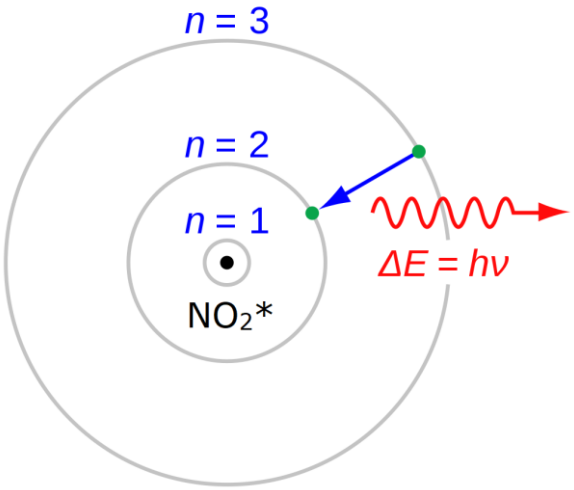
airpointer® NOx module

Chemiluminescence



It is a two-part reaction:

1) Ozone and NO reaction. A dioxygen molecule and an "excited" NO_2 molecule is formed

$$O_3 + NO \rightarrow NO_2^* + O_2$$

2) This "excited" NO_2 molecule returns to its ground state, releasing its excess energy as a photon ($h\nu$) whose center wavelength is about 1100 nm.

$$NO_2^* \rightarrow NO_2 + h\nu \ @1100\ nm$$

Chemiluminescence: quenching

Another way for the excited NO_2 to get rid of its energy is by colliding with another molecule (X).

$$NO_2^* + X \rightarrow NO_2 + X^*$$

To minimize the chance of collision, the reaction chamber is kept under vacuum (P≈0.3 atm).

How is NO measured?

$NO_2^* \rightarrow NO_2 + h\nu$

- Intensity of emitted light is proportional to NO concentration and measured by a PMT

- Only NO can be measured directly

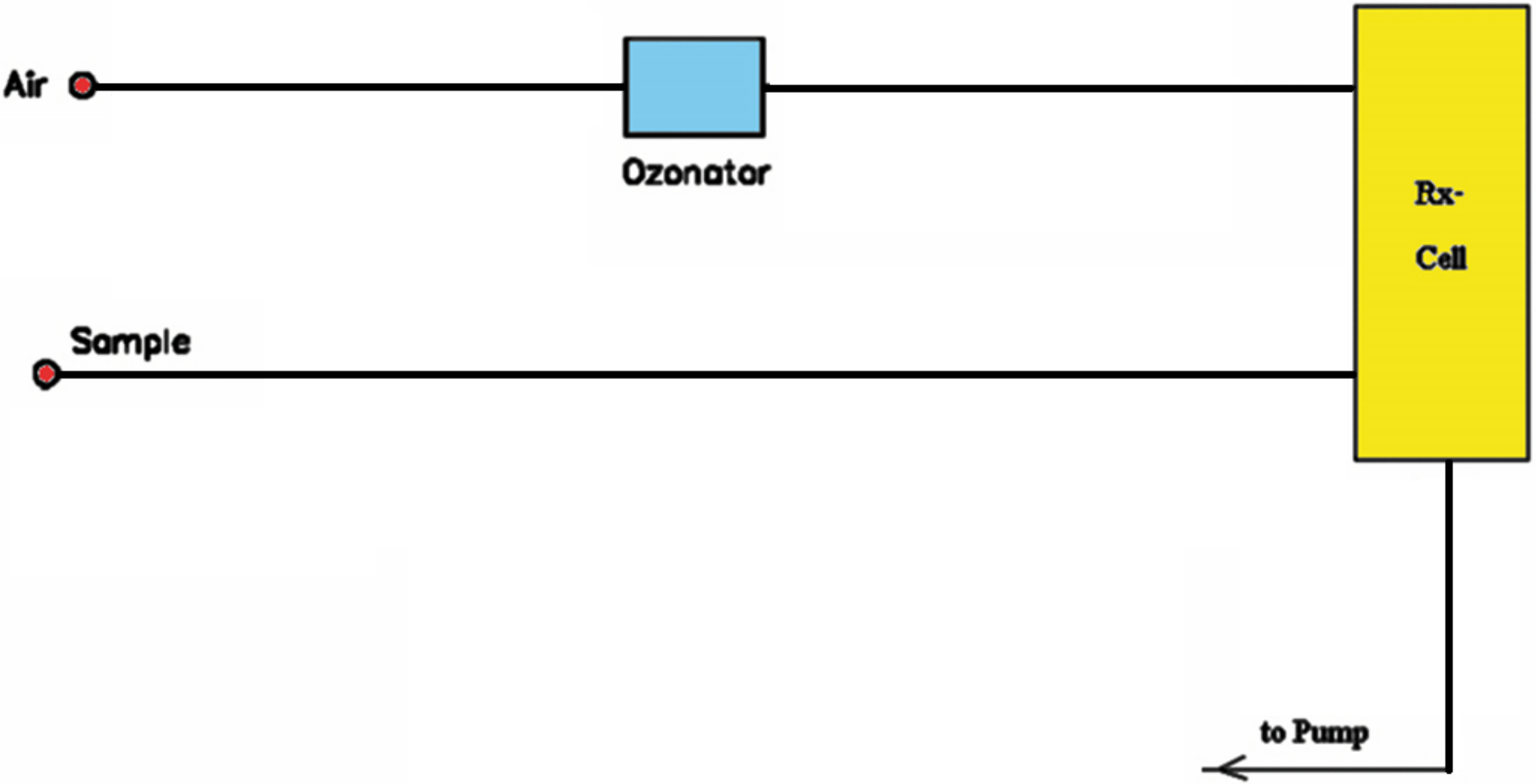
How is NO_2 measured?

- A molybdenum catalyst, heated to ~325 °C, is used to convert NO_2 to NO
- Reduction of NO_2 to NO:

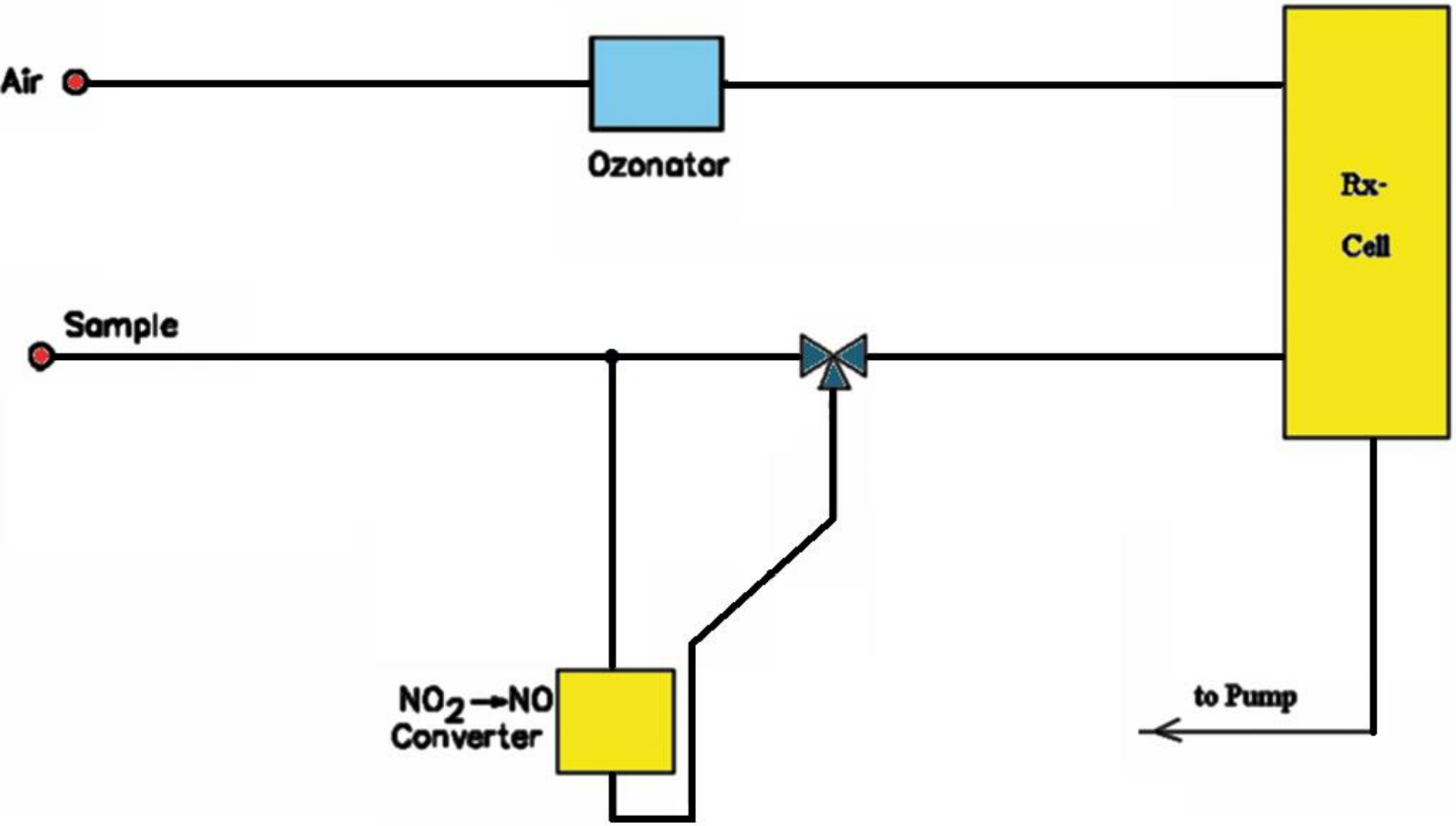
$$3\ NO_2 + Mo \rightarrow 3NO + MoO_3$$

- Thus in the NOx-cycle, the sum of NO + NO_2 is measured
- Calculation for NO_2: c(NOx) – c(NO) = c(NO_2)

Flow schematic (NO)



Flow schematic (NO2)



Problems and solutions

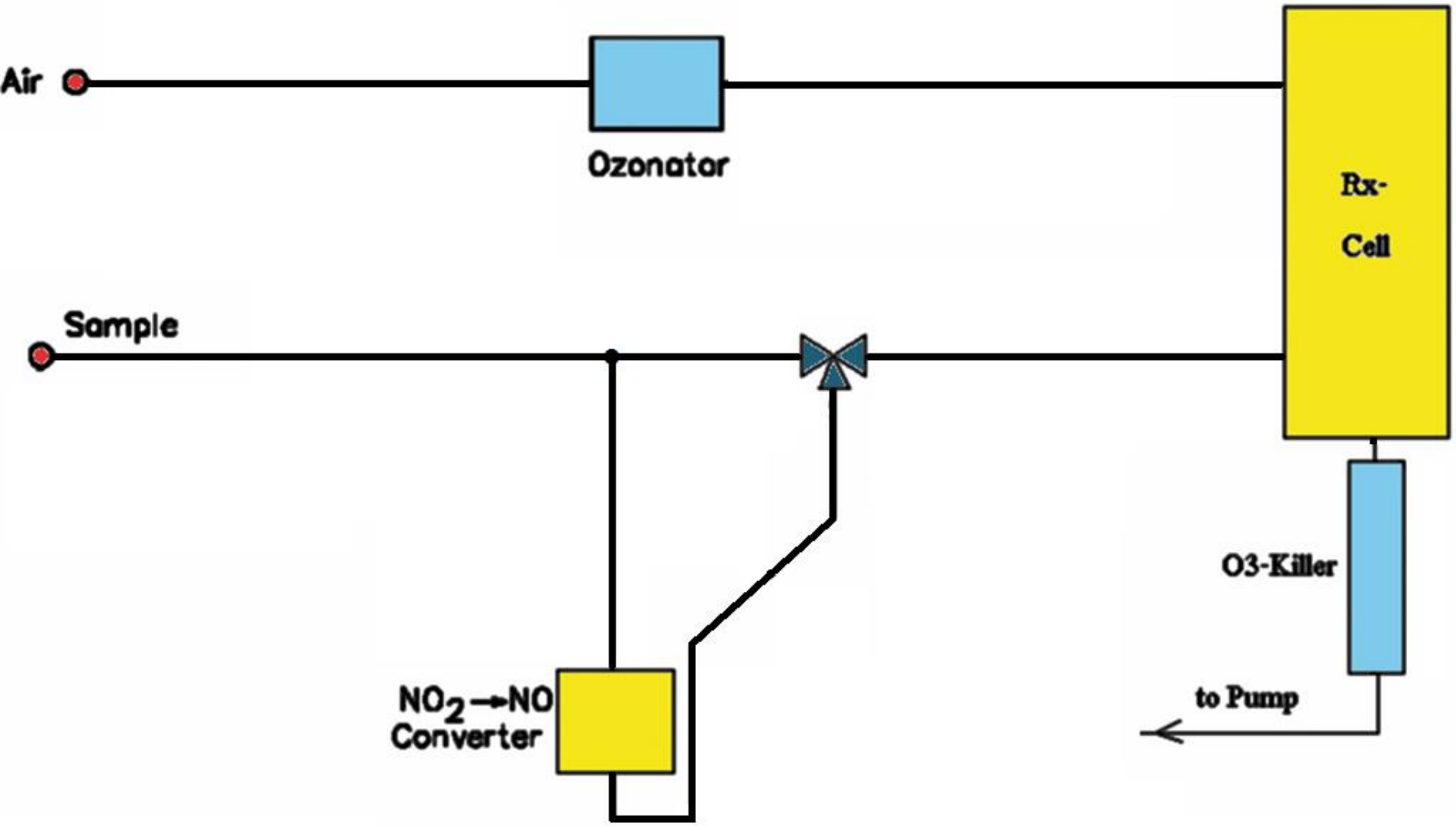
- O_3 is corrosive and toxic
  → Catalytic O_3 killer for low ozone exhaust

- NOx and NO cycle last 8" each: $[NO_2] = [NOx] – [NO]$
  →Delay loop to minimize NO_2-artefacts

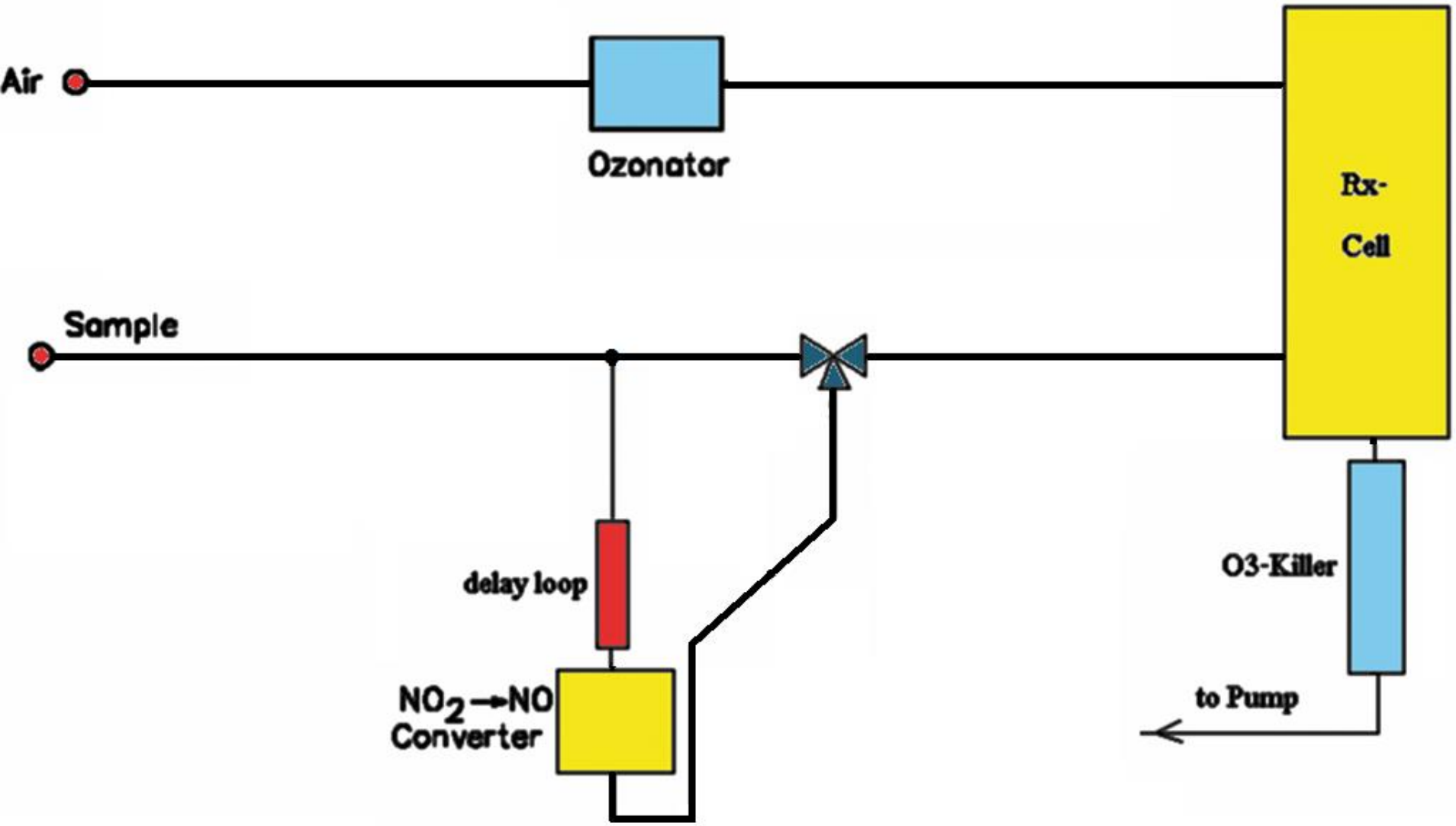
- Ozonator generates unstable compounds (radicals)
  →O_3 cleanser to reduce interfering radicals

- Humidity interference
  → Sample dryer

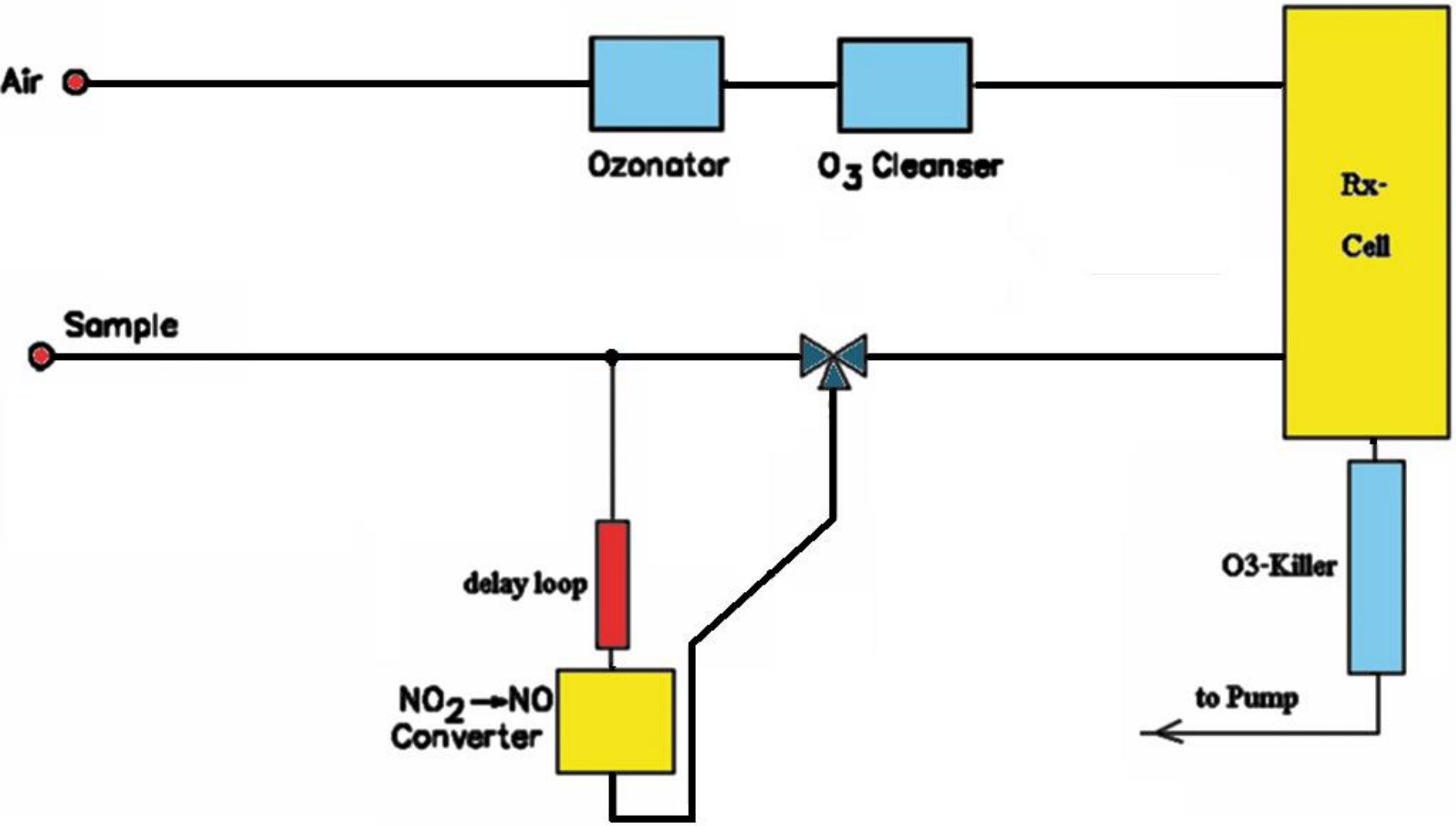
Flow schematic (NO_2)



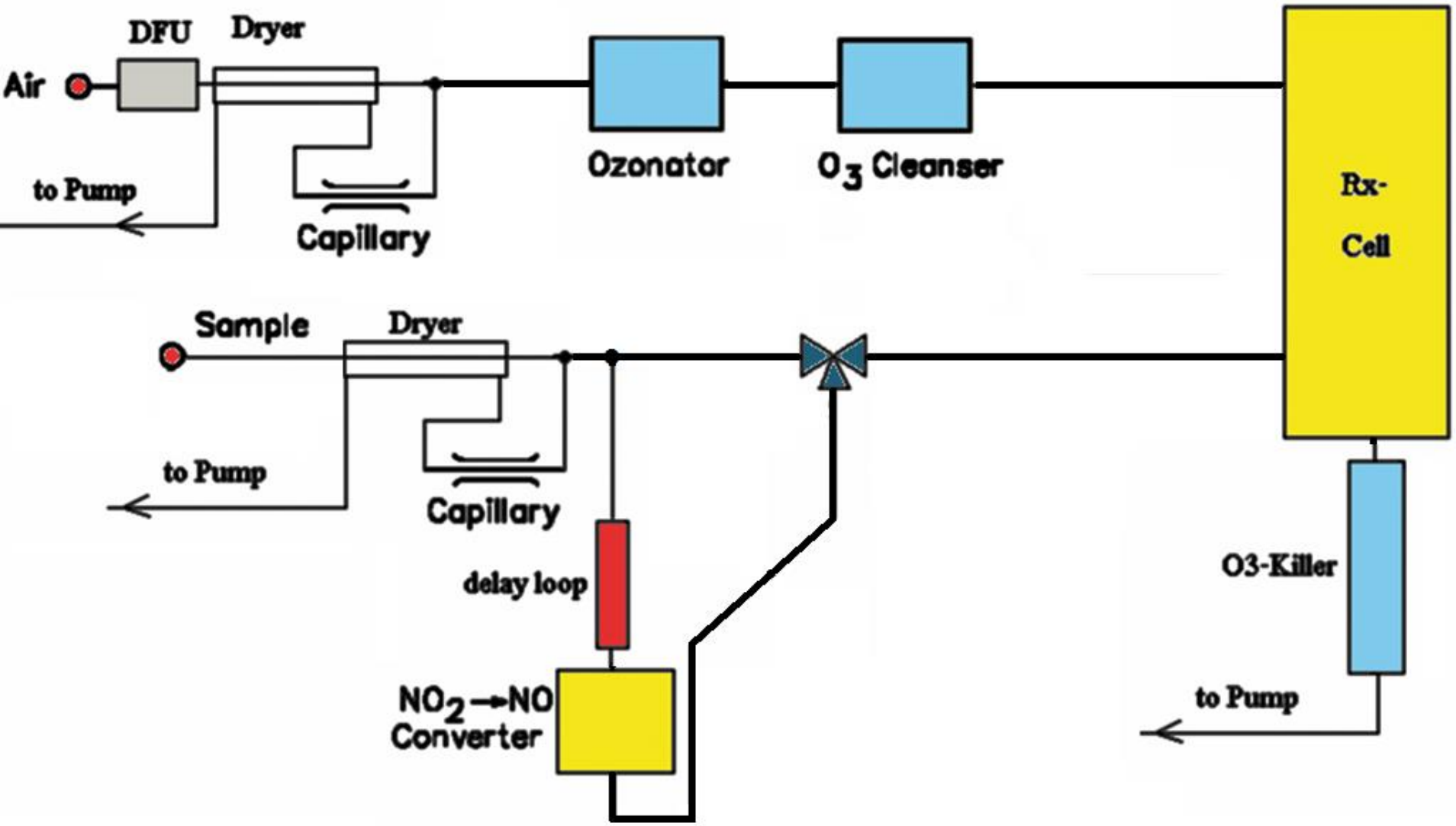
Flow schematic (NO_2)



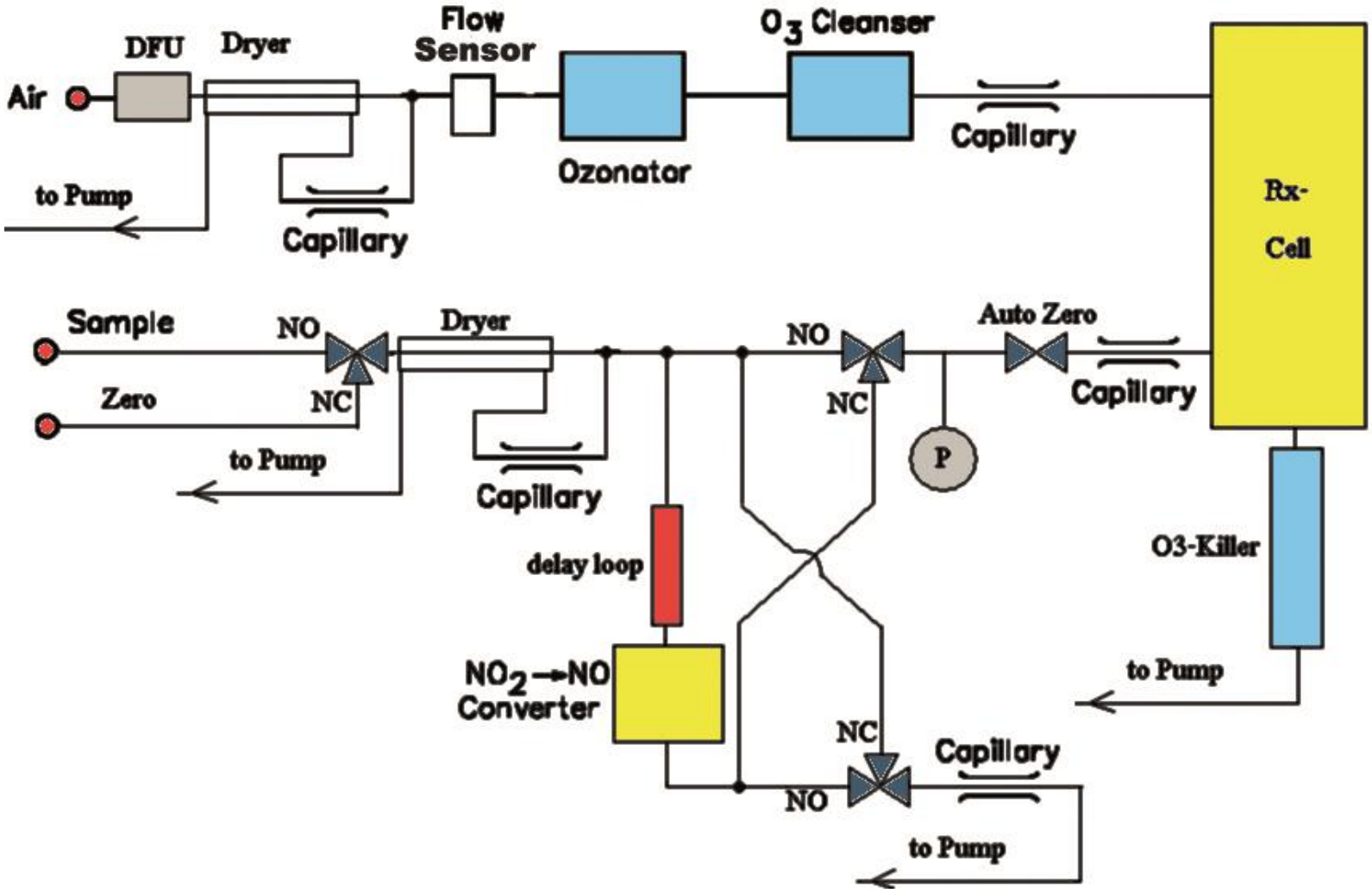
Flow schematic (NO_2)



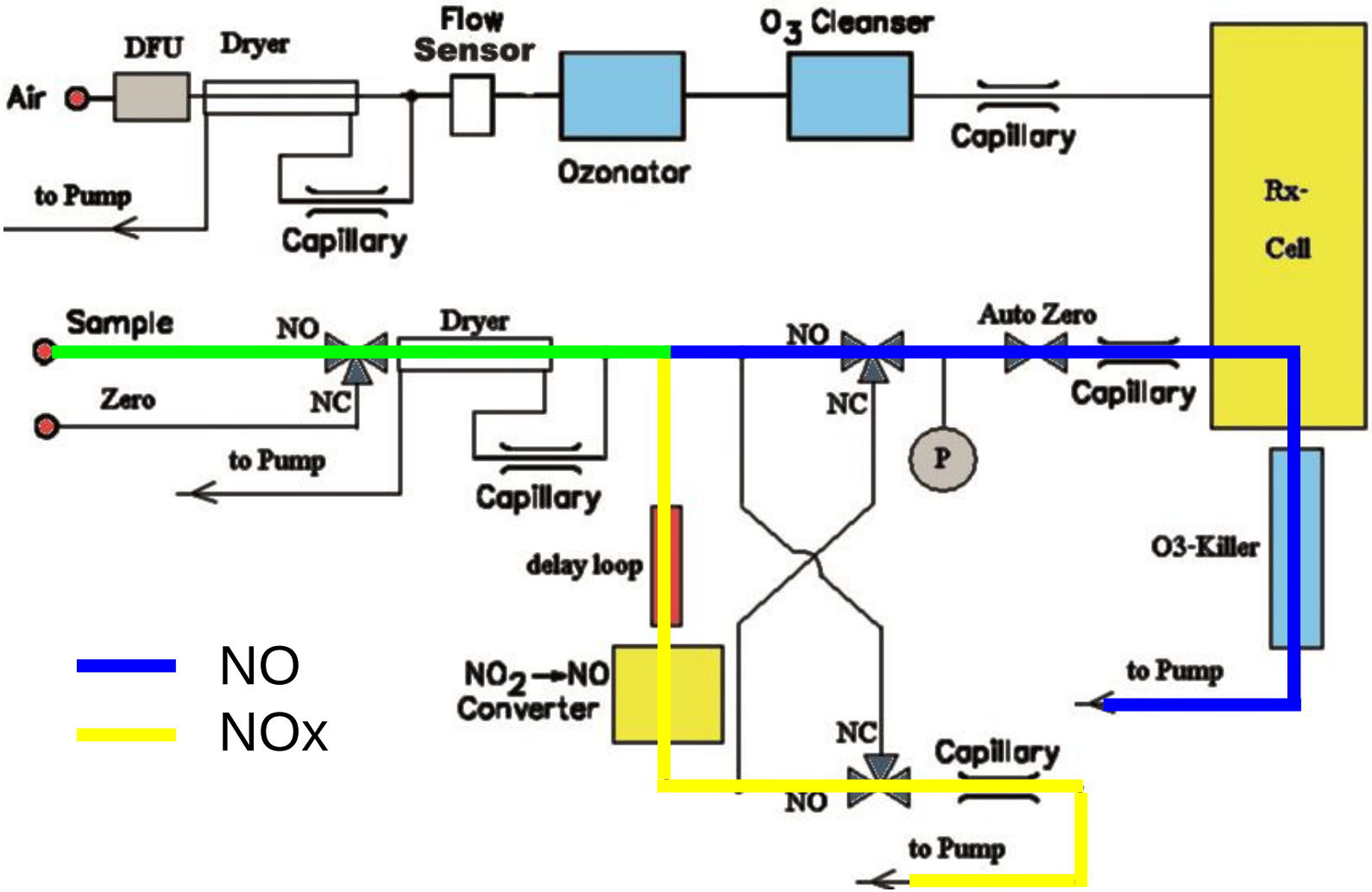
Flow schematic (NO_2)



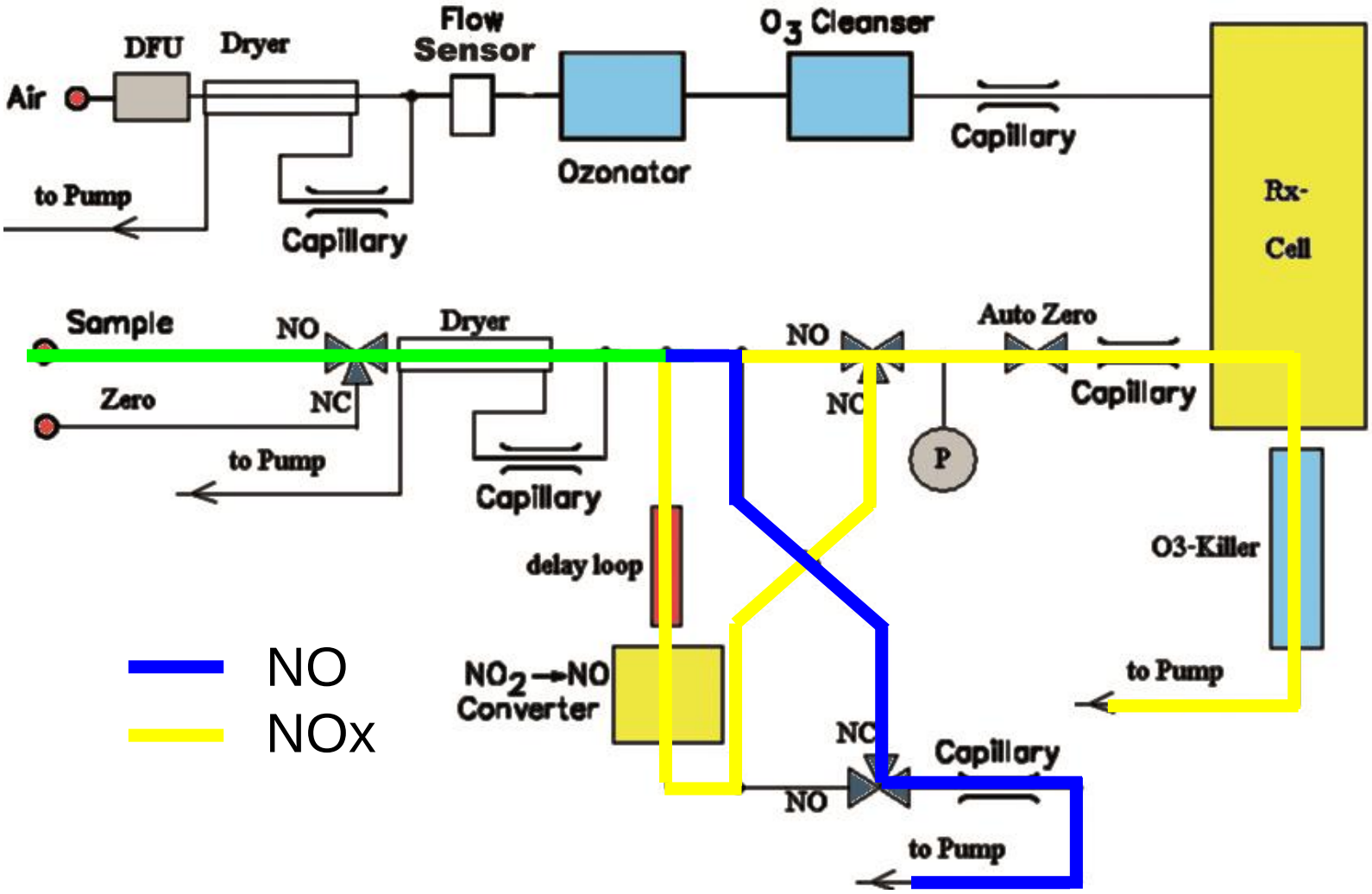
Flow schematic (NO_2)



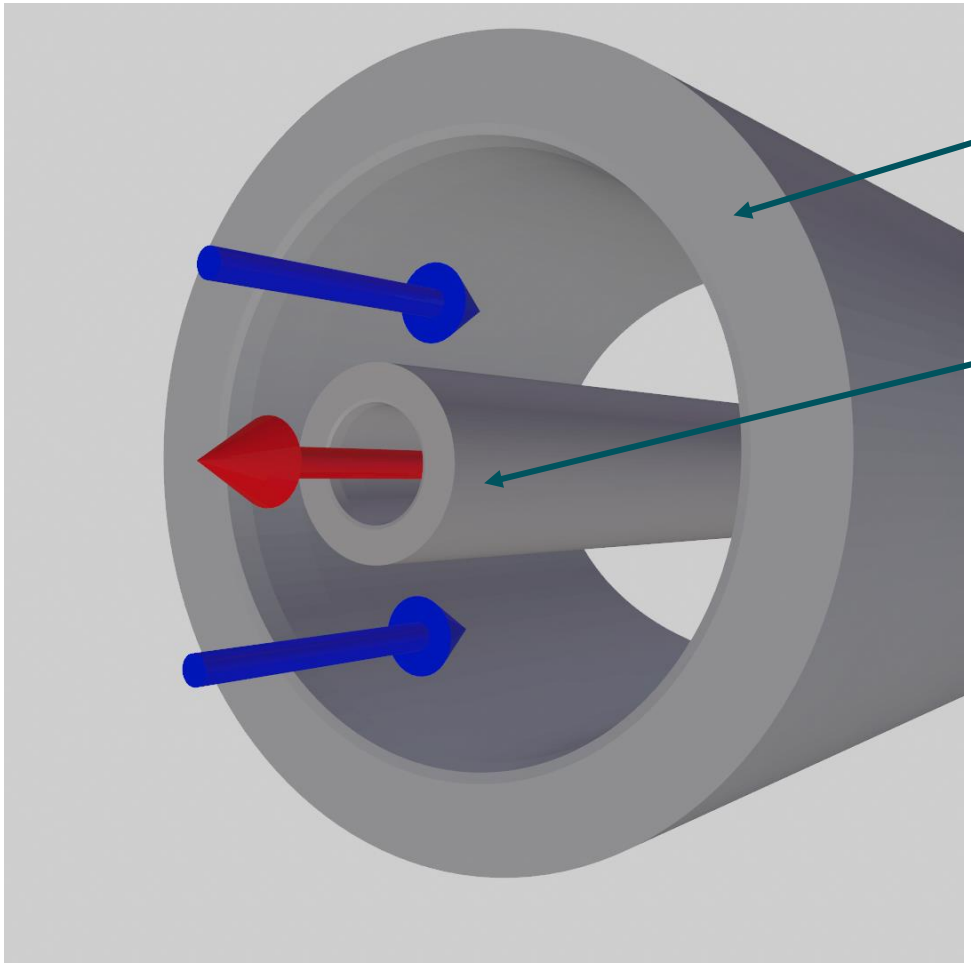
Flow schematic (NO_2)



Flow schematic (NO_2)



Permapure dryer



External Teflon tube

Internal
semi-permeable
membrane (Nafion)

Counter flow to
avoid saturation

Reaction chamber

- Gold plated for maximized sensitivity (improved reflectivity).
- Chamber is under vacuum to prevent quenching so better stability and increased sensitivity.
- Chamber is heated to stabilize flow and thereby improve reproducibility

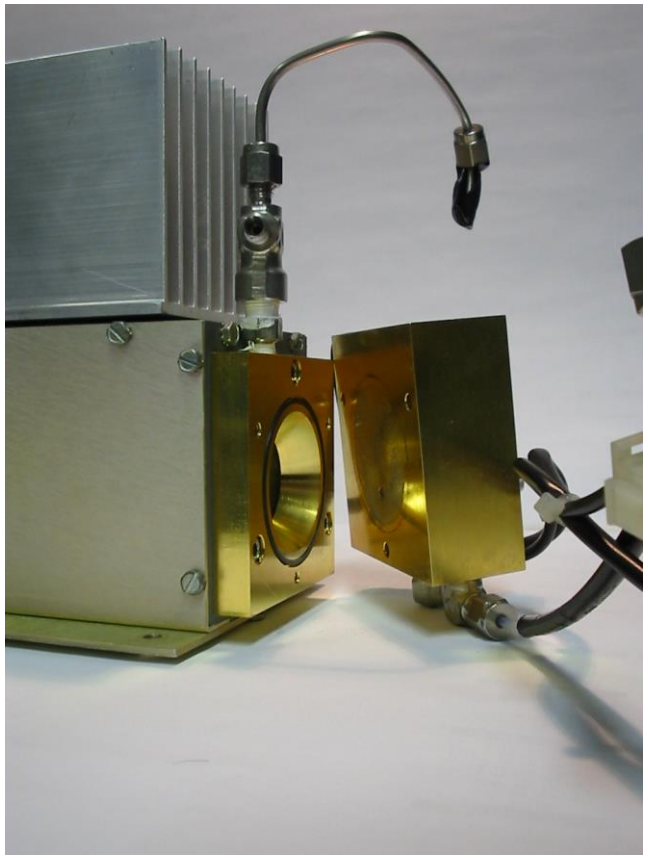
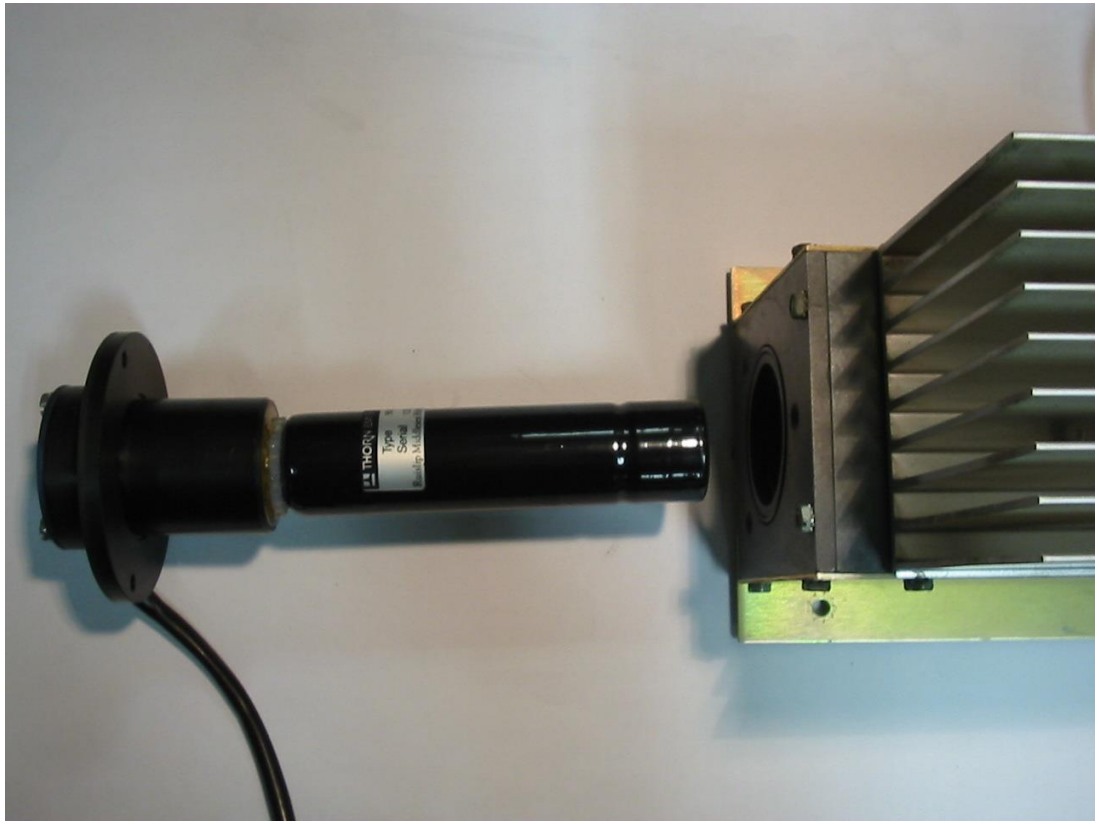


Photo multiplier tube

- Cooled to -2°C to increase sensitivity and stability



NH_3 option

NH_3 → NO_2 converter before the NO_2 → NO converter

Parameters

Actual NOx Values O3Generator: *ON*
no calibration active next automatic calibration cycle starts: 20160909 02:00:00

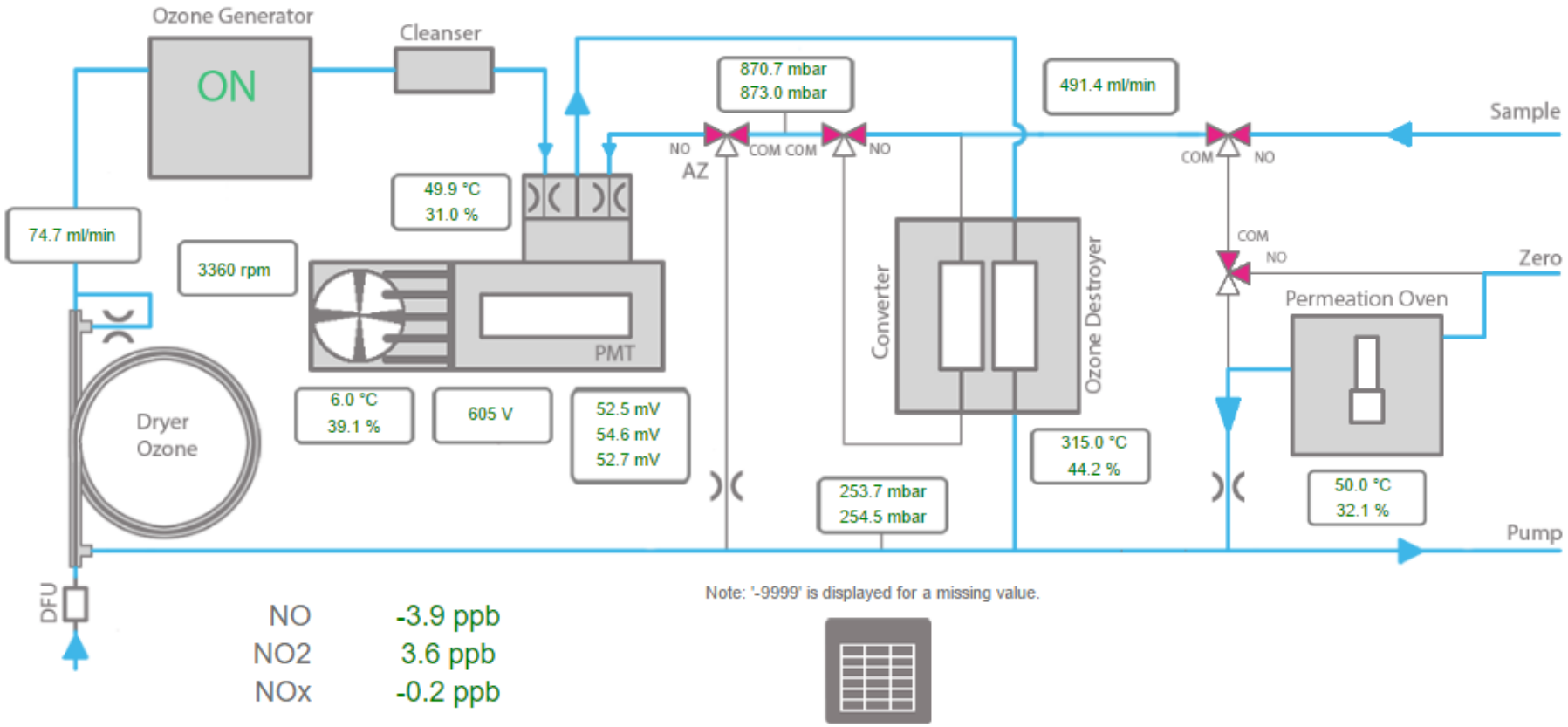
Parameter	Value	Unit	Status: BS-FS-SS	
NO	0.3	ppb	0 0 0	
NO2	1.4	ppb	0 0 0	
NOx	1.7	ppb	0 0 0	

NO_all	0.3	ppb	NO_raw	0.3	ppb	NOStdDev	0.23		NO_Avg (300 sec)	0.4	ppb
NO2_all	1.4	ppb	NO2_raw	1.4	ppb	NO2StdDev	0.30		NO2_Avg (300 sec)	1.0	ppb
NOx_all	1.7	ppb	NOx_raw	1.7	ppb	NOxStdDev	0.25		NOx_Avg (300 sec)	1.3	ppb

PMTSigNO	158.9	Hz	PMTSigNOx	384.3	Hz
PMTSigAuto0	159.2	Hz			
PressNO	902.3	mbar	RCellPressNO	330.2	mbar
PressNOx	902.7	mbar	RCellPressNOx	331.2	mbar
FlowNOx	1145.6	ml/min	FlowO3Gen	96.6	ml/min
Fan_NOx	3390	rpm	HVPS_NOx	-636	V
PMTTemp	-2.0	°C	PowerToPeltier	78.8	%
MolyT	325.4	°C	PowerToMoly	25.8	%
RCellT	50.2	°C	PowerToRCell	39.1	%
PermT	49.8	°C	PowerToPerm	25.6	%

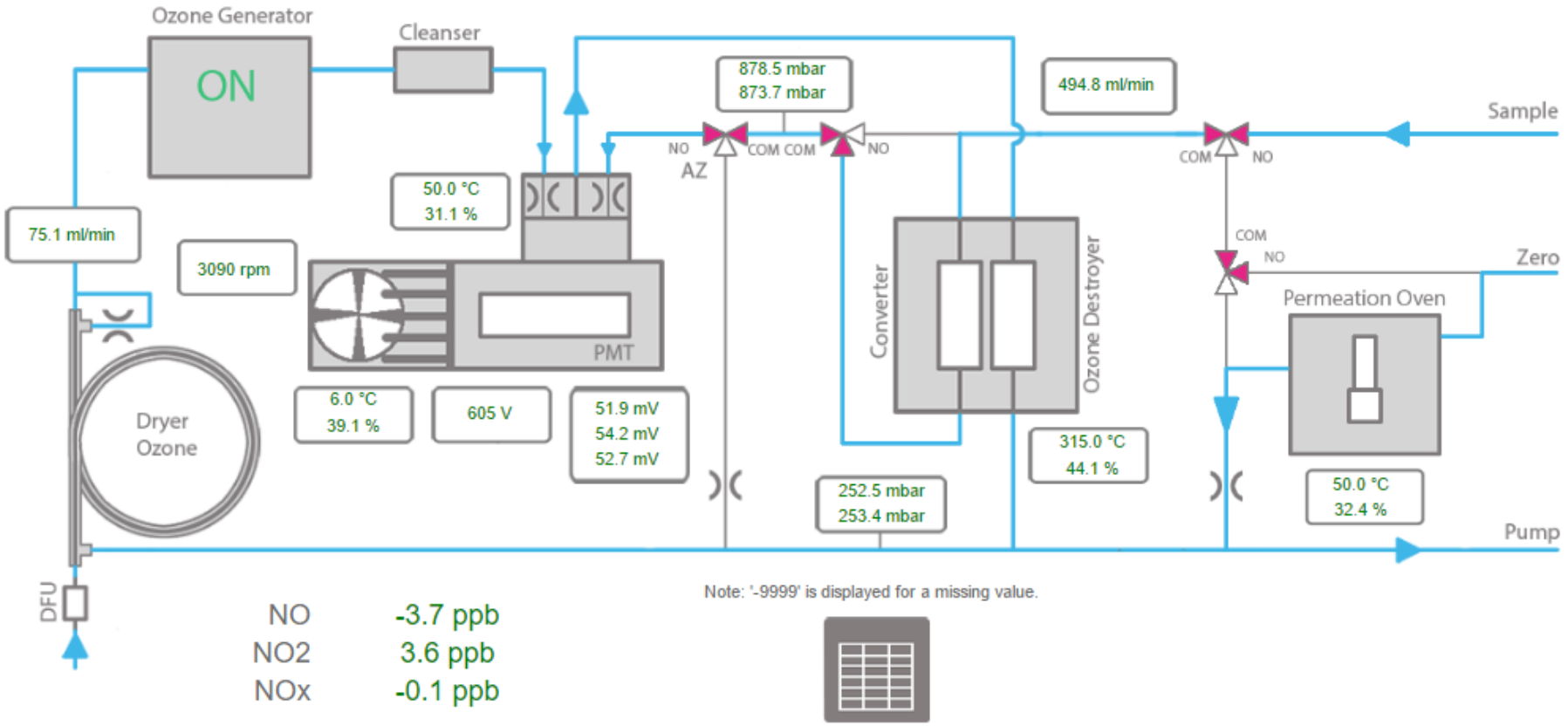
NO Time Constant nr values to TC:	1	StdDev last 10 samples:	0.16
NO2 Time Constant nr values to TC:	1	StdDev last 10 samples:	0.28
NOx Time Constant nr values to TC:	1	StdDev last 10 samples:	0.32
NO Slope:	1.027	NO Offset:	-0.237
NOx Slope:	1.030	NOx Offset:	-0.186
NO2 CE:	1.000	Gain 100 /Offset 5.0 /HVset 630.0 V	O3Gen ON

Parameters

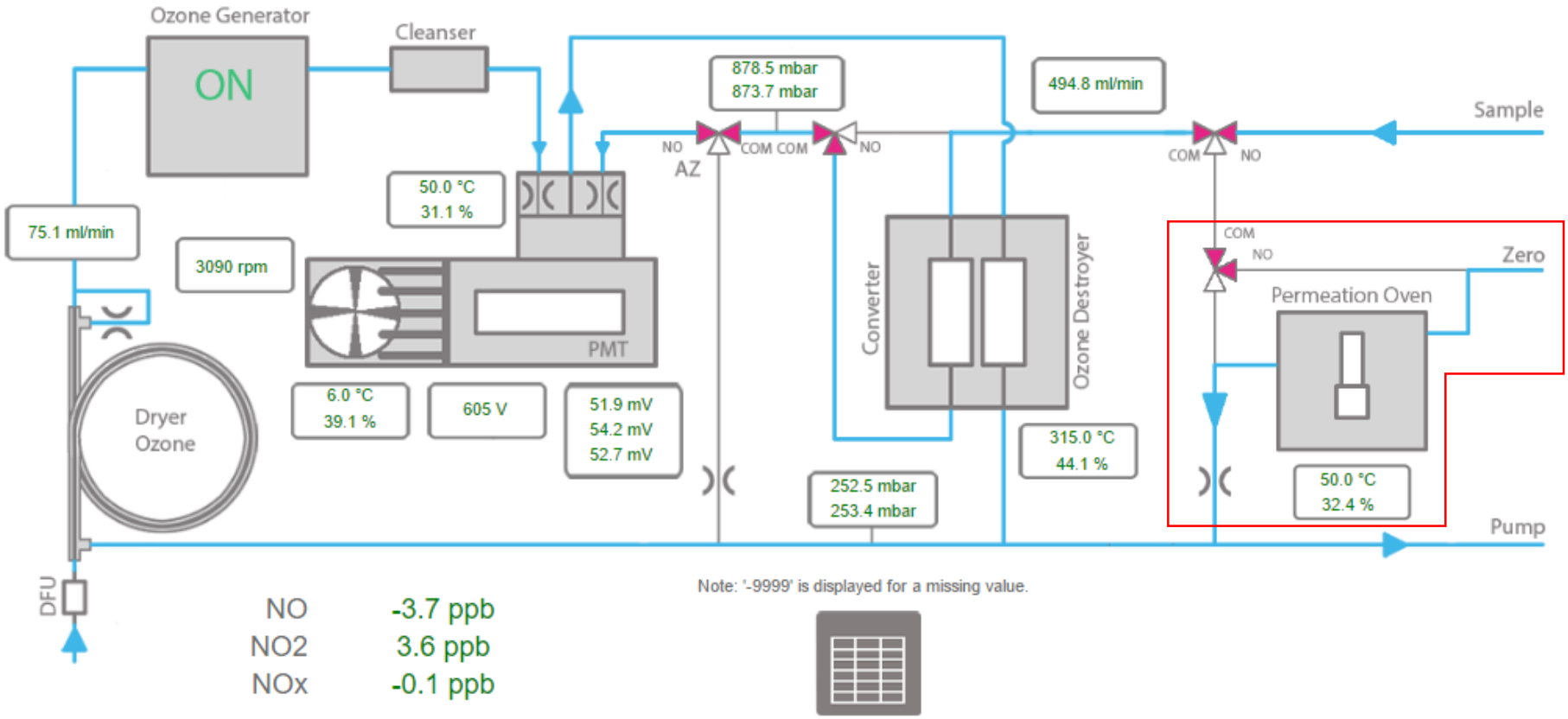


NO	-3.9 ppb
NO2	3.6 ppb
NOx	-0.2 ppb

Parameters


Ozone Generator
ON
Cleanser
878.5 mbar
873.7 mbar
494.8 ml/min
Sample
NO
AZ
COM COM
NO
COM
NO
50.0 °C
31.1 %
75.1 ml/min
3090 rpm
PMT
Converter
Ozone Destroyer
COM
NO
Zero
Permeation Oven
Dryer
Ozone
6.0 °C
39.1 %
605 V
51.9 mV
54.2 mV
52.7 mV
315.0 °C
44.1 %
252.5 mbar
253.4 mbar
50.0 °C
32.4 %
Pump
DFU
NO -3.7 ppb
NO2 3.6 ppb
NOx -0.1 ppb
Note: '-9999' is displayed for a missing value.

Span check



NO	-3.7 ppb
NO2	3.6 ppb
NOx	-0.1 ppb

Calibration

For NO:

- Using external zero air and external NO cylinder

For NO_2:

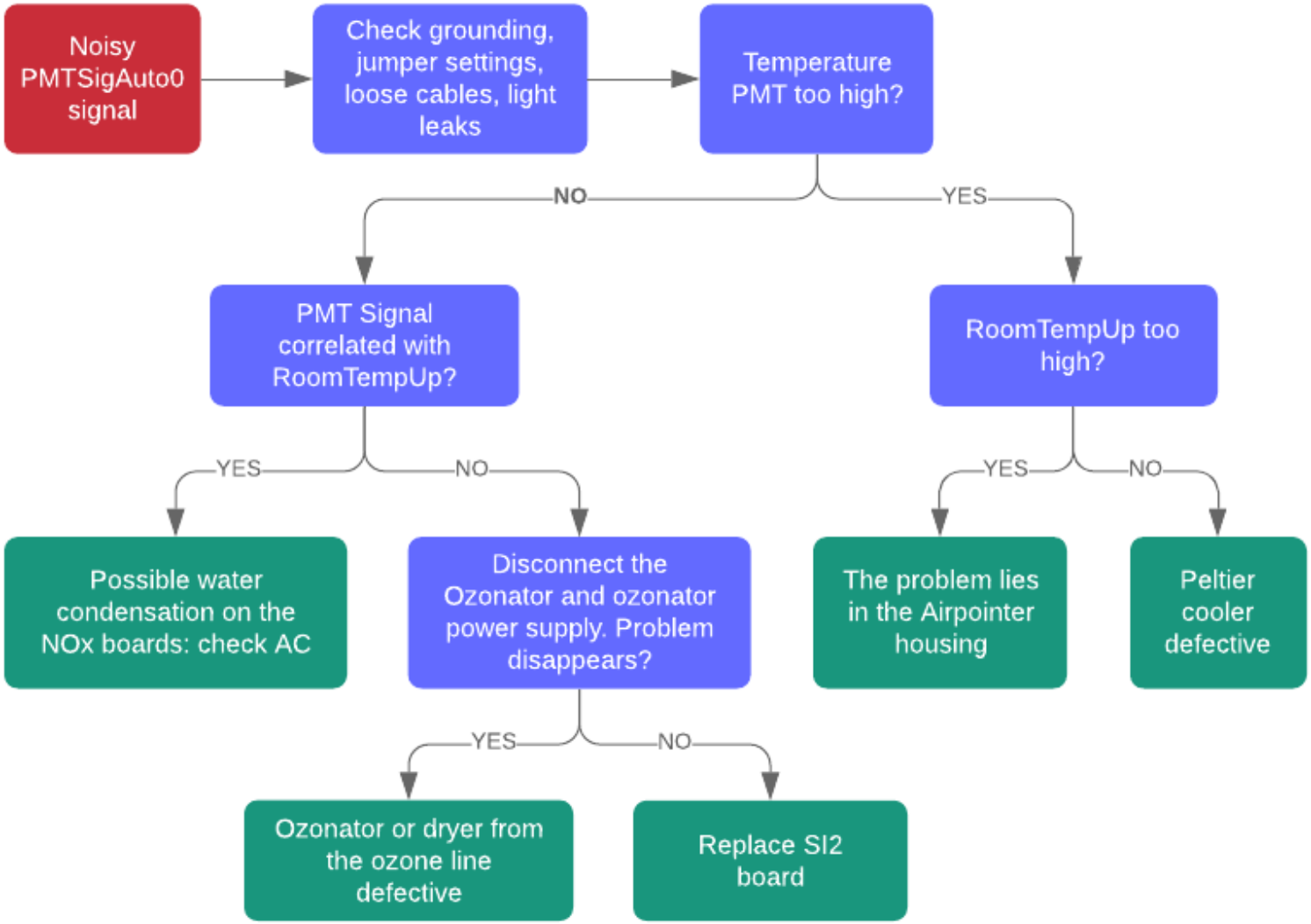
- Using external zero air and external Gas Phase Titration (GPT) module to generate NO_2 from NO and O_3

Preventive maintenance

- Change DFU filters (once a year)
- Test the molybdenum converter efficiency (during each calibration)
- Change o-rings (once a year)
- Clean reaction cell (once a year)

Full schedule available here:
https://www.airpointer.tech/maintenance-schedule/

Troubleshooting NOx



Thank you for your attention!