SWS (Sour Water Stripper) Feed Gas

Description of Process Upset - Sudden and complete loss of the SWS feed stream. The SWS feed stream is approximately 30% H_2S and the balance is equal amounts of water vapour and ammonia

Initial Control Response - Cut in air flow

Tail Gas Analyser Response - If the correct air ratio was being applied to the SWS gas feed then no major change will be observed. However, a gradual reduction in the absolute values of H_2S and SO_2 could be observed and a corresponding increase in unit efficiency. This will be further confirmed by the "Performance Trend" output signal on the Model 900 Air Demand Analyser decreases as the overall recovery efficiency increases.

If too much air was linked to the SWS gas stream (even though the overall air balance to the unit, made up from the requirements of the other feed streams was correct) then with the loss of the SWS gas stream, the unit will quickly become air deficient, i.e. the "Air Demand" signal goes from zero to a positive value.

Confirming Process Indicators

- decrease in reaction furnace temperature
- increase in incinerator outlet temperature and bed ΔT
- possible pluming
- decrease in unit efficiency (refer to stack SO_2 analyser).

2.4.2 Case 4. - Re-Introduction of SWS Feed Gas

As this stream is introduced, confirmation that the correct air ratio is being applied can be referenced directly to the change in the "Air Demand" signal from the tail gas analyser.
The residence time in the unit is approximately 30 - 60 seconds, therefore feedback from the tail gas analyser can be applied promptly to arrive at the optimal air ratio. The response of the analyser and process, is the opposite to that of Case 3 where the SWS feed was lost.

2.5 Case 5. - Hydrocarbon Breakthrough in the Feed

Description of Process Upset - A sudden increase of hydrocarbon (HC) in one of the feed streams. Lightweight hydrocarbons (C_1 and C_2) normally exists in the 0.25 to 1% range in acid gases. An upset usually represents an increase in both the amount (to as much as 5% of the feed) and molecular weight (to C_3, C_4, C_5, C_6, and C_6+) of the hydrocarbons. Bear in mind that a molecule of C_6 hydrocarbon requires almost five times as much air as C_1 and that the hydrocarbon will burn before the H_2S oxidises.

Initial Process Response - There is only a slight increase in the feed gas flowrate and so the air flowrate is also only increased by a small amount. The air demand requirement for the hydrocarbon is considerable but the effect is not noticed until the upset reaches the tail gas, 30 - 60 seconds after the upset.

Tail Gas Analyser Response - The Air Demand control signal goes to positive 5% (maximum control output, 20 mA). The H_2S concentration increases and the SO_2 approaches zero.

Confirming Process Indicators -

- the reaction furnace temperature will show a sudden increase
- the incinerator temperature will increase due to higher H_2S
- depending on the exotherm in the incineration reactor, outlet temperature > 375°C, stack pluming can occur
- serious HC breakthroughs can cause unit trip due to high back end temperature safeguarding

2.6 Case 6. - Pluming Condition

Description of Process Upset - The stack (after the catalytic incinerator) shows a visible plume. The determinants causing the plume need to be established. Assumption - the SRU is on the ratio (2:1) and no process upset has been observed.

Initial Process Response - If the unit is on ratio and the stack is pluming then the overall unit efficiency is likely to be low. This needs to be confirmed.

Although the tail gas analyser is "on ratio" (2:1), the operator must refer to the absolute values of H_2S and SO_2. The higher the absolute values, the lower the overall conversion efficiency within the unit. This will be confirmed further by two additional sources:

- the "Performance Trend" output signal can be useful in giving a signal proportional to overall recovery efficiency, a higher output indicates more sulphur gases in the tail gas and hence lower recovery efficiency

- lower recovery efficiencies will result in higher stack SO_2 emissions indicated by the stack SO_2 analyser

<u>Tail Gas Analyser Response</u>

- It is important in this situation to "trust" the tail gas analyser. Therefore leave the analyser on control until the following process conditions are checked:

- converter bed temperatures. If the observed ΔT across the converter bed No. 1 is < 50 deg.C and < 10 deg.C across converter bed No. 2, this is indicative of low catalyst activity

- higher than normal ΔT across the incinerator reactor bed. If the observed ΔT is > 50 deg.C, this will confirm the low conversions across the converters and account for the higher than expected H_2S in the tail gas. The H_2S is oxidised to produce SO_2, the reaction being extremely exothermic. Note the higher the absolute value of H_2S being fed to the incinerator, the higher the exotherm and therefore ΔT

- sulphur rundown flows. Without flow measuring devices this can only be regarded as a crude and subjective indicator. However, lower sulphur rundown flows confirm low efficiency within the unit or lower throughput.

If any or all of these process indicators is confirmed, then the tail gas analyser can be challenged to make the final confirmation. Change the set-point (normally zero) to +2%. The trim valve will open and the H_2S concentration will decrease as the SO_2 concentration increases in the tail gas.

<u>Confirming Process Indicators</u>

- further increase in incinerator outlet temperature and ΔT
- stack pluming could get worse
- reaction furnace temperature decrease
- SO_2 emission as indicated by stack SO_2 analyser increases

<u>Action</u>

- Return the analyser to "on ratio" control to minimise inefficiency. Prepare unit for heat soak and rejuvenation of the catalytic converters to remedy root cause of inefficiency.

In this case study, the tail gas analyser will be instrumental in determining the root cause of the pluming and subsequent confirmation of the remedial action, i.e. heat soak and rejuvenation procedure.

2.7 Case 7. - Complete Loss of Amine Feed and Attempted Operation on SWS Feed Only

This case is based on actual results from a refinery SRU. After loss of the amine acid gas the operators attempted to operate with SWS gas only. In order to maintain temperatures with the leaner feed of the SWS gas, the operators dramatically increased the air. The result was for the H_2S to go to zero and the SO_2 to increase to 7.0%.

The initial reaction was to disbelieve the analyser and assume it was not functioning, because the H_2S and SO_2 were not reacting in a predictable way. However, the data was quite valid and this was confirmed after the unit went down. This is an excellent illustration of analyser data that is most valuable to the operators providing there is continued confidence in the analyser and trained operators are able to confirm the data from other sources.

Measurement of this extreme excursion of the SO_2 to 7% was possible by virtue of the over range capability of the analyser (the cell and analog output were ranged for only 2%) and by monitoring the signals on an RS 485 digital link.

As in the case of pluming, the analyser is used not for ratio purposes, but to address more serious sudden and short term process upsets.

3.0 Analyser Operation

3.1 Analyser Description

3.1.1 Basics of UV Absorption - Ultraviolet absorption spectrophotometry is commonly used in gas phase process control and emissions applications, especially for the measurement of sulphur species. One of the distinct advantages over infrared techniques is the lack of interference from carbon dioxide and water vapour, which are often present at much higher concentrations than the analytes of interest. However, a factor that often limits the accuracy of a gas phase ultraviolet absorption spectrophotometer is the linearity of response to the species of interest, in particular if a multi-component analysis is to be performed. This problem is overcome in the Model 900 Air Demand Analyser as it is unique in the application of discrete lines of radiation generated by hollow cathode lamps.

In simple terms, optical absorption photometers typically consist of a light source which produces a beam of photons that pass through a sample cell containing the analyte gas and then impinge on a photo detector which converts the number of incident photons to an output voltage. In most cases the output voltage is first measured using a "clean" sample (i.e. the composition of the analyte gas is zero).

This provides a reference voltage, V_{zero} to which samples of the analyte gas are compared. When subsequent samples of the analyte gas are introduced into the cell, the sample voltage from the detector is measured, V_{sample}. The ratio of the reference to the sample voltage is used to determine the analyte concentration through the use of the Beer-Lambert law (2).

3.1.2 **Specifics of the Model M900 Air Demand Analyser ADA** - The Model 900 Air Demand Analyser is comprised of two UV lamps that generate up to 6 wavelengths as well as a filter wheel that contains up to six interference filters, a sample cell and two matched photo detectors. The Model 900 ADA is capable of measuring H_2S, SO_2, COS, CS_2 and sulphur vapour (S_V). The H_2S and SO_2 signals are used to calculate the control signal "Air Demand" that is used to control the trim air to the process. The air demand calculation utilises specific process data from the subject SRU so that the signal is calibrated in terms of actual air requirement for that particular SRU. In addition there is an output for "trend" which is the sum of all sulphur gases and proportional to overall conversion efficiency.

3.1.3 **Sample System** - The sample cell is contained within a temperature controlled oven which also contains a sulphur condenser and an aspirator. All of the temperature zones (four zones: oven, sulphur condenser, electric traced sample and vent line) are controlled by the on board micro controller. The sample system includes two steam jacketed process connection valves and sample probe. In case of low temperature in one of the zones the analyser has an automatic blow back cycle.

3.2 Concept of Using "Air Demand" for the Control Signal

The concept of using a linear algorithm for control purposes rather than H_2S/SO_2 ratio was developed by Western Research some twenty years ago(2). A ratio of 2:1 of $H_2S:SO_2$ is the stoichiometric relationship between the reactants that produces the maximum products, however, ratio is not convenient to use as a control signal. Ratio is non-linear and is more difficult to utilise as a control signal to manipulate the final control element (trim valve).

"Air Demand" on the other hand, is a linear signal and is easily understood in terms of what control action must be taken and of what magnitude. The basic Air Demand equation is ...

$$\textbf{Air Demand} = K\{2[SO_2] - [H_2S]\}$$

When the result is zero the process is in a on ratio condition. The "K" constant is just a scaling factor calculated from the acid gas composition and overall recovery efficiency that characterises a particular SRU. The resultant control signal is scaled to represent a total of 10% (from -5%... 0 ... +5%) of the required process air (under any condition) and this is sufficient to trim the process and still maintain stability in the unit if the control signal is lost. The control signal can be "inverse" or "direct-acting" depending on the operator preference. The normal set up at refineries is as follows:

Process Condition	Air Demand Signal	Analog Output	Control Action
Excess air	-5% to zero	4 - 12 mA	Close trim valve
"On ratio"	zero	12 mA	None
Deficient air	zero to +5%	12 - 20 mA	Open trim valve

As mentioned, 10% of the total air flow is sufficient to trim control most process upsets. Occasionally the Air Demand signal will exceed the -5% or + 5% limits during extreme conditions. If it is desirable to observe these excursions the fourth output (normally assigned to represent the trend) can be scaled for ±10% or even ±20 % Air Demand, and be used for indication purposes. Note this is for indication only and should not be used for control.

3.3 Delineating Process Problems from Analyser Failure

It is not unusual that when the tail gas analyser responds to a process upset in an unexpected way that the analyser is called into question. Although the analyser, like any other complex instrument transducer, is subject to failure it is quite often the case that the data is correct and the operator can make a few simple checks to confirm the veracity of the analyser data. The following information is a list of steps and indicators for this purpose.

3.3.1 Bumping the Process

The first step to take if the analyser data is suspect is to "bump the process" **by making a change in the air flow rate** and seeing if the analyser responds in the expected way. It is not uncommon for the H_2S or the SO_2 signal to go to maximum or minimum in the case that the unit is badly off ratio. For example if the H_2S is at zero and the SO_2 1% (20 mA) then start to cut the air until the SO_2 begins to come down and the H_2S comes up. This may take some time as the process lag time is approximately 30 seconds for an SRU at full load. Also, even as one signal begins to come down it may be some time before the other signal rises as the upstream converters must be on ratio before the result will show in the tail gas. If the analyser responds in this way it is operating properly.

The above procedure can be better observed if the operator has the advantage of **observing the over range signals by means of an optional Modbus communication link.** The analyser has considerable over range capability and although the analogue 4-20 mA outputs will be at maximum at 2% (SO_2) and 4% (H_2S) the signals can be observed up to 4 times over range on the digital link.

If the digital link is not available then the **fourth analogue output can be used for an expanded range of Air Demand** (say -20% ... 0... +20%) and the effect of off-ratio conditions can be observed from this (ie for indication only, not control).

3.3.2 Tuning the Loop

It is not uncommon that a badly tuned control loop can look like an analyser failure because the response to a process change does not give the expected result (in terms of the H_2S and SO_2 responding in opposite and equal amounts). It is worth restating here that the Claus unit can be subject to a turndown of 75% and that this results in a four times increase in process residence time (to approximately two minutes). If the loop is tuned to this state and the unit returns to full load the control loop will not be responsive. There are recommendations for auto gain control and cascading of the feed flow to the trim loop to prevent this from happening.

3.3.3 Analyzer Parameters to confirm Proper Operation/Failure

The following is a quick reference list of basic parameters to check that can usually confirm the analyser operation.

Sample System - The sample system can be the source of problems. If the temperature in the sample lines or the valves drops below the freezing point, then a plug will occur. Quite often the cooling takes place in the steam jacketed valve and the plug occurs in the probe fittings connecting the sample line to the probe. The indications of a plug are...

- the H_2S and SO_2 signals draw a straight line or go to zero.

- the cell pressure drops due to higher vacuum from the aspirator. The change is slight (20 - 30 mm) and can also be affected by process changes.

- if a plug is starting to occur the analyser is slow to respond from a zero check. The analyser should return to full measuring value within 10 seconds of a zero, for sample lines less than 10m. Anything more than this indicates plugging.

The quick remedies for plugging are...

- ensure that the sample line temperature is at least 5 deg C above the process temperature.

- ensure that the process connection valves are sufficiently insulated and have good quality steam (minimum temperature of process plus 5 deg C or a minimum steam pressure of 4 bar, preferably regulated from a higher steam pressure source). This is quite often the source of the problem and often overlooked.

- consider the possibility that NH_3 has broken through the reaction furnace and ammonia salts are forming in the sample line.

The key to sample system problems is to communicate with the QMI (analyser) maintenance people, **quite often a change in the process shows up as a problem in the analyser.** The M900 ADA can be set up to operate under adverse process conditions so it is most important **that the operators communicate with the QMI people to alert them to changing conditions** such as ammonia, higher condenser temperatures, blown demister pads etc.

Photometer

If the photometer fails for any reason the result is easy to recognise as all of the values normally go to zero. There are some exceptions, check the following ....

If there has been adjustment to the sulphur vapour compensation factors or there is a filter problem the S_V comp signal will be erratic.

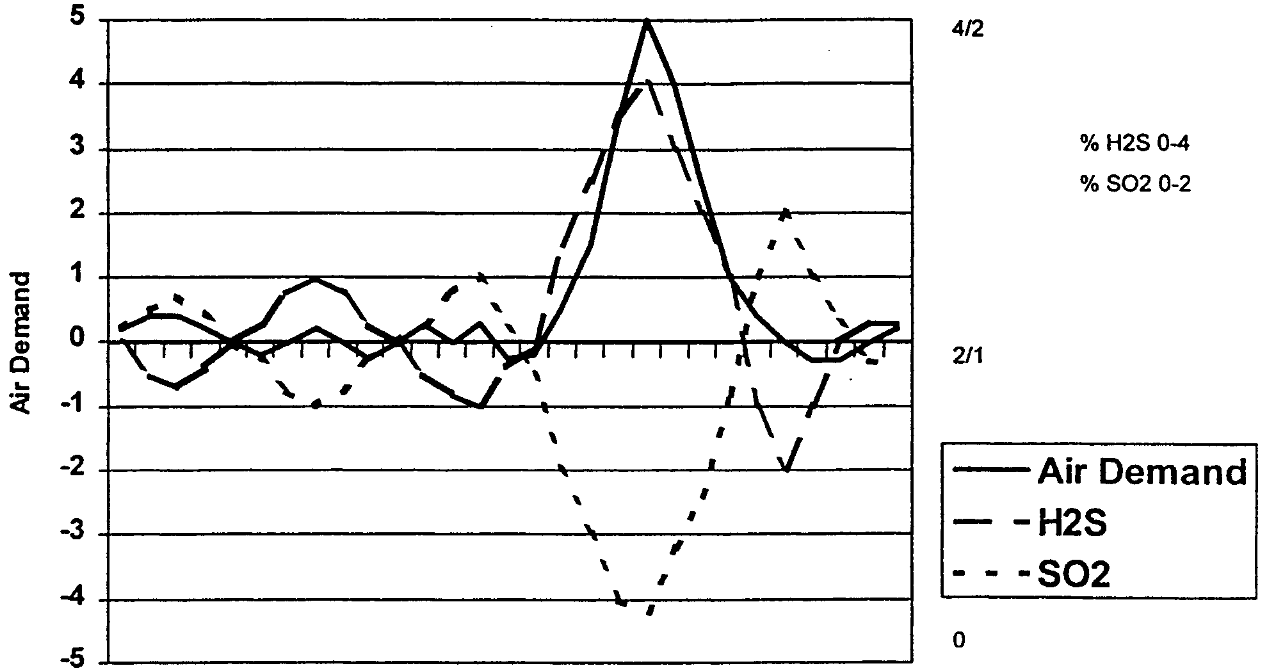
"Neutral Drift" (NDR) is a measure of optically opaque deposits on the windows. This can be from sulphur or ammonia salts. NDR is normally close to zero, values approaching 0.1 indicate 1000 ppm of fouling on the windows and this is considered significant.

References:

1 Sulphur Plant Process Control Analyzer. H. Pascal
Sulphur Recovery, test for Seminar and the Modified Claus Process. R. Hauer, J. Sames
BOVAR Western Research/Global Sulphur Experts

2 The Design and Practical Application of UV Process Photometers. P. Harris, H. Adam
BOVAR Western Research

Case 1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Air Demand
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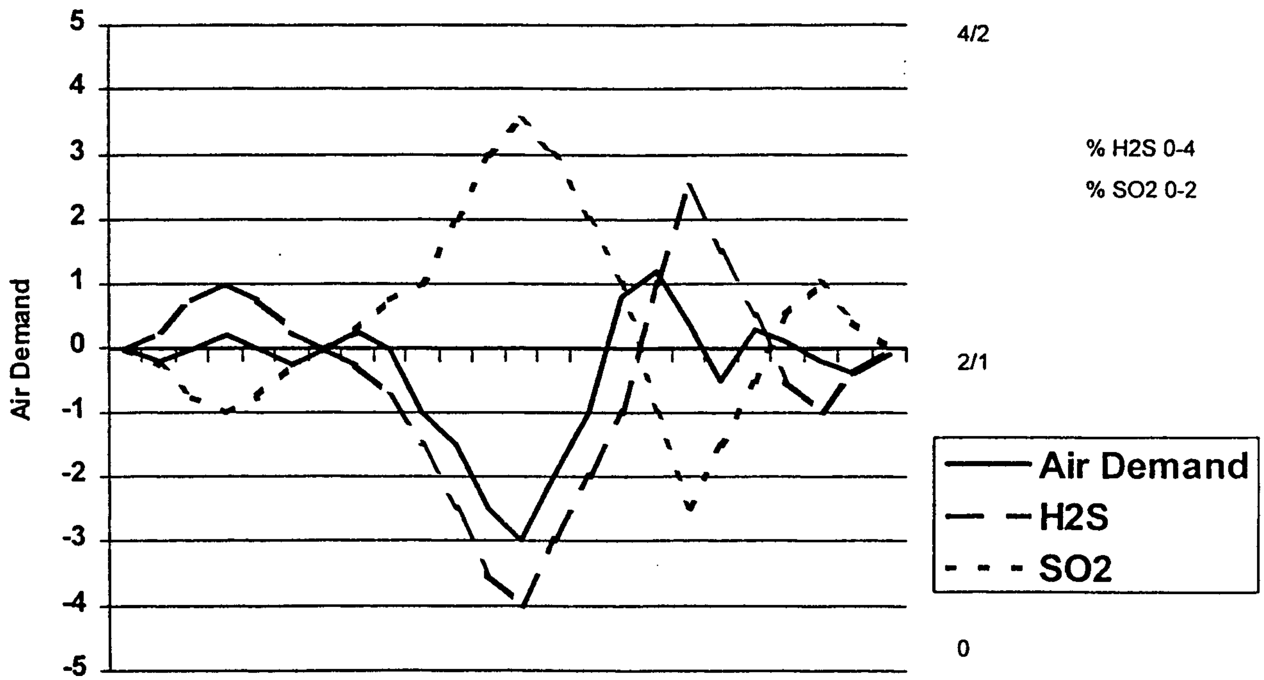
Case 2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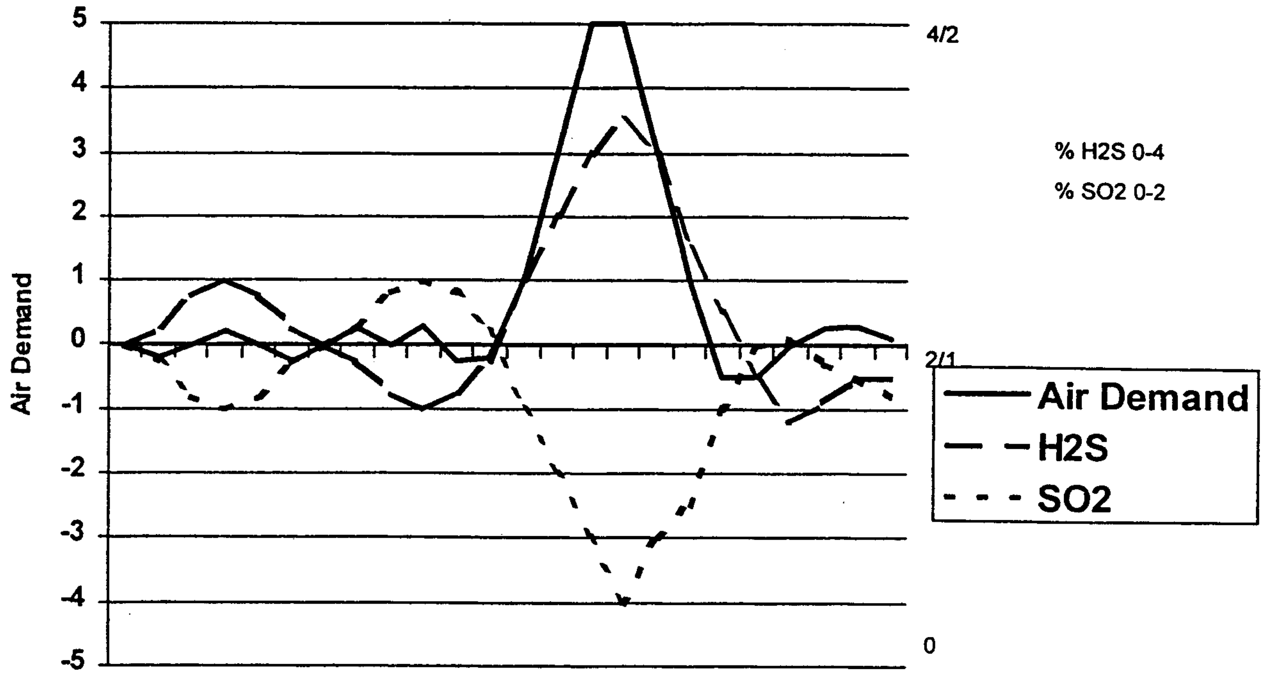
Case 3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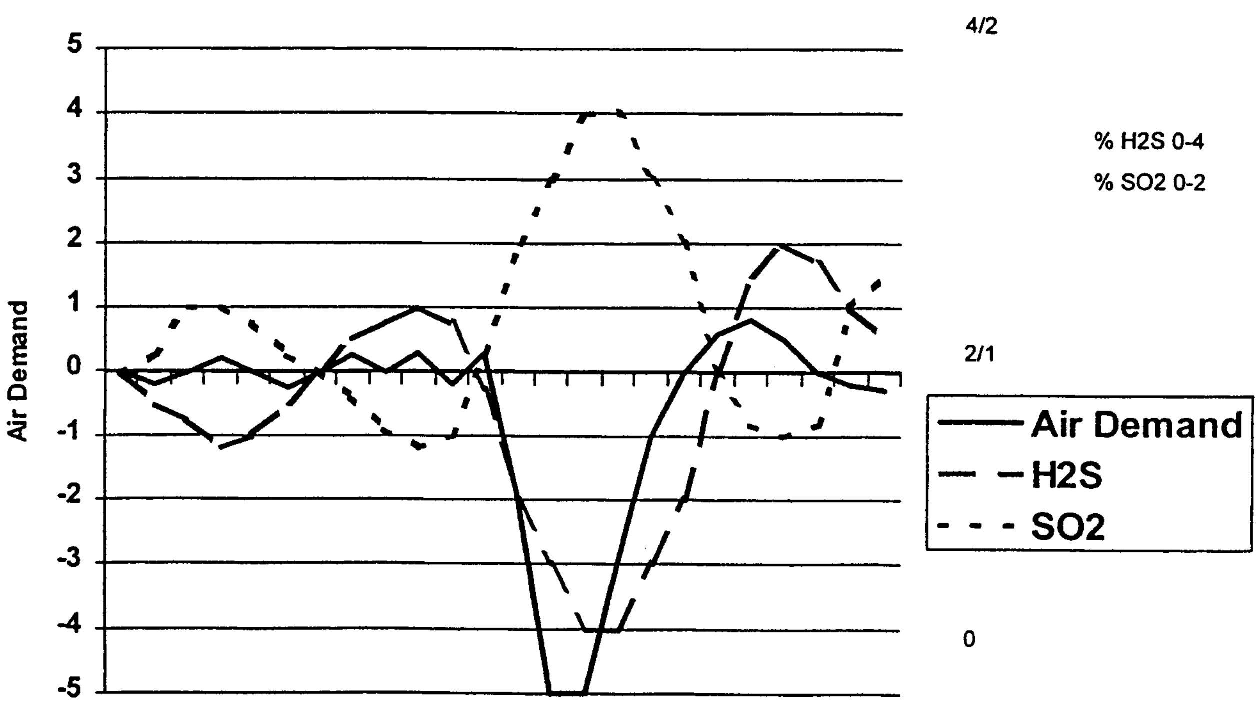
Case 4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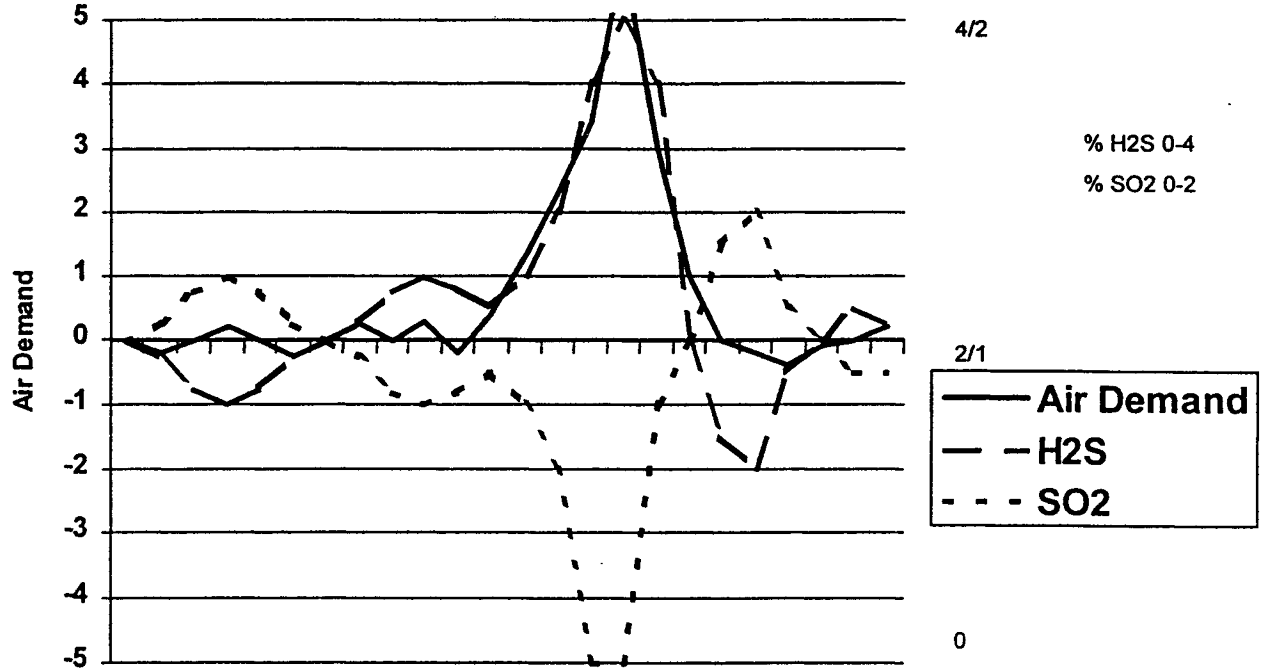
Case 5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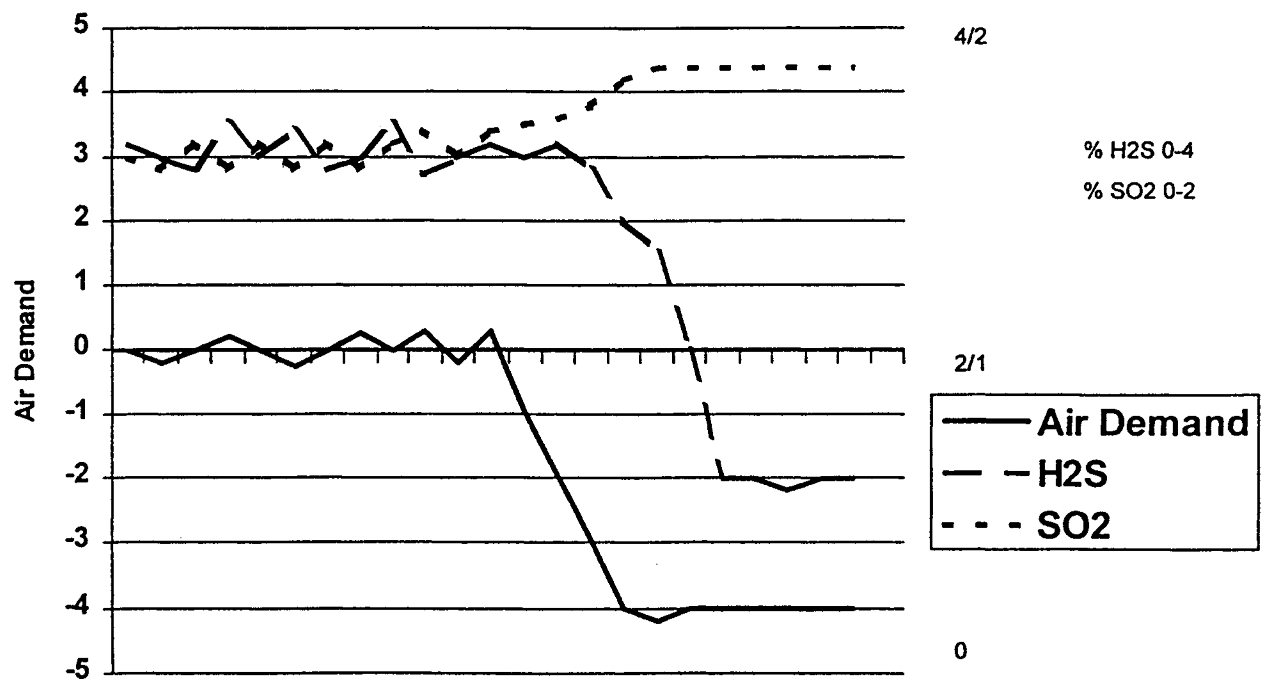
Case 6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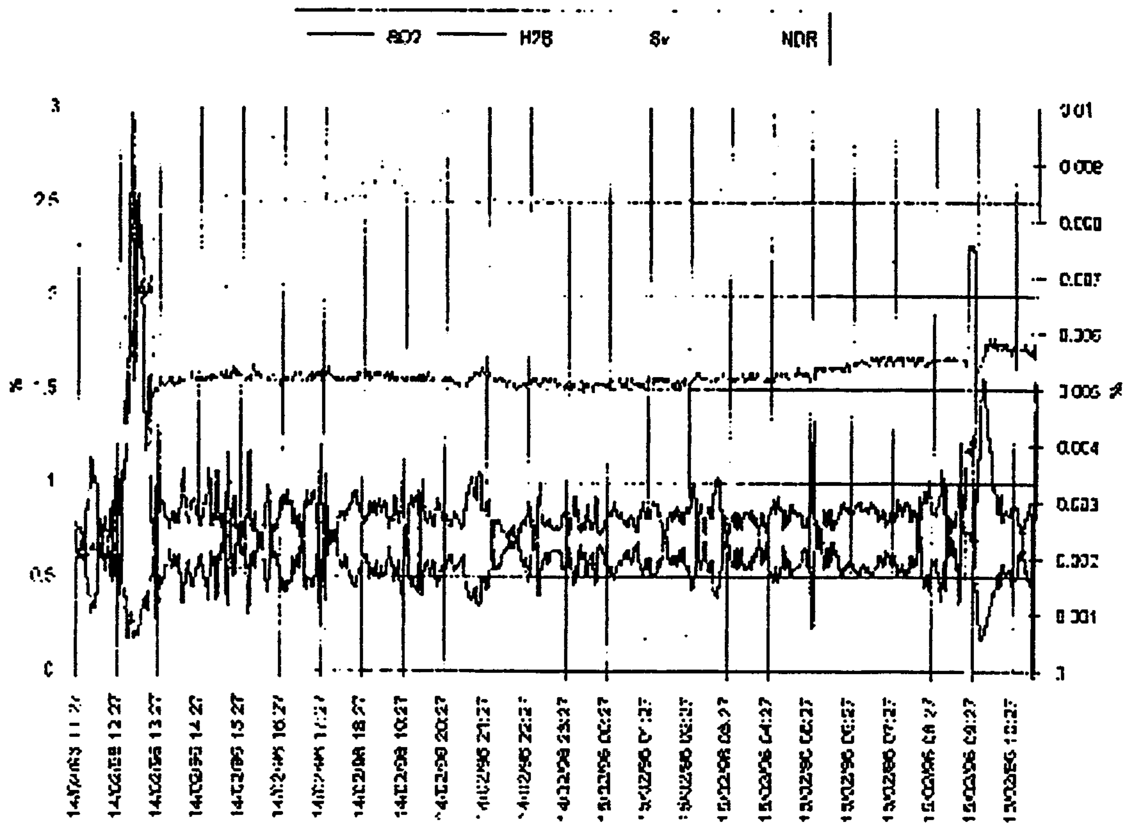
Refinery Tail Gas Analysis (BOVAR 900 analyser)



Refinery Tail Gas Analysis (BOVAR 900 analyser)