

National surface-level ozone analyzers in Russia

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National requirements for ozone analyzers for atmospheric monitoring.

Ozone analyzers must conform to the reference method or equivalent method required by the **GOST 17.2.6.02-85**, (General technical standard. Nature protection. Atmosphere. Automatic gas analyzers for air pollution monitoring), **РД52.04.667-2005**, by the EPA in Appendix D of 40 CFR Part 50.

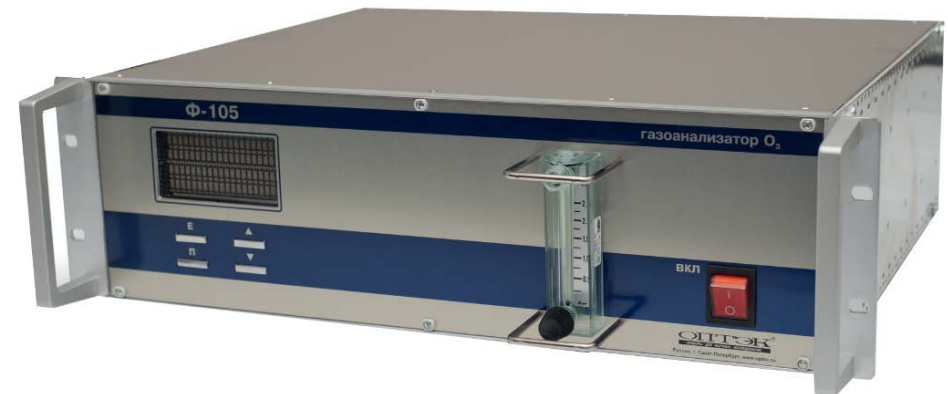
The standard of the Russian Federation applies to automatic gas alarms designed to monitor atmospheric pollution in cities and other settlements, as well as to measure background levels of atmospheric pollution.

OZONE monitoring equipment

Chemiluminescent solid-state ozone analyzer mod. 3.02P-A



Optical UV photometer mod. F-105



The Model 3.02P-A Chemiluminescent Ozone Analyzer

This model combines proven detection technology, easy to use menu-driven software with diagnostic functions to offer flexibility and reliability. It is specified to measure ozone concentrations in ambient air.

The Model 3.02P-A has the following features:

- Automatic continuous measurements
- One block execution
- High sensitivity
- Fast response time
- Linearity
- Menu Driven Software
- Display
- Data output

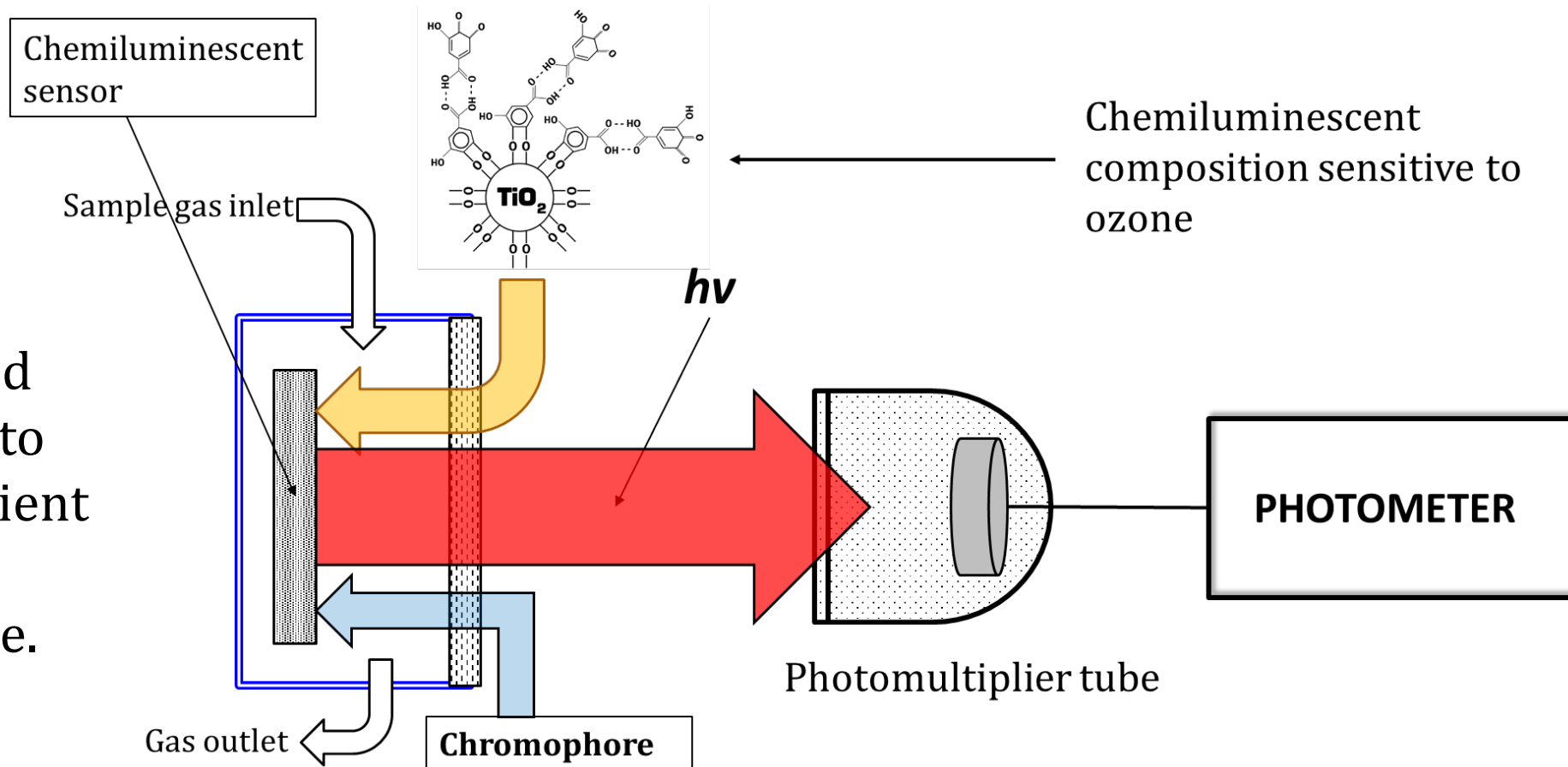


Main regulatory documents for legal development of analyzers in the Russian Federation.

- The type of climate execution - УХЛ 4.2 for ГОСТ 15150
- For protection from environment influences element analyzer belongs to group B1 for ГОСТ 12997.
- For stability to mechanical influences element analyzer belongs to group L1 for ГОСТ 12997.
- For stability to ambient pressure element analyzer belongs to group P1 according to ГОСТ 12977.
- For allowable corner of an inclination element analyzer belongs to group H3 (independent) for ГОСТ 13320).
- For period of warm-up element analyzer belongs to group П-3 (instruments with long time of warm-up) for ГОСТ 13320.
- For time of output signal stabilization element analyzer belongs to group И-3 (inertial) for ГОСТ 13320.
- For level of clamor from element analyzer is not more than 60 dB according to ГОСТ 27883.
- The level of industrial radiohandicapes, influencing on element analyzer, is not more than values designated in ГОСТ23511 and “All-union norms of allowed radiohandicapes” (norms 8- 72)

Principle of Operation. Description of the method of analysis.

Patented technology based on heterogeneous chemiluminescence principle is applied in 3.02P-A gas analyzer, Patent RU 2055347, Patent RU 2493556 C1



Chemiluminescent solid sensor was developed to measure ozone in ambient air. Process scheme is described in the picture.

Block diagram of the 3.02-P-A analyzer

Solenoid Valve

Flow reactor with chemiluminescence sensor

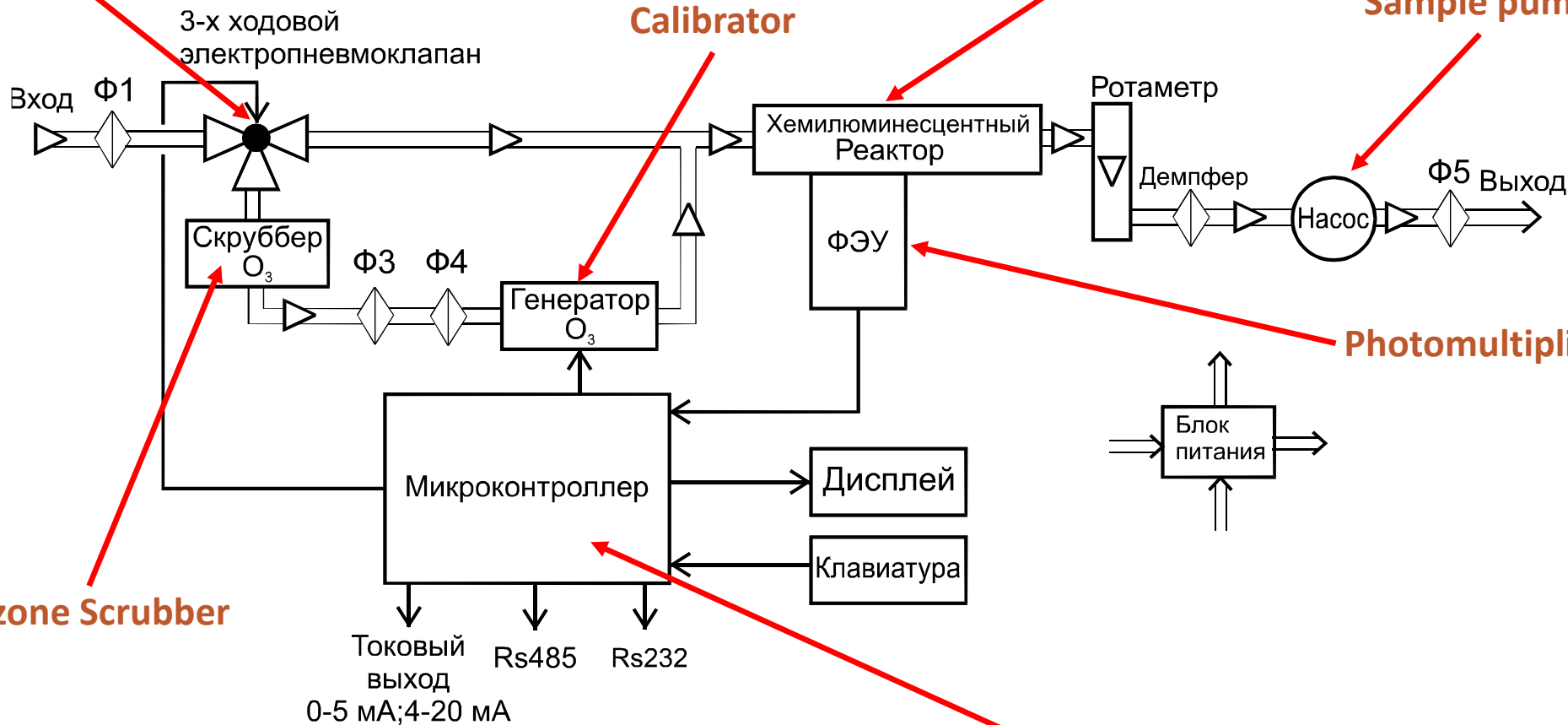
Sample pump

Calibrator

Photomultiplier tube

Ozone Scrubber

Microcontroller



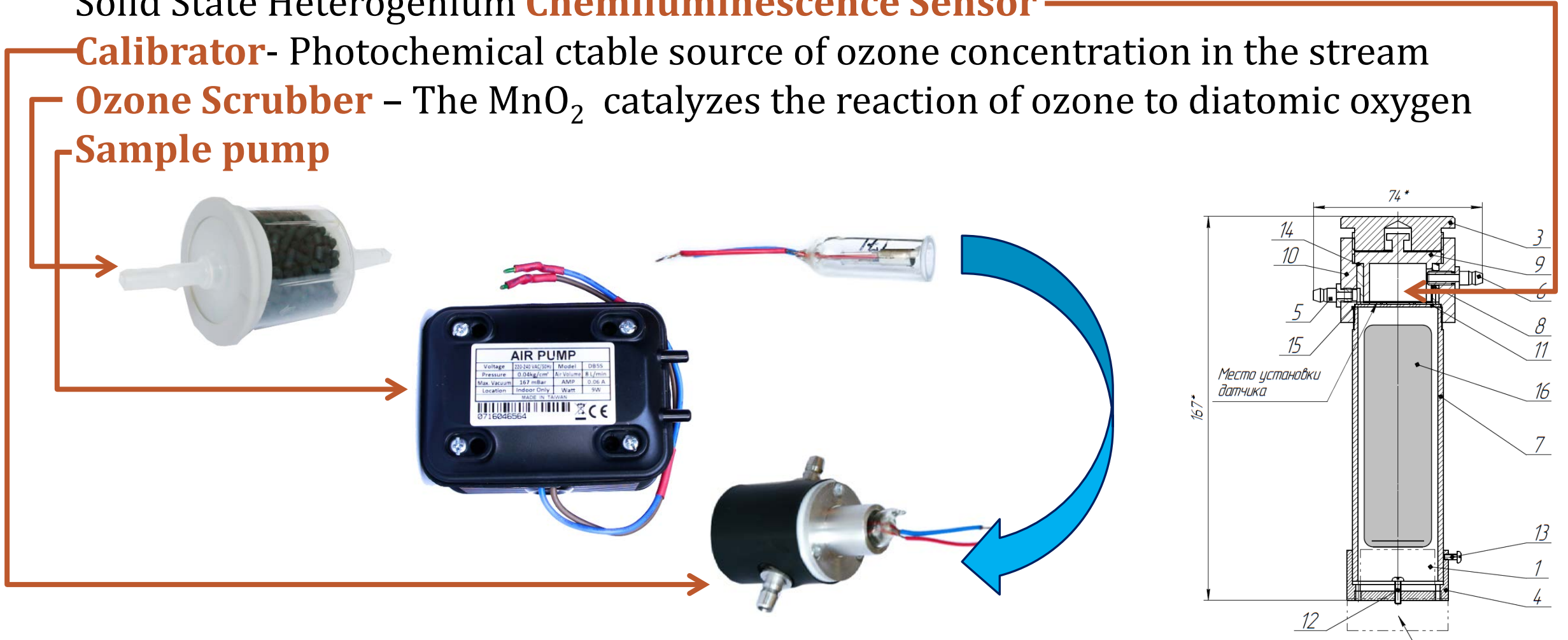
Critical Components of Chemiluminescent Ozone Analyzer

Solid State Heterogeneous **Chemiluminescence Sensor**

Calibrator - Photochemical stable source of ozone concentration in the stream

Ozone Scrubber - The MnO_2 catalyzes the reaction of ozone to diatomic oxygen

Sample pump



3.02P-A Chemiluminescent Ozone Analyzer

Meet EPA designated equivalent method requirements when operated under the following conditions

Specifications

- Range of measuring concentrations:

<u>Measurable range,</u> <u>mcg/m³</u>	The limits of main error	
	<u>reduced, %</u>	<u>relative, %</u>
0 - 30	±20	-
30 - 500	-	±20

1,997 mcg/m³ = 1 ppb O₃ for 20°C in the air

- Resolution: 1 mcg/m³
- Span drift: ± 0,5 parts from main error (7 days)
- Analyzed gas volume flow rate, l / min: 1,8 ± 0,2
- Ambient operation conditions and sample gas parameters
 - temperature: +10...+35 C
 - pressure: 630...800 mm
 - Hg relative humidity: 15...95 %
- Position inclination: not more 20°

3.02P-A Chemiluminescent Ozone Analyzer

- Average time between failures: not less 10000 hours
- Warm-up time: not more 100 min
- Outputs
 - 2 x Current analog outputs
 - 0-5 (4-20) mA
 - 1 RS232 serial port
 - 2 control output relays
(dried contacts)
- Analyzed sample indications stabilization: not more 1 min.
- Dimensions: 410 (L) x 480 (W) x 130 (h)
- Weight: not more 8 kg.
- AC Power supply: 20⁺²²₋₃₃ V, 50±1 Hz
- Power consumption: not more 50 VA
- Limiting content of unmeasured gas components in the analyzed gas mixture (Table 2).

<u>Norms, mg/m³</u>						
<u>CO</u> <u>mg/m³</u>	<u>H₂S</u> <u>mg/m³</u>	<u>SO₂</u> <u>mg/m³</u>	<u>NO</u> <u>mg/m³</u>	<u>NO₂</u> <u>mg/m³</u>	<u>Cl₂</u> <u>mg/m³</u>	<u>Ambient dust,</u> <u>mg/m³</u>
50,0	0,1	0,5	0,5	0,5	1,0	5

Testing the Performance Parameters of a Chemiluminescence Ozone Analyzer mod. 3.02 P-A

February 2008

Environmental Technology Verification Report

JSC OPTEC 3.02 P-A
CHEMILUMINESCENT OZONE ANALYZER

Prepared by
Battelle

Battelle
The Business of Innovation

Under a cooperative agreement with

 **EPA** U.S. Environmental Protection Agency

ETV 

February 2008

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

JSC OPTEC 3.02 P-A
CHEMILUMINESCENT OZONE ANALYZER

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM



Battelle
The Business of Innovation

ETV Joint Verification Statement

TECHNOLOGY TYPE:	CHEMILUMINESCENT OZONE ANALYZER		
APPLICATION:	MEASURING OZONE IN AMBIENT AIR		
TECHNOLOGY NAME:	3.02 P-A		
COMPANY:	JSC OPTEC Ltd.		
ADDRESS:	1985 West Henderson Road	PHONE: (614) 477-1020	
	Columbus, Ohio 43220	FAX: (614) 486-2693	
WEB SITE:	www.optec-corp.com		
E-MAIL:	mkozliner@gmail.com		

A Reexamination of Ambient Air Ozone Monitor Interferences

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ABSTRACT

Achieving compliance with the air quality standard for ozone could cost billions of dollars nationwide. Compliance is judged on ozone measurements made by either the federal reference method (FRM), ethylene chemiluminescence, or the federal equivalent method. A number of laboratory and field studies have examined the accuracy of ozone monitoring instruments, both FRM and FEM, with mixed results. This report summarizes results from a new study of interferences to the FRM, two different FEM configurations, a portable research grade UV photometric instrument and a new solid phase

Ozone analyzers that have been tested

«A Reexamination of Ambient Air Ozone Monitor Interferences»

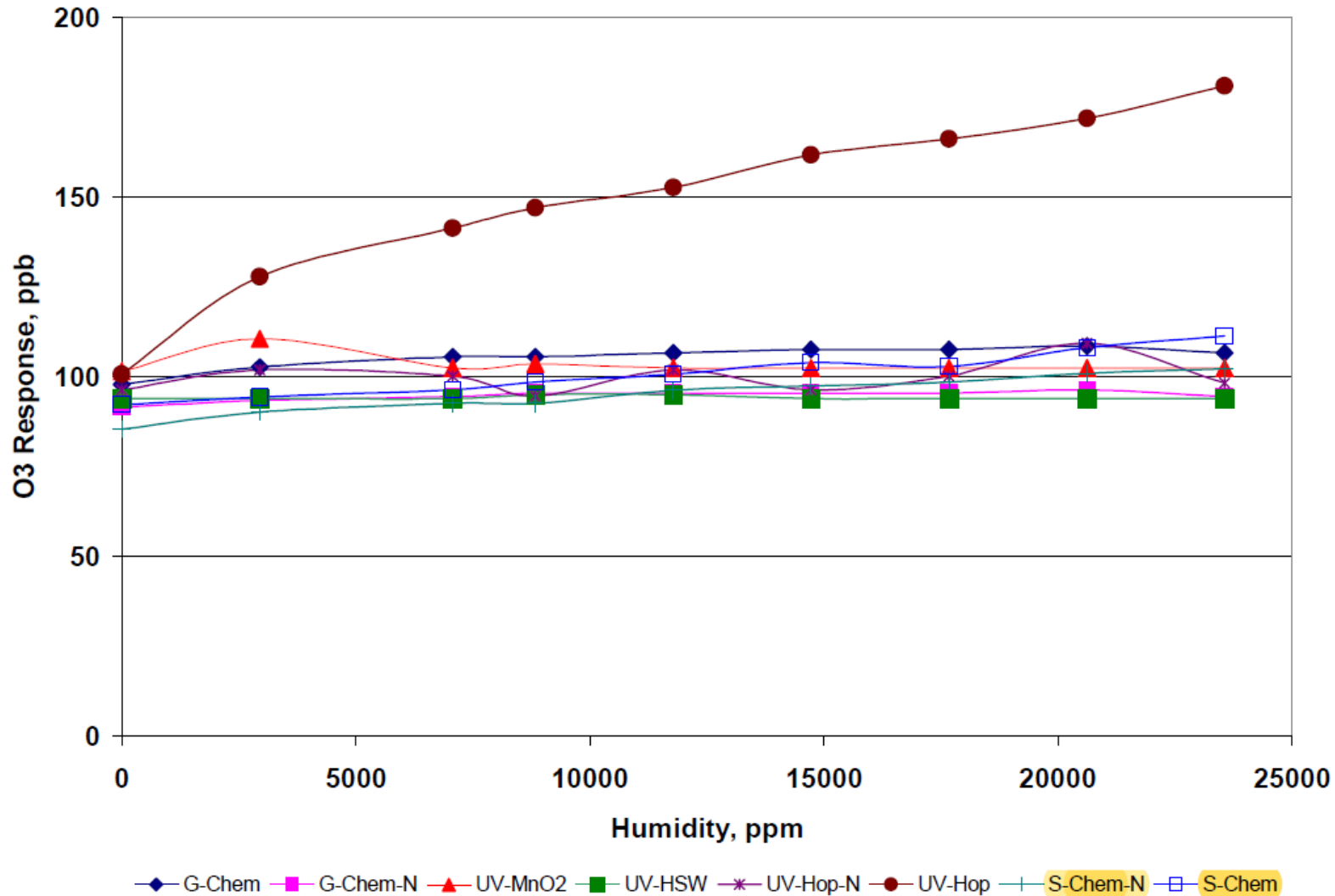
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Darrell W. Joseph (Battelle Science and Technology International, Columbus, OH)

Will M. Ollison (American Petroleum Institute, Washington, DC)

Instrument	Abbreviation	Scrubber	Humidity Equilibration
Bendix ethylene chemiluminescence	G-Chem	No scrubber required	No
Bendix ethylene chemiluminescence	G-Chem-N	No scrubber required	Yes
ThermoEnvironmental UV Model 49	UV-MnO ₂	MnO ₂ unheated	No
Horiba UV APOA-370	UV-HSW	Heated silver wool	No
2B Tech UV Model 202	UV-Hop	Hopcalite unheated	No
2B Tech UV Model 202	UV-Hop-N	Hopcalite unheated	Yes
Optek 3.02 P-A solid-phase chemiluminescence	S-Chem	None	No
Optek 3.02 P-A solid-phase chemiluminescence	S-Chem-N	None	Yes

Response of Ozone Monitors to Increasing Humidity at 100 ppb O₃



Effect of Increasing Water Vapor on Ozone Response at Three Constant Ozone Levels

Ozone Input	55 ppb O ₃	100 ppb O ₃	200 ppb O ₃
<u>Instrument</u>	Change in O ₃ (ppb) per 10 ⁴ ppm H ₂ O		
G-Chem	5	3	10
G-Chem-N	2	1	1
UV-MnO ₂	1	0	0
UV-HSW	2	-1	0
UV-Hop-N	8	2	4
UV-Hop	24	30	32
S-Chem-N	5	7	21
S-Chem	6	8	22

Change in O₃ Response with Increasing Humidity from Static Tests

Instrument

Change in O₃

(% per 10⁴ ppm H₂O)

G-Chem

1.5

G-Chem-N

0.0*

UV-MnO₂

-0.5

UV-HSW

-1.1

UV-Hop-N

-2.2

UV-Hop

-2.0

S-Chem-N

3.2

S-Chem

4.2

* G-Chem-N assumed free from water vapor interference for this test

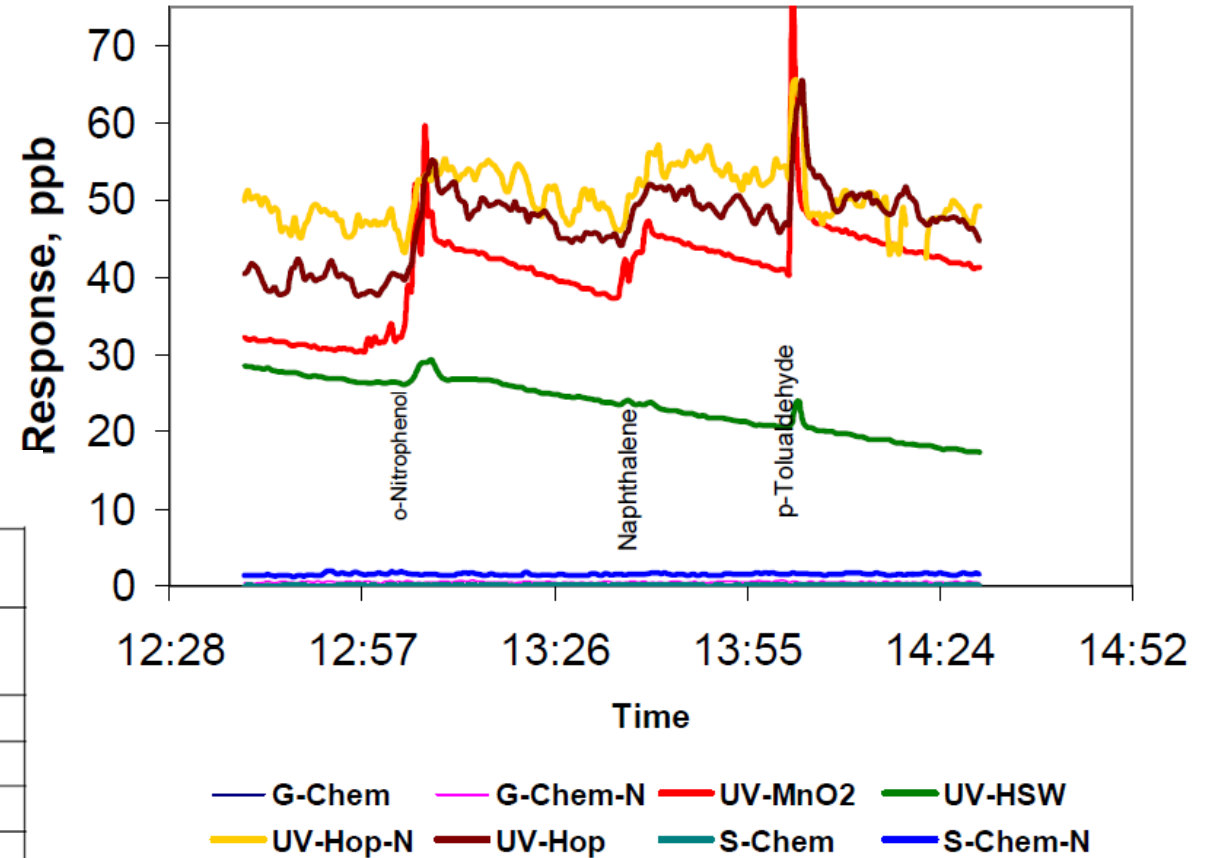
Response Ratio of Ozone to Vapor Phase Mercury

	Test A	Test B
Mercury, ppt	78.7	6.8
Instrument	ppb O ₃ per ppt mercury	
G-Chem	0	0
G-Chem-N	0	0
UV-MnO ₂	0.6	0.3
UV-HSW	0.6	1.1
UV-Hop-N	0.6	1.1
UV-Hop	0.7	1.4
S-Chem-N	0	0
S-Chem	0	0

Response of Ozone Monitors to ppbv Levels of Aromatic Compounds in Dry Air

(Test atmosphere included mercury vapor from an earlier interference test)

Instrument	<u>o-Nitrophenol</u>		<u>Naphthalene</u>		<u>p-Tolualdehyde</u>	
	Low RH	High RH	Low RH	High RH	Low RH	High RH
G-Chem	0	0	0	0	0	0
G-Chem-N	0	0	0	0	0	0
UV-MnO ₂	2.2	2	0.7	0	0.8	0.1
UV-HSW	0.4	0.1	0	0	0.1	0
UV-Hop	1.1	1.7	0.7	0.8	0	0.6
UV-Hop-N	1.8	0	0.6	0.7	0.5	0
S-Chem	0	0	0	0	0	0
S-Chem-N	0	0	0	0	0	0



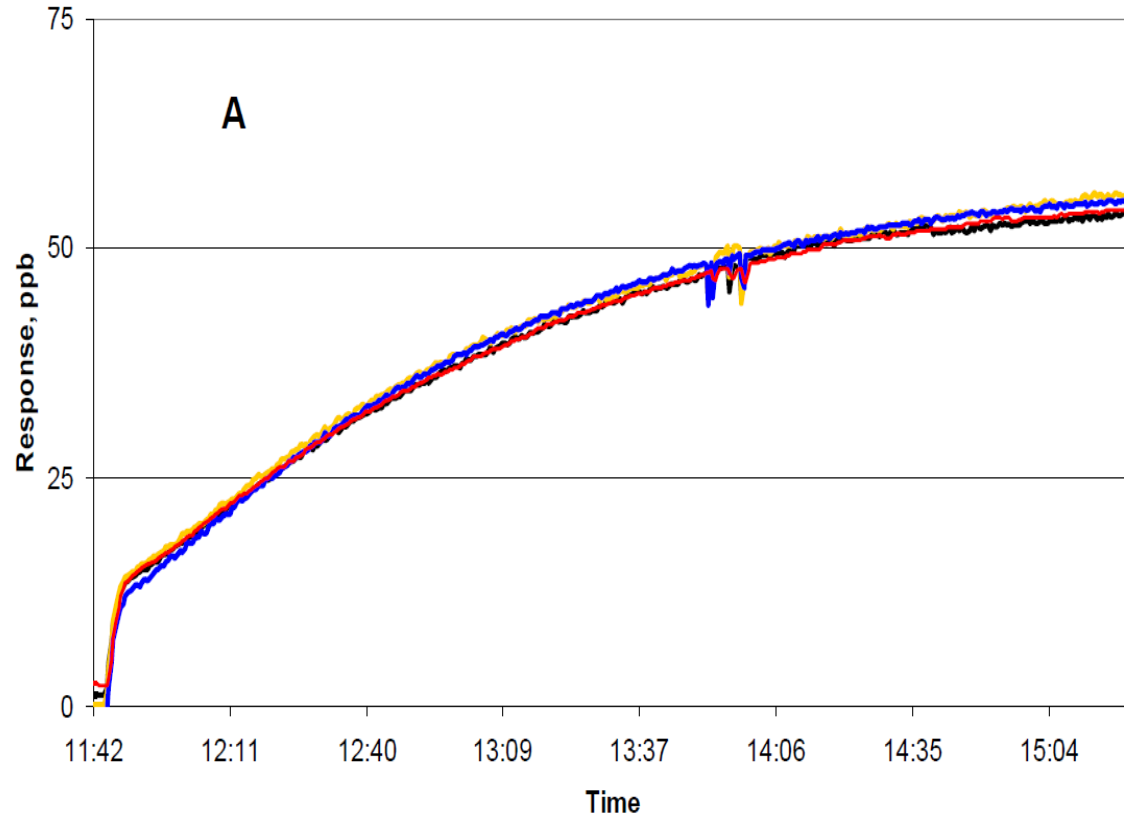
Effect of products of photochemical reactions

	Low Loading test	High Loading Test
Hydrocarbons,* ppmV	0.125	0.50
NO ₂ , ppm	0.06	0.19
Relative Humidity (Initial), %	74	85
Absolute Humidity, ppmV	21,900	23,000

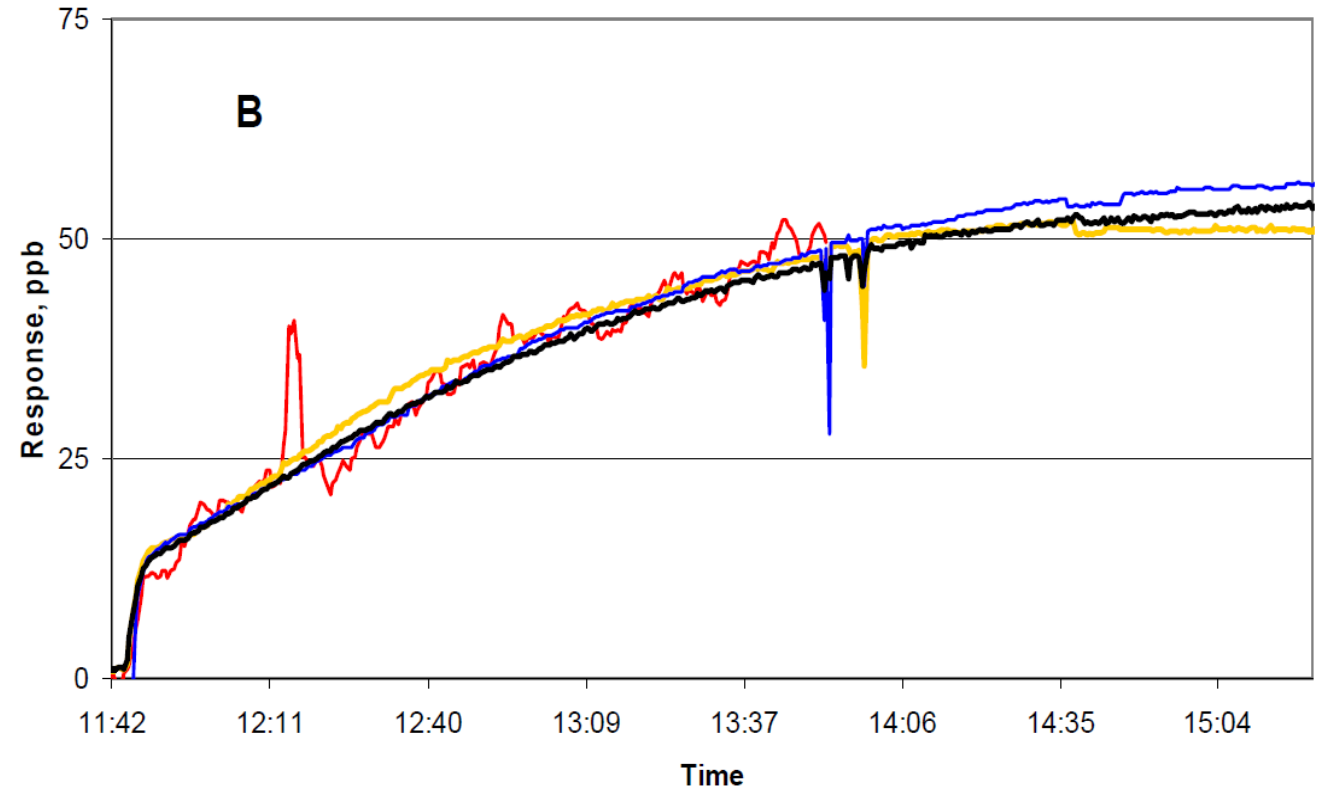
Table 1. Composition of 17-Component Urban Hydrocarbon Mixture.

Compound	Relative Molar Concentration	Compound	Relative Molar Concentration
acetylene	0.136	propylene	0.035
ethane	0.100	trans-2-butene	0.043
propane	0.040	2-methylbutene-2	0.013
2-methylpropane	0.023	benzene	0.029
n-butane	0.099	toluene	0.061
2-methylbutane	0.070	m-xylene	0.069
n-pentane	0.037	p-ethyltoluene	0.025
2-methylpentane	0.044	1,2,4-trimethylbenzene	0.013
ethylene	0.162		

Effect of products of photochemical reactions , (Comparison of Ozone Monitor Results for Low Loading Photochemical Experiment)

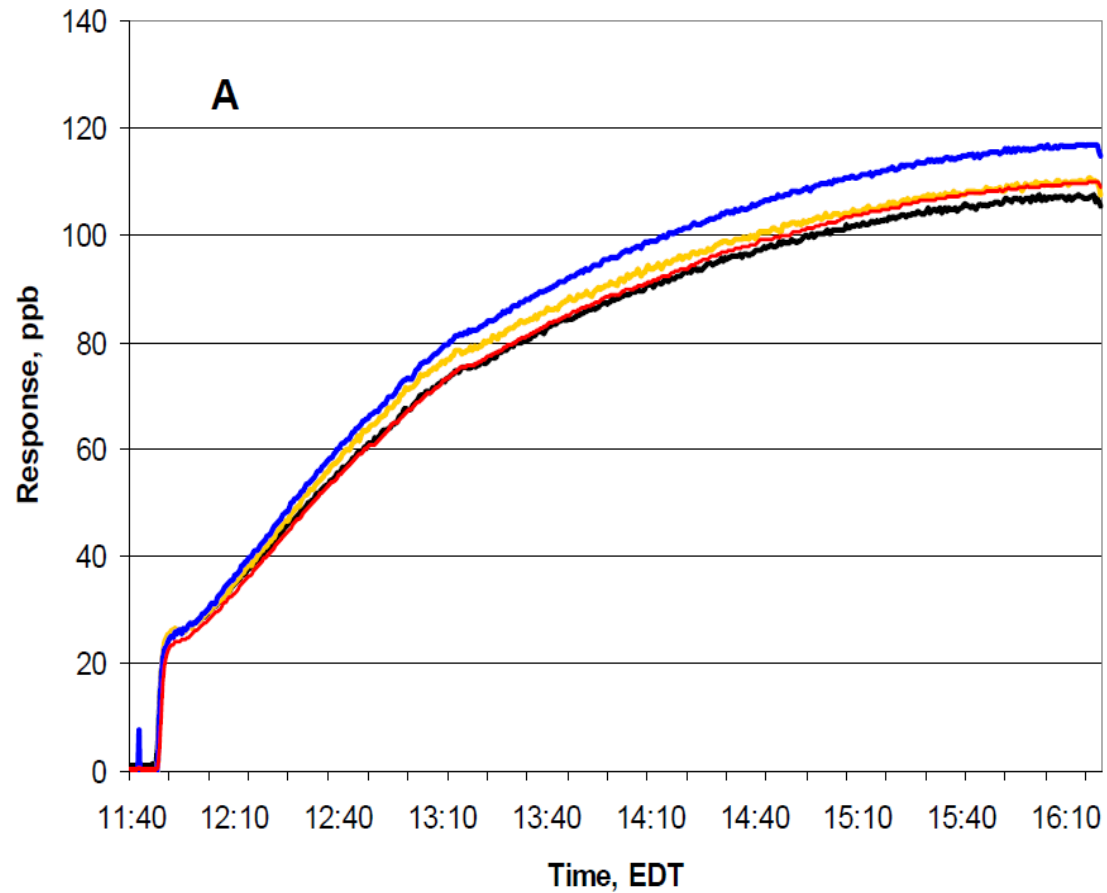


— G-Chem-N — G-Chem — UV-MnO2 — UV-HSW

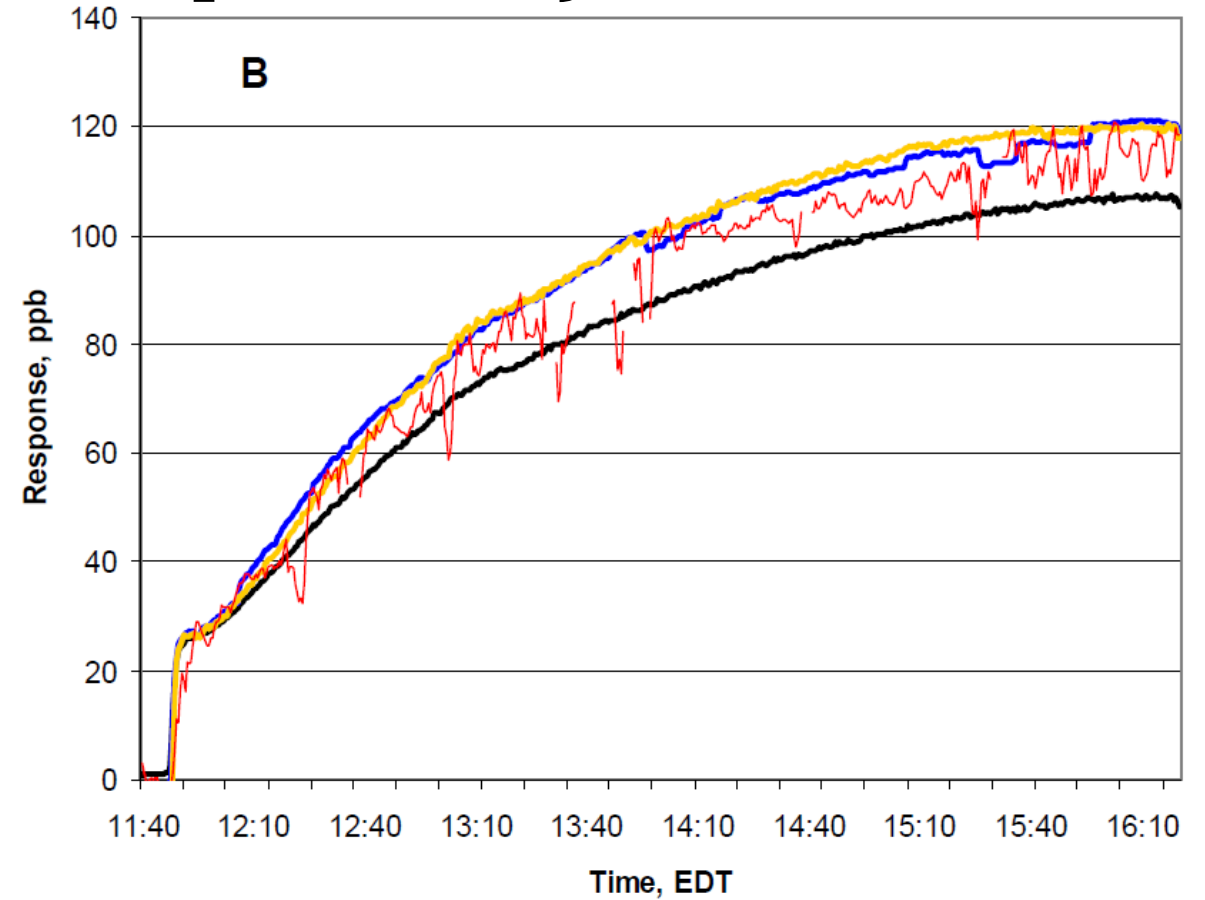


— UV-Hop-N — S-Chem-N — S-Chem — G-Chem-N

Effect of products of photochemical reactions, (Comparison of Ozone Monitor Results for High Loading Photochemical Experiment)

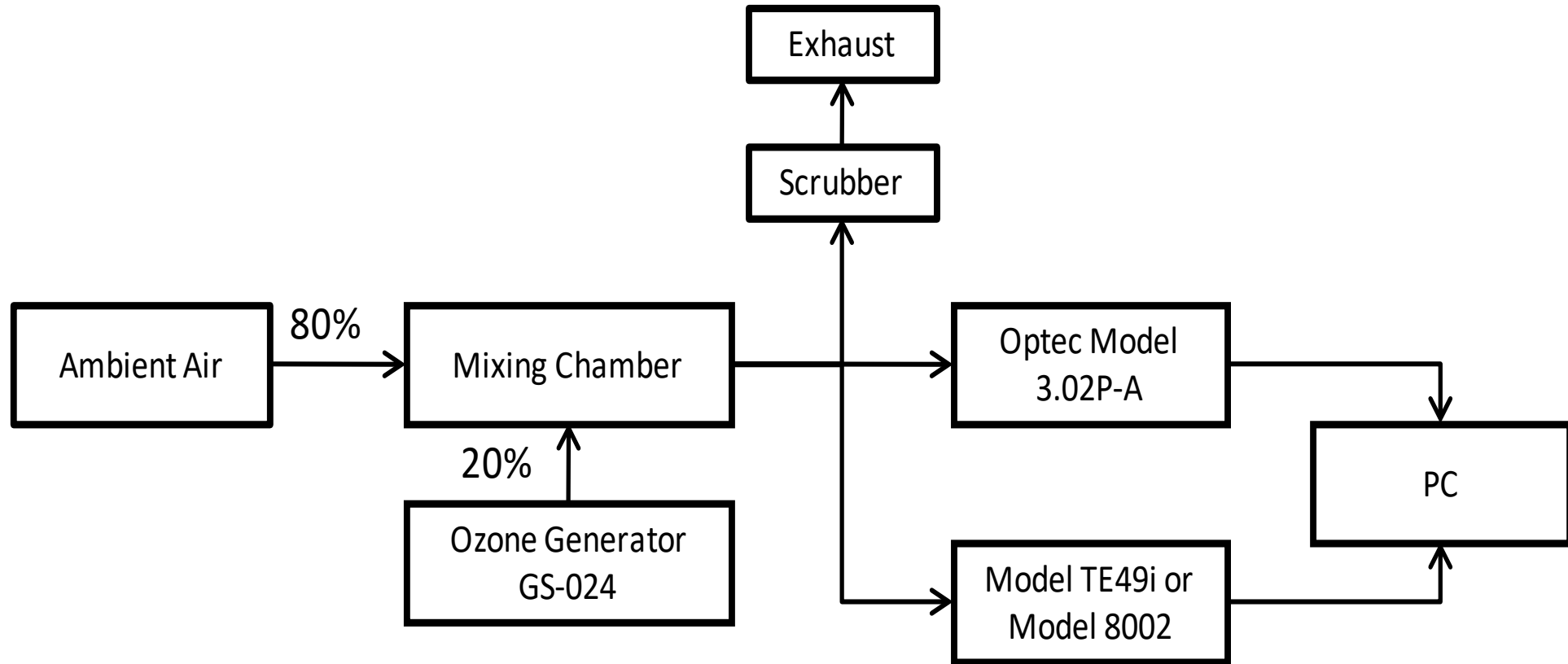


— G-Chem-N — G-Chem — UV-MnO2 — UV-HSW

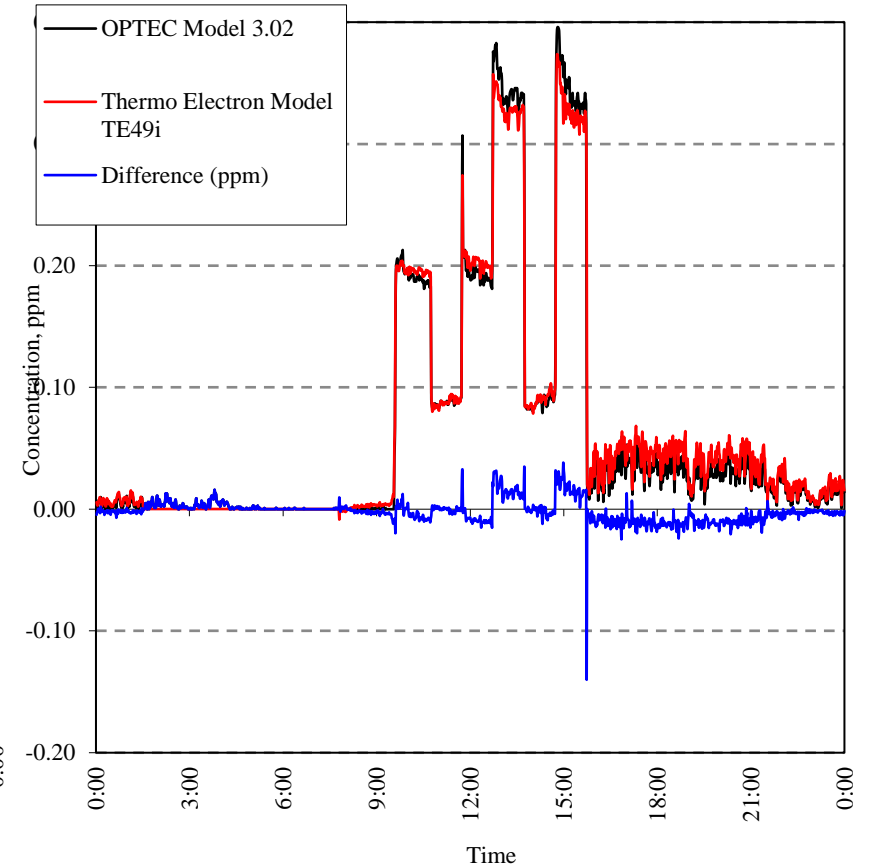
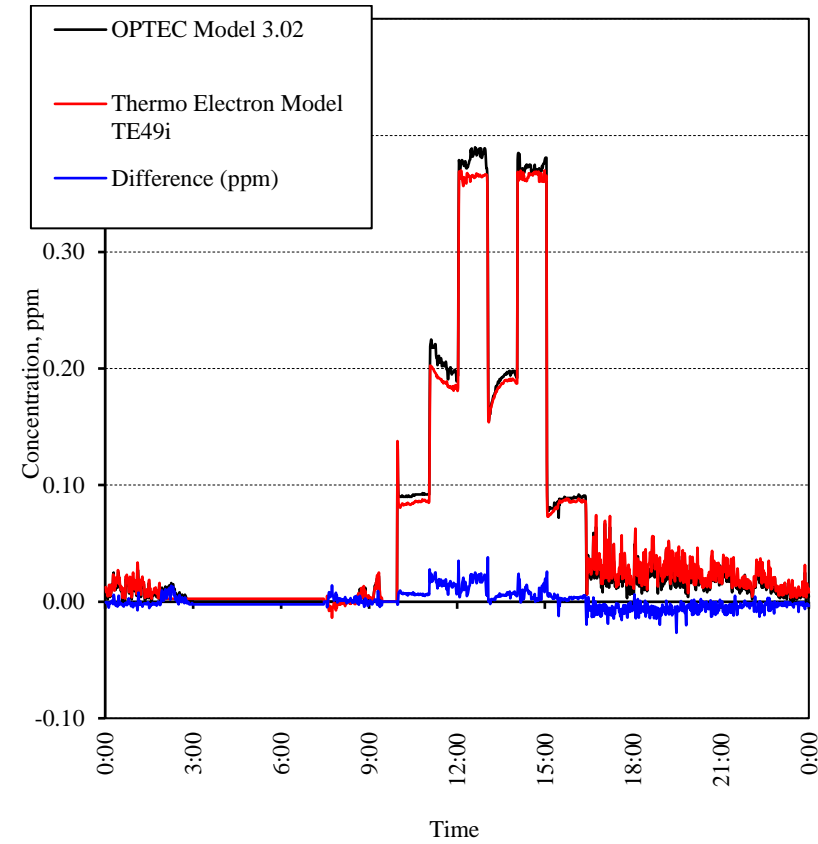
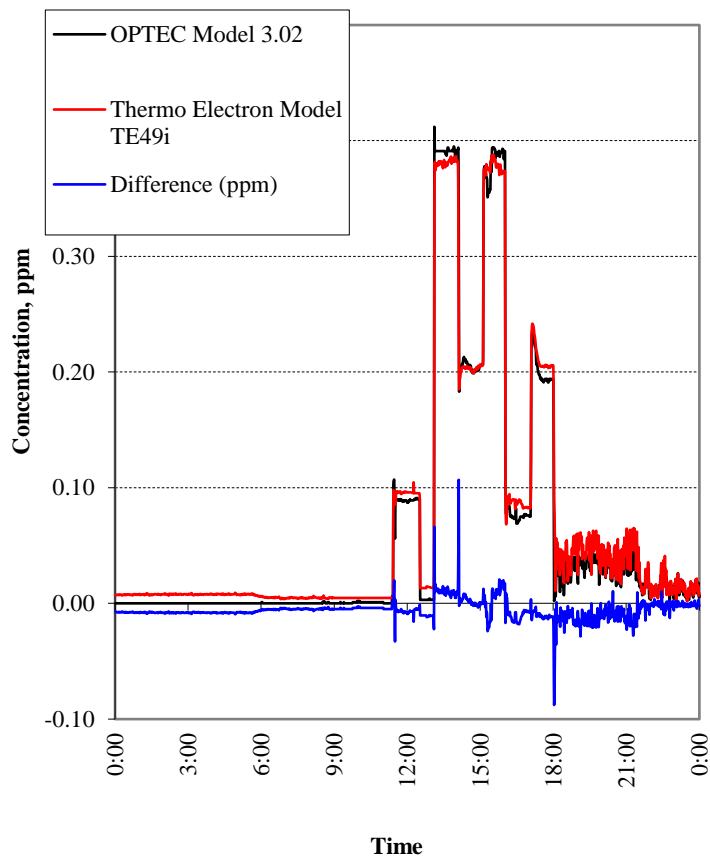


— G-Chem-N — S-Chem — S-Chem-N — UV-Hop-N

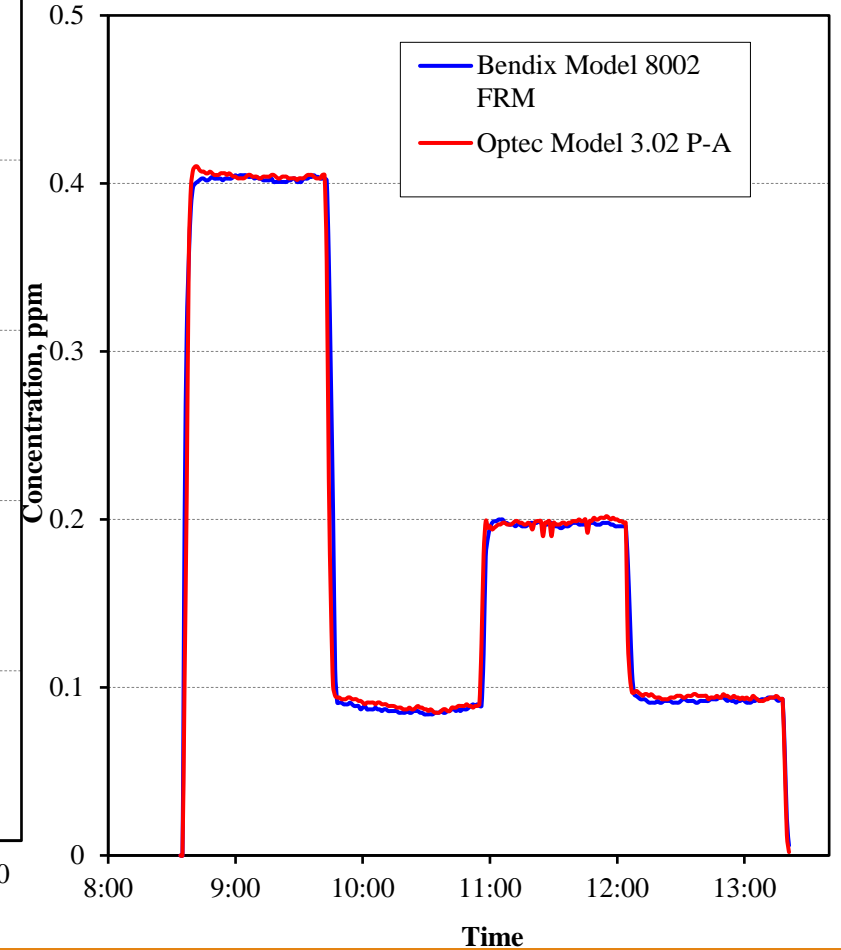
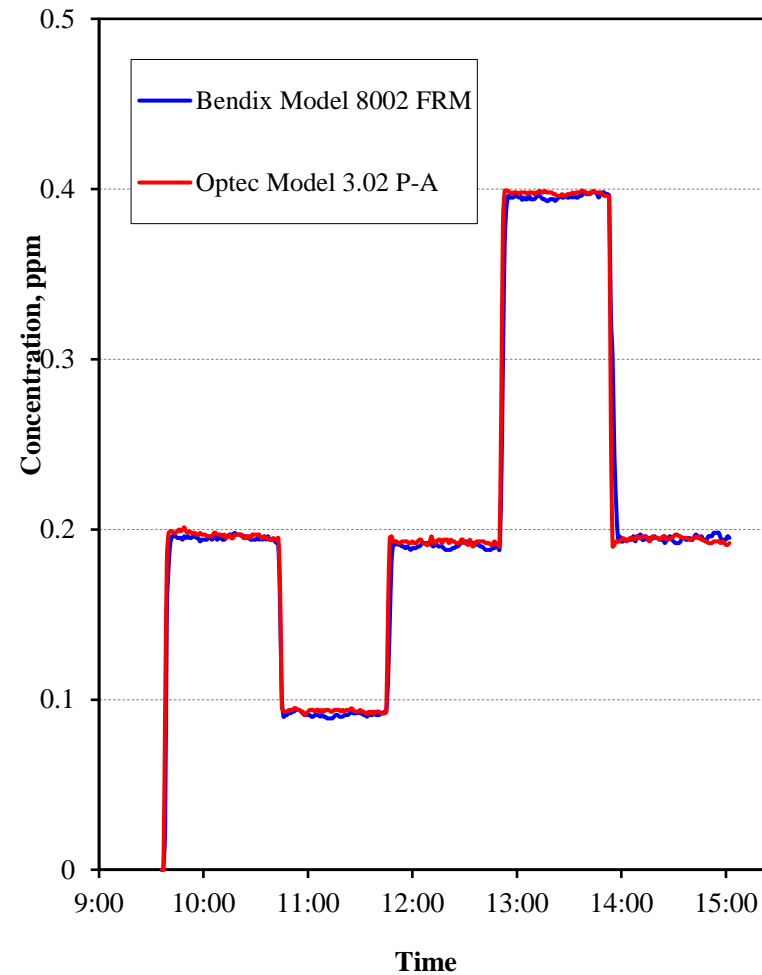
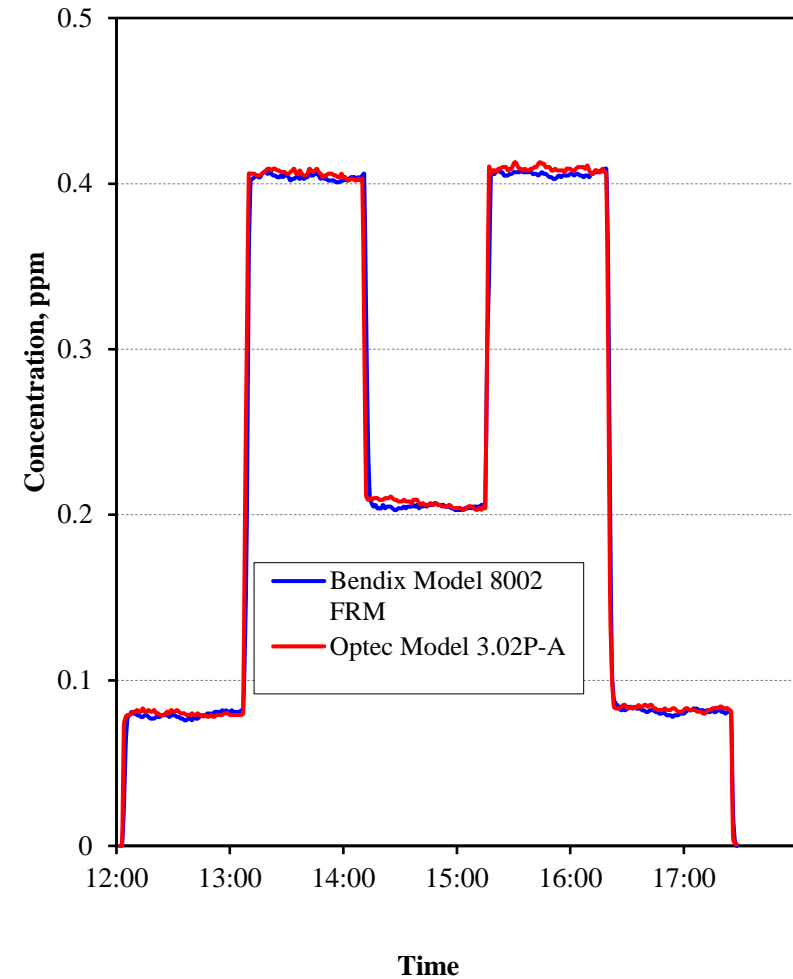
Illustration of testing configuration for comparability measurements of the Model 3.02P-A O₃ analyzer.



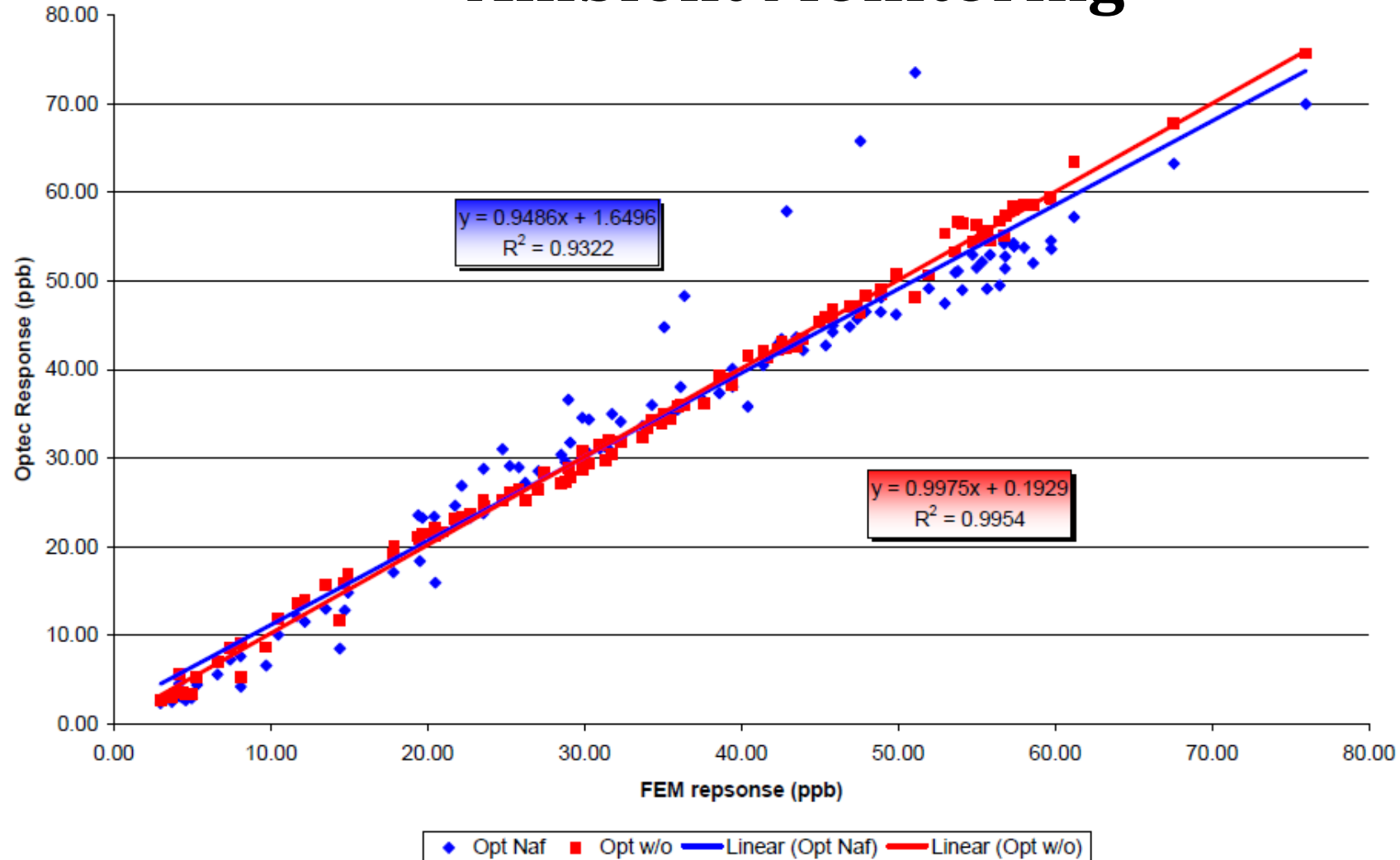
Results of the three days of comparability testing between the Optec Model 3.02 and the Thermo Electron Model TE49i.



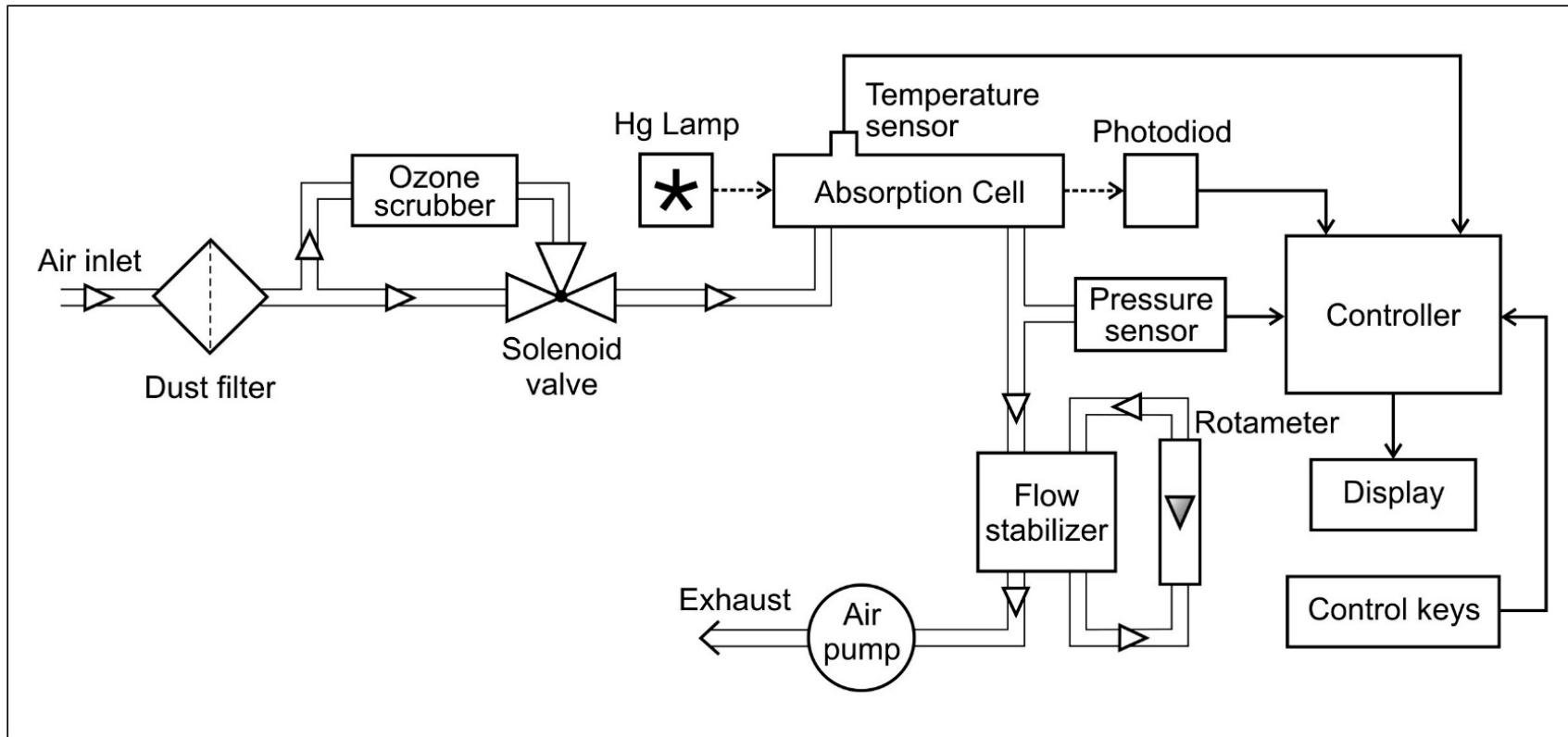
Results of the free day of comparability testing between the Optec Model 3.02 and the Bendix Model 8002 FRM.



Linear Regression of 3.02 P-A and FEM Data During Ambient Monitoring



Schematic diagram of the ozone monitor Optical UV photometer mod. F-105



Technical data of the Analyzer of ozone f-105

Measurement ranges of mass concentration (volume fraction) of ozone mg / m ³ (ppm)	Subranges measurements mg / m ³ (ppm)	Limits of permissible basic error	
		absolute, Δ , mg / m ³ (ppm)	relative, δ ,%
0 – 0,1 (0 – 0,05)	0 – 0,1 (0 – 0,05)	$\pm 0,02$ ($\pm 0,01$)	–
	0,1 – 1,0 (0,05 – 0,5)	$\pm [0,00111 + 0,089C_x^*]$ ($\pm [0,0056 + 0,089C_x^*]$)	–
0,5 – 10,0 (0,25 – 5,0)	CB. 1 – 10,0 (CB. 0,5 – 5,0)	–	± 10

* measured value of mass or volume concentration

At present, 682 ozone analyzers have been produced and are in operation on the territory of the Russian Federation, including chemiluminescent analyzers mod.3.02P-A -609 pieces, ozone analyzers UV-photometers mod.F-105 - 73 pieces.

Thank you for your attention