EPA
United States
Environmental Protection
Agency

Evaluation and Proposal of a New Federal Reference Method for Ozone: Nitric Oxide-Chemiluminescence

Briefing for NACAA

Russell Long

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory

Ozone FRM

United States Environmental Protection Agency

- Federal Reference Methods (FRMs), are set forth in 40 CFR Part 50
  - Provide a specified, definitive methodology for measuring concentrations of criteria ambient air pollutants for comparison to the NAAQS
  - Provide a standard of comparison for determining equivalent methods (FEMs) to the specified reference method that can be used in lieu of the FRM for routine regulatory monitoring
- The FRM for measuring ozone (O_3) in the atmosphere, based upon ethylene-chemiluminescence (ET-CL), was promulgated on April 30, 1971 and later revised on February 8, 1979
  - The ozone FRM is a technically advantageous method
    - Meets performance specifications
    - Free of interferences
  - The ozone FRM is no longer being used for monitoring compliance to the ozone NAAQS due to it no longer being available commercially nor being technically supported by instrument manufacturers = obsolete
- The obsolete status of the existing ozone FRM has resulted in a critical need for ORD to identify, evaluate and propose a new FRM for ozone in the atmosphere capable of satisfying the primary purposes of an FRM

Ozone FRM Research

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Approach

- Emphasis placed on existing Federal Equivalent Methods (FEMs)
  - Methods have already undergone 40 CFR Part 53 performance testing
  - Reviewed and designated by EPA for use in regulatory monitoring
- Other (non FEM) methods also considered
- Comprehensive laboratory evaluations of candidate FRM's
  - Performance specifications of candidate methods determined under controlled laboratory conditions per 40 CFR Part 53 requirements
    - Range
    - Noise
    - Lower detectible limit (LDL)
    - Interference equivalent (IE)
    - Drift (zero and span)
    - Lag time, rise time, fall time
- Ambient evaluations/comparisons of candidate methods
  - July 2011 – Baltimore, MD
  - June-August 2012 – RTP, NC
  - September 2013 – Houston, TX
  - April-June 2014 – RTP, NC
  - July-August 2014 – Denver, CO

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Manufacturer and Model (Abbreviation)	Operation Principle	FRM/FEM Designation No.	Laboratory Testing	Field Deployment
Bendix Model 8002 (Bendix 8002)	Ethylene-Chemiluminescence (ET-CL)	RFOA-0176-007	-	AIRS 2012 and 2014; Houston 2013; Denver 2014
Teledyne API Model T265 (T265)	NO-Chemiluminescence (NO-CL)	EQOA-0611-199	EPA May-July 2013	Baltimore 2011; AIRS 2012 and 2014; Houston 2013; Denver 2014
2B Technologies Model 211 (2B 211)	"Scrubberless" UV Photometric (SL-UV)	EQOA-0514-215	EPA May-July 2013	Houston 2013; AIRS 2014; Denver 2014
2B Technologies Model 205 (2B 205)	UV Photometric (UV-Drier)	EQOA-1410-190	EPA May-July 2013	AIRS 2012 and 2014; Houston 2013
Ecotech Model EC9810 (EC 9810)	UV Photometric (UV-Drier)	EQOA-0193-091	-	Baltimore 2011
Thermo Scientific Model 49i (49i)	UV Photometric (UV)	EQOA-0880-047	EPA May-July 2013	AIRS 2012; Houston 2013

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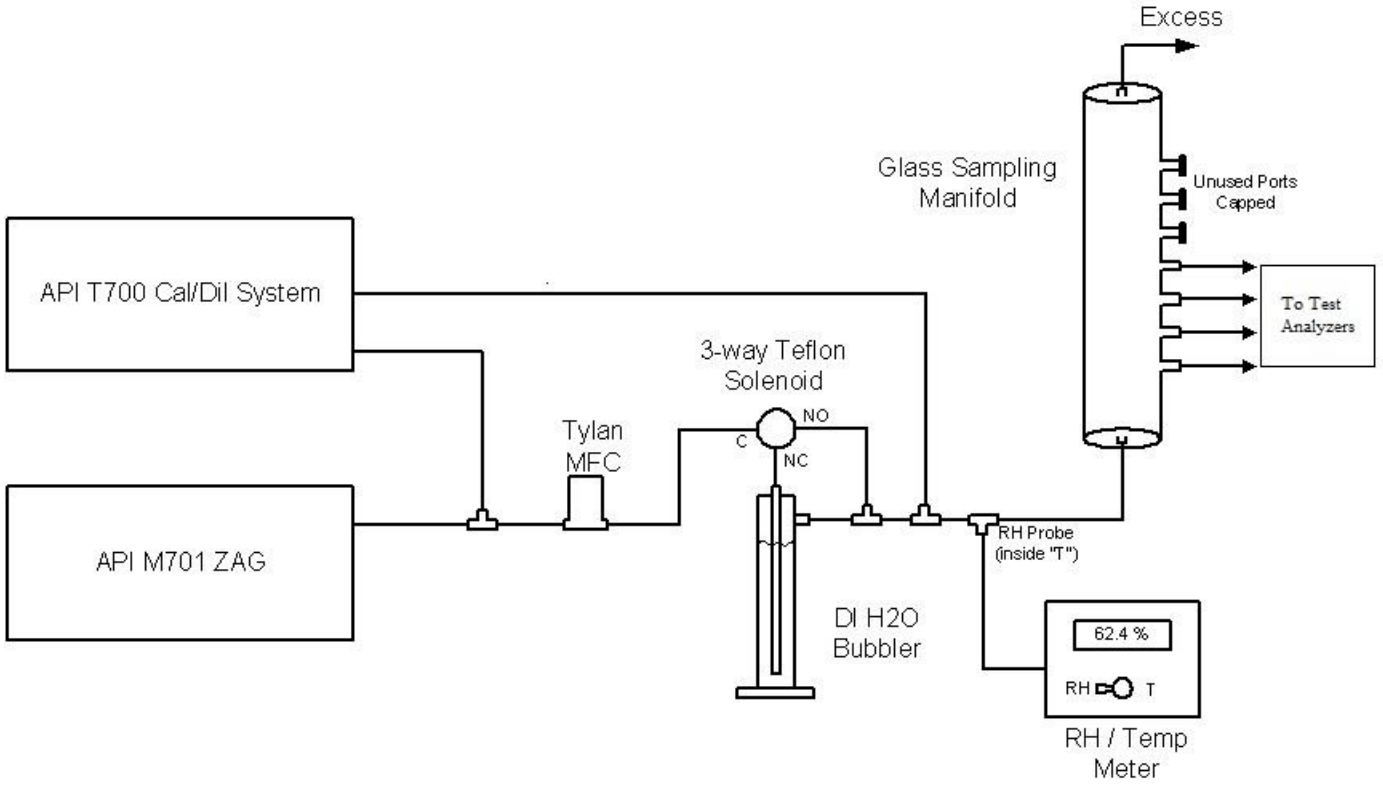
Laboratory Evaluations



Apparatus for performing laboratory based evaluations of candidate FRMs

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Laboratory Evaluations

	Units	Part 53 Specification	T265 (NO-CL)	Bendix 8002 FRM (ET-CL)
Range	ppb	0-500[b,c]	0-100[a] 0-1000[a]	0-500[a]
Noise (S_0) Noise (S_{80})	ppb ppb	5[b], 1[c] 5[b], 1[c]	0.064 0.433	NA NA
LDL	ppb	10[b], 3[c]	0.6[a]	NA
Interference Equivalent • Water Vapor • H_2S • CO_2	 ppb ppb ppb	60 (total)[b] ±20[b], ±5[c] ±20[b], ±5[c] ±20[b], ±5[c]	 0.02 0.001 -0.1	 0.02 NA 0.11
Zero Drift Span Drift (80% URL)	ppb %	±20[b], ±4[c] ±5[b], ±3[c]	0.036 0.3	NA NA
Lag Time	minutes	20[b], 2[c]	<1	NA
Rise Time	minutes	15[b], 2[c]	<1	NA
Fall Time	minutes	15[b], 2[c]	<1	NA

[a] As designated or published by instrument manufacturer
[b] Current 40 CFR Part 53 specifications
[c] Proposed 40 CFR Part 53 specifications

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Laboratory Evaluations

	Units	Part 53 Specification	49i (UV)	2B 205 (UV-Drier)	2B 211 (SL-UV)
)Range	ppb	0-500[b,c]	0-500[a] 0-1000[a]	0-500[a]	0-2000[a]
Noise (S_0) Noise (S_{80})	ppb ppb	5[b], 1[c] 5[b], 1[c]	0.155 0.350	0.473 0.602	0.310 0.479
LDL	ppb	10[b], 3[c]	1[a]	2[a]	1[a]
Interference Equivalent • Water Vapor • H_2S • CO_2	 ppb ppb ppb	60 (total)[b] ±20[b], ±5[c] ±20[b], ±5[c] ±20[b], ±5[c]	 1.626 -0.042 -0.23	 0.765 -0.082 -0.09	 0.209 0.01 0.03
Zero Drift Span Drift (80% URL)	ppb %	±20[b], ±4[c] ±5[b], ±3[c]	0.109 -0.3	-0.427 -0.2	0.082 -0.1
Lag Time	minutes	20[b], 2[c]	<1	<1	<1
Rise Time	minutes	15[b], 2[c]	<2	<1	<1
Fall Time	minutes	15[b], 2[c]	<2	<1	<1

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Nightly Span and Zero Results

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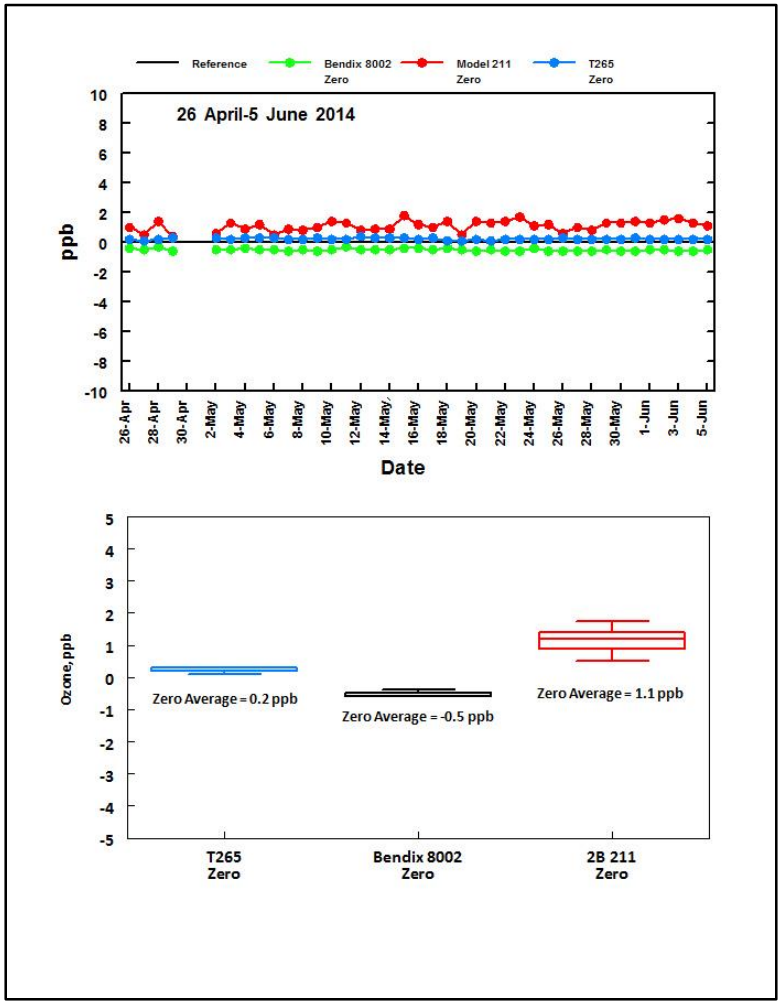

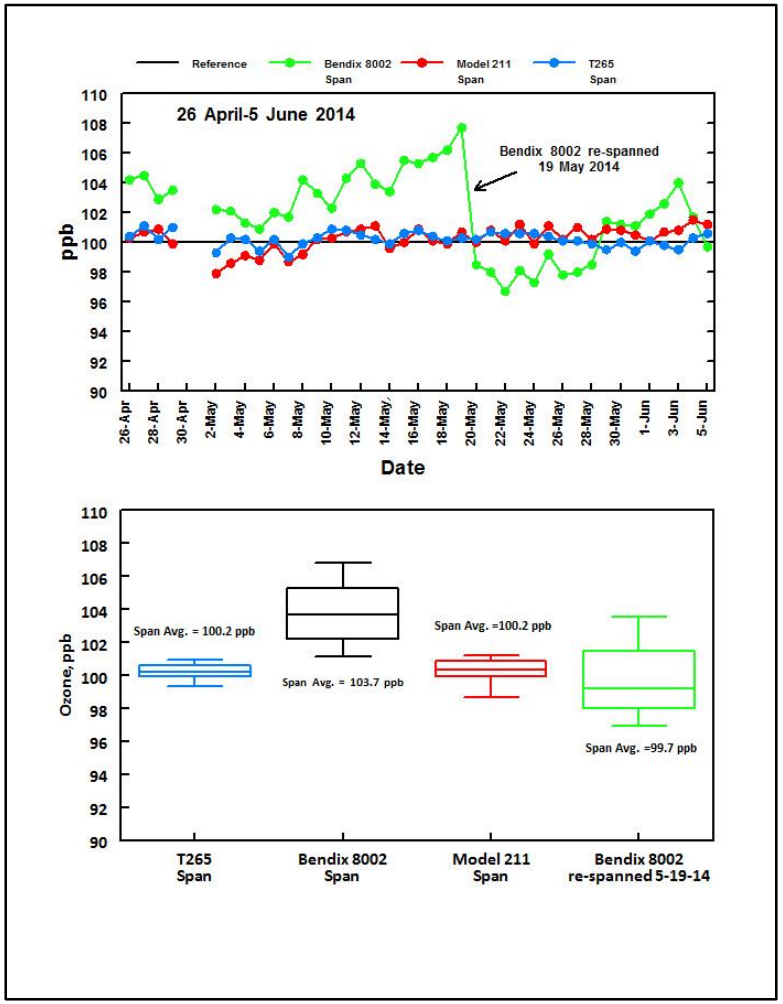

- During the ambient evaluation periods (AIRS RTP, NC Spring 2014 shown above), automated nightly zero and span checks were conducted.
- Ambient data correction factors were obtained (as needed) from analysis of the zero and span check data results.

Baltimore, MD
1-31 July 2011

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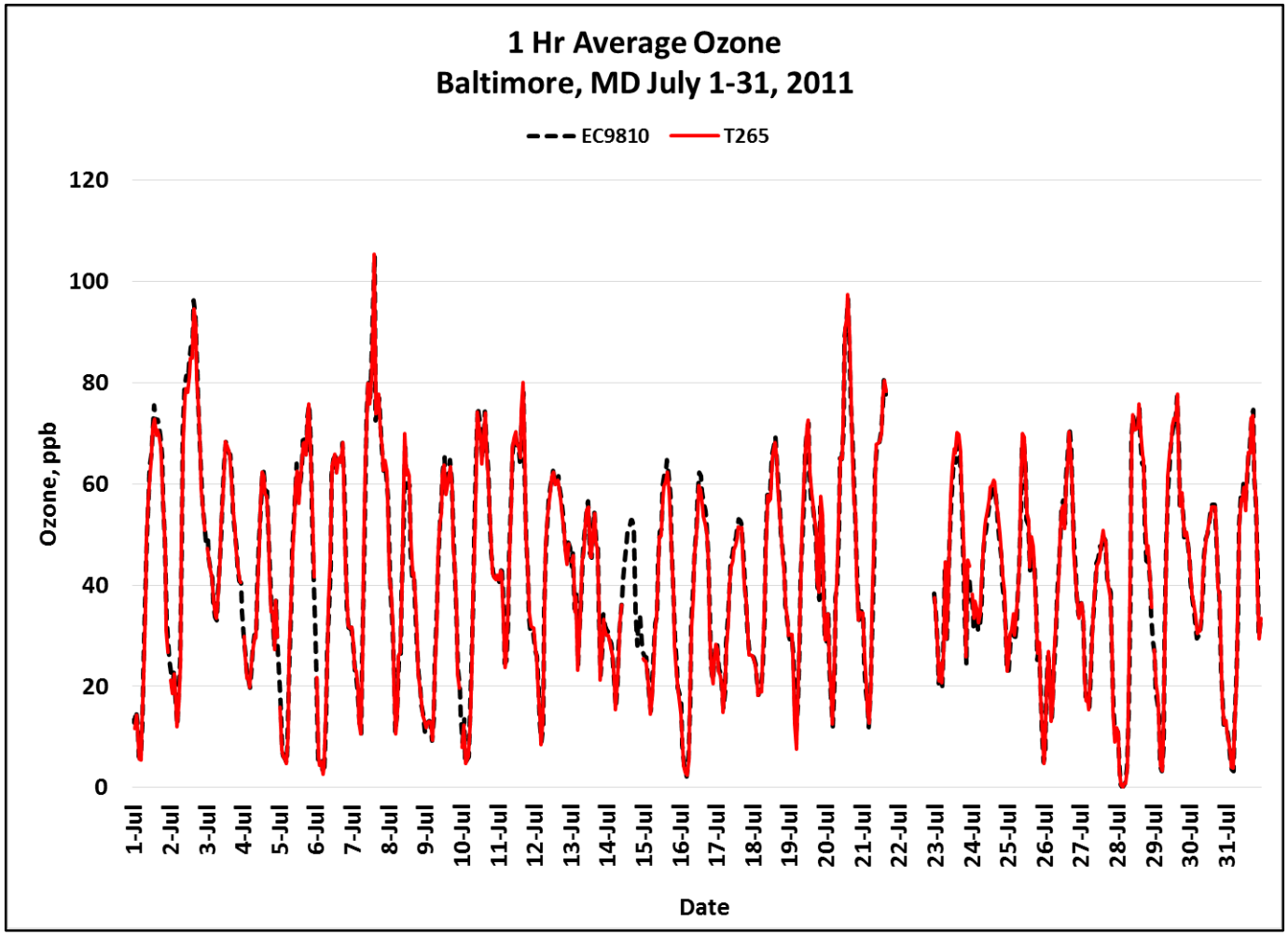

- **A very robust comparison was observed between the T265 (NO-CL) and the EC9810 (UV-Drier) methods for 1 Hr average and Maximum Daily Eight Hour Average (MDA8) ozone concentrations during the July 2011 Baltimore, MD evaluation.**

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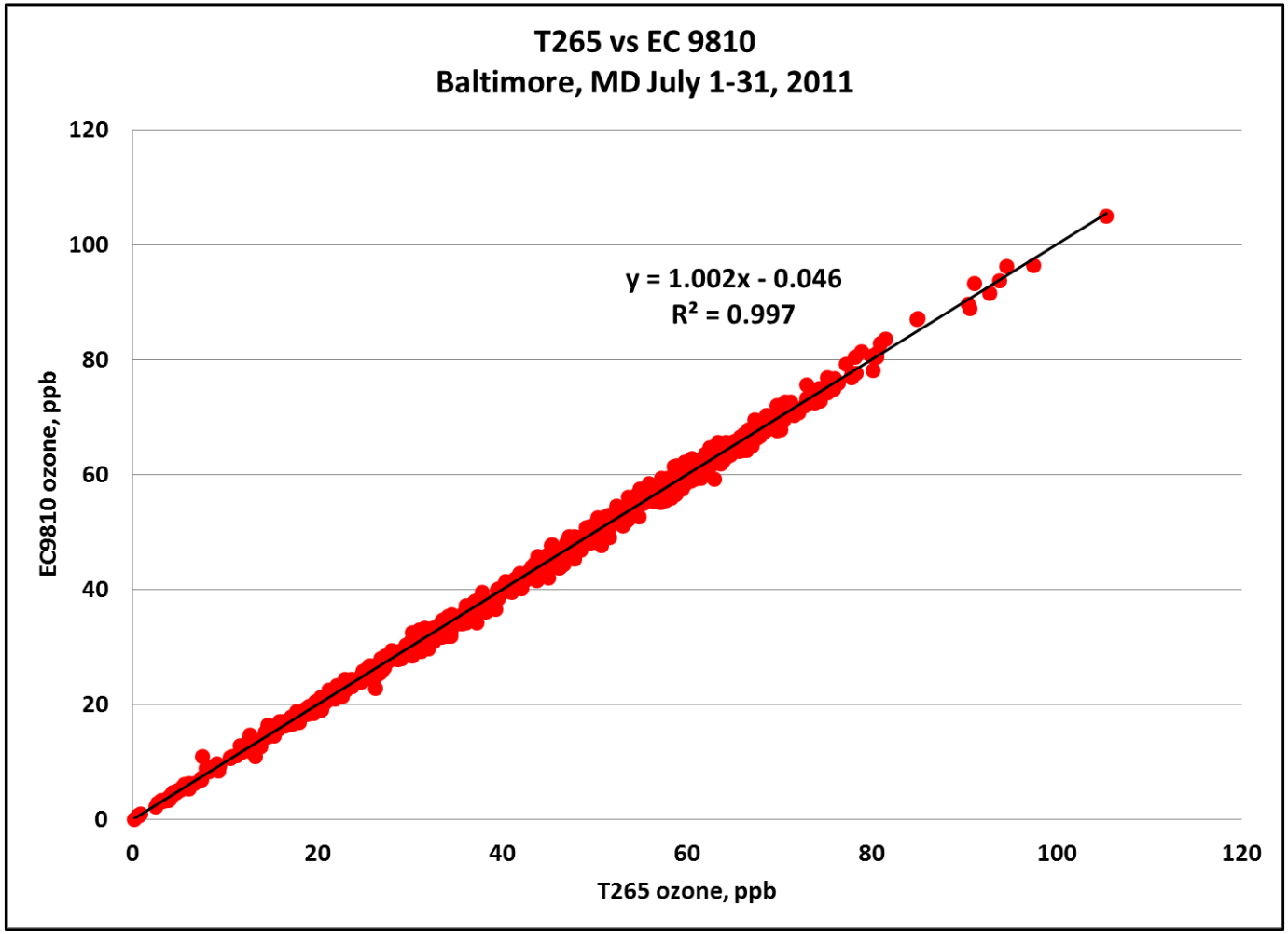

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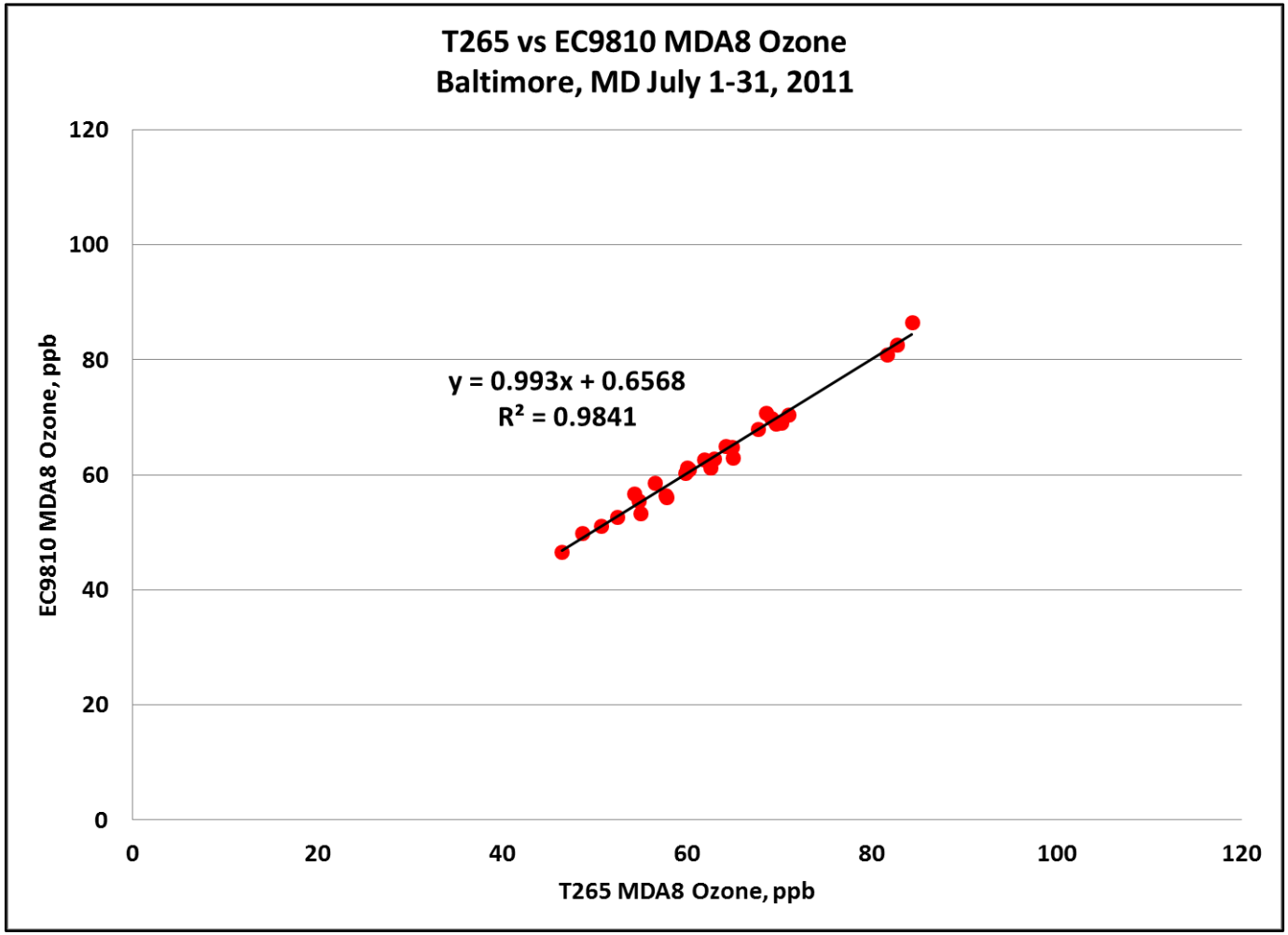

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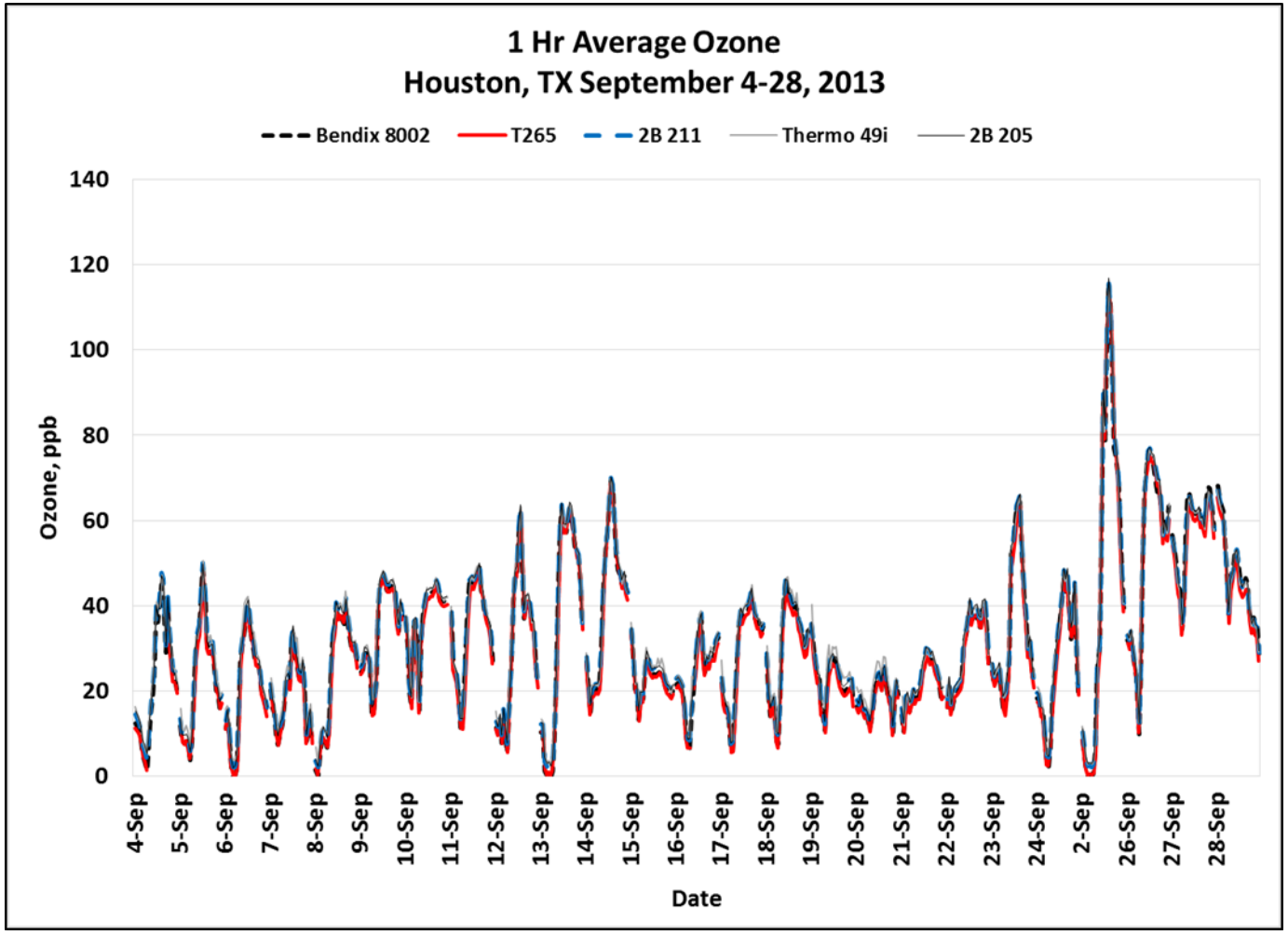
Houston, TX
04 – 28 September 2013



- **Excellent agreement was observed between the Bendix 8002 (ET-CL), the T265 (NO-CL), and the 2B 211 (SL-UV) for 1 Hr average and Maximum Daily Eight Hour Average (MDA8) ozone concentrations during the September 2013 Houston, TX evaluation.**
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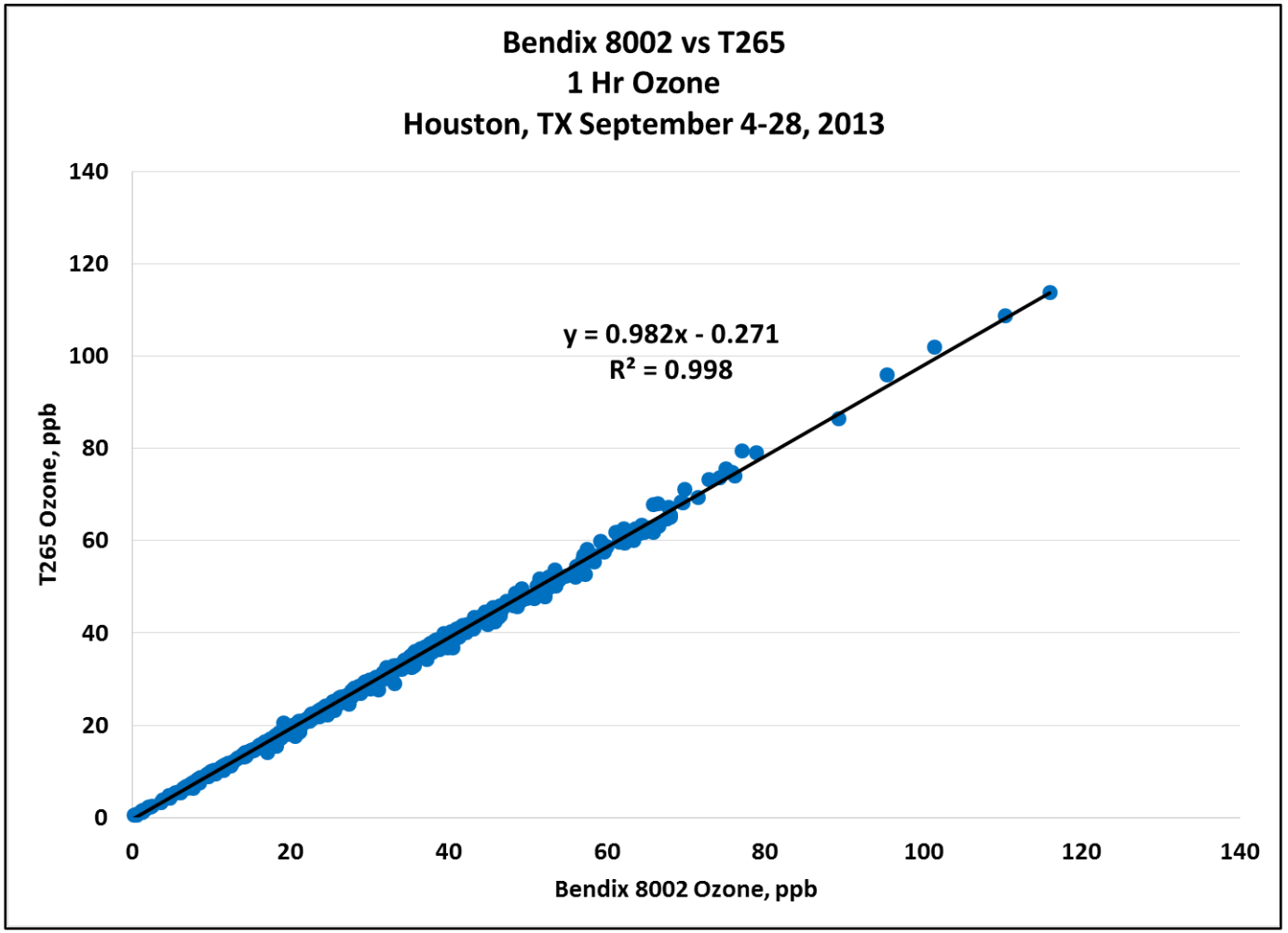

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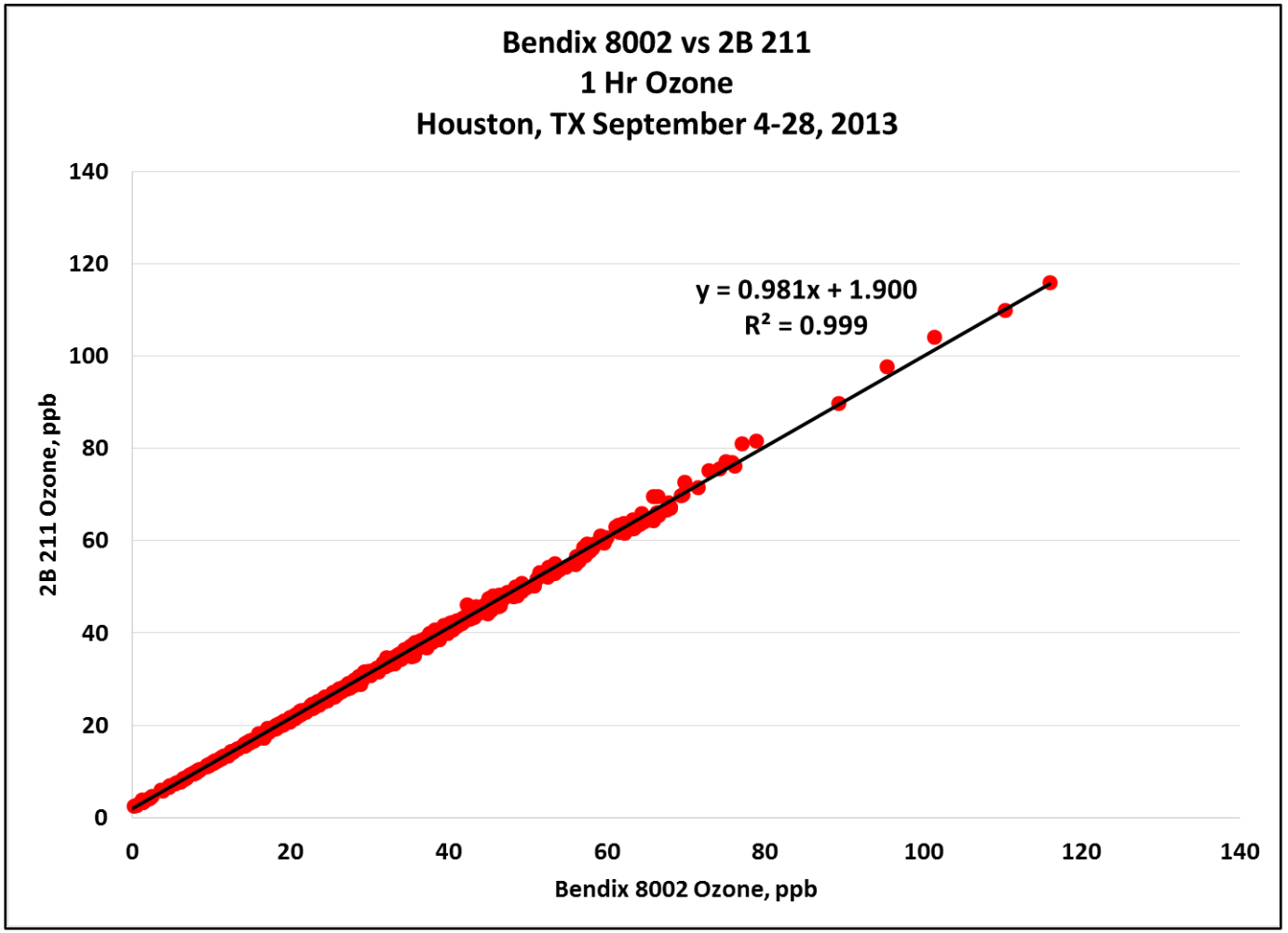

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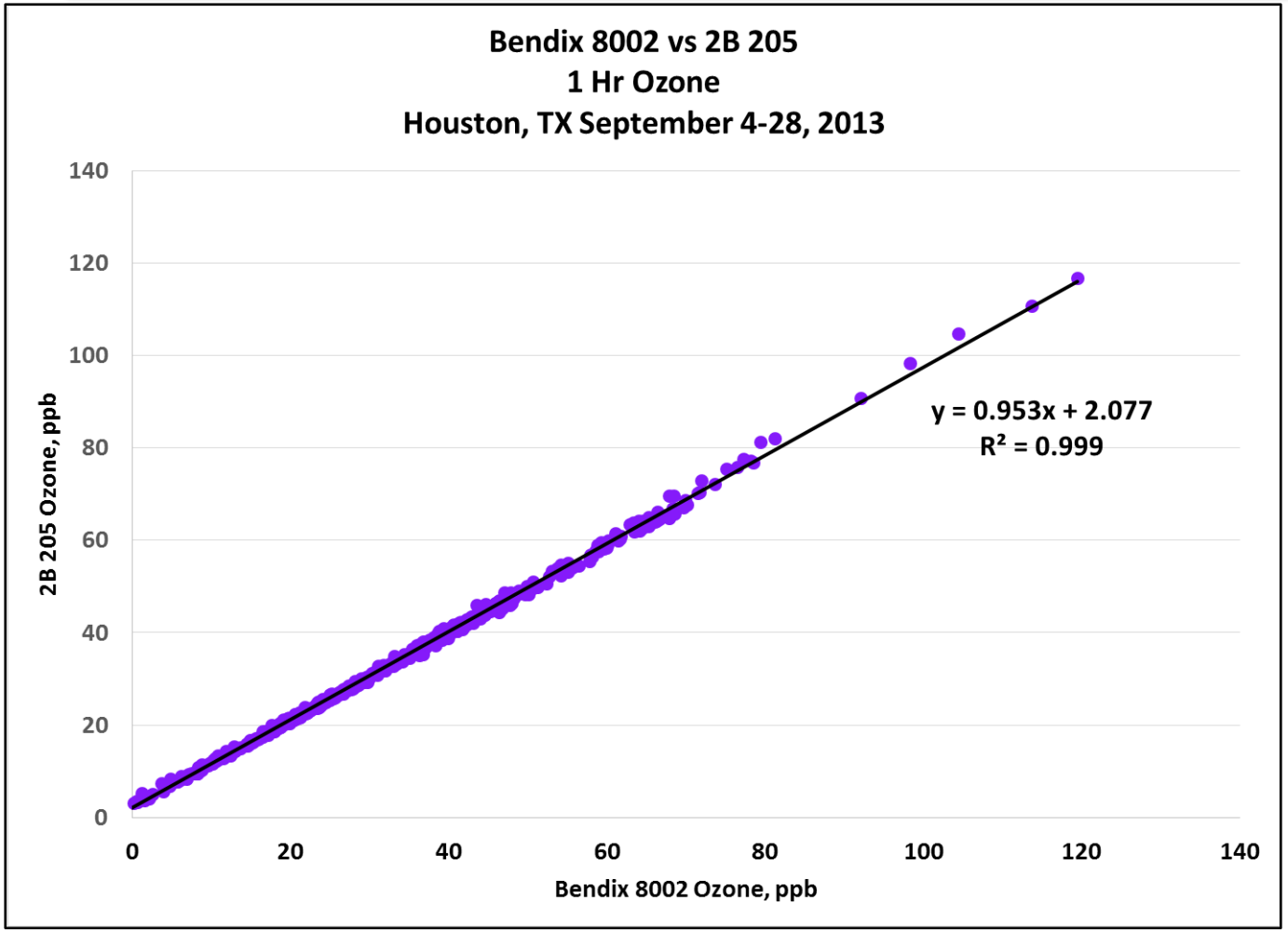

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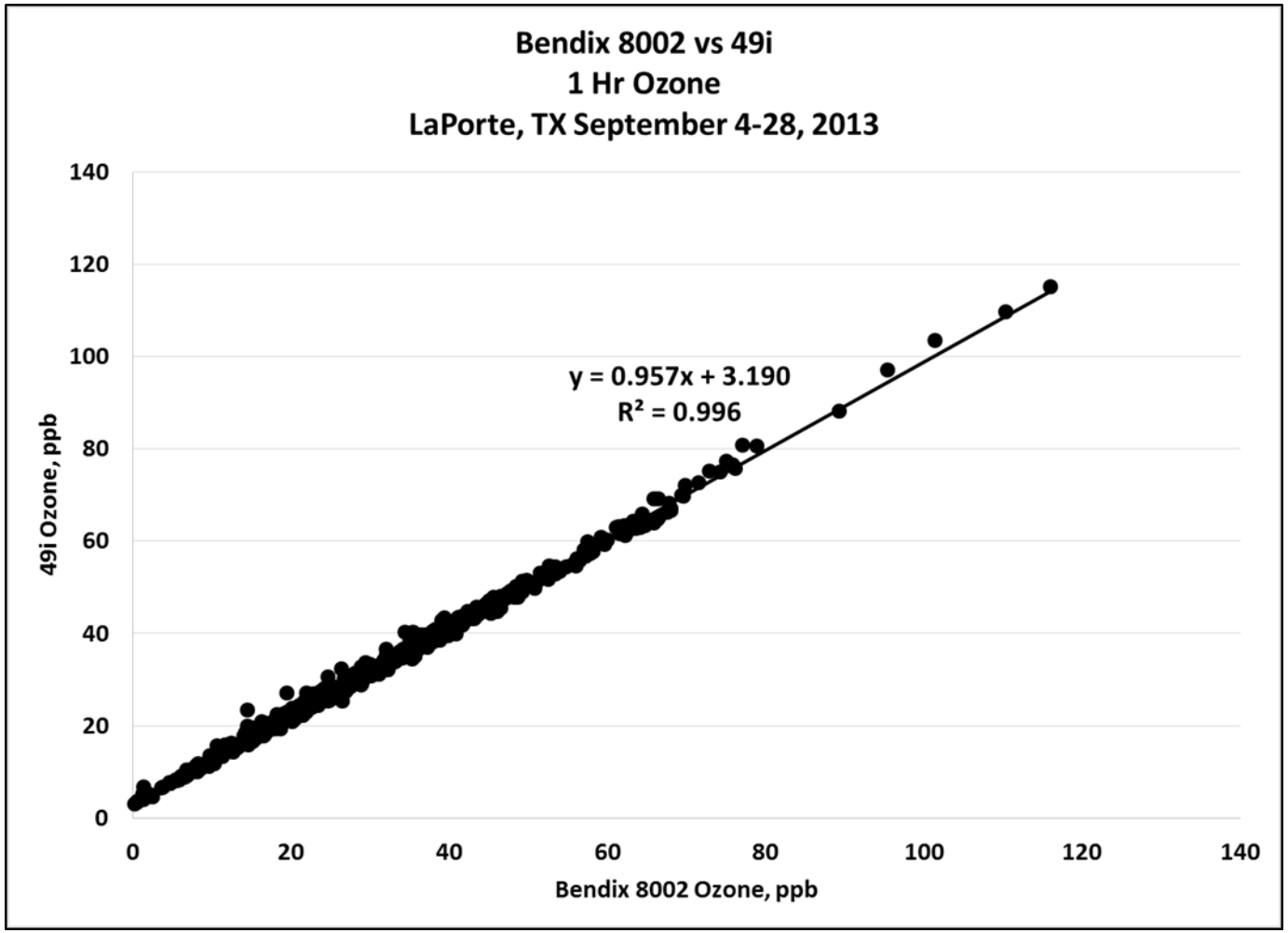

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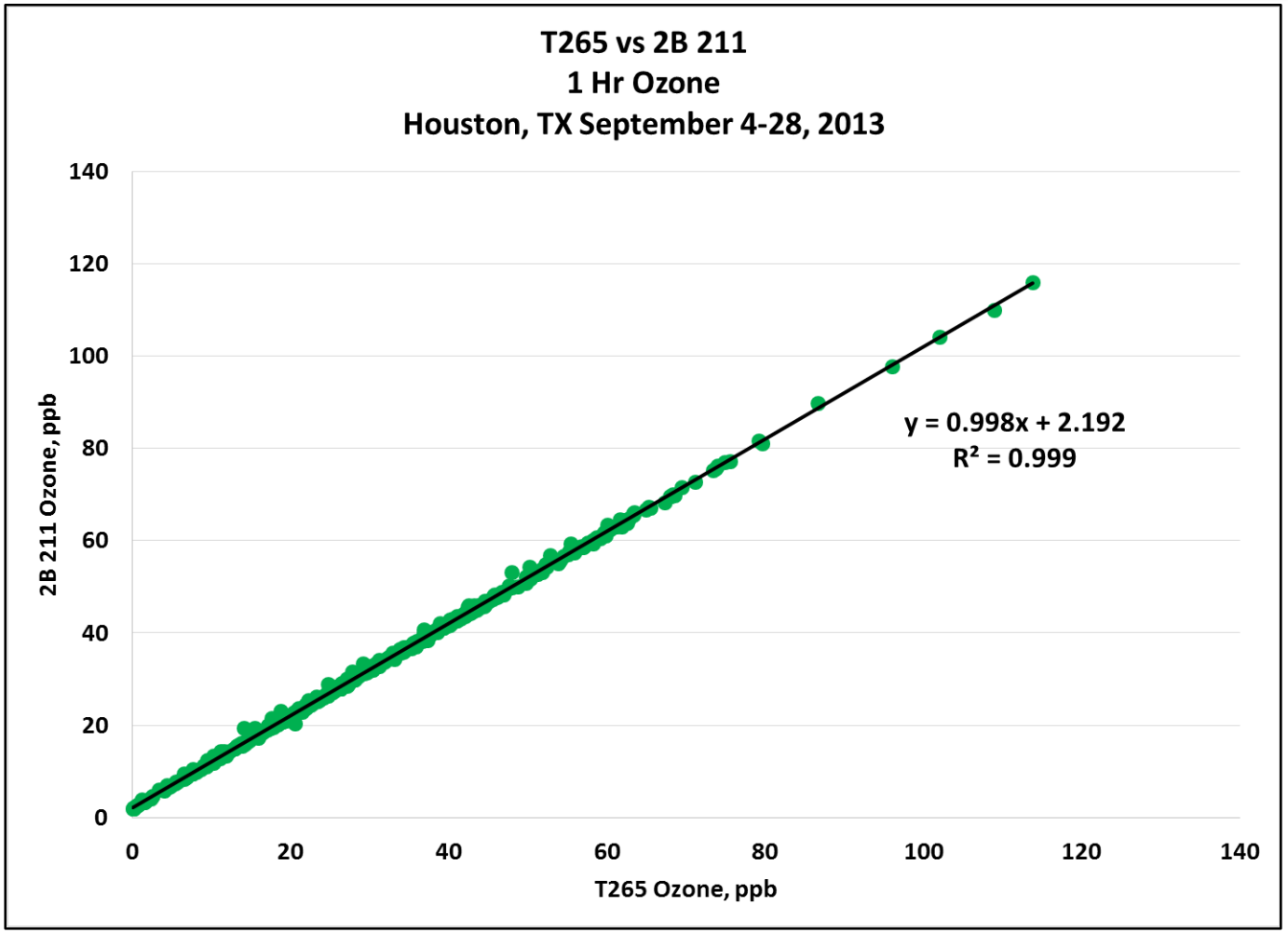

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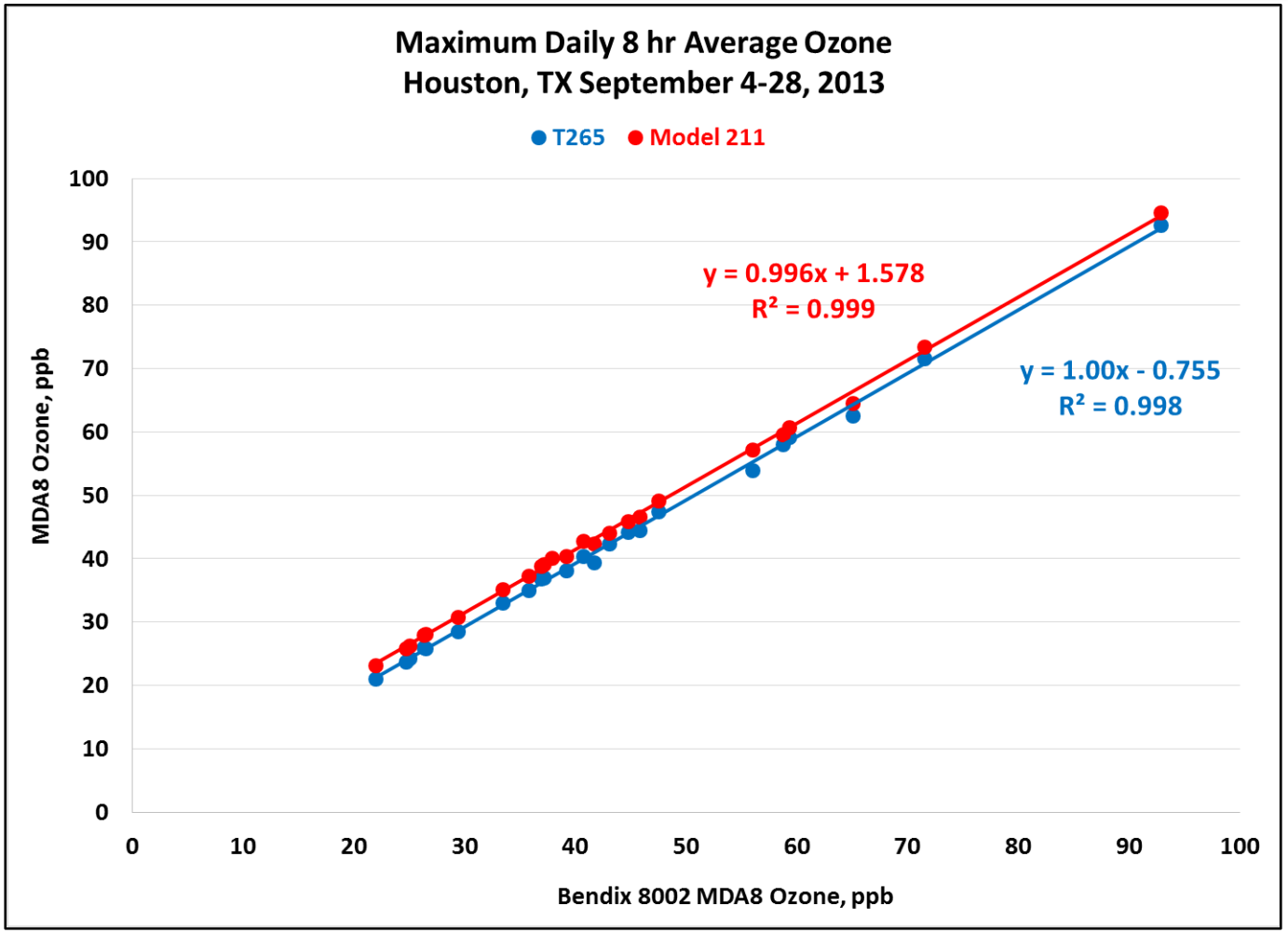

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Denver, CO
14 July – 12 August 2014

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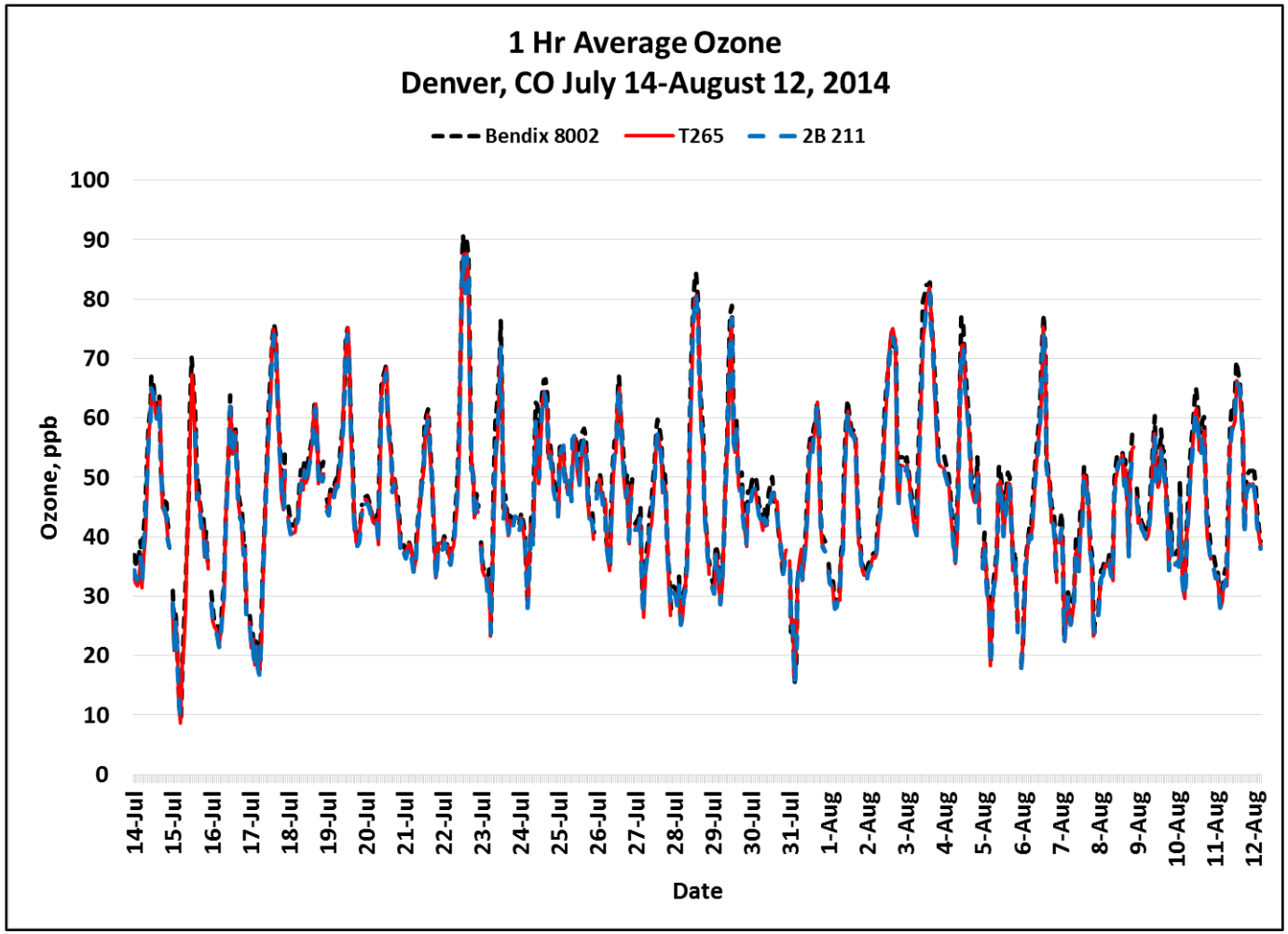

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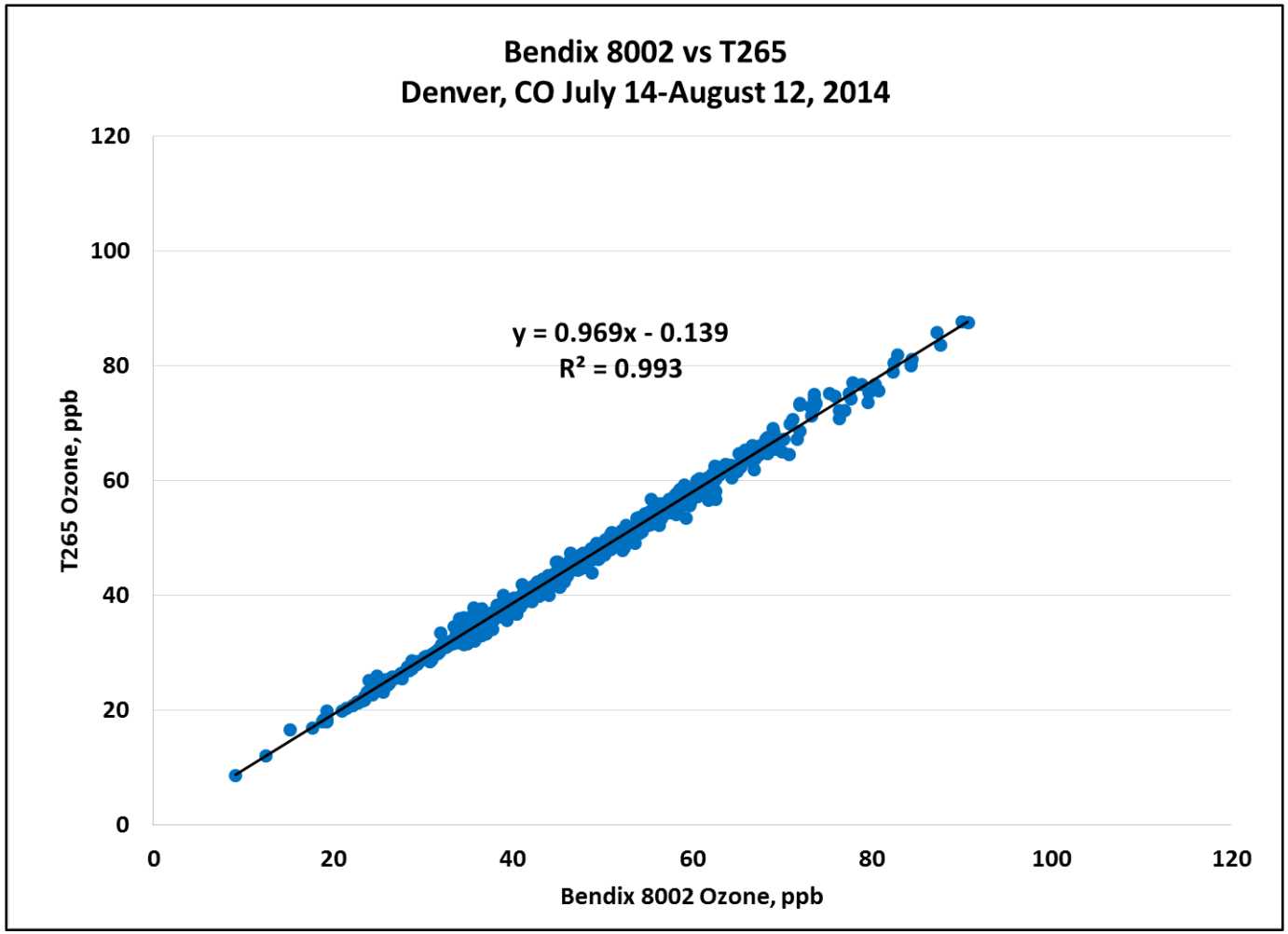

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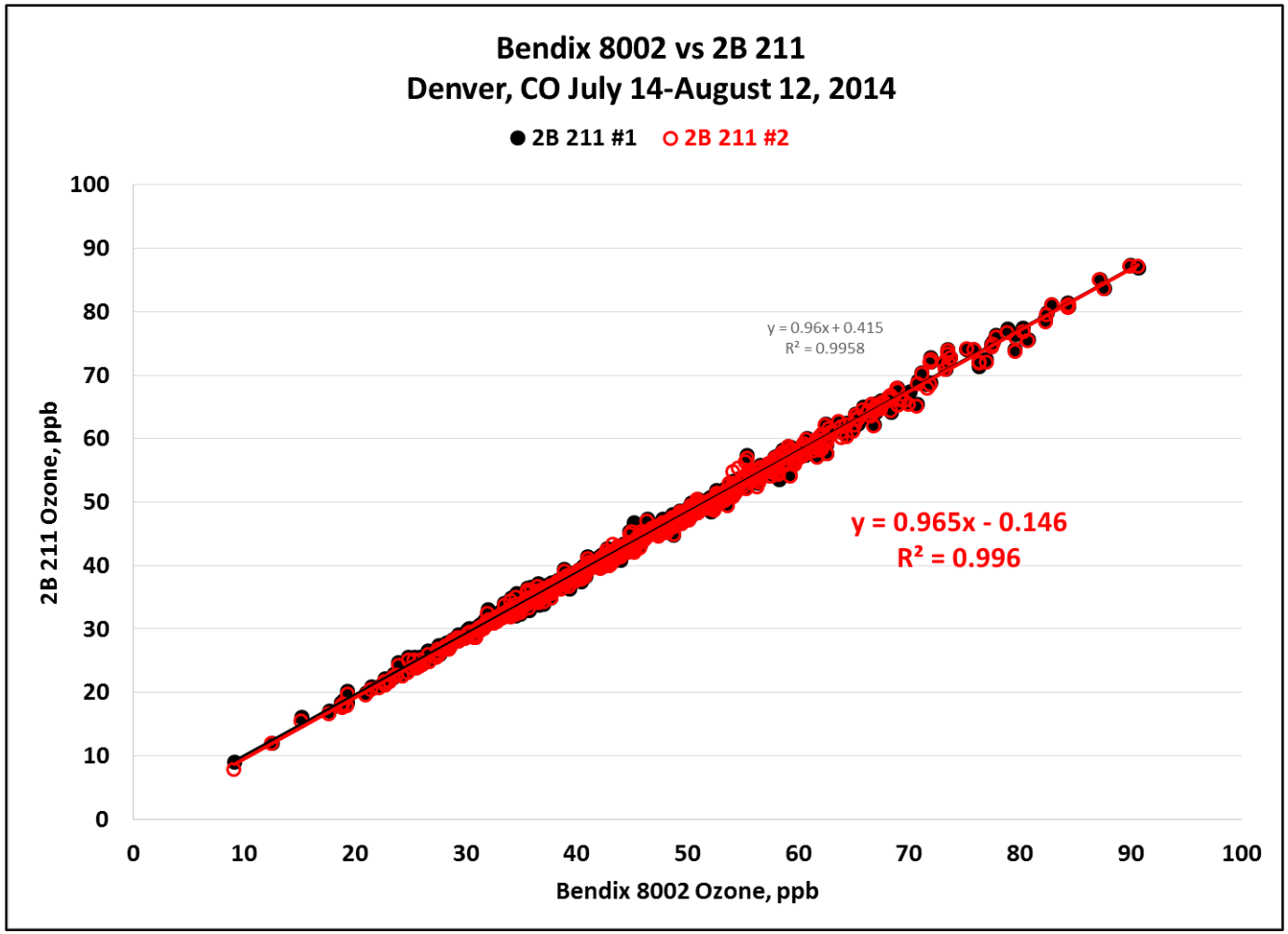

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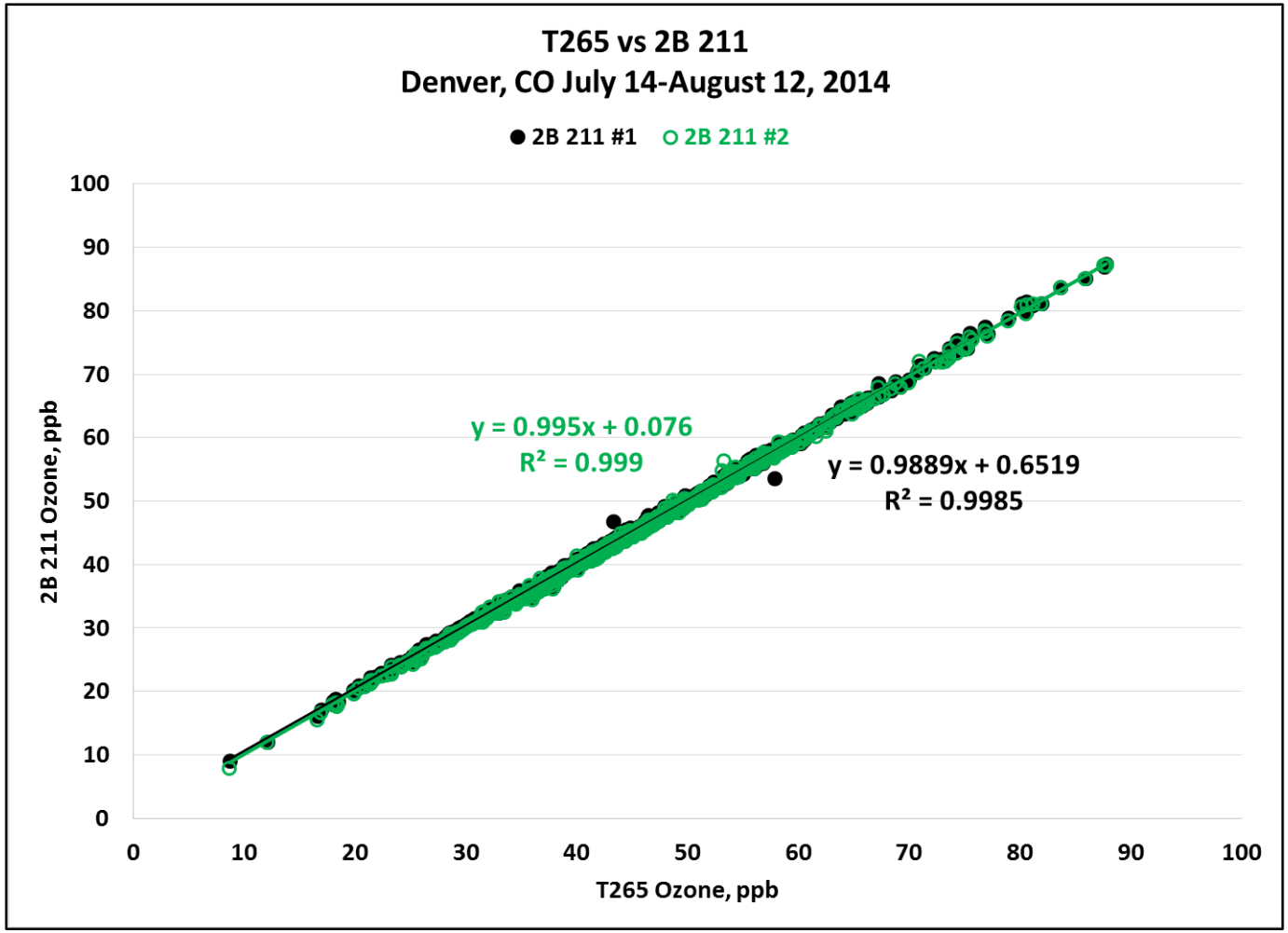

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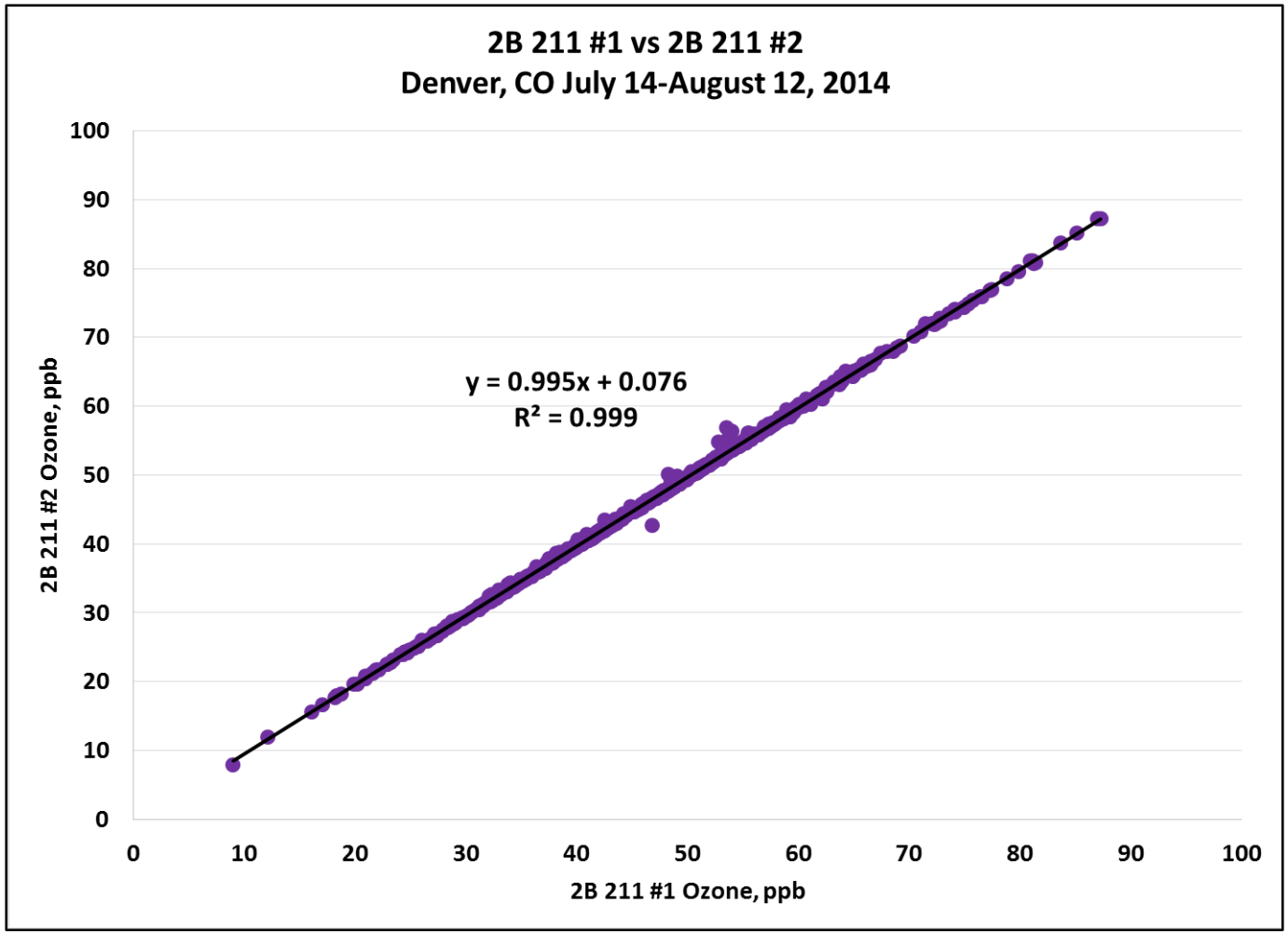

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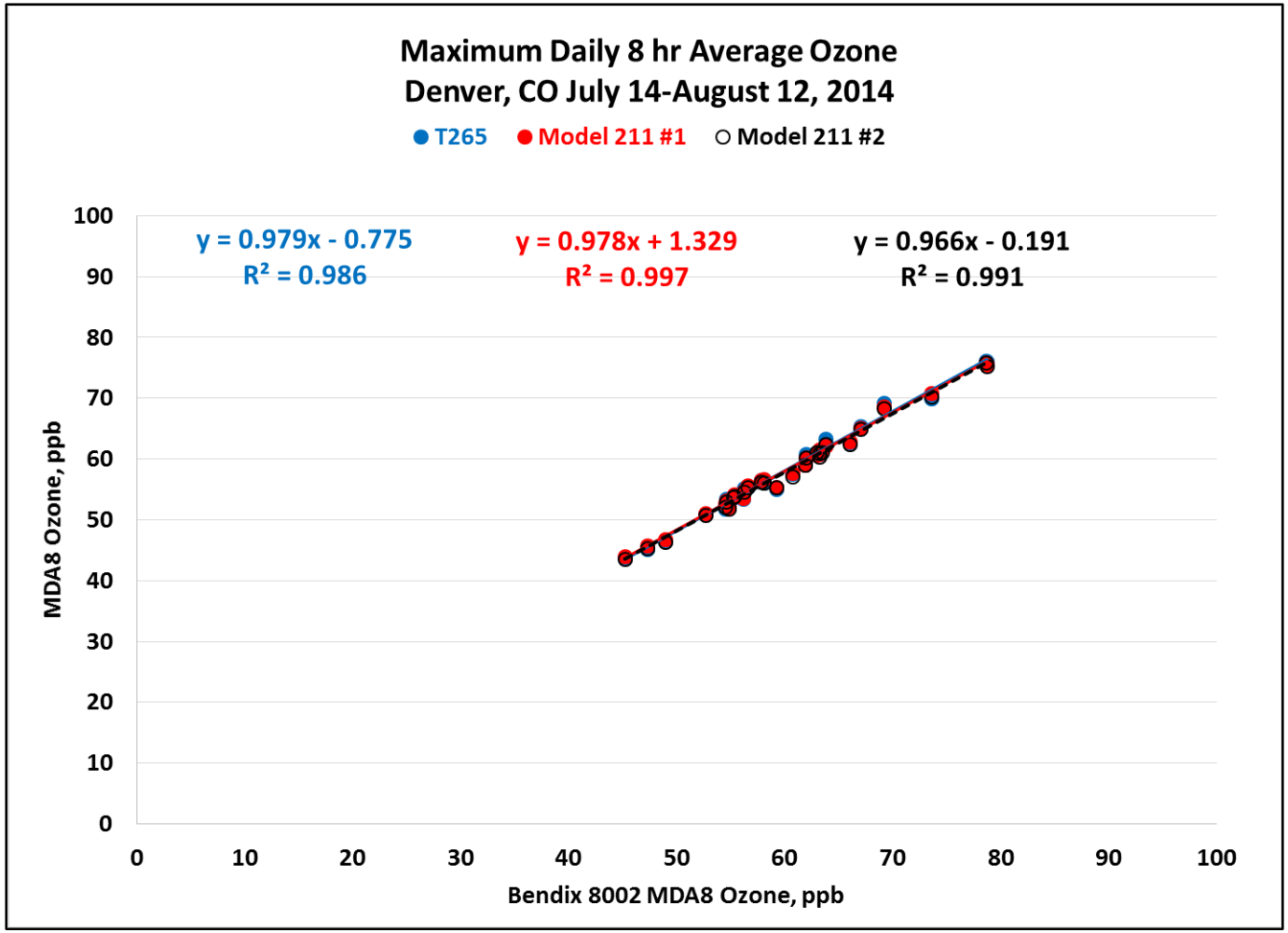

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Status of Ozone FRM Research

United States Environmental Protection Agency

- Comprehensive laboratory evaluations of candidate FRM's – **complete**
  - Performance specifications of candidate methods determined under controlled laboratory conditions per 40 CFR Part 53 requirements
- Ambient evaluations/comparisons of candidate FRM's – **complete**
- Selection of a new FRM for ozone – **complete**
  - Measurement of ozone in the atmosphere by NO-Chemiluminescence (NO-CL)
- ORD presents ozone FRM materials to CASAC AMMS for peer review and consensus – **complete**
- FRM in Regulatory text for submission to Federal Register and Inclusion as Appendix D in 40 CFR Part 50 – **complete**
- Draft suggested changes to 40 CFR part 53 regarding new ozone FRM/FEM performance specifications – **complete**
- Proposed rulemaking (including new FRM and changes to 40 CFR Part 53) signed by EPA Administrator on November 26, 2014 and published in Federal Register on December 17, 2014

References

- Technical Report: Performance of the Proposed New Federal Reference Method for Measuring Ozone Concentrations in Ambient Air, EPA/600/R-14/432/October, 2014
- National Ambient Air Quality Standards for Ozone; Proposed Rule, Federal Register/Vol. 79, No. 242/December 17, 2014

Implications and Conclusions

United States Environmental Protection Agency

- **Results obtained in laboratory and ambient evaluations, indicate that the NO-CL method meets and exceeds all requirements for proposal of a new FRM for ozone.**
- **Results obtained in laboratory and ambient evaluations also suggest that the SL-UV may, upon further evaluation, also meet the requirements to serve as an additional ozone FRM.**
- **ORD is prepared to respond to the received comments on the proposed ozone rulemaking and will support final rulemaking for the ozone NAAQS.**
- **A peer reviewed journal manuscript detailing this work is currently undergoing Agency clearance and will be submitted for publication in 2015.**

Proposed Ozone FRM

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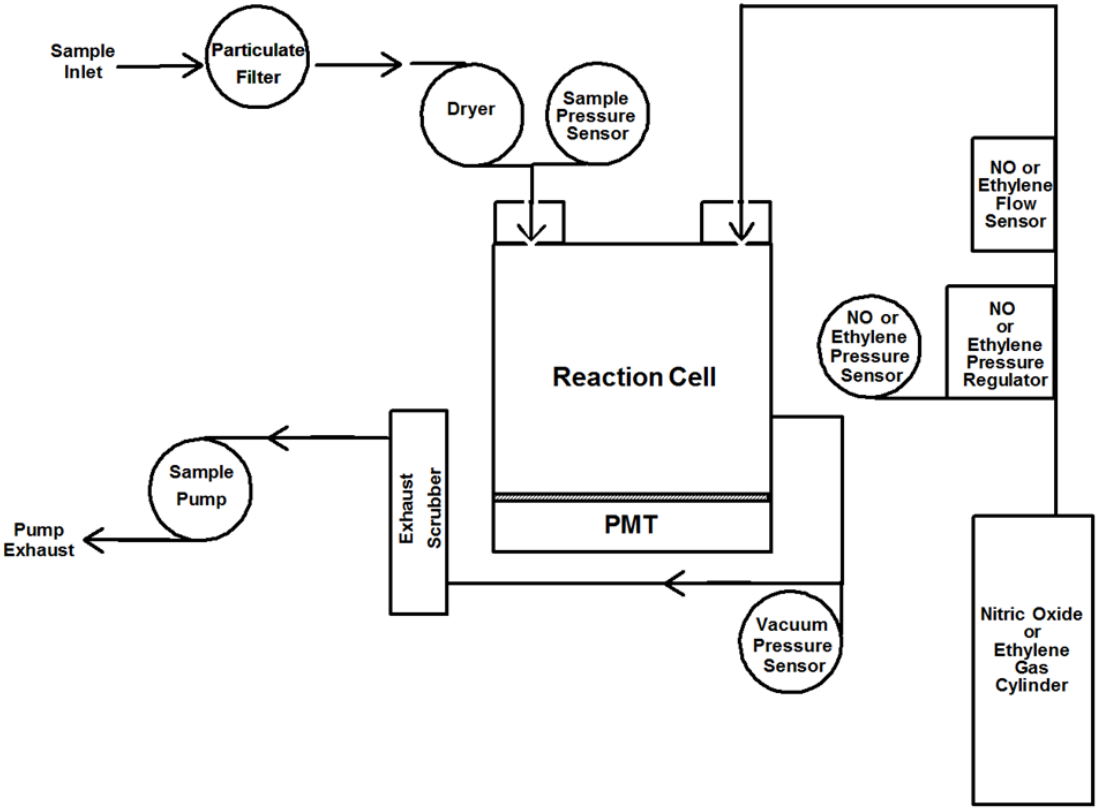

Measurement Principle

- Based on quantitative measurement of the chemiluminescence from the gas-phase reaction of ozone in an air sample with excess nitric oxide (NO) or Ethylene.
- Measurement system is calibrated by reference to O_3 concentration standards produced and assayed according to the same existing calibration procedure prescribed in 40 CFR Part 50, Appendix D.
- Analyzers implementing this measurement principle would include:
  - A reaction cell where the gas phase reaction occurs (containing a window through which the light can be detected)
  - A photomultiplier tube (or equivalent) detector and associated electronics to measure the light produced
  - A pump and flow control system for sampling the ambient air
  - A dryer to control sample air humidity
  - A supply of NO or Ethylene contained in a high-pressure gas cylinder (which may be either internal or external to the analyzer).

Acknowledgements/Disclaimer

United States Environmental Protection Agency

ORD Ozone FRM Methods Research Team
Melinda Beaver, Rachelle Duvall, Eric Hall, Surender Kaushik, Jim Szykman

Acknowledgements

- U.S. EPA, OAR/OAQPS/AAMG
- Alion Science and Technology
- MDE
- TCEQ
- CDPHE
- NASA
- NOAA
- CASAC AMMS

Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.