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Technical Report

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EVALUATION OF THE BECKMAN 951A ATMOSPHERIC NOx ANALYZER

by

Sherman D. Funk

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Engineering Staff
Engineering Operations Division
Mobile Source Air Pollution Control
Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105

Abstract

The primary method used for the measurement of NOx emissions by EPA and the automotive industry is by the chemiluminescence process. Several improvements have been made in these instruments since the original vacuum type NOx analyzers. EPA has taken the opportunity to evaluate some of these instruments in an effort to refine its analysis capability.

Although other instruments have been evaluated in various degrees by EPA and the industry, this report discusses the Beckman 951A which has a history of wide usage and previous evaluations.

Bench testing and operational comparisons were completed in the EPA laboratory over a period of six weeks. Although the 951A still demonstrates need for improvement in certain areas, it met all EPA requirements and advertised specifications. The test results correlated to within ±0.5% of full scale to the presently used Teco 10A. The 951A has been found to be an acceptable alternative to the vacuum type chemiluminescence analyzer.

I. INTRODUCTION

The NOx analyzer evaluation project on which this report is written is the result of earlier investigations into improved state of the art instrumentation for the analysis of vehicle NOx emissions. These investigations led to the Beckman atmospheric NO/NOx analyzer. Two Beckman versions (the 951 and the 951A,) have been evaluated at this laboratory. Since the 951A has been tested to a greater degree it will be the one addressed in this report.

II. BACKGROUND

EPA EOD has used the vacuum type NOx analyzers for Light Duty vehicle emission testing since 1972. The vacuum pumps associated with the Teco 10A models have been a constant source of maintenance problems and a potential cause of leaks. In addition, the use of pure oxygen for ozone generation has always been a safety concern. These problems and concerns as well as the development of the atmospheric NOx analyzers, prompted the search for a better instrument to measure NOx.

In the past few years, a number of atmospheric NOx analyzers have been advertised and considered by the EPA laboratory. However, only a few have ever had extensive evaluation. One was the Philco-Ford version. The report, completed in June 1974 indicated it was an acceptable instrument for light duty vehicle emissions testing. Inquiries to industry laboratories revealed that the Beckman 951 had also been extensively tested and used in the industry. These data, coupled with our limited resources to evaluate instruments in general, prompted us to select the 951 for a more thorough evaluation. A Beckman 951 was purchased and was tested for a period of time. However, during the evaluation period the newer version the 951A, was developed. Although the basic detectors are unchanged, the 951A utilizes improvements in flow control and regulation. The company claimed the 951 could not be upgraded to a 951A configuration, but provided a 951A for additional testing. The following test plan was developed to assess the performance of the 951A relative to our current instrumentation.

III. TEST PLAN

A test plan to evaluate this instrument was designed and implemented in three parts.

A. Preliminary Checkout
   A basic analyzer checkout procedure was preformed in a specifically designed equipment test rack by the following steps.

   1. Stability, Noise, Speed of Response, and Repeatability checks were made by performing the following:

a. Select 0-100 PPM range on the instrument and an appropriate span gas.

b. Alternatively pass zero and span gas through the instrument while in the NOx position of the converter for a period of 75 seconds each.

c. Using a stopwatch, measure the time from a gas input change until reading indicates 90% of full scale.

d. During these tests observe traces for noise, stability, and repeatability.

2. Using procedure given in manual, set pots for range attenuation compatability.

3. Perform standard procedure for converter efficiency checks.

4. Run a curve check on the 0-100 PPM and the 0-250 PPM ranges and process data.

5. In order to check flow sensitivity, perform the following tests.

a. With the instrument adjusted for normal operation, pass a span gas through the instrument for 45 seconds.
b. Record reading on the chart recorder.
c. Adjust instrument by-pass flow up to 2400 CCM and down to 400 CCM in 200 CCM steps.

B. Comparison Tests
The Beckman unit was plumbed into the auxiliary by-pass line of the Teco 10A system in Analysis Site A001. A series of ten FTP and two HWFET was run. These produced 64 sample bag comparisons from actual certification tests.

C. CO_2 Interference Test
Two sets of four mixtures of NOx and CO_2 were blended and then measured on the Teco 10A and the 951A both in the NOx and the NO modes (see Appendix C). The Teco 10A was assumed to be interference free.

IV. SUMMARY OF RESULTS

The results of our tests can be summarized as follows:

A. Speed of response - Time from external valve change (zero to span) to 90% FS-Fast response switch position - 6.3 sec; Slow response switch position - 10.4 sec. Installed in Analyzer bench - Fast response switch position - 11.4 sec. Slow response switch position - 15.8 sec.

B. Attenuation Accuracy - Ability to match measurements from one range to another was less than ± 0.5 of full scale error.

C. Converter efficiency at final temperature setting (601° F) 98.15%. Converter has a fairly flat response curve within the operating range (See Appendix E).

D. Linearity - -0.4% non-linear on 0-100 PPM range; +0.1% non-linear on 0-250 PPM range.

E. By-Pass Flow Sensitivity - No change in output while by-pass flow was changed from 400 CCM to 2400 CCM in 200 CCM steps. Sample pressure remained the same. However, a 0.1 PSIG change in sample pressure caused a 1.0% of full scale change in output of analyzer in the same direction.

F. Precision - Zero and span settings were repeatable to less than $\pm 0.5\%$ of full scale.

G. Noise (degree of random and periodic deviations of output) average peak to peak - noise was no greater than 0.3% of full scale.

H. Stability - Zero and span drifts were less than $\pm 1\%$ of full scale for a period of four hours of continuous runs.

I. Comparison tests to Teco 10A - 64 comparisons produced a mean difference of +0.33 PPM. These were no greater differences than 0.7 PPM (See Appendix B). Corrected sample (Sample-Background) values from these same tests were compared and correlated to a mean difference of +0.04 PPM (See Appendix B 1). A series of 10 blended SAC bag measurements resulted in differences of less than ± 0.5 PPM.

J. Response to CO_2 - Response to CO_2 was less than 1 PPM at concentrations near the top of the CO_2 operating range for light duty emissions. (See Appendix C).

K. There are a number of potential problem areas with the Beckman 951A:

   1. The extensive use of miniature thin wall teflon tubing in the unit, some areas in which (capillary tubing, especially) inadvertent pinching or damage could cause abnormal operation. Capillaries should be made of some kind of hard material.

   2. It is difficult to make the NO bypass flow balance adjustment using the NO_2-free NO gas method since opening and closing the door cause a 0.5% difference in output. The door must be opened and the HV interlock set to make an adjustment with the bypass compensator valve. It is not known why this door causes a difference in output.

Another area, which may be part of the problem, is that the sample capillary is positioned so that closing the door presses against it. This could possibly affect capillary flow. This has not been proven, but the design should be improved.

3. Higher temperatures of the converter cause different responses at different concentrations causing some apparent non-linearity. It is not known why this occurs. It is recommended to run at the lower end of the temperature operating range.

4. The NO bypass valve knob kept coming loose although it was re-installed a number of times. Also, the NO/NOx mode switch kept coming loose even though it was tightened repeatedly.

5. The sample flow rate came no where near 200 CCM at 4 PSIG as the manual recommends. It also turns out that 200 CCM is the incorrect recommended flow as per Al Roddan of Beckman. We recommend a sample flow rate of 160 CCM. This should be set with a calibrated rotameter. Our pressure setting turned out to be 4.35 PSIG on the gauge.

6. This analyzer also exhibits some of the same problems as Teco 10A.

   a) Noise was measured up to an average of 0.3% of full scale peak to peak, sometimes a little higher.

   b) Generally, chemiluminescent analyzers have relatively slow response in comparison to other emissions analyzers primarily due to sample flow. Even though it is about 3 seconds faster than the Teco 10A the 951A would still slow down testing. Response time for analyzer alone from gas change at inlet port to 90% of full scale is 6.3 seconds. When installed in the analytical bench, this increased to 11.4 seconds as compared to the Teco 10A response of 14.8 seconds.

   c) Similiar to the 10A there are sluggish problems after a period of non-use (2 to 3 days) for the first few hours. If used continuously there are less problems.

   d) There also appears to be some sluggishness when returning to a span reading after reading a bag, although this is not serious.

VI. DISCUSSION

The Beckman 951A continuously analyzes a flowing gas sample and determines levels of nitric oxide (NO) or Oxides of Nitrogen (NOx)

($NO + NO_2 = NOx$). It utilizes the chemiluminescent method of detection. To determine NO, sample NO is quantitatively converted into NO_2* by oxidation with molecular ozone produced within the analyzer from air or oxygen supplied by an external cylinder. Approximately 10% of the NO_x molecules are elevated to an electronically excited state accompanied by the emission of photons. These photons strike the photomultiplier detector, generating a low level DC current. The current is amplified to drive an output indicating device, (recorder and/or meter). NOx determination is identical to that described above except that, before entry into the reaction chamber, the sample is routed through a converter where the NO_2 component is converted to NO.

After receipt of this instrument it was installed in a specifically designed checkout bench for preliminary tests. It was then installed in the A001 exhaust analytical bench as shown in Appendix D. During these tests a number of problems and issues of concern arose.

During initial checkout we found very poor sensitivity and occasional loss of zero. It was found that the ozone and exhaust lines were reversed on the reaction chamber fittings. This apparently had been done by the Beckman service man. We also found that the high voltage was 100 volts higher than nominal. He had also raised this to increase sensitivity. When we corrected the reversal, the sensitivity problem was corrected. The higher than necessary voltage created excessive dark current. When we lowered the voltage to nominal, this corrected the zero (dark current) problem.

We found that the recommended sample pressure of 4 PSIG only produced 138 CCM of sample capillary flow rather than the 200 CCM that the manual indicated. After additional investigations with GM and the Beckman design engineer, John Harman, it was finally decided to run at the 160 CCM flow rate that was the originally recommended value since no one seemed to know where the 200 CCM recommendation originated. GM is running at the 160 CCM rate also. We set this flow from a calibrated rotameter and marked it on the pressure gauge. It reads approximately 4.35 PSIG. Bypass flow was set at 2 liters per minute.

It was found that after running a few converter efficiency checks that the pressure matching method for NO bypass flow balance was inadequate since some readings were higher in the NO mode than the NOx mode. This was corrected by using a known NO_2 free cylinder of NO and setting the flow balance until the readings were the same in both modes.

Initial curve checks on the instrument on ranges 0-100 PPM and 0-250 PPM were less than 1% non-linear. Checks on 0-50 PPM were -1.2% non-linear and on 0-5000 PPM were 6% non-linear. However, gases on these ranges are non-dependable and no emphasis was placed on these checks. However, after installing the instrument in the analytical bench and during a series of converter temperature adjustments to find the best converter efficiency it was found that the higher temperature settings near the top end of the recommended range resulted in some abnormal curve plots, primarily on the 0-100 PPM range. It was really never determined why these higher temperatures caused more non-linearity on that one range. Possible causes could be NO_2 in the cylinders with some unknown reaction occurring in the converter. This same phenomenon was encountered in an EPA evaluation in March 1973 of a Ford modified Teco 10A and is discussed in excerpts from that report in Appendix G. These problems were not investigated since time did not allow. Since the higher temperatures 650° - 700°F not only caused this negative response but affected the stability to some degree it was decided to run the converter on the low end of recommended operation (605°F) that would give 98%+ converter efficiency and still result in acceptable curve linearity. It should be noted that each time the converter temperature was changed it was necessary to re-adjust the NO bypass balance.

During our check out previous to the actual comparison tests. The converter heater blanket element opened. The Beckman service rep was contacted. He then brought out a new one and it was installed and worked satisfactorily.

A final converter efficiency of 98.1% was accepted with a temperature of 607°F. Although it was found that 100% efficiency could be achieved at 691°F, 99% at 689°F and 98.4 at 697°F that the lower setting was more acceptable for all-around operation. More than sixteen settings and efficiency checks were made (See Appendix E).

The bag comparison tests were completed by the Light Duty team on actual certification tests. (Results are on Appendix B and B-1. Although the one to one comparisons of all bags, sample and background indicate a slight bias for the 951A to read in the positive direction (Mean difference of +.33 PPM with a standard deviation of 0.168), the corrected samples (sample minus background) correlated to a mean difference of +0.04 PPM with a standard deviation of 0.152. All readings were on 0-100 PPM range. The definite positive bias of the 951A could not be explained. However the magnitude is so small that it is not considered significant.

CO_2 interference checks were made by C&M personnel with blended bags of CO_2, NOx and air. (See Appendix C for results.) The different results of the two tests can be explained by the fact that the interference level is below standard instrument variability.

VII. CONCLUSIONS/RECOMMENDATIONS

A. The Beckman 951A is an acceptable instrument to measure light duty vehicle NOx emissions. It meets all EPA requirements and Federal Register specifications. However, for testing on ranges above 0-1000 PPM, in order to achieve the required linearity, different combinations of sample and ozone capillary flow plus the use of oxygen for ozone may have to be used.

B. Since, (a) the 951A uses the less expensive and safer air rather than oxygen for ozone, (b) it is an atmospheric type analyzer thereby eliminating the need for a vacuum pump, (c) it provides a slightly faster response than the 10A, (d) its NOx emission measurement results correlate satisfactorily with the presently used Teco 10A, (e) its configuration and plumbing requirements are compatible with our analytical benches, and (f) there is a significant amount of historical data available on these units from other laboratories, it is recommended as an equivalent, if not an improved alternative to the vacuum type NOx analyzers and could be used to replace them in Light Duty Certification and E&D Light Duty analytical benches.

VIII. BIBLIOGRAPHY

1. Interferences in Chemiluminescent Measurement of NO and NO_2 Emissions from Combustion Systems, R. Matthews, R. Sawyer, and Robert Schefer, Dept. of Mechanical Engineering, University of California, Berkley, Calif. Nov. 1977.

2. Ford Motor Company Intra-Company Memo, Atmospheric Pressure Chemiluminescent NOx Analyzer, R. Ford and J. Westveer, July 25, 1972.

3. Memo from Thermo-Electron Corp to D. Paulsell, EPA, NOx Converter Efficiency Test Expression, John Dunlay, Sept. 17, 1973.

4. Pressure Quenching in the Chemiluminescent Nitric Oxide-Ozone Reation, William Zolner, Ph.D., Thermo-Electron Corp.

5. EPA Inter-Office Memo, Report on NO/NOx Analyzer Investigation Progress, S.D. Funk, March 28, 1980.

6. Beckman Sales Literature, 1980.

7. EPA EOD Engr. Staff Project Sub-Task Summary, Atmospheric NOx Analyzer Evaluation, S.D. Funk, Sept. 2, 1980.

8. Technical Report, Evaluation of Philco-Ford Chemiluminescent NOx Analyzer, June 1974.

9. Technical Evaluation of Ford Motor Co. Alternate Test Equipment and Procedures, D. Paulsell, March 1973.

IX. APPENDICES

A. Beckman 951A and 951 Schematic Flow Diagram. A-1 Beckman 951A and 951 Differences

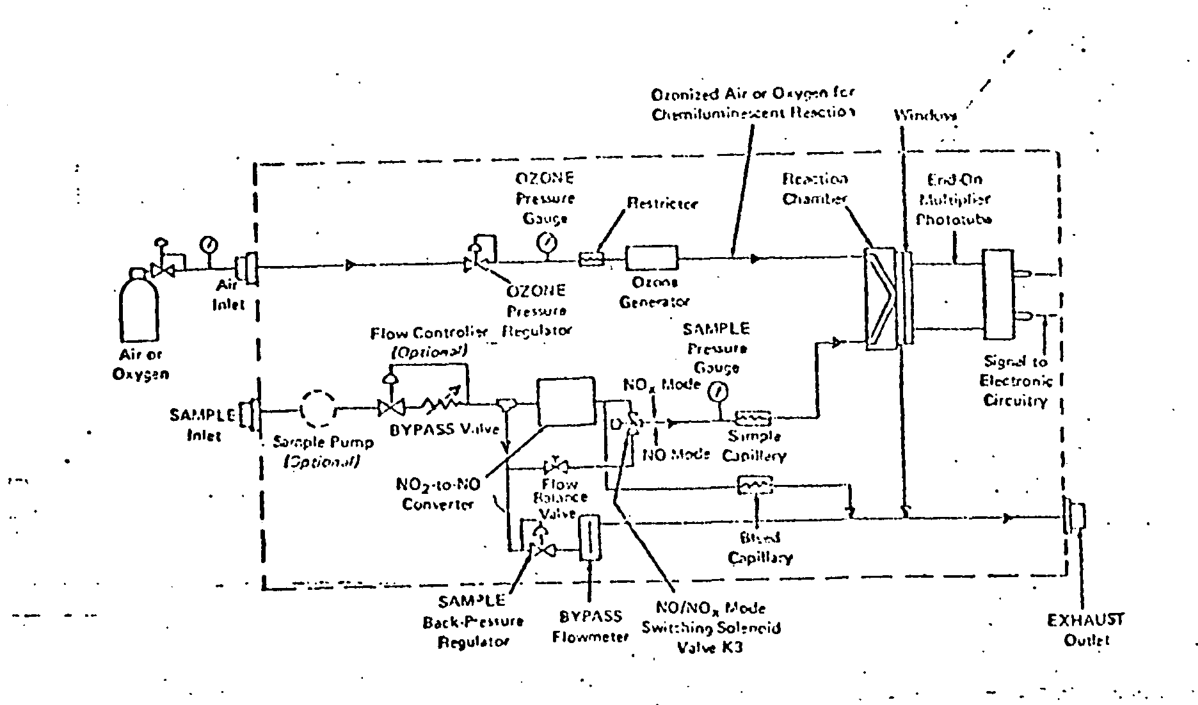
B. NOx Exhaust Sample Bag Comparison Table B-1 Corrected NOx Sample Comparisons

C. CO_2 Interference Table $C_{1\&2}$ Graphs

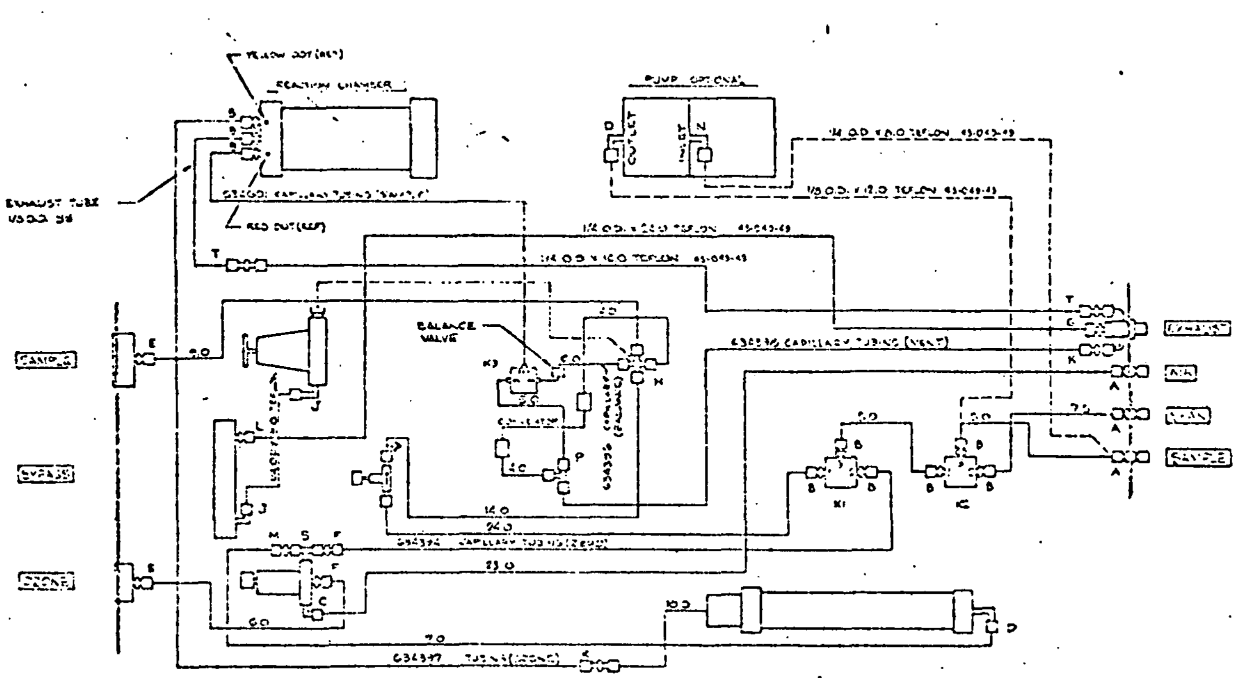
D. Beckman 951A Plumbing Connections in Analytical Bench

E. Converter Efficiency Graph

F. Excerpt from an EPA Technical Evaluation of a Ford Modified Teco 10A.



FLOW DIAGRAM OF BECKMAN 951A



FLOW DIAGRAM OF BECKMAN 951

Differences in Beckman 951A and 951

In the Beckman 951A:

1. A type J thermocouple output of converter temperature is provided.
2. Pressure settings and flows are visible thru the new front panel window.
3. Trim pots to separately trim each range have been added.
4. The span and zero solenoids are removed.
5. An led indicator showing converter cycling has been added.
6. Converter temperature adjust is now from front panel.
7. Improved flow balancing thru use of needle valve. The use of a needle valve has improved flow balancing.
8. Internal ozonator on/off switch has been added.
9. Internal changes of flow configuration and pressure regulation have been made.

NOx EXHAUST SAMPLE BAG COMPARISONS
Diff. = 951A - 10A

BECKMAN VS. TECO
READINGS = PPM

DATE	TEST #	BAG 1 and 4						BAG 2 and 5						BAG 3 and 6					
		BG			SAMP			BG			SAMP			BG			SAMP		
		951A	10A	DIFF	951A	10A	DIFF	951A	10A	DIFF	951A	10A	DIFF	951A	10A	DIFF	951A	10A	DIFF
11-20-80	80-6816	0.7	0.6	+0.1	27.9	27.9	0.0	0.8	0.2	+0.6	9.7	9.1	+0.6	0.3	0.1	+0.2	19.5	19.1	+0.4
11-20-80	80-6823	0.7	0.2	+0.5	60.3	60.3	0.0	0.6	0.1	+0.5	13.8	13.1	+0.7	0.3	0.0	+0.3	43.7	43.6	+0.1
11-20-80	80-6819	0.6	0.1	+0.5	2.5	2.2	+0.3												
11-20-80	80-6820	0.8	0.3	+0.5	21.9	21.6	+0.3	0.7	0.3	+0.4	7.1	6.7	+0.4	0.7	0.3	+0.4	11.3	10.9	+0.4
11-21-80	80-6825	0.6	0.1	+0.5	22.0	21.6	+0.4	0.6	0.1	+0.5	4.3	3.8	+0.5	0.3	0.0	+0.3	12.4	12.1	+0.3
11-21-80	80-6833	0.7	0.1	+0.6	13.5	13.3	+0.2	0.5	0.0	+0.5	5.1	4.6	+0.5	0.3	0.0	+0.3	11.6	11.3	+0.3
11-21-80	80-6830	0.5	0.2	+0.3	16.5	16.3	+0.2	0.5	0.2	+0.3	7.1	6.8	+0.3	0.3	0.1	+0.2	17.9	17.8	+0.1
11-21-80	80-6828	0.5	0.2	+0.3	14.7	14.4	+0.3	0.5	0.2	+0.3	4.1	3.7	+0.4	0.3	0.1	+0.2	5.7	5.6	+0.1
11-20-80	80-6824	0.6	0.1	+0.5	80.8	80.1	+0.7												
11-20-80	80-6864	0.4	0.2	+0.2	26.4	26.2	+0.2	0.4	0.2	+0.2	8.5	8.4	+0.1	0.2	0.1	+0.1	12.9	12.8	+0.1
11-21-80	80-6869	0.7	0.2	+0.5	41.7	41.4	+0.3	0.4	0.2	+0.2	10.3	9.9	+0.4	0.4	0.2	+0.1	18.1	17.9	+0.2
11-21-80	80-6865	0.7	0.2	+0.5	2.3	1.8	+0.5	0.5	0.3	+0.2	0.8	0.6	+0.2	0.6	0.3	+0.3	2.1	1.9	+0.2

MEAN DIFFERENCE + 0.33 PPM or
0.33% of
FULL SCALE ON 0-100 PPM RANGE
STD DEV. 0.168

CORRECTED NOx SAMPLE COMPARISONS
951A (SAMP. - BG) - 10A (SAMP -BG)
CORRECTED SAMPLES

DATE	TEST #	BAG 1-4 TRANS COLD			BAG 2-5 STABLE COLD			BAG 3-6 TRANS. HOT			
		951A	10A	DIFF	951A	10A	DIFF	951A	10A	DIFF	
11-20-80	80-6816	27.2	27.3	-0.1	8.9	8.9	0.0	19.2	19.0	+0.2	READINGS = PPM
11-20-80	80-6823	59.6	60.1	-0.5	13.2	13.0	+0.2	43.4	43.6	-0.2	
11-20-80	80-6819	1.9	2.1	-0.2							
11-20-80	80-6820	21.1	21.3	-0.2	6.4	6.4	0.0	10.6	10.6	0.0	
11-21-80	80-6825	21.4	21.5	+0.1	3.7	3.7	0.0	12.1	12.1	0.0	
11-21-80	80-6833	12.8	13.2	-0.4	4.6	4.6	0.0	11.3	11.3	0.0	
11-21-80	80-6830	16.0	16.1	-0.1	6.6	6.6	0.0	17.6	17.8	-0.2	
11-21-80	80-6828	14.2	14.2	0.0	3.6	3.5	+0.1	5.4	5.5	-0.1	
11-20-80	80-6824	80.2	80.1	+0.1							
11-20-80	80-6864	20.2	26.0	0.0	8.1	8.2	-0.1	12.7	12.7	0.0	
11-21-80	80-6869	41.0	41.2	-0.1	9.9	9.7	+0.2	17.7	17.7	0.0	
11-21-80	80-6865	1.6	1.6	0.0	-0.3	-0.3	0.0	1.5	1.6	-0.1	

MEAN DIFF -0.12
STD DEV. .18

MEAN DIFF +.04
STD. DEV .10

MEAN DIFF. -0.04
STD. DEV. 0.11

TOTAL TESTS
MEAN DIFF =-0.043 PPM
STD DEV = 0.152

CO_2 INTERFERENCE

RANGE 0-100PPM

(NOx ANALYZERS BECKMAN 951A vs. TECO 10A)

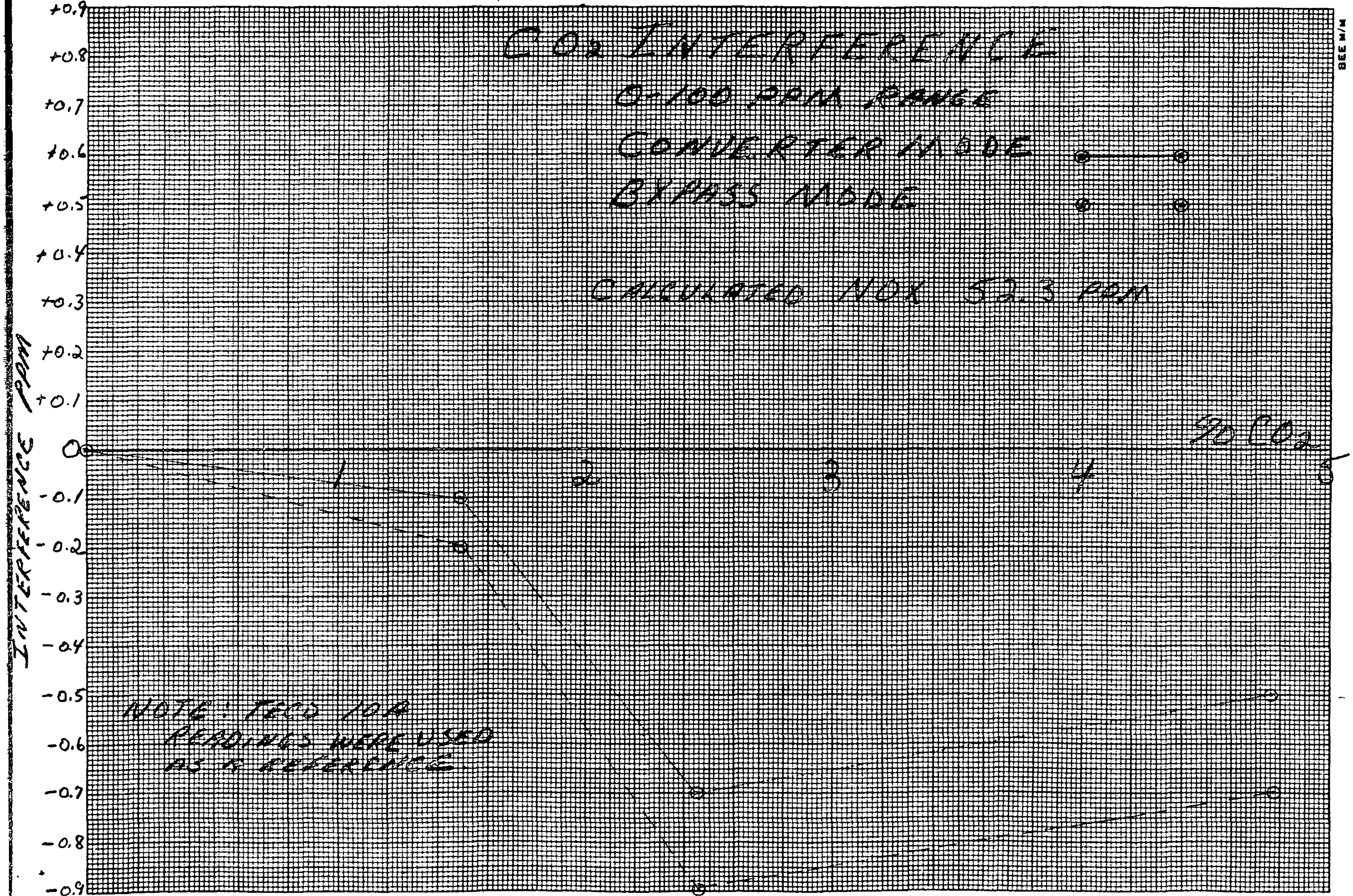
	CALC. BLEND		MEASURED PPM					OFFSET 951A-10A		BIAS @ 0% CO_2 951A-10A		INTERFERENCE OFFSET - BIAS	
	PPM NOx	CO_2%	CO_2%	NOx		NO		NOx	NO	NOx	NO	NOx	NO
				951A	10A	951A	10A						
BAG 1	52.3	0	0	51.6	50.8	41.9	40.9	+0.8	+1.0	+0.8	+1.0	0	0
2	52.3	1.5	1.47	51.9	51.2	41.2	40.4	+0.7	+0.8			-0.1	-0.2
3	52.3	2.5	2.45	49.6	49.5	34.0	33.9	+0.1	+0.1			-0.7	-0.9
4	52.3	4.81	4.77	51.1	50.8	38.9	38.6	+0.3	+0.3			-0.5	-0.7
5	52.3	0	0	51.1	50.2	41.6	41.3	+0.9	+0.3	+0.9	+0.3	0	0
6	52.3	1.5	1.45	51.2	50.5	40.7	40.6	+0.7	+0.1			-0.2	-0.2
7	52.3	2.51	2.47	30.9	50.2	40.2	39.9	+0.7	+0.3			-0.2	0.0
8	52.3	4.81	4.77	51.3	50.7	41.3	41.0	+0.6	+0.3			-0.3	0.0

NOTE: Bias is defined as the difference between the 951A and the 10A readings at 0% CO_2. 10A is considered with no interference.

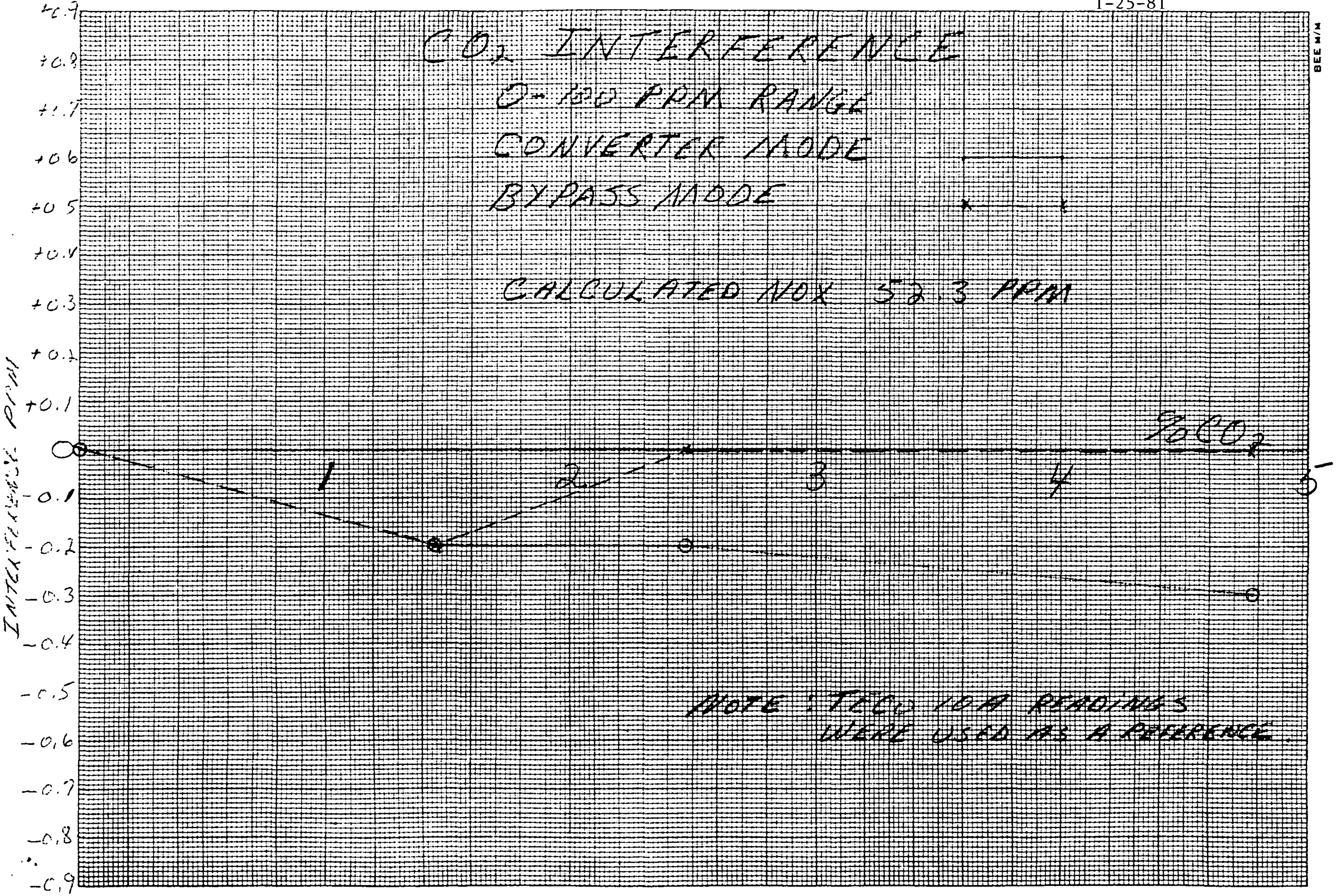
Offset is defined as the difference between the 951A and the 10A with interference and bias combined.

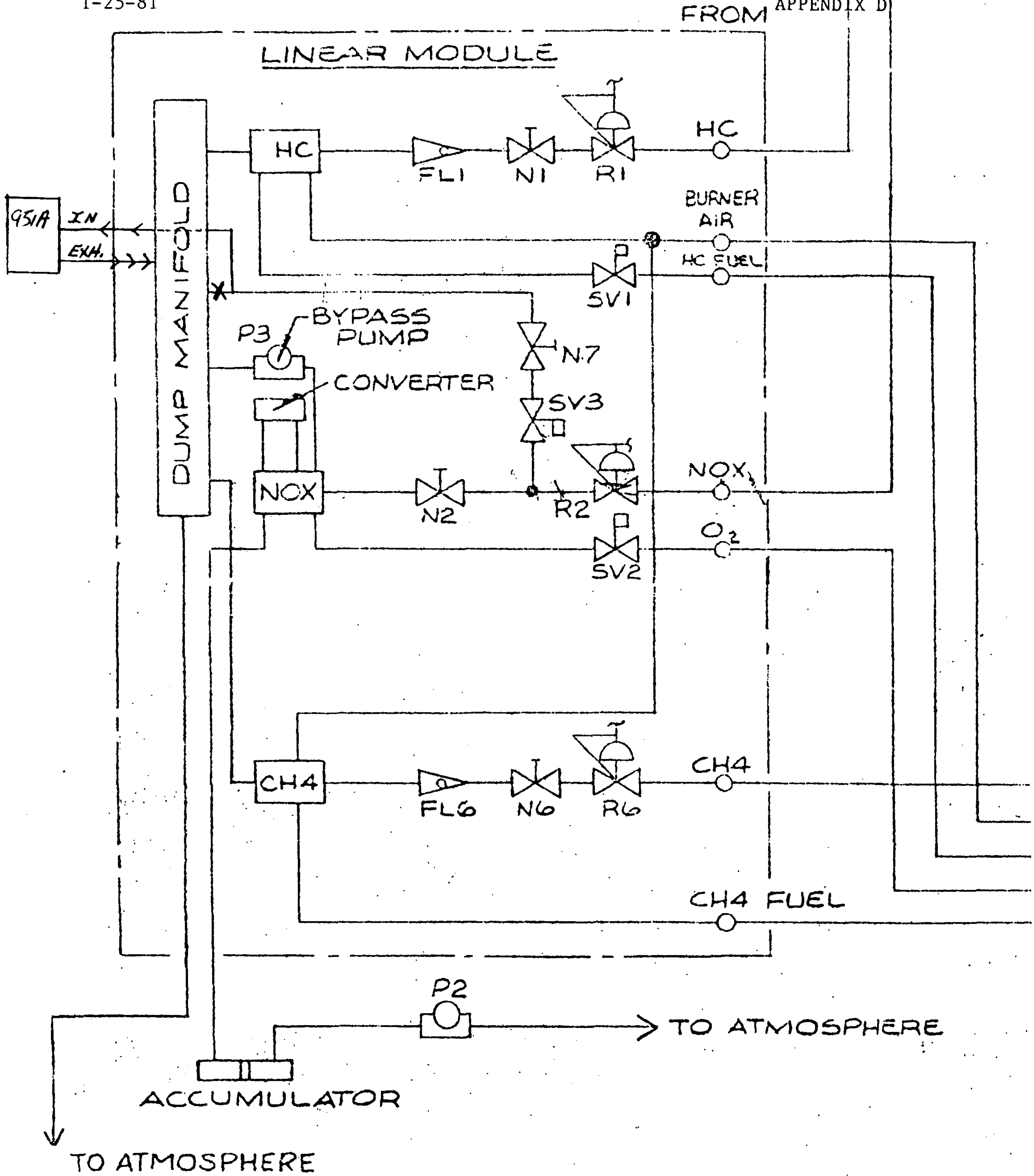
Interference is calculated by subtracting the bias from the offset at various levels of CO_2.

TEST # 1
BAGS 1-4



BAES 5-8

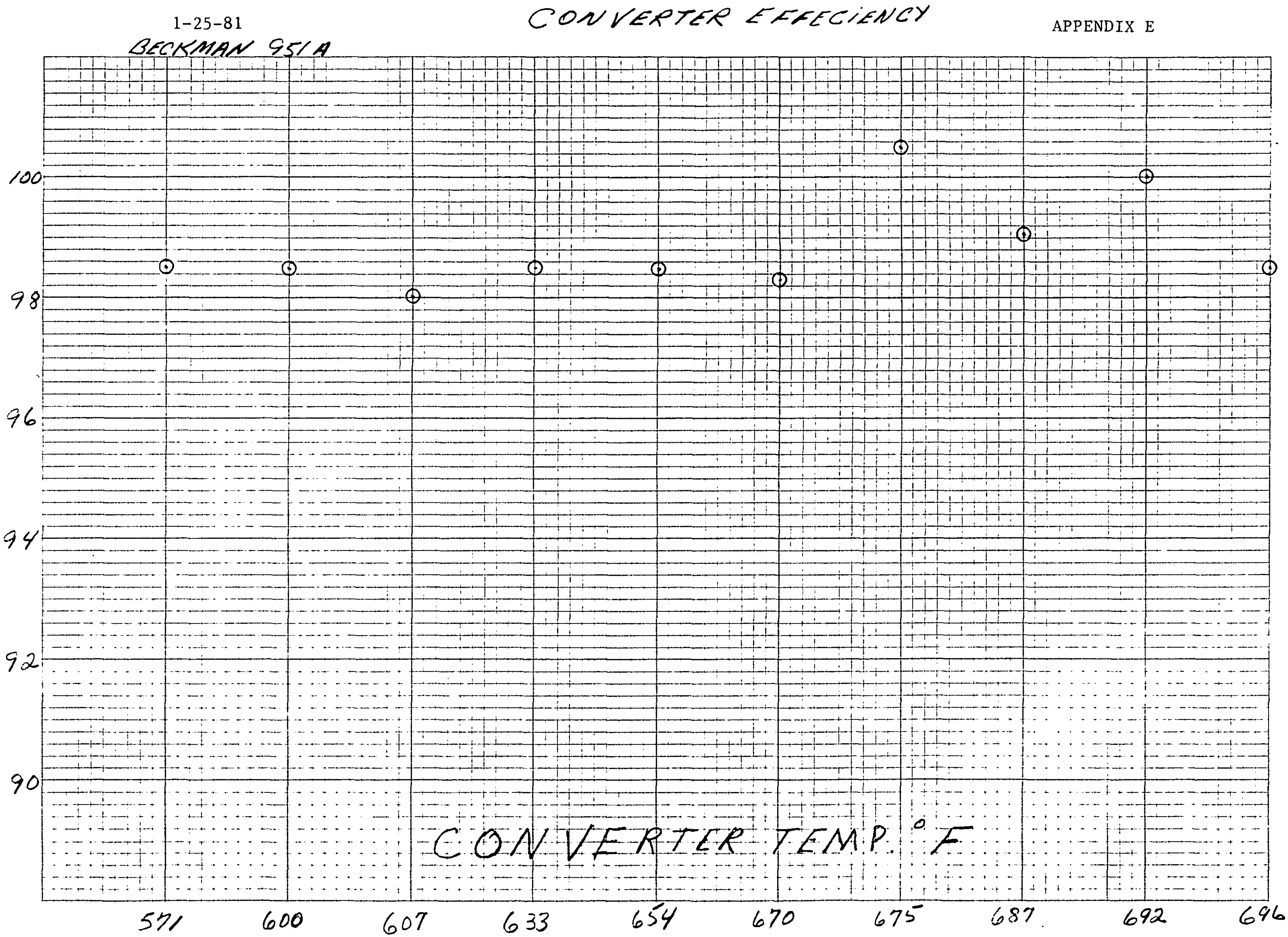

CO2 INTERFERENCE
0-100 PPM RANGE
CONVERTER MODE
BYPASS MODE
CALCULATED NOX 52.3 PPM
% CO2
INTERFERENCE PPM
+0.9
+0.8
+0.7
+0.6
+0.5
+0.4
+0.3
+0.2
+0.1
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
1
2
3
4
5
NOTE: TECO 10A READINGS
WERE USED AS A REFERENCE.



NOTE:

1. VACUUM PUMP P2 LOCATED IN BC
2. ACCUMULATOR LOCATED UNDEF
   FLOOR ON SITE
3. ENCLOSURE DENOTED AS — - —
4. ANALYZER DENOTED AS HC (TYP.

1-25-81


CONVERTER EFFECIENCY
BECKMAN 951A
100
98
96
94
92
90
CONVERTER TEMP. °F
571
600
607
633
654
670
675
687
692
696

TECHNICAL EVALUATION OF A FORD MODIFIED TECO 10 A, MARCH 1973

the back pressure with precision during the measurement period.

The converter temperature and flow were studied to assess their affect on measured values. A valve is positioned in the bypass line of the converter to simulate the pressure drop of the converter and thus achieve balanced flows and resultant equivalent readings as per above discussion. See Fig. 1C.

One perplexing characteristic concerning the converter was the lower values obtained for the span gas in the convert mode than in the bypass mode. Initially it was thought to be a flow unbalance, but tests showed increased loss of NO reading as the converter temperature increases. There are a series of reactions which may occur to produce this effect:

a) $2NO_2 \rightarrow 2NO + O_2$

b) $O_2 + 2C \rightarrow 2CO$

c) $2NO + 2CO \rightarrow N_2 + 2CO_2$

Reaction (c) requires a reducing atmosphere and is enhanced in the +400°C temperature range. In the case of bag analysis from CVS, the absence of the reducing atmosphere makes this reaction unlikely. These reactions are speculative, but theoretically could cause the effects; however, operation at the recommended temperature of 475°C produces negligible losses as well as high conversion efficiency. See Fig. 1D.

E. Several miscellaneous aspects of operation are mentioned here as areas of possible improvement. In this particular instrument, the sample pump bypass valve, N_2, was teed to the sample pressure regulator bleed off tube, both connected to the exhaust fan. The influence of the pump backflow on the regulator changed a span value from 90.7 to 88.5, or -2.5%. This effect simply reflects a change in sample flow. The bypass, bleed off, and reaction chamber exhaust should all be independently vented to the exhaust fan. See Fig. 1C.

A gage to monitor the sample capillary back pressure to ± .5"H_2O and a finer control metering valve should be installed in the sample line to assure flow equivalence during all measurements.