

LCCP

Thomas G. Grumbles

VISTA

To SID Pitts

Date 7/14

fyi

Have you been involved in this?

TGS

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To: G. L. FOSHEE, Westlake, LA.

Route: _____

From: G. W. BACON, Houston, TX.

Copy: _____

Date: July 11, 1986

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Subject: H₂S IN REFINERY FUEL GAS

X-7: _____

Interoffice
Communication

VISTA

Hydrogen sulfide in refinery fuel gas obtained from Conoco poses potential safety problems for workers in the Lake Charles chemical complex. Currently Conoco is to inform Vista when H₂S content in the refinery fuel gas exceeds 100 ppm. PED has been requested to verify the existing standard and make recommendations as necessary.

The current 100 ppm limit for notification appears to be based on SO_x permit limits for burning RFG in the VCM or LAB plants. (E. O. Strand-IOC-4/8/86). Conoco refinery off gas specifications are for a normal concentration of H₂S at 25 ppm and a maximum concentration of 80 ppm. See Table I. It should always be assumed that H₂S is present in the refinery fuel gas.

The 100 ppm limit is also acceptable from a safety standpoint. Based on published data, exposure to H₂S in concentrations up to 100 ppm, for short time periods, does not cause permanent injury. If the pipeline concentration is 100 ppm, there is little chance of a worker being exposed to H₂S at this concentration unless there is a significant leak. However at concentrations above 100 ppm, H₂S deadens the sense of smell. It would be possible for a worker to attempt to fix a leak when the H₂S concentration is high enough to kill without being able to detect the presence of H₂S. Therefore, Vista should be informed when the concentration exceeds 100 ppm. Table II shows the effect of H₂S on humans for various concentration levels.

There are several potential problem areas for hydrogen sulfide within the plant. These problem areas include: 1.) Blowdown of the steam plant fuel gas drum, and 2.) Leakage from valves and fittings within the area. Blowing down the fuel gas drum involves forcing accumulated water in the fuel gas drum into a containment vessel. The water contains dissolved H₂S which is highly corrosive. Corrosion could cause leaks in the blowdown line or possible rupture of this line. Leakage from valves and fittings is probably the source of detectable hydrogen sulfide in the area. If pipeline concentrations become excessive, concentration levels could exceed the threshold limit value (TLV) of 10 ppm. It is necessary that plant personnel be aware of excessive H₂S levels in the fuel gas so that appropriate safety precautions can be taken.

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We also evaluated systems for detecting H_2S in refinery fuel gas. Two methods exist for such a detection system. The first method includes an "On-Line" analysis of H_2S in the refinery fuel gas pipeline. The second method involves placement of ambient air sensors at strategic locations within the steam and ethylene plants.

Under normal conditions refinery fuel gas H_2S content does not pose a safety problem. The advantage of an "On-Line" detection system is that when an upset occurs, potential safety problems are immediately identified. The usefulness of the "On-Line" system is dependent on the accuracy and timing of reports received from Conoco. If several hours elapse before Vista is informed, then Vista should consider purchasing an "On-Line" detection system. The primary disadvantage to "On-Line" analysis is that it does not provide information on the exposure level to workers in the area on a continuous basis. Plant personnel are presently investigating various options for an "On-Line" analysis system. Table III gives information and purchase price of several systems on the market.

The advantage of ambient air sensing is that the concentration of H_2S which workers are exposed is a known quantity. A warning can be given at the TLV, 10 ppm, and an evacuation alert at the maximum peak concentration, 50 ppm. One disadvantage is that if Conoco does not report an upset condition, workers could be exposed to concentrations as high as 1000 ppm if an accident were to occur while working in the area. This could occur before an ambient air system could give adequate warning. Also, complete ambient air monitoring around the refinery fuel gas network would be more expensive than "On-Line" monitoring. Total cost of an ambient air system is dependent on the number of sensors employed. The average cost for ambient air sensing is about \$1500/sensor.

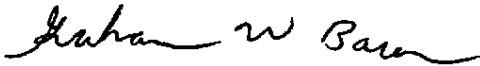
In conclusion, Vista should be informed when the H_2S concentration in the refinery fuel gas exceeds 100 ppm for three reasons.

1. H_2S deadens the sense of smell above 100 ppm.
2. 100 ppm is the limit for burning RFG at the LAB and VCM plants.
3. 100 ppm is above the maximum H_2S concentration specified in contracts.

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In addition, plant personnel should determine if the present warning system from Conoco is adequate for pipeline concentrations of H_2S . If not, Vista should proceed with plans for an "On-Line" hydrogen sulfide detection system. "On-Line" detection offers several advantages over ambient air monitoring. It offers the earliest warning for potential problems, it is less expensive, and it covers the entire refinery fuel gas network. If there are any questions or comments, please call me.



G. W. Bacon

/mb

Attachments

cc: JAD, THH, RHG, PDC, RJS, RLP, JCS, BHS, SAR,
SSP, DDZ, JCL, JV
LRB
CRD, FEL, PFF, TWH, TGG

- LCCP
- LAB
- Houston

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TABLE I

GAS SPECIFICATION
CONOCO REFINERY OFF GAS

	<u>MAXIMUM</u>	<u>MINIMUM</u>	<u>TYPICAL</u>
Total Sulfur, gr/MCF	50	0	10 - 20
PPM	80	0	16 - 32
H ₂ O, dew point °F	- 35	- 100	- 50
, LB H ₂ O/MMCF	10	1	5

HEAT CONTENT

HHV, BTU/SCF	1160	900	1100
LHV, BTU/SCF	1060	810	1000

COMPOSITION, MOL %

	<u>LOW BTU</u>	<u>NORMAL</u>
N ₂	1.7	1.6
CO ₂	0.2	0.2
CO	1.0	0.6
H ₂	24.9	17.0
C ₁	59.8	51.8
C ₂	2.4	5.0
C ₂	9.8	20.5
C ₃	0.1	1.9
C ₃	0.1	1.4
C ₄	0	0
IC ₄	0	0
NC ₄	<u>0</u>	<u>0</u>
	100.0	100.0

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TABLE II

EFFECTS OF HYDROGEN SULFIDE INHALATION ON HUMANS⁽¹⁾

<u>CONCENTRATION</u> (PPM)	<u>EFFECT</u> (Less Than Twenty Minutes)
1000 +	Immediate Unconsciousness, Death
200 - 1000	Unconsciousness, Respiratory Paralysis, and Possible Death
100 - 200	Eye Damage, Burning Throat, Deadened Sense of Smell
25 - 100	Burning Eyes, Headache, Dizziness
1 - 25	Irritation of Eyes and Respiratory System, Rotten Egg Odor
10	Threshold Limit Value for Eight-Hour Exposure ⁽²⁾
50	Maximum Allowable Peak Exposure ⁽³⁾

REFERENCES

- (1) Adapted from "Occupational Exposure to Hydrogen Sulfide" Criteria Document, National Institute of Occupational Safety and Health, (NIOSH), May 1977.
- (2) NIOSH Standard
- (3) OSHA Standard

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TABLE III

ON-LINE H₂S DETECTION SYSTEMS

MANUFACTURER:	Tracor Atlas Inc.
METHOD:	Lead Acetate Tape
DESCRIPTION:	H ₂ S contacts lead acetate sensing tape. Lead sulfide forms and tape darkens. Rate of darkening, which is detected by light deflection is proportional to H ₂ S concentration.
RANGE:	20 ppb 100%
ADVANTAGES/ DISADVANTAGES:	This system is widely used and is H ₂ S specific. The mechanical tape drive is subject to breakdown. Tape must be replaced every two weeks. Three minute measuring cycle. This system is employed by Conoco.
PRICE:	\$13,000

MANUFACTURER:	I.T.T. Barton
METHOD:	Titration
DESCRIPTION:	Hydrogen sulfide is titrated by a bromine reagent. The reagent is generated by passing a current through an electrolytic solution. Excess reagent is maintained in the solution by the generating current. Net generating current is proportional to H ₂ S concentration.
RANGE:	0 - 1000 ppm
ADVANTAGES/ DISADVANTAGES:	Must use a filter to make H ₂ S specific. Bromine solution must be replaced every two weeks.
PRICE:	\$10,000

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TABLE III (Con't.)

MANUFACTURER:	Texas Analytical
METHOD:	Solid State Sensor
DISCRIPTION:	Sensor detects H ₂ S by diffusion/adsorption. Interaction between the sensor and H ₂ S results in a decrease in resistance proportional to the H ₂ S concentration.
RANGE:	Any Range within 0 - 1%
ADVANTAGES/ DISADVANTAGES:	Lower cost, continuous analysis
PRICE:	\$4,600
MANUFACTURER:	Western Research Inc.
METHOD:	UV Adsorption
RANGE:	0 - 25 ppm
ADVANTAGES/ DISADVANTAGES:	Not suitable for RFG, low range and high cost
PRICE:	\$19,500

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