# USER'S GROUP MEETING

September 11, 2018

$NO_X$ CONVERTER EFFICIENCY TESTING

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WELCOME

# QUESTIONS

1. DOES EVERYONE HERE KNOW WHAT NOx CONVERTER EFFICIENCY TESTING IS?

# QUESTIONS

2. IS ANYONE HERE REQUIRED NOW BY THEIR REGULATORY AGENCY OR ARE ANTICIPATING THAT THEY WILL BE REQUIRED TO CONDUCT THIS TEST ON A ROUTINE BASIS?

# WHAT / WHY / HOW

- WHAT?
  - BACKGROUND ON $NO_X$ CONVERTER
- WHY?
  - REASON FOR TESTING
- HOW?
  - METHODS

# WHAT

- WHAT IS $NO_X$?
  - $NO_X$ IS <u>NOT</u> A MOLECULE
  - $NO_X$ IS A MAN MADE NAME FOR THE SUM OF THE NITRIC OXIDE (NO) MOLECULE AND THE NITROGEN DIOXIDE ($NO_2$) MOLECULE – $NO_X = NO + NO_2$
  - DOES <u>NOT</u> INCLUDE THE $N_2O$ MOLECULE (NITROUS OXIDE)

# WHAT

- FORMATION OF $NO_X$ IS <u>NOT</u> FUEL DEPENDENT LIKE $SO_2$
- MOST IS CREATED FROM THE HEAT OF COMBUSTION
  - $N_2 + O_2 + HEAT = 2NO$
- THEREFORE IT IS PRESENT ON <u>ALL</u> COMBUSTION SOURCES

# WHAT

- IF PRIMARILY NO IS FORMED FROM THE HEAT OF COMBUSTION – WHY BE CONCERNED WITH $NO_2$?
  - NO IS NOT A STABLE MOLECULE
  - GIVEN ENOUGH TIME AND OXYGEN, ALL NO WILL CONVERT TO $NO_2$

# WHAT

- $NO_X$ IS TYPICALLY LIMITED IN PERMIT BY REGULATORY AGENCIES AS IT IS A CONTRIBUTOR TO PHOTOCHEMICAL SMOG AND ACID RIAN

# WHAT

- SOME PERMITS STATE THAT $NO_X$ IS TO BE REPORTED AS "$NO_2$"
- WHAT IS MEANT IS THAT THE MOLECULAR WEIGHT OF $NO_2$ IS TO BE USED IN THE MASS CALCULATION

# WHAT

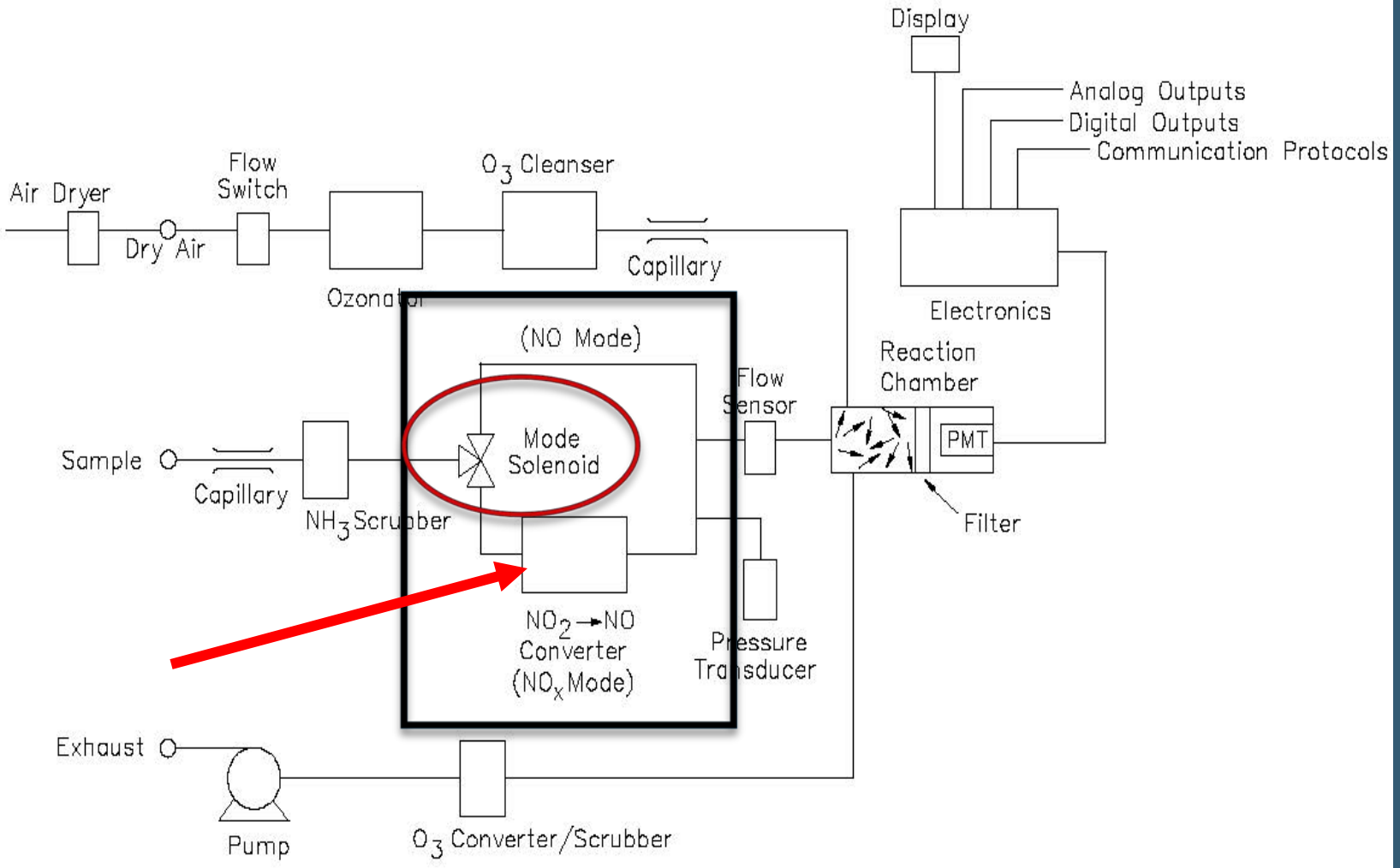
- IF NOX IS NOT A MOLECULE, AND $NO_X$ ANALYZERS ARE "MOLECULE COUNTERS", HOW IS $NO_X$ MEASURED?
  - SHORT ANSWER – IT IS NOT MEASURED.
  - ONLY THE NO MOLECULE IS MEASURED – THAT IS, A $NO_X$ ANALYZER IS REALLY A NO ANALYZER

# WHAT

- IN THE US, MOST ACCEPTABLE TECHNOLOGY FOR NOX ANALYSIS, IS THE CHEMILUMINESCENT ANALYZER (CLA, CLD)
- CHEMICAL LIGHT
  - $O_3 + NO = O_2 + NO_2^*$
- ANALYZER + SAMPLE CONDITIONING

# WHAT

- THE $NO_2$ MOLECULE IS CONVERTED TO NO IN THE SAMPLE CONDITIONING PRIOR TO DETECTION AND THE ANALYZER'S RESULT IS REPORTED AS $NO_X$ ($NO + NO_2$)
- A $NO_X$ CONVERTER IS REALLY A $NO_2$ TO NO CONVERTER


Display
Analog Outputs
Digital Outputs
Communication Protocols
Air Dryer
Flow Switch
$O_3$ Cleanser
Dry Air
Capillary
Ozonator
Electronics
(NO Mode)
Reaction Chamber
Flow Sensor
Mode Solenoid
PMT
Sample
Capillary
$NH_3$ Scrubber
Filter
$NO_2 \rightarrow NO$ Converter ($NO_x$ Mode)
Pressure Transducer
Exhaust
Pump
$O_3$ Converter/Scrubber

# 42i/LS

# WHY

- TWO TYPES OF CONVERTERS

1. STAINLESS STEEL
   - HIGH TEMPERATURE ≈ 650 $^{0}$C+
   - INDEFINITE LIFE BUT CAN BECOME CONTAMINATED
   - PREFERRED FOR HIGH $NO_2$ CONCENTRATIONS
   - WILL CONVERT $NH_3$ SLIP TO NO

# WHY

2. RARE EARTH CATALYST
   - MOLYBDENUM ≈ 300 $^0$C
   - VITREOUS CARBON ≈ 200 $^0$C
   - WILL NOT CONVERT $NH_3$ TO NO
   - HAVE LIMITED LIFE
     - LIFE = CONCENTRATION X TIME
     - RATED @ 100,OOO ppm/hr
       - 1 PPM FOR 100,000 HOURS
       - OR 10 PPM FOR 10,000 HOURS

# WHY

- NORMALLY $NO_X$ WAS 95% NO AND 5% $NO_2$
- HOWEVER WITH AMMONIA AND/OR UREA INJECTED SCR – THIS RELATIONSHIP CAN BE CHANGED
- HAVE SEEN $NO_X$ WITH 20% $NO_2$ DOWNSTREAM OF SCR

# WHY

THEREFORE EFFICIENCY OF $NO_2$ TO NO (NOX) CONVERTER BECOMES IMPORTANT

EFFICIENCY ABOVE 90% IS REQUIRED

# WHY

- NJDEP TECHNICAL MANUAL #1005 – QUARTERLY
- SCAQMD – ANNUALLY
- SDAQMD – ANNUALLY
  - PIO PICO – QUARTERLY VIA LETTER – CONTESTED
- SJVAQMD – ANNUALLY
- MOST ANALYZER MANUFACTURES - ANNUALLY

# NJDEP Technical Manual #1005

- For each chemiluminescence based NOx analyzer, a converter efficiency check must be conducted as the last step of each quarterly audit required by Section VI of this document as well as 40 CFR Part 60 and/or Part 75.

# HOW

- 40CFR60 APPENDIX A, METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

- THREE PROCEDURES

# $NO_2$ CAL GAS CYLINDER

- 8.2.4.1 Introduce $NO_2$ converter efficiency gas to the analyzer in direct calibration mode and record the $NO_X$ concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E-7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art $NO_2$ calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

# $NO_2$ CAL GAS CYLINDER

- TYPICAL LIFE OF $NO_2$ CYLINDER IS SIX MONTHS
- NEW CYLINDER FOR EVERY ANNUAL TEST

# $NO_2$ CAL GAS CYLINDER

- *7.1.4 Converter Efficiency Gas. What reagents do I need for the converter efficiency test?* The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show $NO_2$ conversion at the concentrations encountered in the source. A test gas concentration in the **40 to 60 ppm** range is **suggested**, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, $NO_2$ is required. For the alternative converter efficiency tests in section 16.2, NO is required.

# $NO_2$ CAL GAS CYLINDER

- THE "SUGGESTED" USE OF 40 TO 60 ppm $NO_2$ GAS PER 7.1.4 IS INAPPROPRIATE FOR LOW RANGE $NO_X$ ANALYZERS

- ON 10 ppm FSR ANALYZER USE $NO_2$ GAS LESS THAN 9 ppm

# 40CFR60 Apx A Method 7e

- 8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

# 40CFR60 Apx A Method 7e

- *16.2 Alternative $NO_2$ to NO Conversion Efficiency Procedures.*
- You may use either of the following procedures to determine converter efficiency in place of the procedure in section 8.2.4.1.
- 16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123-78.

# TEDLAR BAG

- 16.2.2 Bag Procedure. ..... Fill a Tedlar or equivalent bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid- to high-level NO in $N_2$ (or other appropriate concentration) calibration gas.

# TEDLAR BAG

- (1) Immediately attach the bag to the inlet of the $NO_X$ analyzer (or external converter if used). .....Measure the $NO_X$ concentration for a period of **30 minutes**. If the $NO_X$ concentration drops more than 2 percent absolute from the peak value observed, then the $NO_2$ converter has failed to meet the criteria of this test.

# 40CFR86.123-78

- 40CFR86-SUBPART B ….TEST PROCEDURES - §86.123-78-OXIDES OF NITROGEN ANALYZER CALIBRATION
- 40CFR86 - CONTROL OF EMISSIONS FROM NEW AND IN-USE HIGHWAY VEHICLES AND ENGINES
  - MONTHLY TEST ON ALL $NO_X$ ANALYZERS

# 40CFR86.123-78

- SIMPLIFIED TO FOUR STEP PROCEDURE
  - ASSUMES NO $NO_2$ IN SPAN CYL
- USES CURRENT $NO_X$ SPAN CYLINDER OF NO + IA
- REQUIRES A “CE TESTER”

# CE TESTER

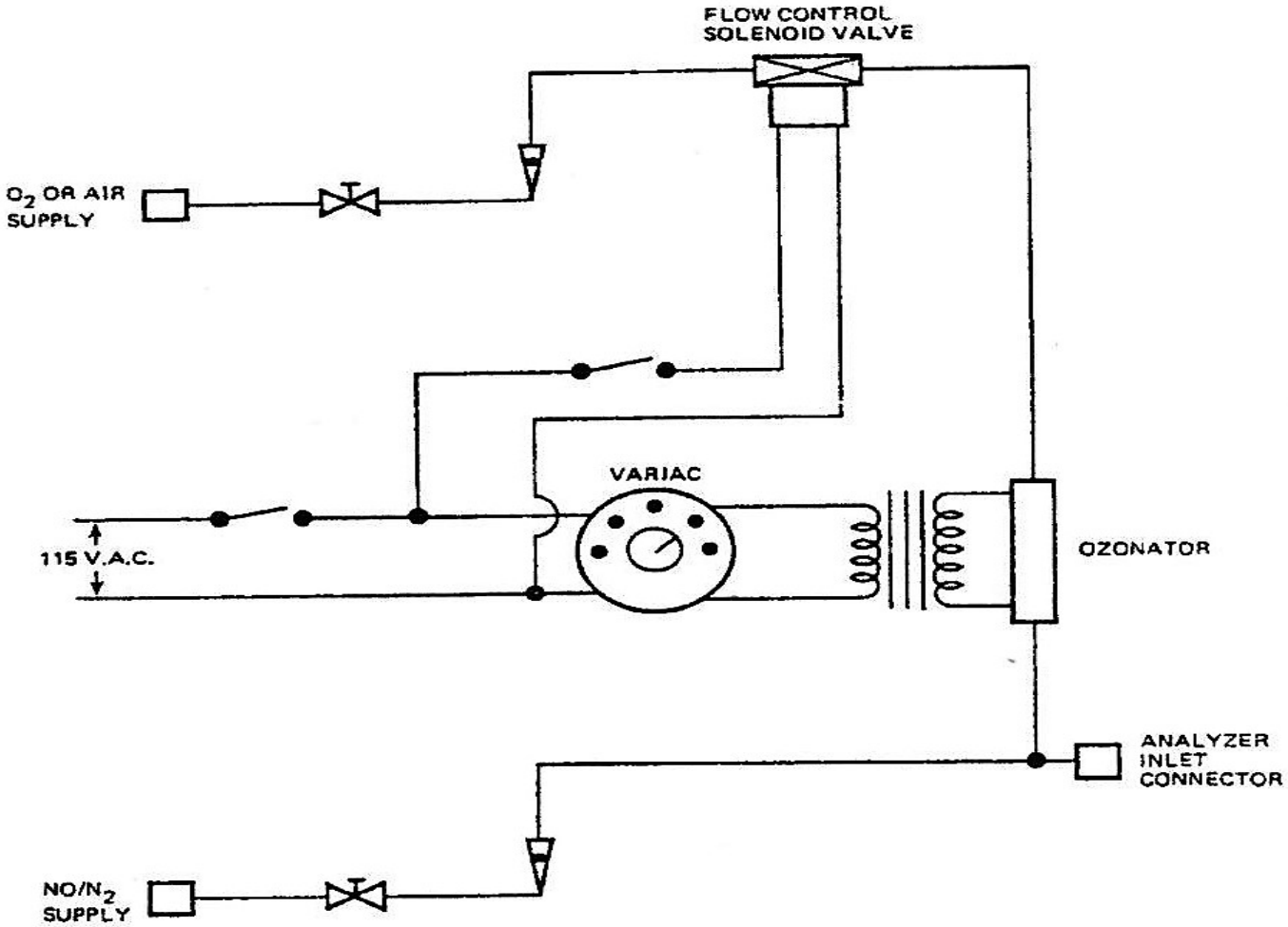



FIGURE D79-4 $NO_x$ CONVERTER EFFICIENCY DETECTOR

# 40CFR86.123-78

- STEP 1
  - NO MODE ON ANALYZER
    - ( $NO_2$ TO NO CONVERTER BYPASSED)
  - SPAN ANALYZER ON DAILY SPAN GAS
  - BASELINE VALUE

# CE TESTER – STEP 1

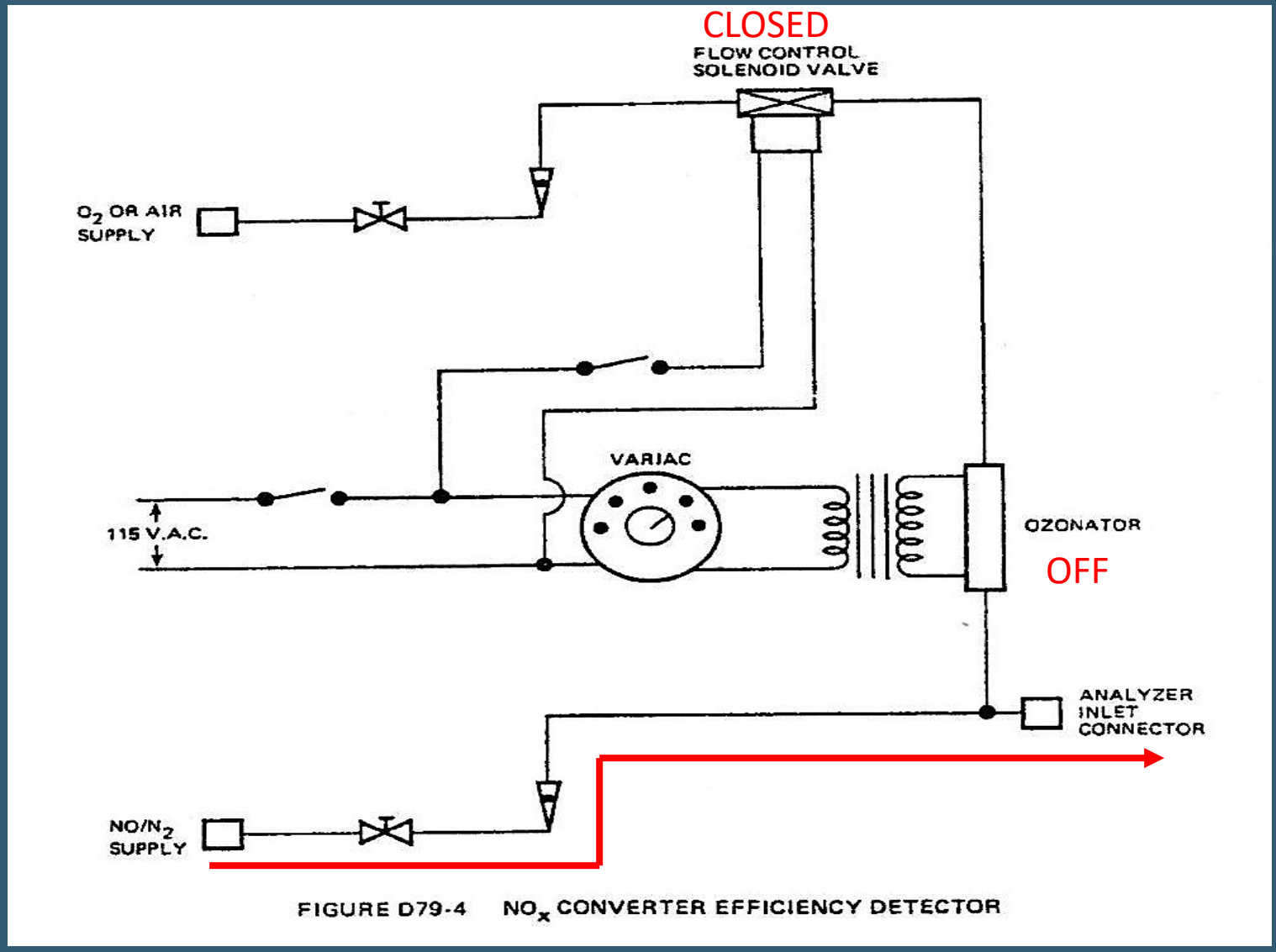
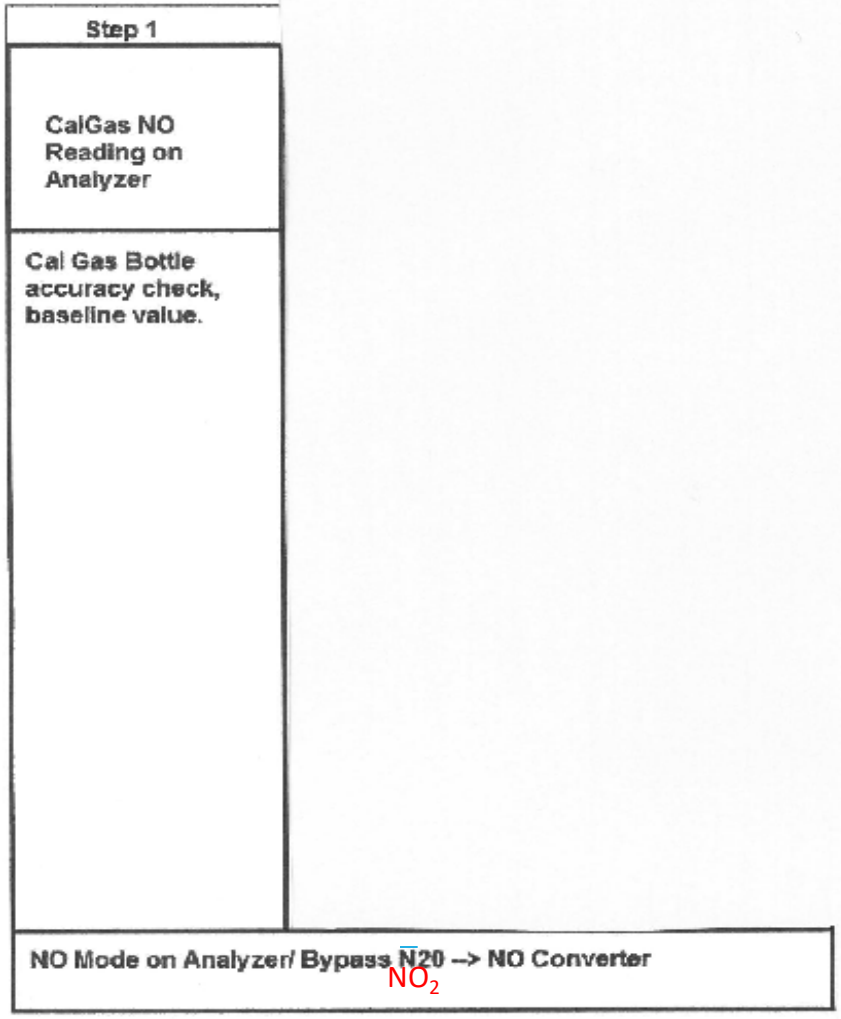



FIGURE D79-4 $NO_x$ CONVERTER EFFICIENCY DETECTOR

# STEP 1


Step 1
CalGas NO Reading on Analyzer
Cal Gas Bottle accuracy check, baseline value.
NO Mode on Analyzer/ Bypass N20 --> NO Converter
$NO_2$

# 40CFR86.123-78

- STEP 2
  - ADD SMALL AMOUNT OF INSTRUMENT AIR TO SPAN GAS
  - DILUTE ANALYZER RESPONSE TO APPROX. 90% OF BASELINE VALUE.

# CE TESTER – STEP 2

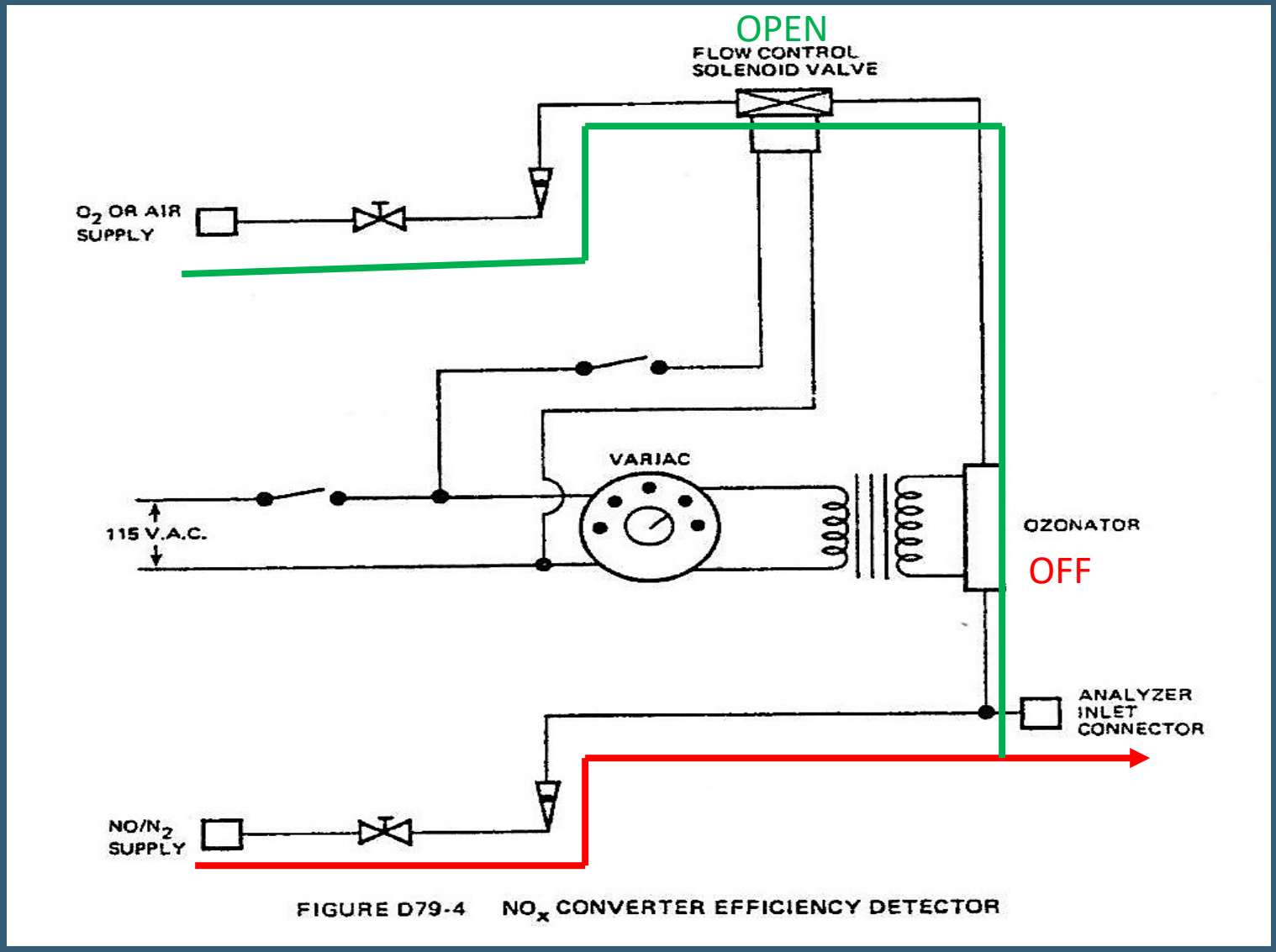
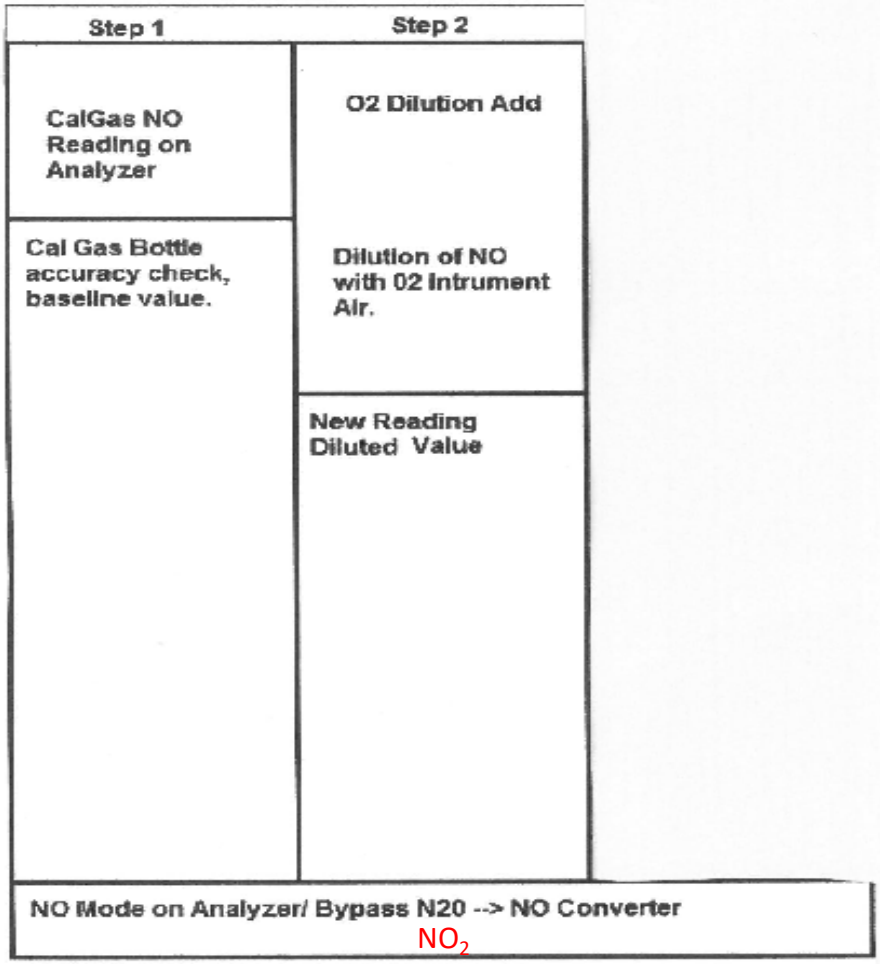



FIGURE D79-4 $NO_x$ CONVERTER EFFICIENCY DETECTOR

# STEP 2


Step 1
Step 2
CalGas NO Reading on Analyzer
O2 Dilution Add
Cal Gas Bottle accuracy check, baseline value.
Dilution of NO with 02 Intrument Air.
New Reading Diluted Value
NO Mode on Analyzer/ Bypass N20 --> NO Converter
$NO_2$

# 40CFR86.123-78

- STEP 3
  - TURN ON OZONATOR
  - ADJUST OZONE GENERATOR IN CE TESTER SO THAT ANALYZER RESPONSE IS APPROX. 20% OF BASELINE VALUE
    - $NO + O_3 = NO_2 + O_2$
  - ANALYZER IN NO MODE – WILL NOT MEASURE $NO_2$

# CE TESTER – STEP 3

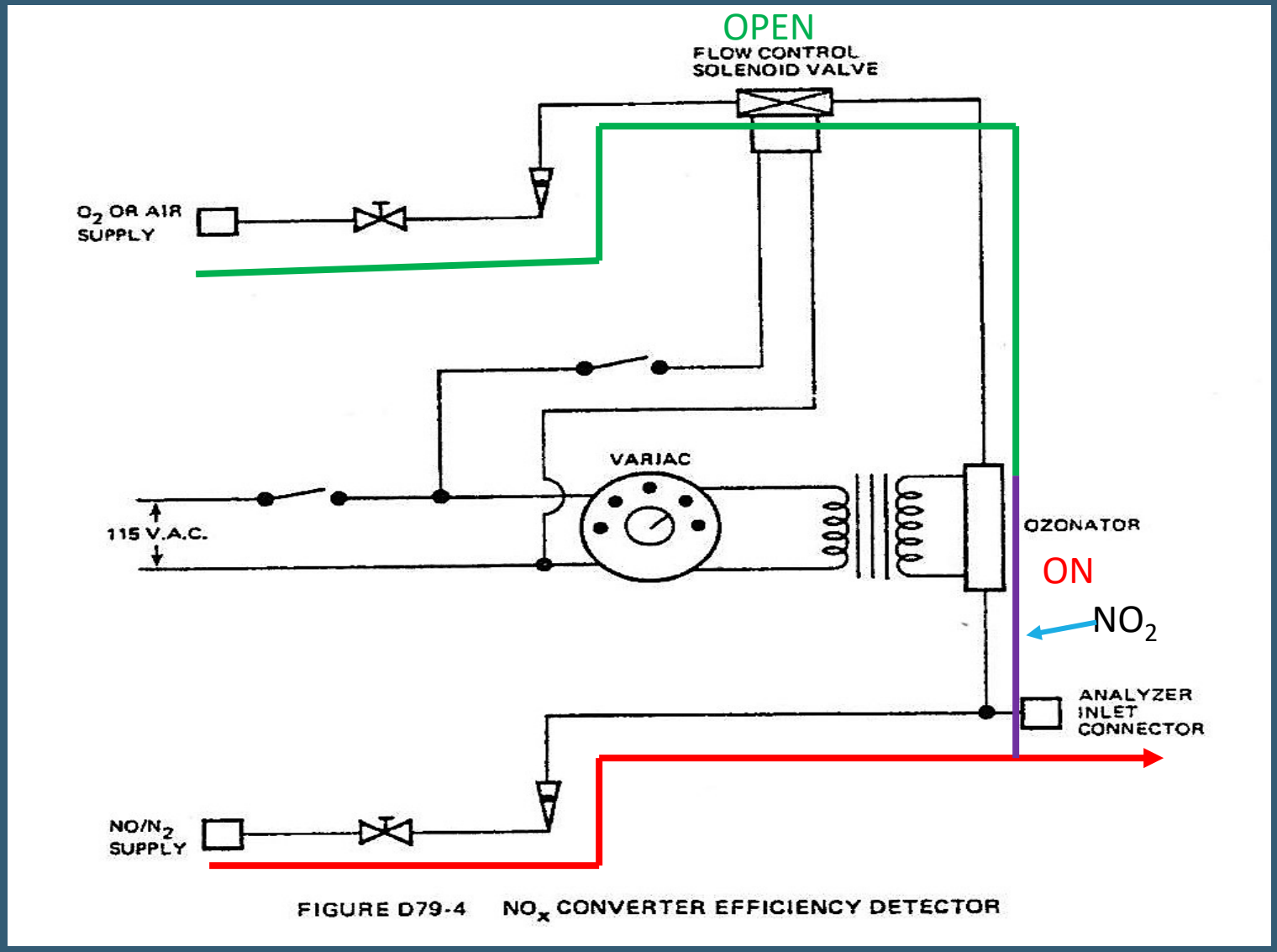
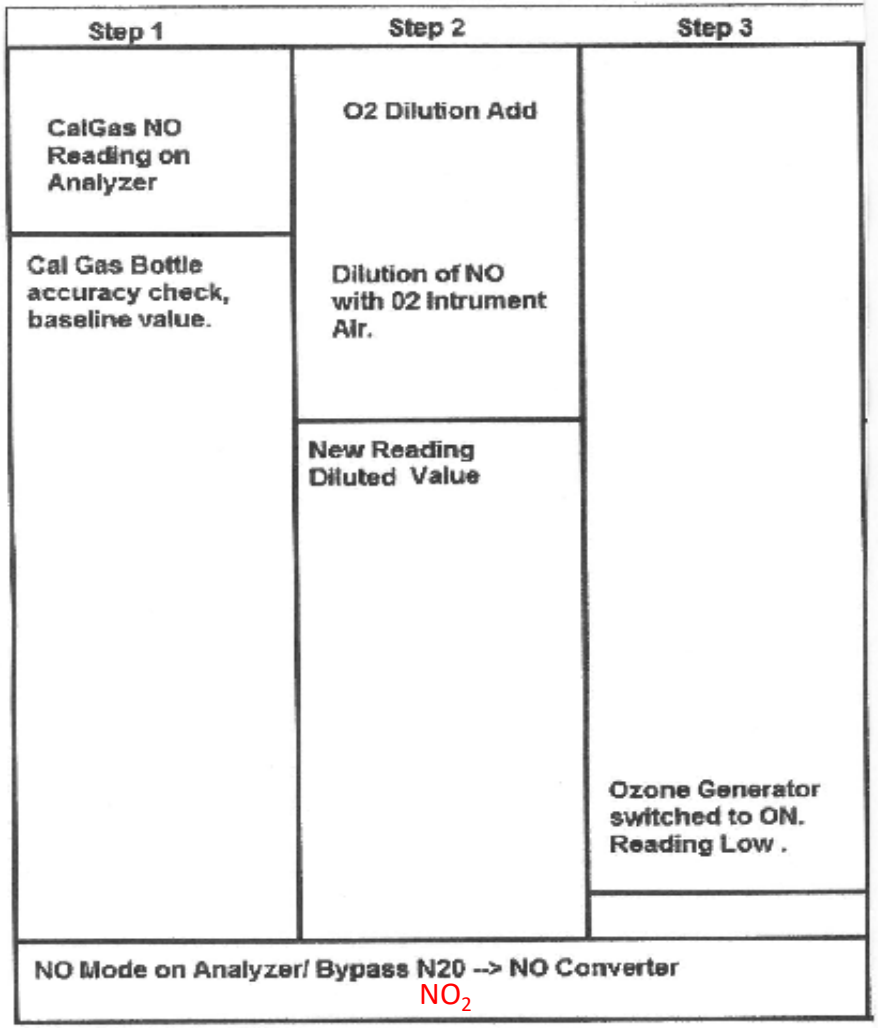



FIGURE D79-4 $NO_x$ CONVERTER EFFICIENCY DETECTOR

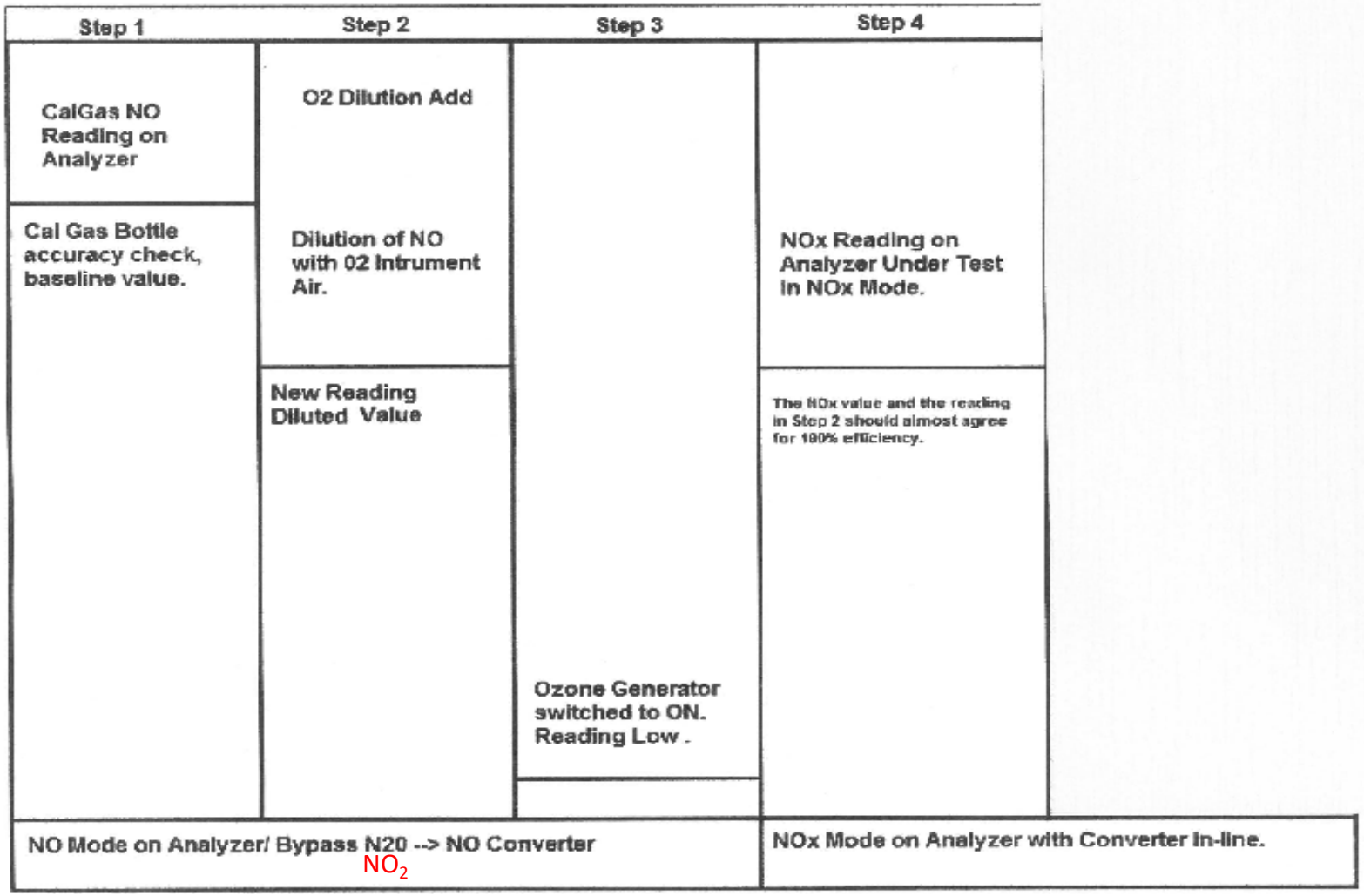
# STEP 3


Step 1
Step 2
Step 3
CalGas NO Reading on Analyzer
O2 Dilution Add
Cal Gas Bottle accuracy check, baseline value.
Dilution of NO with 02 Intrument Air.
New Reading Diluted Value
Ozone Generator switched to ON. Reading Low .
NO Mode on Analyzer/ Bypass N20 --> NO Converter
$NO_2$

# 40CFR86.123-78

- STEP 4
  - $NO_X$ MODE ON ANALYZER
    - SAMPLE IS PASSED THROUGH $NO_2$ TO NO CONVERTER
  - ANALYZER VALUE SHOULD INCREASE TO BE CLOSE TO STEP 2 VALUE
  - IF IT WERE EQUAL YOU WOULD HAVE 100% EFFICIENCY

# STEP 4


Step 1
Step 2
Step 3
Step 4
CalGas NO Reading on Analyzer
O2 Dilution Add
Cal Gas Bottle accuracy check, baseline value.
Dilution of NO with 02 Intrument Air.
NOx Reading on Analyzer Under Test in NOx Mode.
New Reading Diluted Value
The NOx value and the reading in Step 2 should almost agree for 100% efficiency.
Ozone Generator switched to ON. Reading Low .
NO Mode on Analyzer/ Bypass N20 --> NO Converter
NO2
NOx Mode on Analyzer with Converter In-line.

# 40CFR86.123-78

- EFFICIENCY CALCULATION

$$\frac{\text{STEP 4 VALUE} - \text{STEP 3 VALUE}}{\text{STEP 2 VALUE} - \text{STEP 3 VALUE}} \times 100 = \%\ \text{EFFICIENCY}$$

| Step 1 | Step 2 | Step 3 | Step 4 | Converter Efficiency Calc. |
|---|---|---|---|---|
| CalGas NO Reading on Analyzer | O2 Dilution Add | | | Calculate Converter Efficiency. |
| Cal Gas Bottle accuracy check, baseline value. | Dilution of NO with 02 Intrument Air. | | NOx Reading on Analyzer Under Test in NOx Mode. | |
| | New Reading Diluted Value | Ozone Generator switched to ON. Reading Low . | The NOx value and the reading in Step 2 should almost agree for 100% efficiency. | Step 4 Value -- Step 3 Value<br>Step 2 Value -- Step 3 Value<br>X<br>100<br>=<br>% Efficiency |
| NO Mode on Analyzer/ Bypass N20 --> NO Converter | | | NOx Mode on Analyzer with Converter In-line. | |

# CE TESTER

- STAND ALONE MANUAL OPERATION
- FULLY AUTOMATIC OPERATION UNDER PLC CONTROL CAN BE BUILT INTO SYSTEM
- CeDAR REPORT JUST LIKE CGA/LINEARITY

# QUESTIONS?