

REFERENCES

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Appendix A

ANALYSIS REPORT

TO: P. Stepanoff DEPT.: PS& Research, Iron Run
FROM: J. H. Phillips, K. C. Tewari DEPT.: CRSD-A, R&D 3/x. 5673,4791
DATE: 28 October 1986 Problem Solving Laboratory
SUBJECT: GC/ECD Analysis of Iron and Nickel Carbonyls

Sample No.: S627010

cc: J. H. Frost; F. A. Lucrezi; G. J. Mantell; P. Rao; T. L. Slager

SUMMARY: A packed column gas chromatograph equipped with an electron capture detector (GC/ECD) has been set up to measure nickel tetracarbonyl (Ni(CO)₄) and iron pentacarbonyl (Fe(CO)₅) in syngas. A dynamic gas diluter was utilized for calibration of the instrument and the determination of method linearity. The GC/ECD and dynamic diluter were found to be linear over five orders of magnitude. The detection limit and quantitation limit for Ni(CO)₄ were 0.03 ppb and 1.0 ppb, respectively. The detection limit and quantitation limit for Fe(CO)₅ were 0.15 ppb and 0.27 ppb, respectively. The concentration of Ni(CO)₄ and Fe(CO)₅ in syngas cylinder S627010 as measured by GC/ECD was in good agreement with the traditional method of analysis.

PROBLEM DEFINITION/SAMPLE DESCRIPTION: Both Fe(CO)₅ and Ni(CO)₄ are known to be catalyst poisons at trace levels in the liquid methanol process. The traditional method of Fe(CO)₅ and Ni(CO)₄ analysis consists of wet scrubbing followed by atomic absorption analysis for iron and nickel. The Process Gas Group requested an analytical technique with a faster turnaround time to allow a more rapid response to catalyst poisoning. Tests were also scheduled in which various materials would be evaluated for their ability to remove metal carbonyls from the syngas. Due to the large volume of gas required for the traditional method, a new technique which used a smaller sample size would be preferred. The syngas consists of approximately 37% H₂, 36% CO₂, 20% CO, and 0.9% N₂.

ANALYTICAL PROCEDURES: The 5890 GC/ECD and 3393A integrator were purchased from Hewlett-Packard. A slight modification was made to the gas sampling valve system according to Figure 1. The column was silanized prior to packing and conditioned overnight at 100°C before use. The GC/ECD operating conditions are listed in Table 1, and typical chromatograms can be found in Figure 2. The dynamic gas diluter utilized two Tylan GC260 mass flow controllers and was designed and assembled at APCI. A schematic diagram of the dynamic diluter can be found in Figure 3.

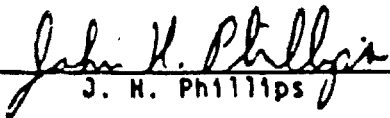
Request No.: None
Charge No.: (7-7-1557.71)
Notebook No.: 9189-12
Method No.: 274
Phone Date: 10/27/86
Sample Receipt Date: 10/6/86

lkw:4022w

RESULTS AND DISCUSSION: Once the instrumental conditions described in Table 1 were set up, a standard cylinder containing 22 ppm Fe(CO)_s and 8 ppm Ni(CO)₄ was connected to the gas sampling loop. Since both carbonyls eluted much more rapidly than expected, a liquid standard of 6 ppm Fe(CO)_s was injected to confirm the retention time of that component. Next, the dynamic gas diluter was utilized to produce accurate, real time, low level carbonyl standards for a calibration curve. In this work, the standard cylinder was diluted with nitrogen, and the dynamic gas diluter outlet was connected directly to the gas sampling loop. The data obtained from this procedure is listed in Table 2, and log-log plots of the standard curves can be found in Figures 4 and 5. Both Fe(CO)_s and Ni(CO)₄ calibration curves were linear down to 1.0 ppb. Below 1.0 ppb, the quantitation of Ni(CO)₄ was difficult since it eluted on the tail of an impurity in the nitrogen. In the syngas matrix, this problem is not expected, and lower detection and quantitation limits should be achievable for Ni(CO)₄.

To confirm the accuracy of the GC/ECD technique, a standard cylinder and a syngas cylinder (SG27010) were analyzed simultaneously by GC/ECD and the traditional method. First the syngas cylinder was analyzed. During the 30 minute scrub time, seven GC/ECD measurements were taken. Next, the standard cylinder was placed in line. During the 40 minute scrubbing time, the standard cylinder was analyzed by GC/ECD to arrive at standard response factors for the iron and nickel carbonyl peaks. For this work, the standard cylinder was connected to the dynamic diluter prior to the GC/ECD. In this way, the external calibration standard could be dynamically diluted until the area counts of the external standard approximated the area counts in the sample. The Ni(CO)₄ area counts stabilized almost immediately, however, the Fe(CO)_s area counts were extremely low until about 30 minutes into the analysis. Since the traditional method found no significant variation from previous measurements, we are assuming that Fe(CO)_s requires a significant period of time to equilibrate in the dynamic diluter. After the levels of Fe(CO)_s and Ni(CO)₄ in the standard cylinder were determined by the traditional method, a response factor for each analyte was calculated. By applying these response factor to the average area counts in the syngas, Fe(CO)_s and Ni(CO)₄ concentrations were calculated (Table 3).

The GC/ECD technique is able to accurately and precisely measure less than 1.0 ppb concentrations of Fe(CO)_s and/or Ni(CO)₄ in syngas. The sample volume required for the 1.0 ppb quantitation limit is 1.0 ml, and the analysis time is under 3.0 minutes. Personnel from CRSD-Analytical will be available to help PSG researchers utilize the GC/ECD instrument for future measurements. A CRSD-Analytical method, entitled "Analysis of Trace Levels of Fe(CO)_s and Ni(CO)₄ in Syngas", is currently being written.


J. H. Phillips


K. C. Tewari

tkw:4022w
Attachments

Table 1

GC/ECD Operating Conditions

Column:	6' x 2 mm i.d. (.25" o.d.) glass
Packing:	10% squalane on 100/120 mesh chromosorb W (H/P)
Carrier:	5% methane in Argon at 60 ml/min.
Oven:	31°C, isothermal
Injector:	31°C, 1 ml gas sampling loop
Detector:	31°C, Ni ⁶³ Electron Capture
Integrator:	3393A Hewlett-Packard

Table 2

Calibration Standards for Ni(CO)₄ and Fe(CO)₅

<u>Ni(CO)₄</u>			<u>Fe(CO)₅</u>		
<u>ppb</u>	<u>Counts</u>	<u>% rsd</u>	<u>ppb</u>	<u>Counts</u>	<u>% rsd</u>
8,000.	2.044ee7	3.2	22,000.	1.195ee8	2.8
800.	2.622ee6	1.8	2,200.	1.926ee7	4.8
63.	3.778ee5	13.0	540.	4.033ee6	3.1
6.3	7.561ee4	4.7	54.	2.268ee5	3.9
1.26	1.809ee4	1.9	10.8	4.052ee4	4.1
0.63	1.141ee4	4.4	5.4	1.866ee4	2.0
0.315	8.789ee3	4.6	2.7	1.089ee4	2.2
0.063	3.417ee3	5.3	0.54	2.563ee3	9.0
0.0315	2.748ee3	3.2	0.27	1.330ee3	16.0
			0.216	2.370ee2	28.1
			0.162	2.020ee2	31.0

Table 3

Calibration Results GC/ECD vs. Traditional Method

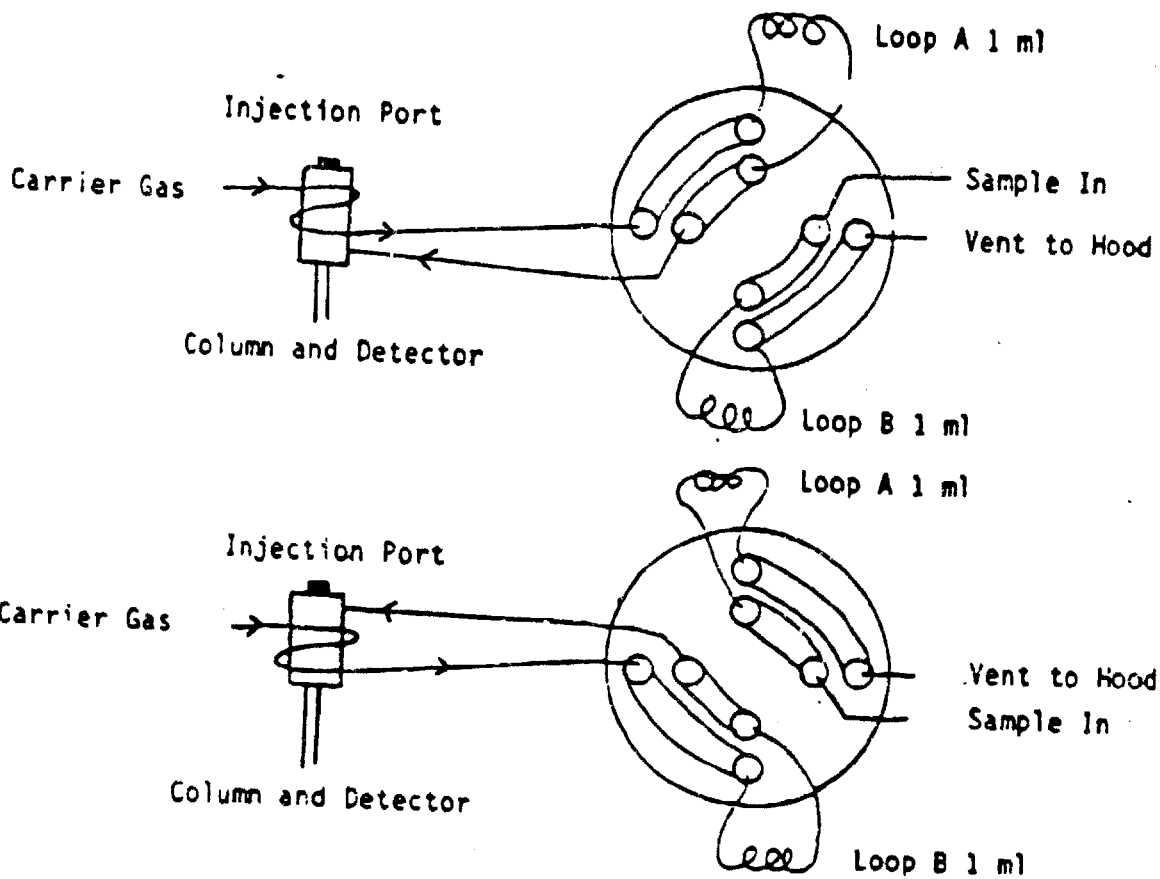
Standard Cylinder Calibration and GC/ECD Response Factors

Ni(CO) ₄	15.0 ppm by A.A.	4,730,000 cts/ppm	1.7 %rsd (n=3)
Fe(CO) ₅	9.9 ppm by A.A.	8,230,000 cts/ppm	3.0 %rsd (n=3)

Syngas Sample (S627010): Analysis by A.A. and GC/ECD

Ni(CO) ₄	0.056 ppm by A.A.	0.063	2.0 %rsd (n=7) by GC/ECD
Fe(CO) ₅	0.47 ppm by A.A.	0.54	3.5 %rsd (n=7) by GC/ECD

Position 1



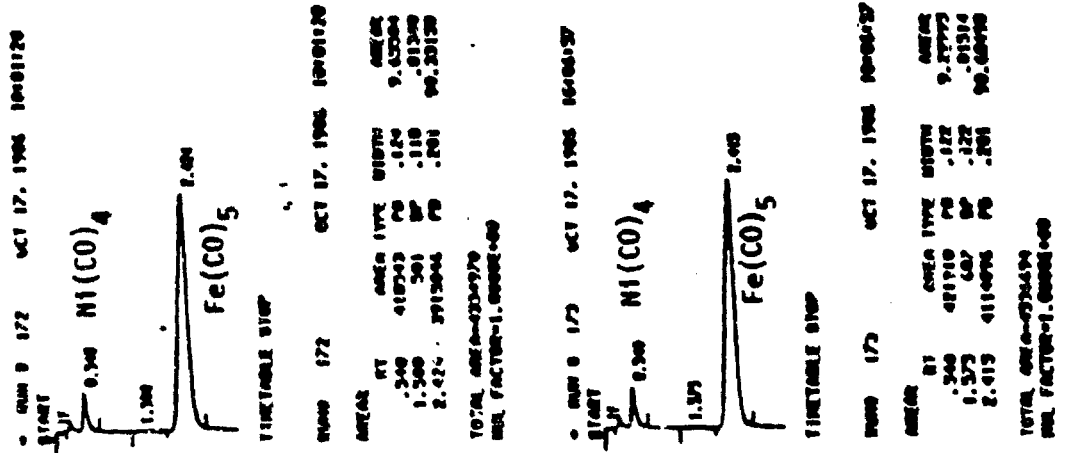
Position 2

Figure 1

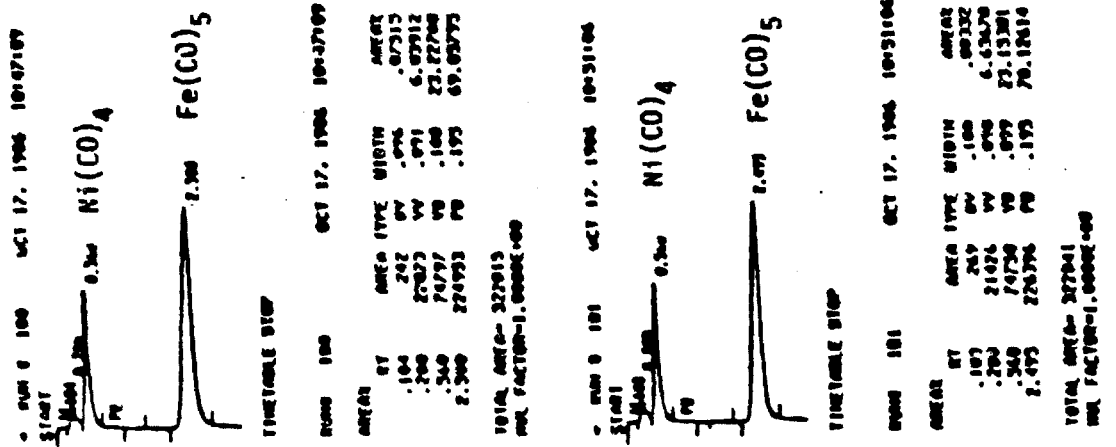
Eight Port Sample Valve Configuration

GC/ECD Chromatograms

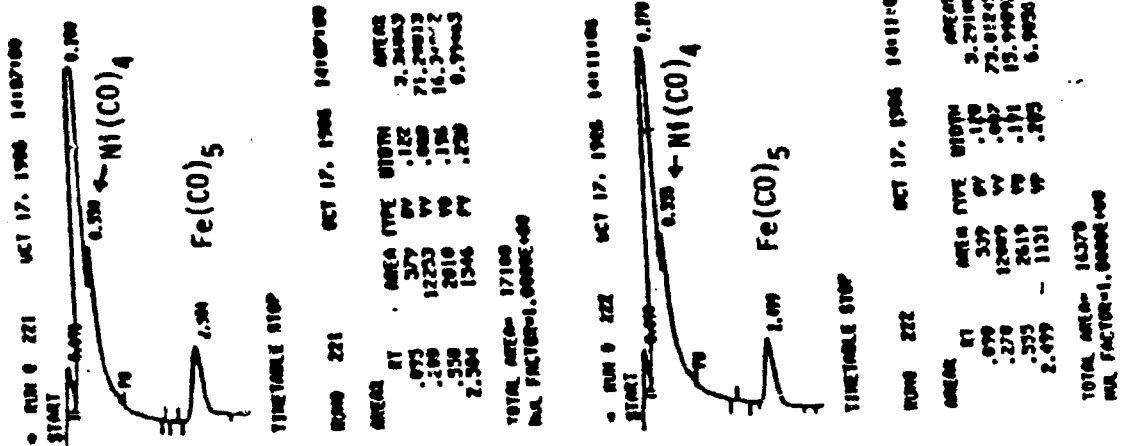
63 ppb Ni(CO)₄
540 ppb Fe(CO)₅
In Nitrogen



6.3 ppb Ni(CO)₄
54 ppb Fe(CO)₅
In Nitrogen



0.03 ppb Ni(CO)₄
0.27 ppb Fe(CO)₅
In Nitrogen



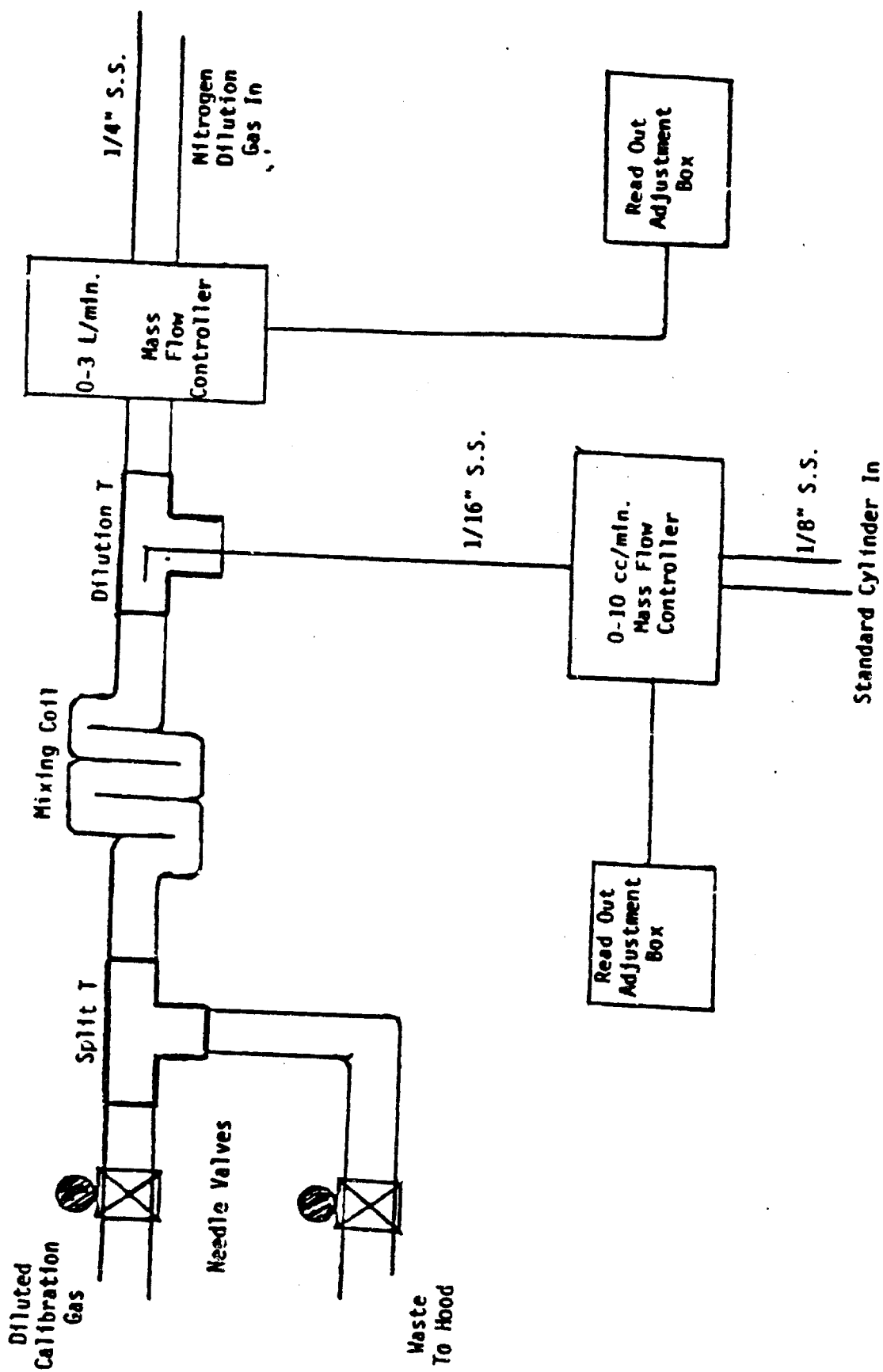


Figure 3
Dynamic Gas Diluter Schematic Diagram

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LOG PREP COUNTS

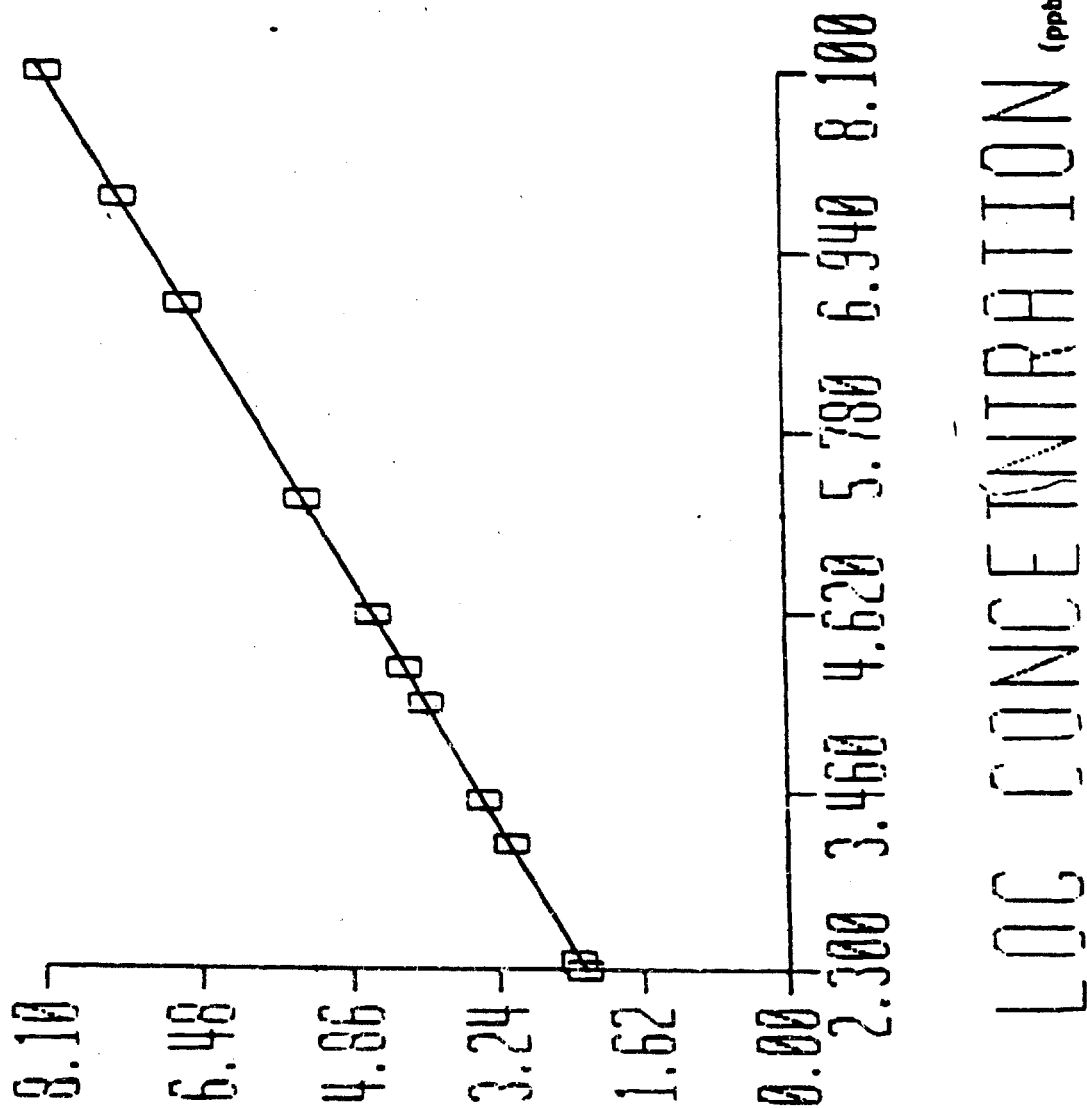


Figure 5

NICKEL DIETHYLHYDROXYL

LOG PPM COUNTS

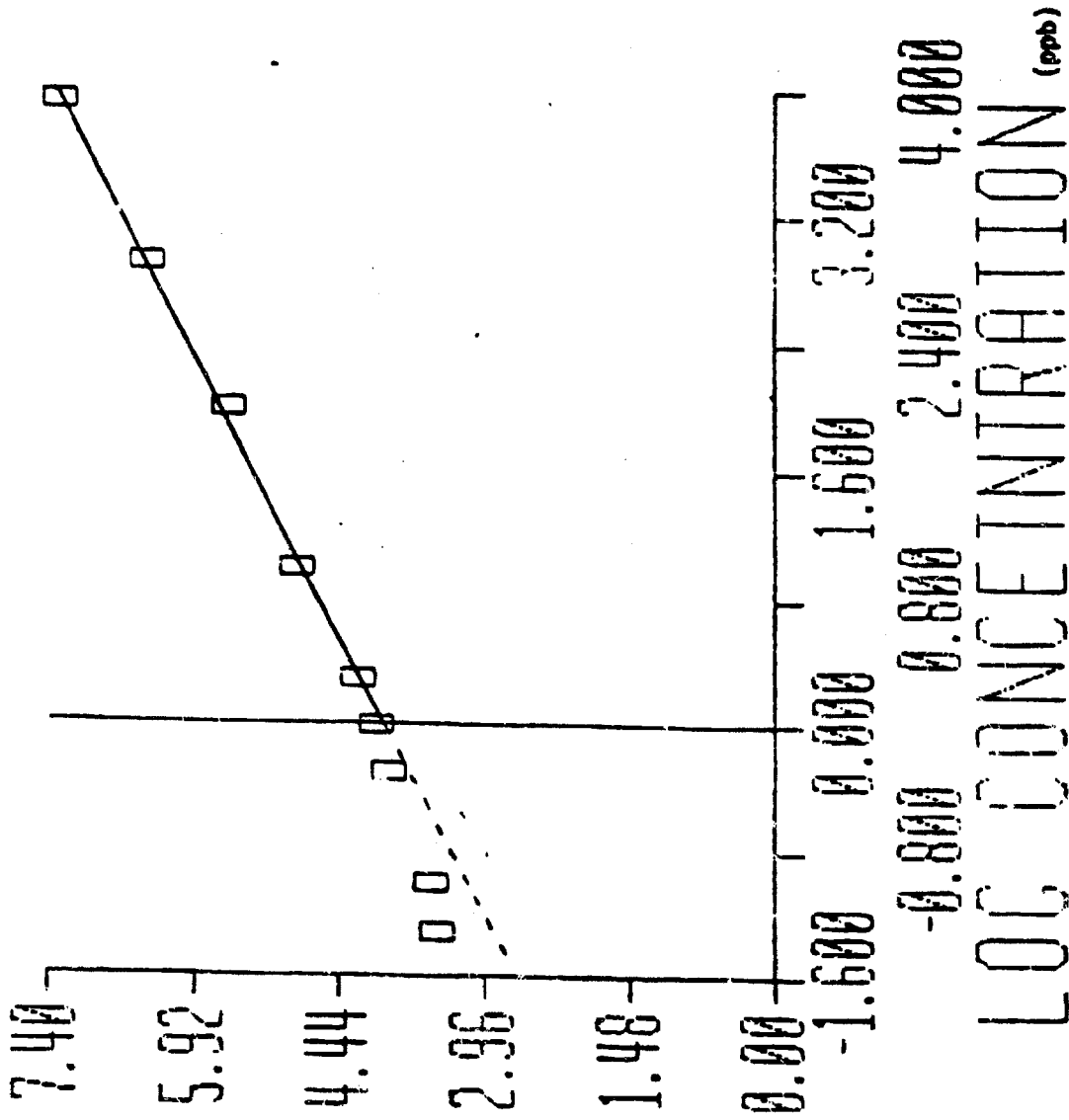


Figure 4

Memorandum

Ali
PRODUCT

To: T. H. Hsiung Dept.: PSG Research/Iron Run
From: P. J. Maroulis Dept./Ext: CRSD-Analytical/R&D #3
Date: 4 December 1987
Subject: Method Summary for Determining Low ppmv Levels of H₂S and COS

cc: R. J. Coraor
J. H. Frost
T. C. Golden
J. B. Wallace

An analytical method has been developed for determining H₂S and COS to 0.5 ppmv in a mixture of 30% H₂, 20% N₂, 10% CO, and 40% CO₂. The separation is performed with a 4' Hayesep Q column heated to 50°C using He carrier gas with a flow rate of 30 ml/min. The eluted gases are detected with a photolionization detector (PID) equipped with a 11.7 ev lamp. The system is plumbed around a 10-port Nitronic 50 Valco gas sampling valve (GSV). All sampling and valving lines are constructed of teflon (1/8" OD). A gas tight syringe can be used in place of the GSV to introduce the sample via a GC septum.

For developing this method an 84 ppmv H₂S and 75 ppmv COS in 30% H₂, 20% N₂, 10% CO, and 40% CO₂ gas mixture purchased from Specialty Gases was used. This standard was dynamically blended to lower concentrations with a diluent gas mixture of 30% H₂, 20% N₂, 10% CO, and 40% CO₂ using two Tylan mass flow controllers. All the dilution lines and transfer lines were constructed of teflon. Swagelock fittings constructed of 316 stainless steel were used where needed. A low residence time was maintained for H₂S and COS in the lines to minimize losses. This was done by using high flow rates and low volume lines (i.e., short lines and small diameters).

Table 1 contains the conditions used to achieve the separation of H₂S and COS from the matrix gas. It was necessary to separate the CO₂ from the H₂S and COS since it produced a large negative response with the PID. Figure 1 shows the separation of 1.8 ppmv H₂S and 1.6 ppmv COS as well as the negative CO₂ response prior to the H₂S. The CO₂ is adequately separated from H₂S for quantitation at these levels. However, for concentration below ≈300 ppbv in a 40% CO₂ mixture, better resolution is needed for good quantitation.

Table 2 contains the calibration data generated for H₂S and COS in the syn-fuel matrix. Area counts and response factors are given for concentration ranges of 0.5 ppmv to 84 ppmv for H₂S and 0.5 ppmv to 75 ppmv for COS. The data indicate the H₂S and COS responses are linear using the PID over this concentration range.

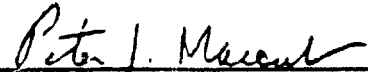
To: T. H. Hsiung

2

4 December 1987

The PID sensitivity was found to decay =3-4% per day. This is probably due to the decay of the lamp and clouding of the detector window. A constant PID sensitivity can be achieved by increasing the lamp intensity each day. This may not be necessary for this phase of the project since there is adequate signal for the required 0.5 ppmv detection limit. However, the GC-PID system must be calibrated each day whether the lamp sensitivity is adjusted or not to obtain maximum accuracy.

A standard analytical method is being written. If you have any questions, please contact me.


P.J. Maroulis

cjd

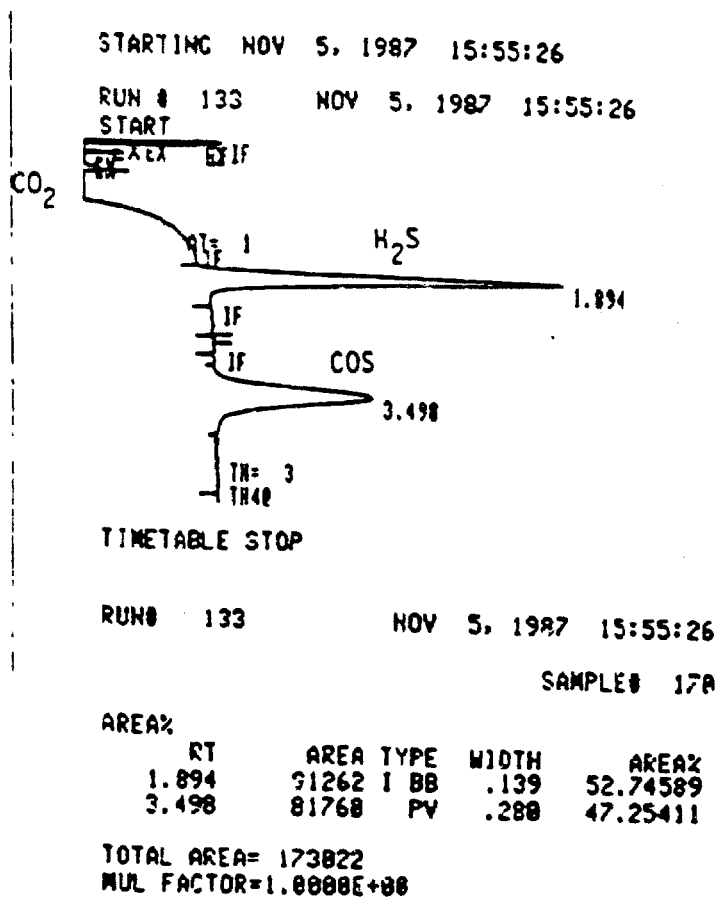
Table 1Gas Chromatographic Conditions

Column Packing:	Hayesep Q
Column Tubing Material:	FEP Teflon
Column Size:	4' x 1/8" O.D. x 0.059" I.D.
Column Temperature:	50°C
Carrier Gas	He
Carrier Gas Flow Rate:	30 ml/min.
Sample Volume:	1.0 ml
Detector:	Photoionization
Detector Lamp	11.7 eV

Table 2H₂S and COS Calibration Data

<u>H₂S</u>			<u>COS</u>		
<u>Concentration (ppmv)</u>	<u>Area (counts)</u>	<u>Response (counts/ppmv)</u>	<u>Concentration (ppmv)</u>	<u>Area (counts)</u>	<u>Response (counts/ppmv)</u>
0.59	30,232	51,241	0.53	30,361	57,285
1.80	92,853	51,585	1.61	81,023	50,324
8.26	422,215	51,116	7.37	352,702	47,856
29.1	1,507,391	51,765	26.0	1,277,758	47,606
84.0	4,326,556	51,507	75.0	3,459,066	46,121

Figure 1. Chromatogram Showing the Separation of 1.8 ppmv H₂S and 1.6 ppmv COS from 30% H₂, 20% N₂, 10% CO, and 40% CO₂



APPENDIX B

Derivation of Kinetic Model

At the start of kinetic measurements ($t = 0$), there is a known amount of impurity in the gas phase, y_0 , and a known amount of impurity adsorbed on the carbon, n_1 . As the kinetic experiment starts ($t > 0$), the gas phase impurity is exposed to the adsorbent and during adsorption the gas phase concentration, y , decreases as a function of time.

Mass Balance at Any Time

$$W \frac{dn}{dt} = \frac{PV}{RT} \frac{dy}{dt}$$

where

- W = adsorbent weight
- n = number of moles in gas phase
- t = time
- P = total pressure, constant
- V = total void volume, constant
- T = temperature, constant
- y = impurity concentration

Let $a = PV/WRT$, then

$$\frac{dn}{dt} = a \frac{dy}{dt}$$

APPENDIX B
(continued)

Integrating yields:

$$\int_{n_1}^n dn = a \int_{y_0}^y dy$$

$$(n - n_1) = a (y - y_0) \quad \text{or} \quad (1)$$

$$n = n_1 + a (y - y_0)$$

Rate of Mass Transfer

The rate of mass transfer is given by:

$$\frac{\partial n}{\partial t} = k(y - \bar{y}) \quad (2)$$

where k is the mass transfer coefficient in units gmole/gm/sec.

If the adsorption isotherm is linear, then it can be described by:

$$n = K \bar{y} \quad (3)$$

APPENDIX B

(continued)

Combining equations 2 and 3 yields:

$$\frac{\partial n}{\partial t} = k \left(y - \frac{n}{K} \right) \quad (4)$$

Combining equations 1 and 4 yields:

$$\begin{aligned} a \frac{\partial y}{\partial t} &= k \left[y - \frac{n_1 + a(y - y_0)}{K} \right] \\ &= k \left[y (1 - a/k) - \left(\frac{n_1 - ay_0}{K} \right) \right] \end{aligned}$$

Let $b = 1 - a/k$

$$c = \frac{n_1 - ay_0}{K}$$

Substitution leaves:

$$a \frac{\partial y}{\partial t} = k [by - c]$$

Integrating:

$$\int_{y_0}^y \frac{dy}{(by-c)} = \frac{k}{a} \int_0^t dt$$

$$\frac{1}{b} \ln (by - c) \Big|_{y_0}^y = \frac{k}{a} t$$

APPENDIX B

(continued)

Evaluating leaves:

$$\ln \frac{by - c}{by_0 - c} = \frac{b}{a} kt \quad (5)$$

Substituting values for b and c leave:

$$by_0 - c = y_0 - n_1/k$$

and

$$by - c = y \left(1 - \frac{a}{k}\right) - \frac{1}{k} (n_1 - ay_0)$$

Substituting these values into equation 5 yields:

$$\ln \frac{y(1-a/k) - \frac{(n_1 - ay_0)}{k}}{y_0 - n_1/k} = \left(\frac{k-a}{ak}\right) kt$$

or

$$\ln \frac{y(1-a/k) - \frac{(n_1 - ay_0)}{k}}{y_0 - n_1/k} = \exp \left(\frac{k-a}{ak}\right) kt$$

Thus by plotting the left hand side of the above equation vs. $t \left(\frac{k-a}{ak}\right)$ yields a straight line with a slope of k in units of gmole/gm/sec.

Appendix C

Memorandum

PRODUCTS

To: T. H. Hsiung Dept.: PSG Research
From: A. T. Perka Dept./Ext.: PSG Process Engineering/7943
Date: 31 August 1987
Subject: Revised Design Levels for Syngas Catalyst Poisons Study

cc: A. D. Bixler R. L. Madnick - Chem Systems
D. M. Brown E. Schmetz - DOE
E. P. Holley/D. J. Silkworth M. C. Stewart - EPRI
J. Klosek W. H. Heber - EPRI
D. S. Lubbers/G. W. Roberts P. C. Williamson - TVA
R. B. Moore T. L. Wright - TVA
D. W. Studer
R. F. Weimer

add. R.W. Wetherington

This is an update to D. W. Studer's memo of 8 June 87 entitled "Preliminary Design Levels for Syngas Catalyst Poisons Study", reflecting some recently discovered information. Several entries require comment:

- A new column has been added, showing gas turbine fuel specs. The numbers here indicate that if LPMEOH is used in a configuration which also includes a gas turbine, the levels of chlorine, iron and nickel in the feed to the LP unit will probably have already been lowered significantly to meet GT specs.
- The results from the Shell gasifier PDU given in Reference 6 show iron carbonyl levels before AGR in the 0.5-1 ppm range for both coals tested. On this information the iron carbonyl adsorber feed limit has been lowered to 5 ppm, to reflect a greater confidence in a lower amount entering the AGR system. This value still reflects a considerable safety factor over the maximum value one would expect given the Shell gasifier data.
- Several new references show nickel carbonyl concentrations between 0.004-0.1 ppm, and based on this information the adsorber feed limit has been lowered from 10 to 1 ppm nickel.
- New information on halides and nitrogen compounds have led to an increase in their adsorber feed limits.
- A range of water compositions is given because the value would depend on the acid-gas removal system used.
- A second table has been added containing newly acquired information on a large number of trace elements. It is not clear at this time if all of them are a problem for our catalyst, but they are presented here for completeness.

I hope this updated list of contaminants will be helpful. As before, any comments or additional input from the distribution would be most appreciated.

Alan T. Perka
A. T. Perka

TABLE 1
MAJOR TRACE CONTAMINANTS IN LPMEOH SYNGAS FEED

<u>Trace Component</u>	<u>Design Concentration, ppmv</u>		<u>Turbine Fuel Gas Specs, ppmv (7)</u>
	<u>Adsorber Feed Limit</u>	<u>Catalyst Design Limit(1)</u>	
Sulfur Compounds*			
H ₂ S	5 (2)		
COS	10 (2)		
Total Sulfu	15 (2)	0.06	
Halides			
Chloride	20 (3,8,10)		<10
Fluoride	5 (8,10)		
Total Halides		0.01	
Hydrocarbons			
Ethylene, Benzene and Other Unsaturation	2 (8)	300	
Acetylene	1 (8,9)	5.0	
Nitrogen Compounds			
NH ₃	5 (4,8,9,10)	10.0	
NO _x	0.001 (8,10)	0.1	
HCN	6 (5,8)	0.01	
Oxygen		1500	
Water	0-1500 (11)		
Solaxol (polyethylene glycol dimethyl ether)	0.02**		
Formate	49 (8)		
Iron, as Fe(CO)₅	5 (6)	0.01	0.1
Nickel, as Ni(CO)₄	1 (6,8,9,10)	0.01	0.1

* Much higher levels have been reported. Limit set based on apparent economic operating range of guard bed materials (13).

** Based on a vapor pressure of 0.0007 mm Hg at 77°F. and assuming no entrainment of liquid.

4526H

TABLE 2
MISCELLANEOUS TRACE ELEMENTS IN LPMEOH SYNCOG FEED

<u>Trace Component</u>	<u>Design Concentration, ppbv</u>		<u>Turbine Fuel Gas Specs, ppbv(7)</u>
	<u>Adsorber Feed Limit</u>	<u>Catalyst Design Limit(1)</u>	
Arsenic	1 (8,9)	Absent	
Barium	4 (8)		
Beryllium	20 (8)		
Boron	30 (9)		
Cadmium	0.5 (9)		
Chromium	0.9 (9)		
Cobalt	0.6 (9)		
Lead	0.4 (10)		2,000
Mercury	1 (6,10)		
Molybdenum	10 (8)		
Potassium/Sodium	10 (13)	Absent	500
Selenium	0.2 (8)		
Silver	0.1 (8)		
Thallium	0.1 (8)		
Vanadium	10 (6,8)	Absent	2,000

Calcium

4526H

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10. EPRI Final Report #AP-2215 "Coal Gasification Environmental Baseline Studies", Texaco, Inc., March 1982.
11. APCI memo, J. Klosek, "Cool Water Syngas Location and Condition: Guard Bed Tests", 14 August 1987.
12. APCI memo, A. T. Perka, "Intermediate-Level Sulfur Removal in LPMEOH Feed Streams, 6 August 1987.
13. No reference, guess only.