A calibration system for low range GPT calibrations of high sensitivity NOx and NOy monitors.

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NCore Gas Calibration Needs

- NCore gas monitoring requirements include Ozone and trace level CO, SO_2 and NOy.

- The NCore Quality Assurance requirements include:
  - Multipoint calibrations – as needed to 6 months
  - Span and Precision checks – 24 hrs to 2 weeks
  - Converter Efficiency checks – 2 weeks to monthly
  - Low level detection tests - annually

- The NCore Technical Assistance Document (TAD) recommends automated audits and "on the fly" real-time level 1 data validation

NOy Calibration Requirements

- NOx&y analyzers are only able to detect NO. In order to know if the NOx&y and NO_2 data are valid, it is vitally important to know if & how well the converter is working.

- The NCore TAD recommends that Multipoint calibrations be performed for both NO and NO_2 at the same concentrations.

- Dilution of NO_2 is possible from gas cylinders but is not recommended due to the long stabilization period for each point as well as the instability of certified cylinder concentrations.

- Gas Phase Titration (GPT) is preferable because it produces reliable NO_2 concentrations without long stabilization periods.

GPT NO$_2$ Calibrations

- GPT calibrators use Mercury vapor lamps to produce ozone which reacts with cylinder NO to produce NO$_2$.

- The lamps are unstable and inconsistent at the levels needed to produce ozone for low level GPT calibrations.

- Simply increasing the flow rate or decreasing the reaction volume limits the calibrator's dynamic range and may make the calibrator un-usable for higher level GPT calibrations.

- The limitations of the API Model 700E's ozone generator sets the lower limit of its NO$_2$ output to 50 ppb.

API 700EU   vs   API 700E

- Internal Photometer with GPT to < 3 ppb NO_2
- Support for 2 Pollutant Flow controllers
- Supports External Valve Driver (automates site)

- Internal Photometer with GPT 30 - 50 ppb NO_2
- Support for 2 Pollutant Flow controllers
- Supports External Valve Driver (automates site)

The API Model 700EU

- A flow fraction controller is installed after the ozone generator to permit less than 100% of the generated ozone to react with NO

M701

P

NO-in-N2

GPT FLOW FRACTION CONTROLLER

GPT
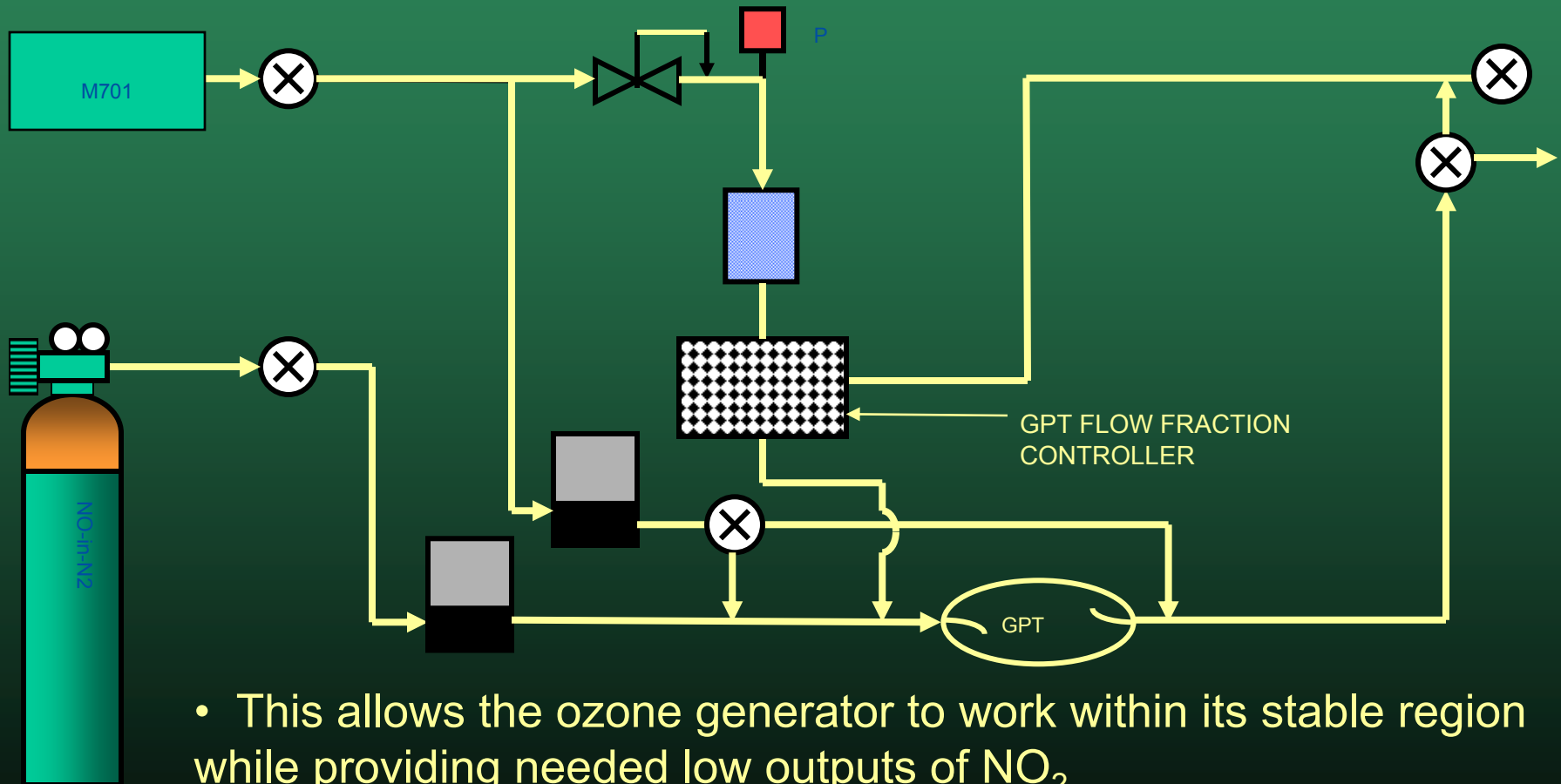
- This allows the ozone generator to work within its stable region while providing needed low outputs of NO_2.

Typical GPT steps

Name	Description	Values Obtained for Converter Efficiency Calculations (1)
GPTPS	Optional step. Used to increase the accuracy of the O_3 concentration during GPT generation mode.	
GPT	Produces NO2 test gas using GPT with the ozone generator ON. The O_3 lamp drive value is used from the previous GPTPS.	[NO]rem, [NOx]rem
GPTZ	Delivers NO gas only for determining baseline ("orig") NO and NOx values. Ozone generator is OFF.	[NO]orig, [NOx]orig

(1) 40 CFR part 50 Appendix F, "Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescence)"

GPTPS Step

- GPTPS stands for "GPT Pre-Set"
- Optional step. Used just prior to GPT step to increase O_3 accuracy.
- User sets target NO and O_3 value identical to GPT.
- M700EU generates ozone and flows zero air in place of NO gas (no titration takes place.)
- M700EU uses internal photometer to "dial-in" O_3 concentration requested.
- Once concentration has stabilized, O_3 generator drive value is stored for the requested O_3 concentration point.
- The stored O_3 generator drive value is then used during subsequent GPT step.

GPT Step

- O_3 and NO are mixed at the specified concentrations.

- O_3 value should be no more than 80% of the NO value to ensure complete reaction of O_3.

- $O_3 + NO \rightarrow NO_2 + O_2$

- Stoichiometric ratio is 1:1 between O_3 and NO2.

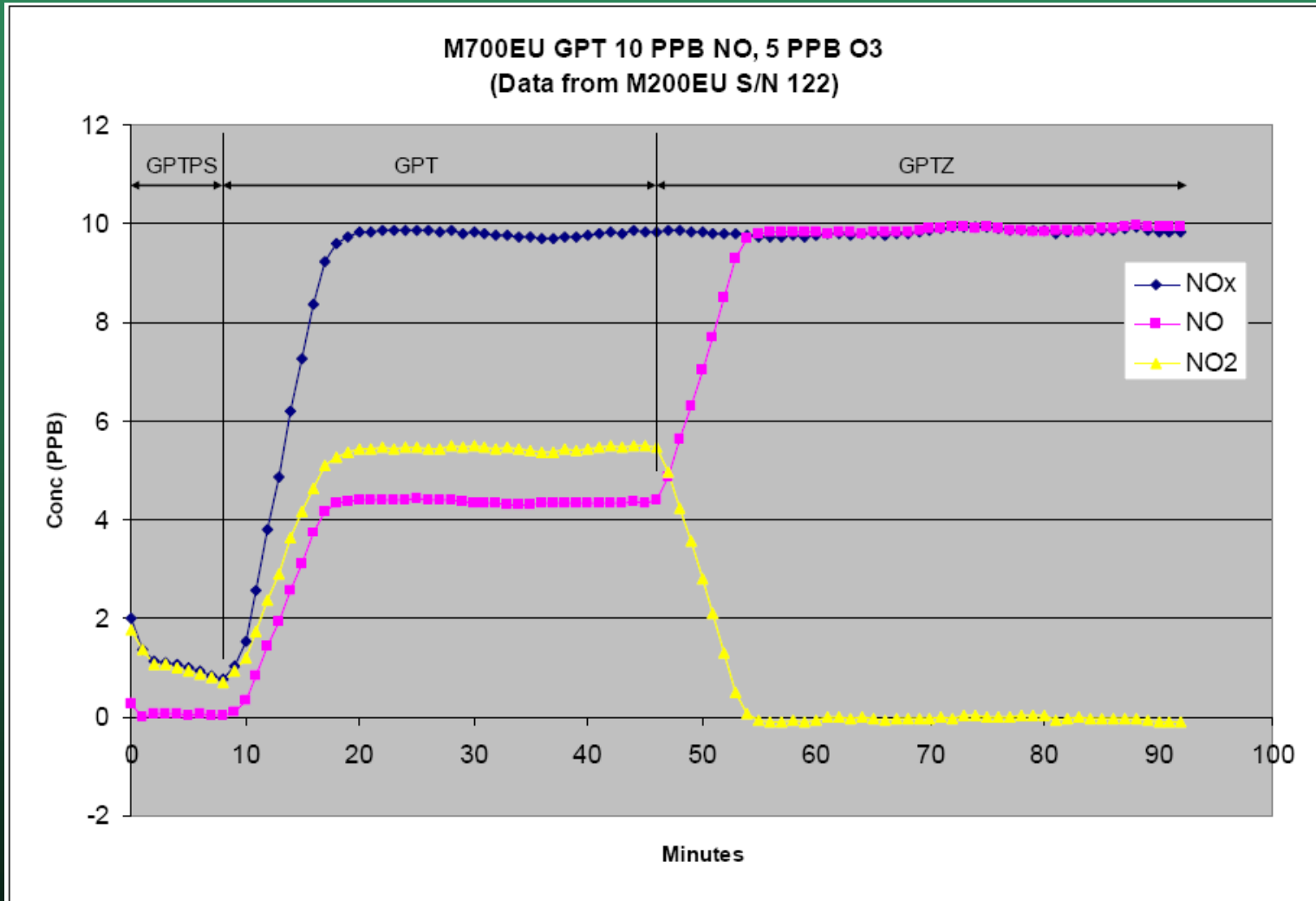- Resultant NO value is recorded as $[NO]_{rem}$, NO_X value as $[NOx]_{rem}$
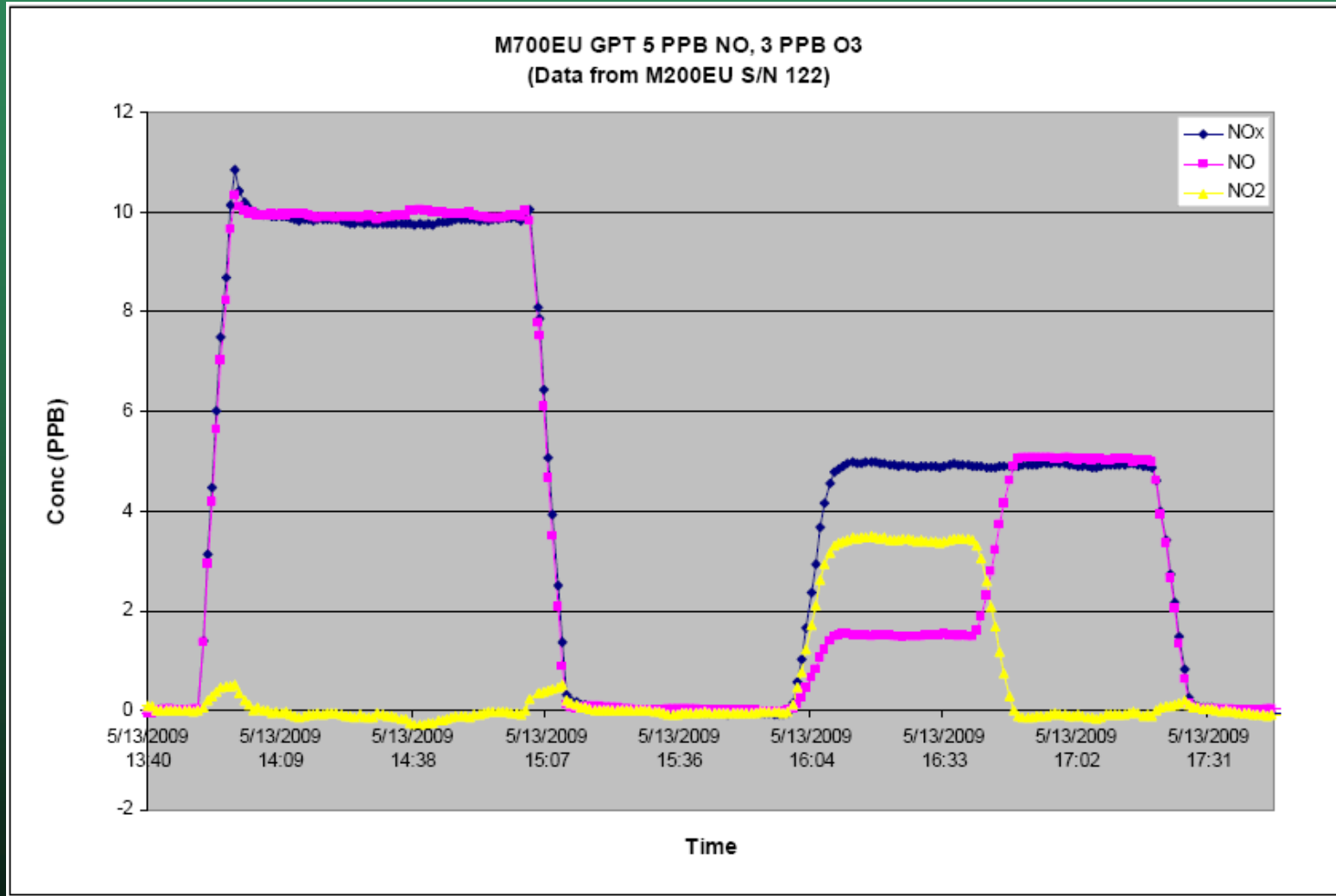
GPTZ Step

- Delivers NO gas only.

- Identical to GPT step except O_3 generator is OFF.

- Used for determining baseline ("orig") NO and NOx values.

- Resultant NO value is recorded as $[NO]_{orig}$, NO_X value as $[NOx]_{orig}$

M700EU Performance

M700EU GPT 10 PPB NO, 5 PPB O3
(Data from M200EU S/N 122)

M700EU Performance

M700EU GPT 5 PPB NO, 3 PPB O3
(Data from M200EU S/N 122)

Conclusions

- NCore calibrators must be able to deliver NO_2 at the same concentrations as NO.

- External valve drivers and advanced data acquisition systems permit automated audit sequences and automatic level 1 validation.

- The support for 2 pollutant flow controllers provides accuracy at the low levels needed for calibration levels at NCore clean (rural) sites and for low level detection tests.

- Accurate GPT convertor efficiency tests may reduce the need for additional convertor checks with diluted NPN/IPN.

End of Presentation

Typical Gas Standards

- NYSDEC Primary NO Cylinder (NIST)
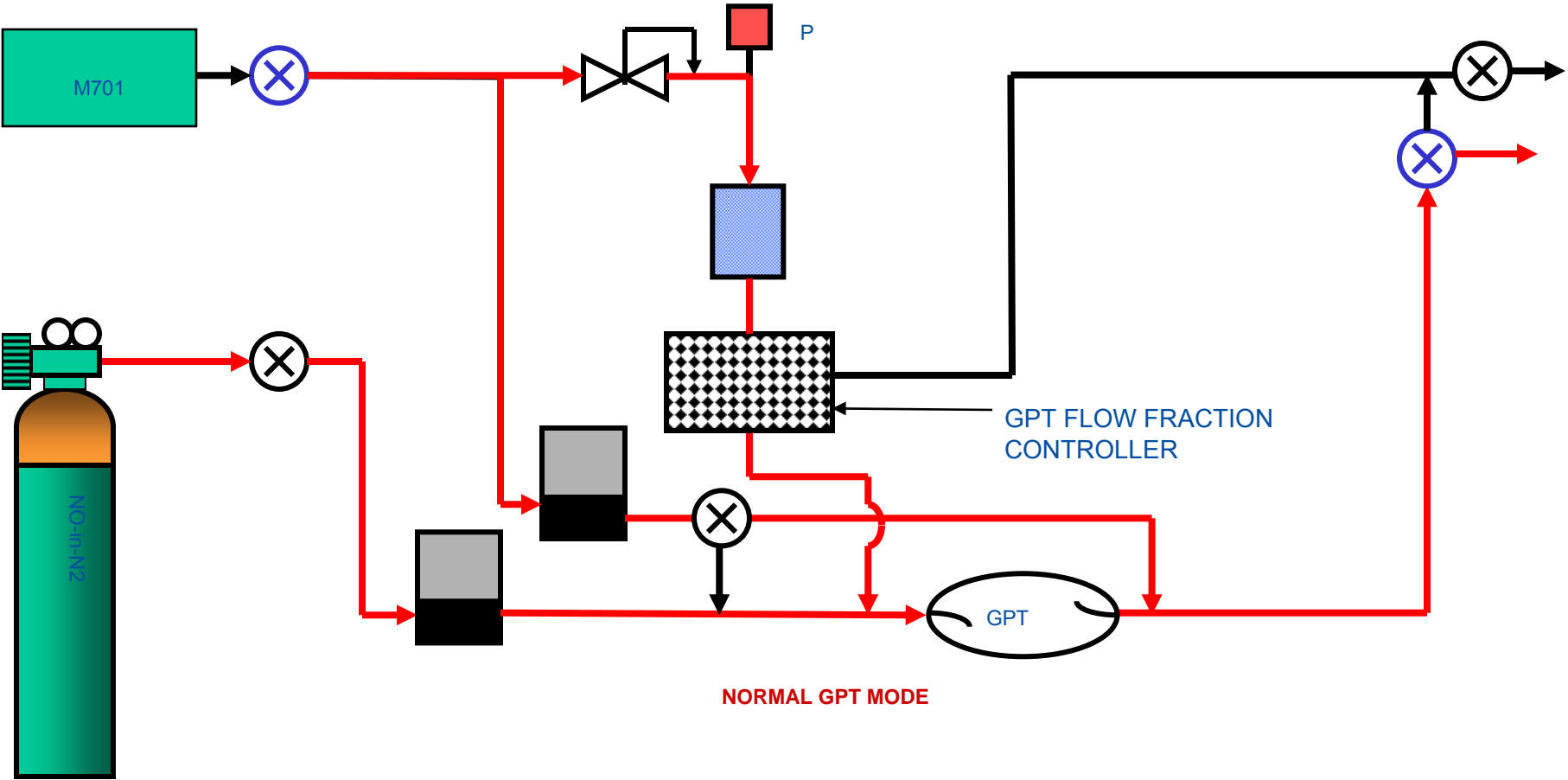
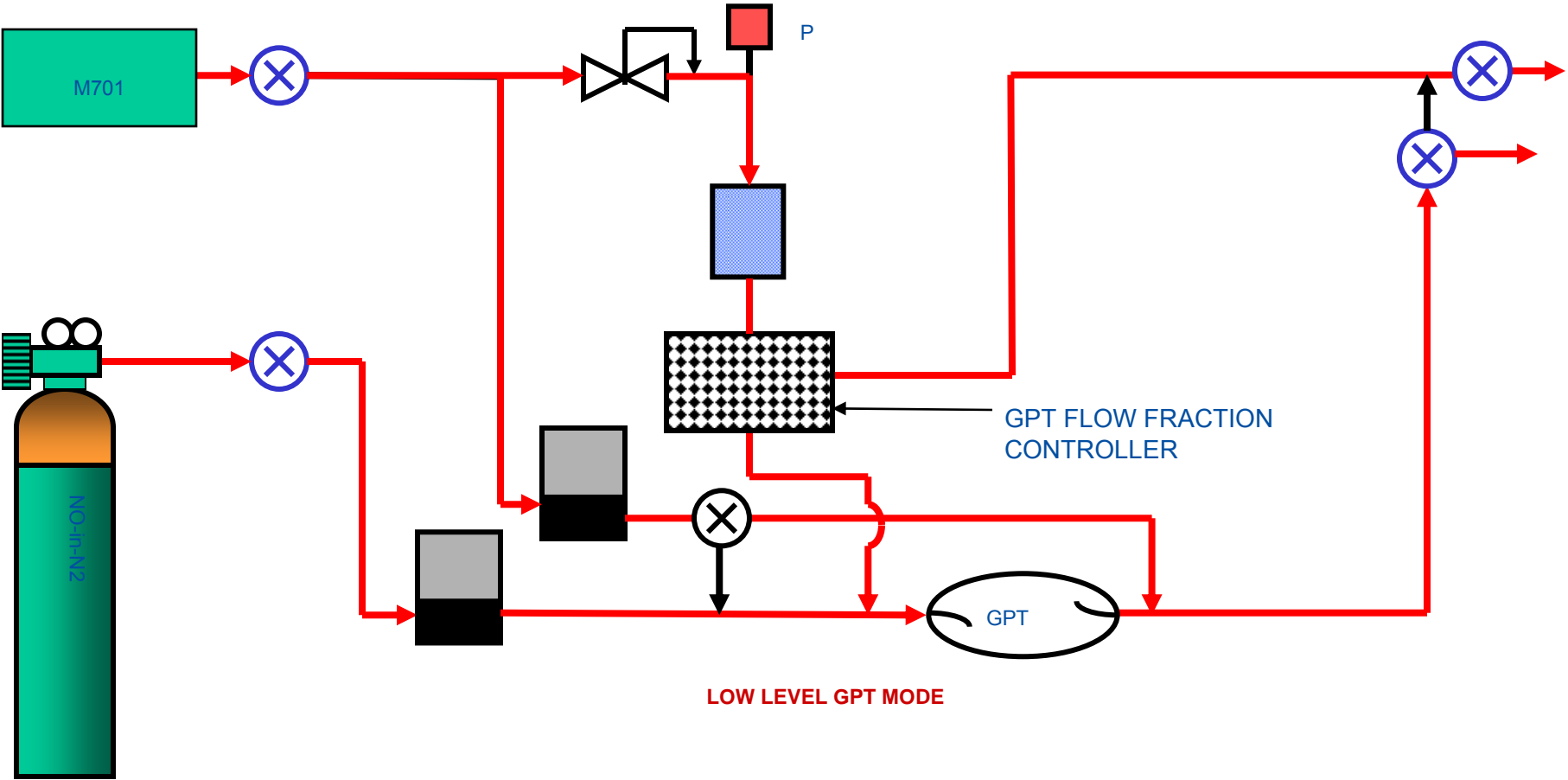 48.52 ± 0.32 ppm NOx

  48.52 ± 0.32 ppm NO
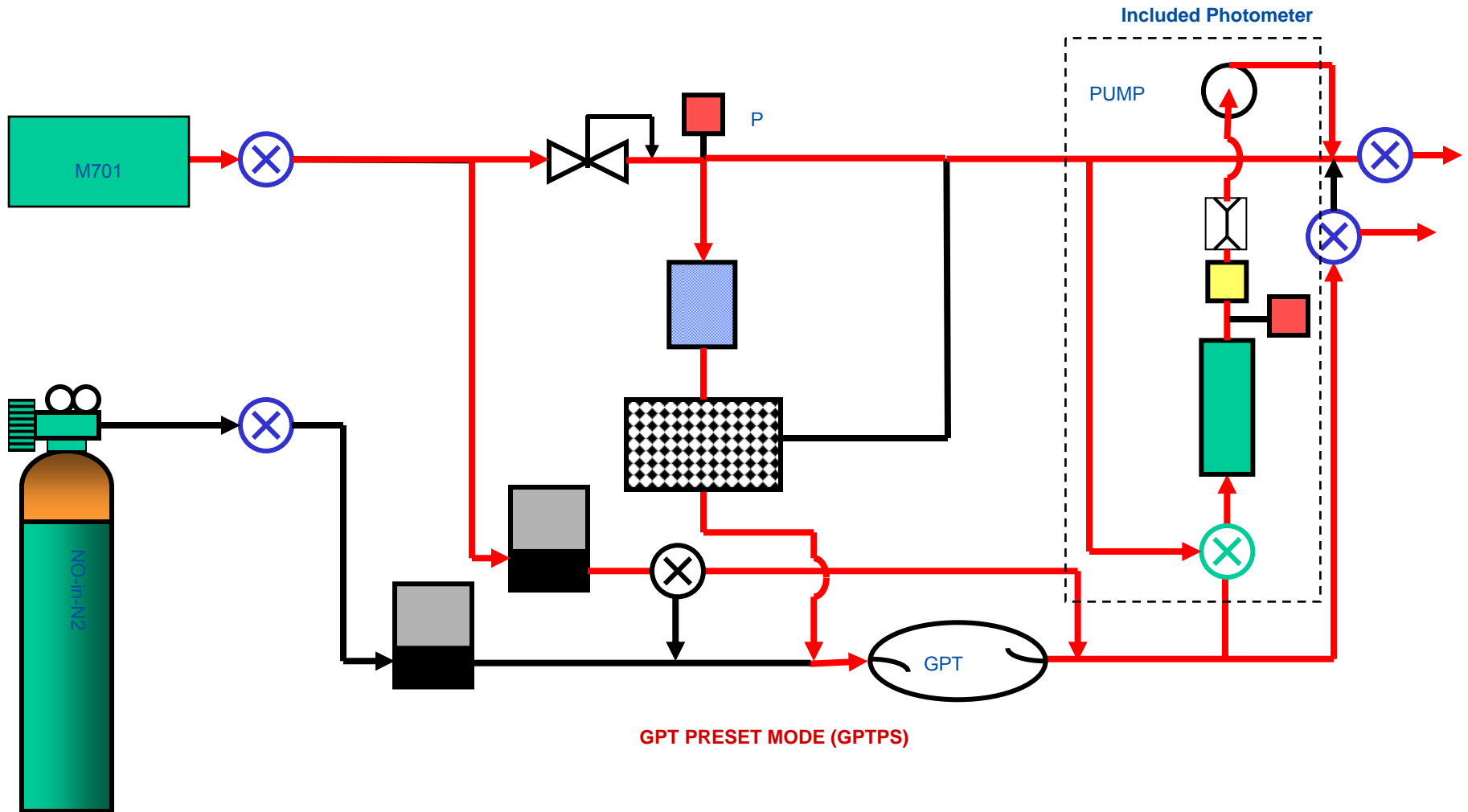
  Balance Nitrogen

The specifications permit > 1% NO_2

The Model 700EU GPT

M701

NO-in-N2

P

GPT FLOW FRACTION
CONTROLLER

GPT

NORMAL GPT MODE

The Model 700EU GPT

M701

P

NO-in-N2

GPT FLOW FRACTION
CONTROLLER

GPT

LOW LEVEL GPT MODE

The Model 700EU GPT

Included Photometer

PUMP

P

M701

NO-in-N2

GPT

GPT PRESET MODE (GPTPS)

The Model 700EU GPT

M701

NO-in-N2

O3 OFF

P

GPT

GPTZero MODE (GPTZ)
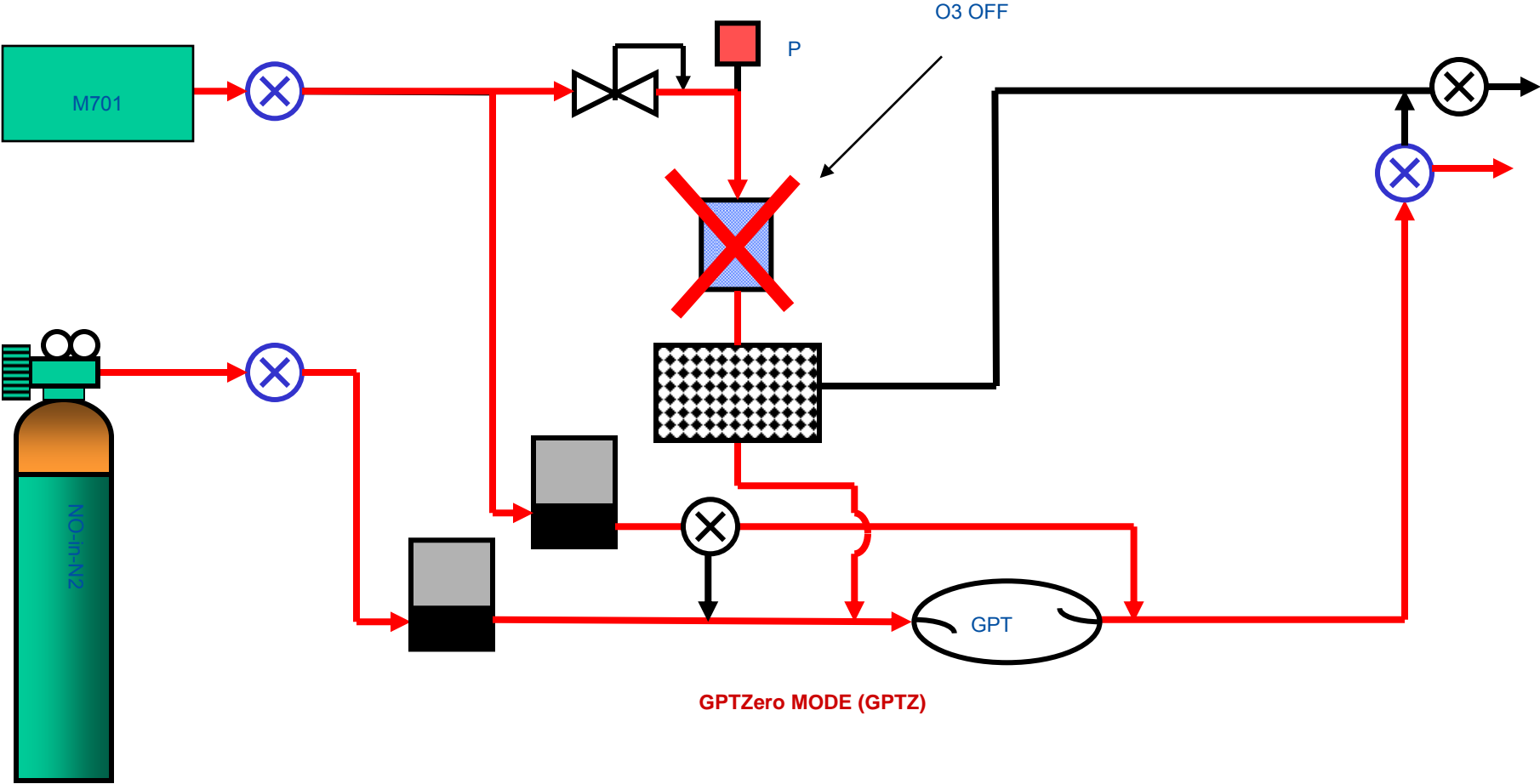
The Model 700E GPT Option

M701

NO-in-N2

REG

P

GEN

CF

GPT

V
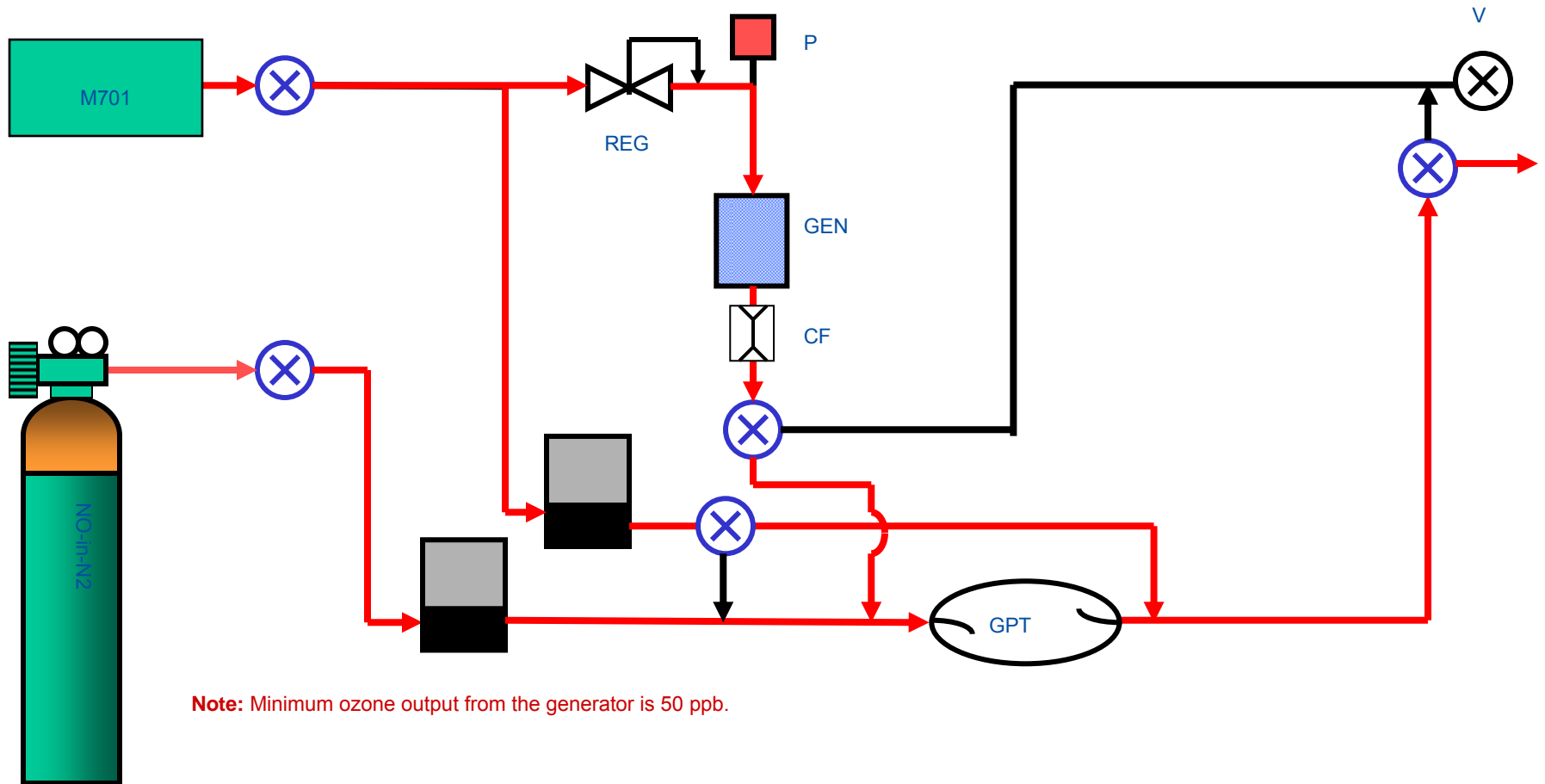
Note: Minimum ozone output from the generator is 50 ppb.

M700EU Performance

NYS Department of Environmental Conservation