



NOx Analysis Accuracy and Reliability: New Technologies and Old Methods

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Overview

- Evolution of Gas Sensing Instruments
- New Technologies
 - Electro-chemical
 - Micro Sensor Technology
 - Spectroscopy
- Reference Method Testing
 - Low level NO_x
 - Performance Specification 2
 - Changes in Method 7E
 - Low level protocol gas
- Sampling Systems
 - Sample Probe
 - Sample lines
 - Gas conditioning
- Summary
 - Shortcomings
 - Further research
 - Alternative (PEM)

Evolution of Gas Sensing Instruments

- Phase 1 - Discrete Instrumentation
- Phase 2 - Multi-gas Modular Instrumentation
- Phase 3 - Micro-technology
- Phase 4 - MEMS Technology
- Phase 5 - Nano-micro Hybrid
- Phase 6 - Nano-miniaturization

Advantages of Miniaturization

- Smaller
- Lower cost/redundancy
- Faster response
- Increased sensitivity
- High specificity
- Less drift
- Multi-gas sensing

New Technology Options

- Electrochemical
 - Emerging technology
 - Developmental stage
- Micro-Electro-Mechanical Systems (MEMS)
 - Research stage
 - Much more complex
- Spectroscopy
 - Well known
 - Not economical in most instances

Electrochemical Sensor Technology

- Sensing Cell
 - Permeable membrane
 - Chemically absorbing/reacting media
 - Change electrical/mechanical properties
- Concentration measurement
 - Reference electrode used for measurement
 - Difference between measured and reference provides concentration signal
 - Concentration signal typically a direct electrical signal with no signal processing required
- Sensitivity depends on type of cell and material

□ Electrochemical Sensors

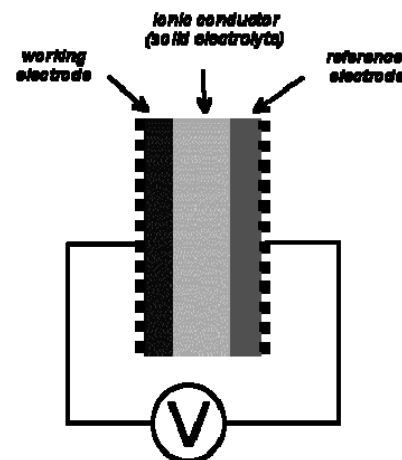
- Been around for years
 - Originally developed for ambient work
- Sensing cells for CO₂, CO, NO, NO₂, O₂, SO₂ and NH₃
- Issue: Poisoning over life of cell
 - Some mfr use dual cells with switching
 - Flush off-line cell w/ambient air
- Drawback: Cell replacement
 - Cost and labor

Electrochemical Recent Advances

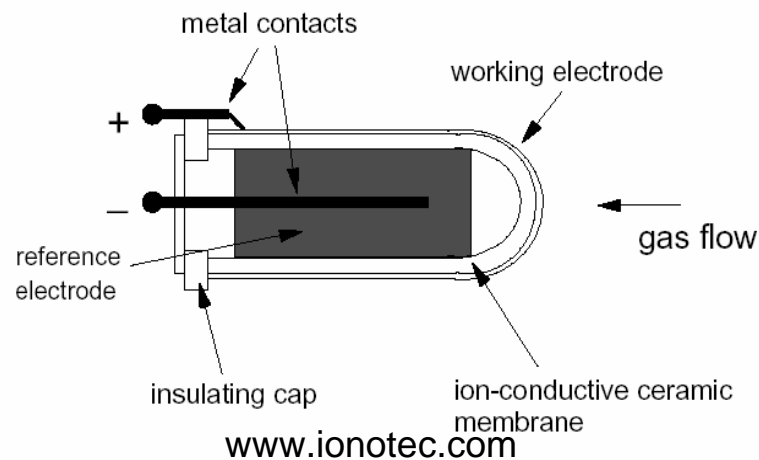
- Use of nanoparticles
 - Improving sensitivity by increasing surface area
 - Smaller packages
 - Improved selectivity through new electrolytes and membranes
- Weak areas:
 - Sample conditioning
 - Cross sensitivity issues with common stack gases
- Dilution system would be revolutionary

Potentiometric/Amperometric

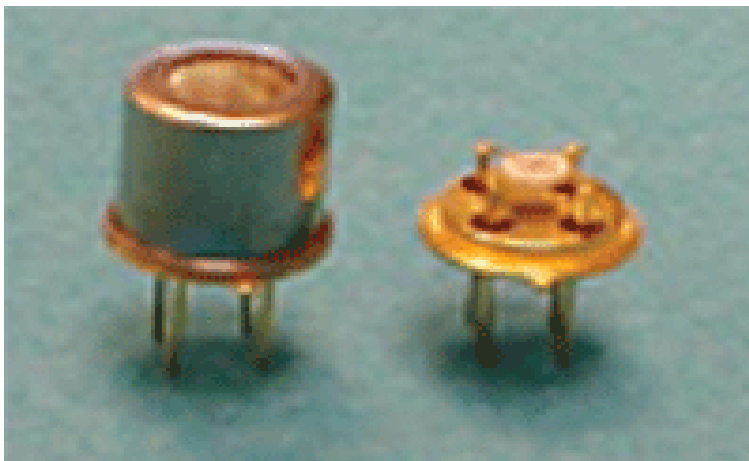
- Electrochemical cell in a casing with a permeable membrane
- NO_x permeate the membrane and contact with the internal gel or electrolytes of the sensor
- Reaction takes place (oxidizing or reducing) inducing a voltage differential or current
- Manufacturers report <1ppm detection limit
- Large cross sensitivity
- DOE funded research underway for NO_x/CO/O₂ system



www.fkf.mpg.de



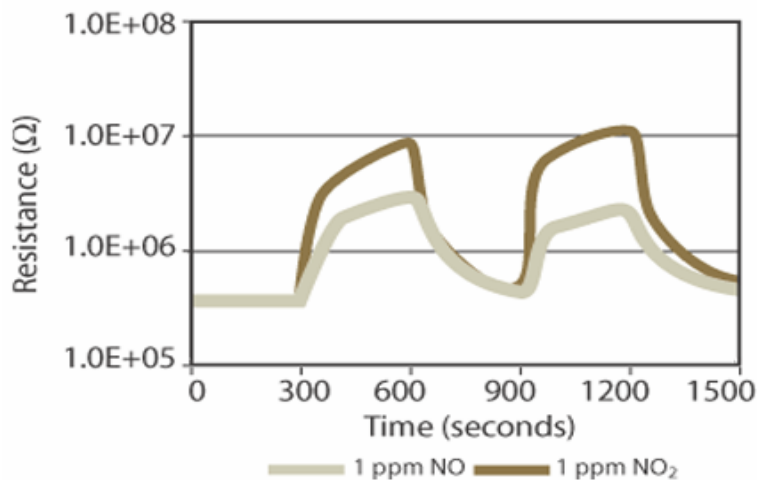
www.ionotec.com



www.isa.org

Metal Oxide Sensor

- Metal Oxide Semiconductor (MOS) material is sintered to a substrate
- Heating wire is included in substrate
- Reaction with NO/NO₂ occurs when material is heated
- Resistance is measured
- Response to low level NO_x
- Time response is long (~5 minutes)

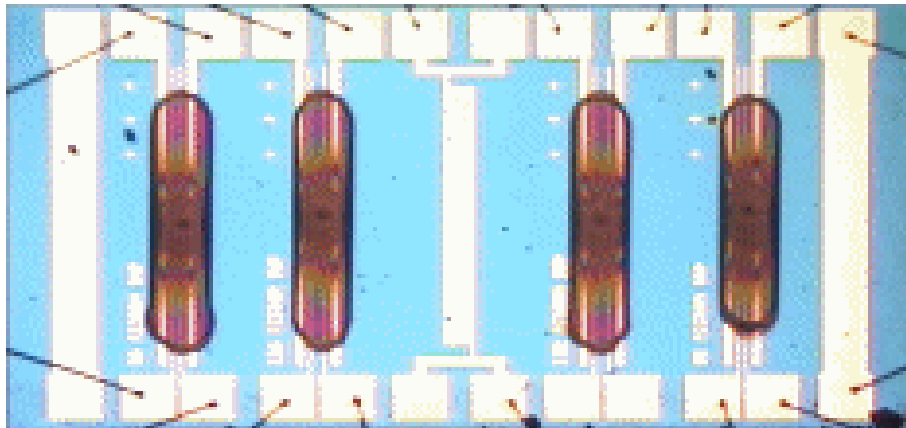


Chemiresistors

- Potential for eventual in-situ use
- Temp will be of concern re: polymer life
- Saturation of polymer and regeneration an issue
- Mostly lab applications
- Ambient concentrations

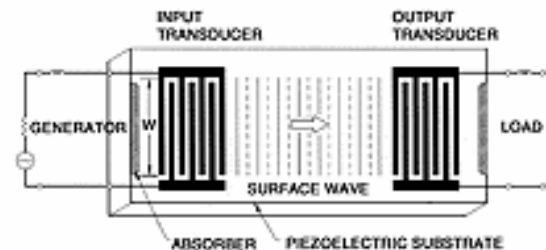
Chemiresistors

- Changes in resistance due to gas absorption onto a polymeric film
- Film swells during absorption
- Time limitation for absorption to occur

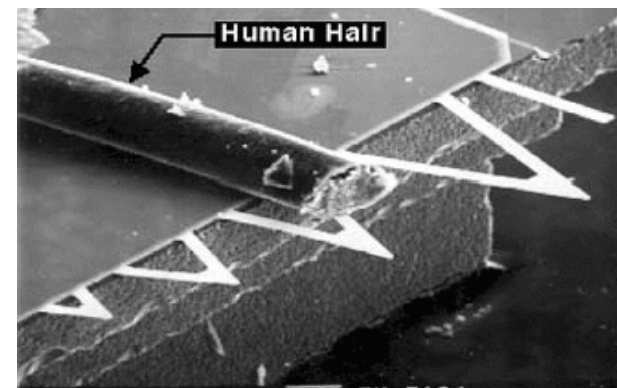


Acoustic Wave Sensors

- Structure that is induced to oscillate at resonant frequency
- Coating selectively adsorbs NO or NO₂
- Added mass changes the resonant frequency
- More research needed for performance specifications



www.sensorsmag.com



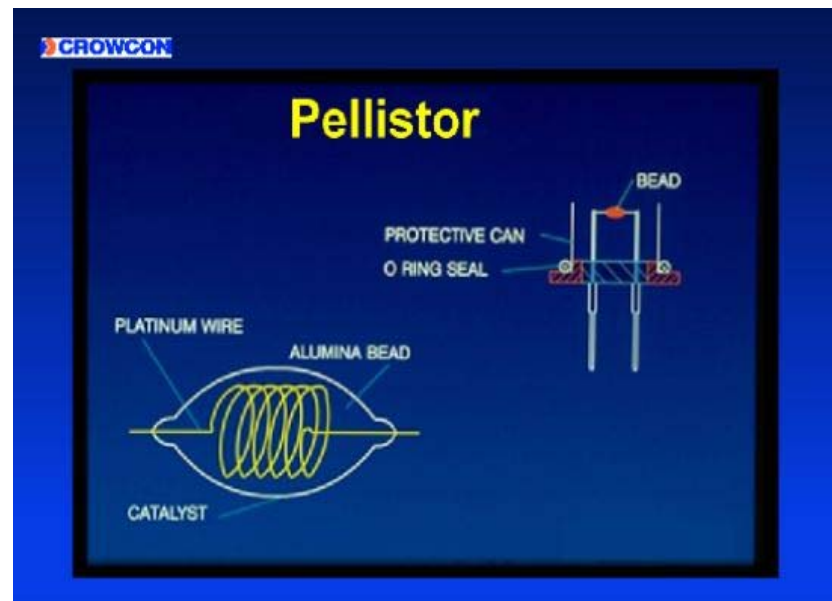
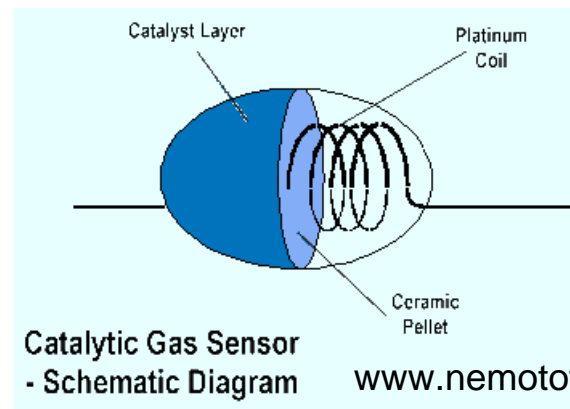
www.ornl.gov

Catalytic Calorimeter

- Well-established technology
- Used for combustibles
- New catalysts sensitive to other gases
- Performance degrades for low concentration measurements

Catalytic Calorimeter

- Catalytic reaction at interface dependent on temperature of sensor
- Resistance of wire changes with temperature
- Performance poor at concentration <50 ppm

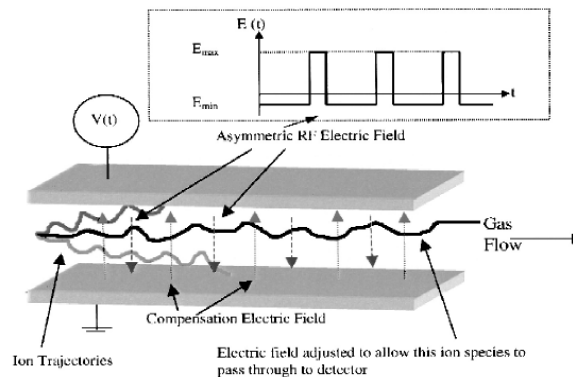


Ion Mobility Spectrometer

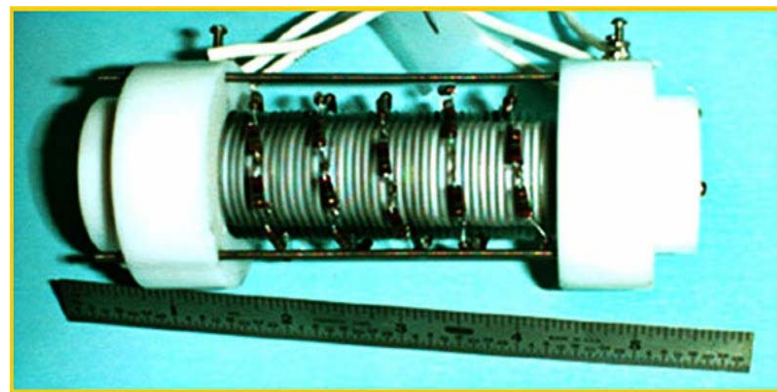
- Recently finding its way to stack applications
 - Ammonia (Particle Measurement Systems)
 - ppt range
 - Low sulfur applications only
- MEMS technology reducing size and cost

Ion Mobility Spectrometer

- Work by ionizing a gas sample
- Charge of the particles used in electric field to accelerate them over a known distance
- Micromachining used to create IMS with volume of 0.6cm^3
- Ambient pressure
- Further development necessary

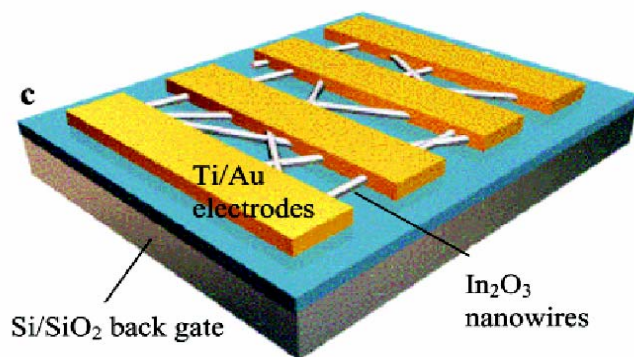


Miller et al.

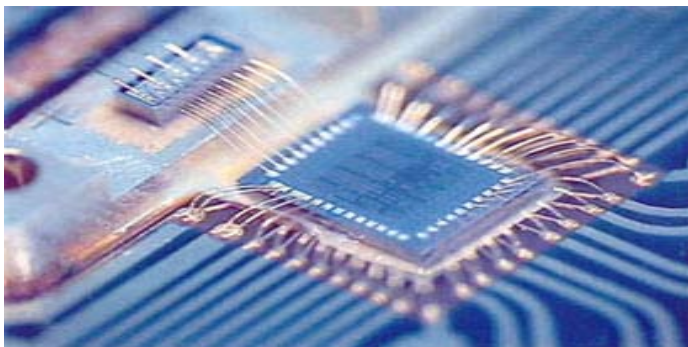


Argonne National Lab

Nano Technology



Zhang et al



nanosens.nl

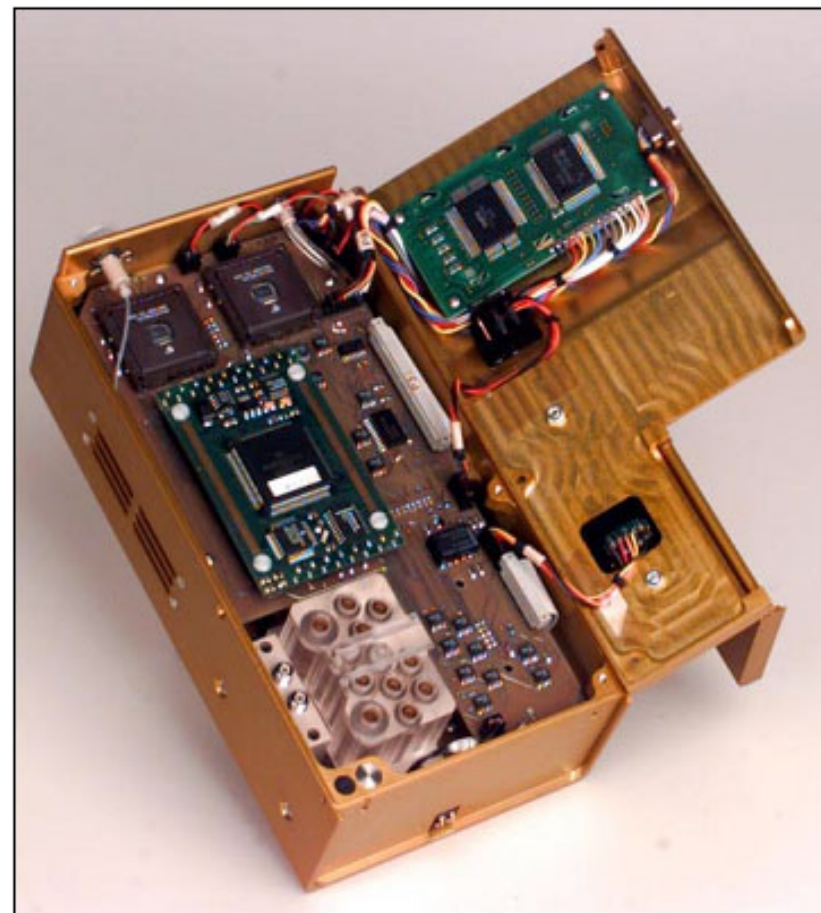
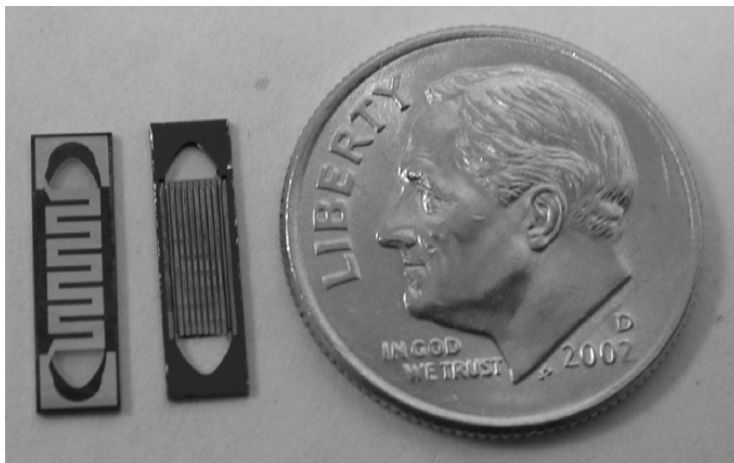
- Nanowires/Nanotubes
 - Constructed of semiconductors
 - 100 nm diameter
 - Change of conductance when contacting NO₂
 - Sensitivity between 5 ppb - 0.5 ppm with 5 second response time
 - More work to be done in area

Integrated MicroSystems

- Greatly benefitting from MEMS technology
- Tricorder

Integrated MicroSystems

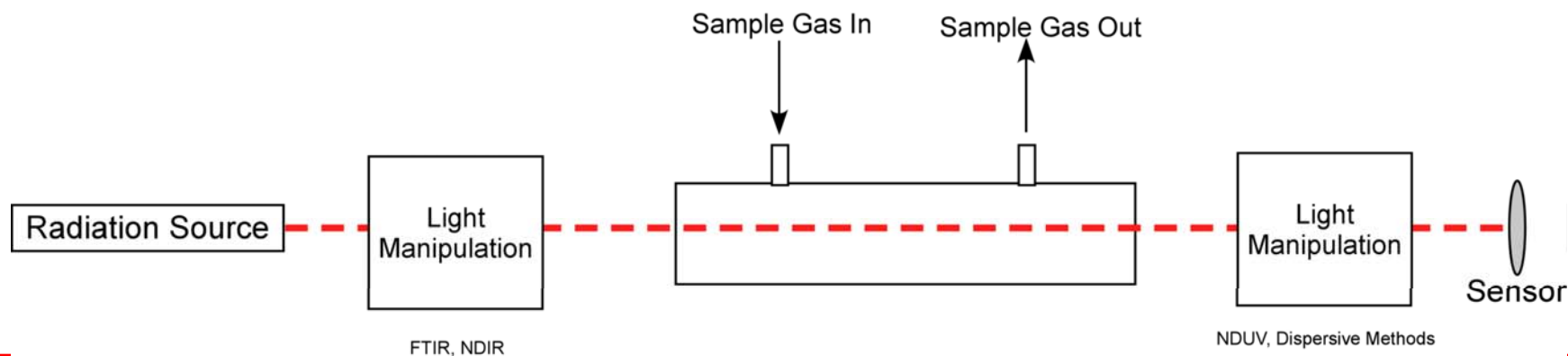
- zNose (www.znose.com)
 - Gas chromatograph
- MicroChemLab
 - (Sandia National Lab)
 - Preconcentrator
 - Gas Chromatograph
 - SAW sensor

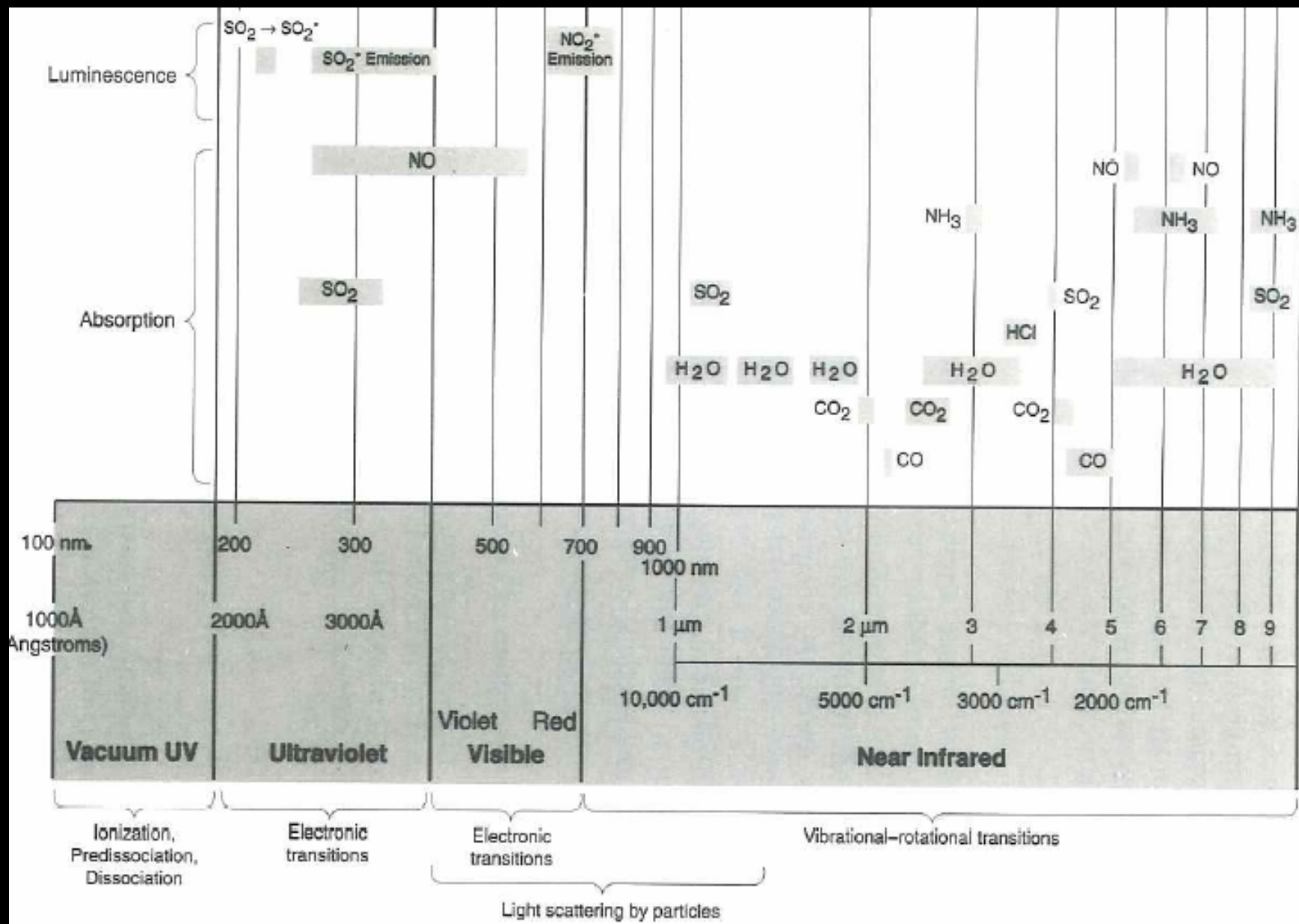


www.sandia.gov

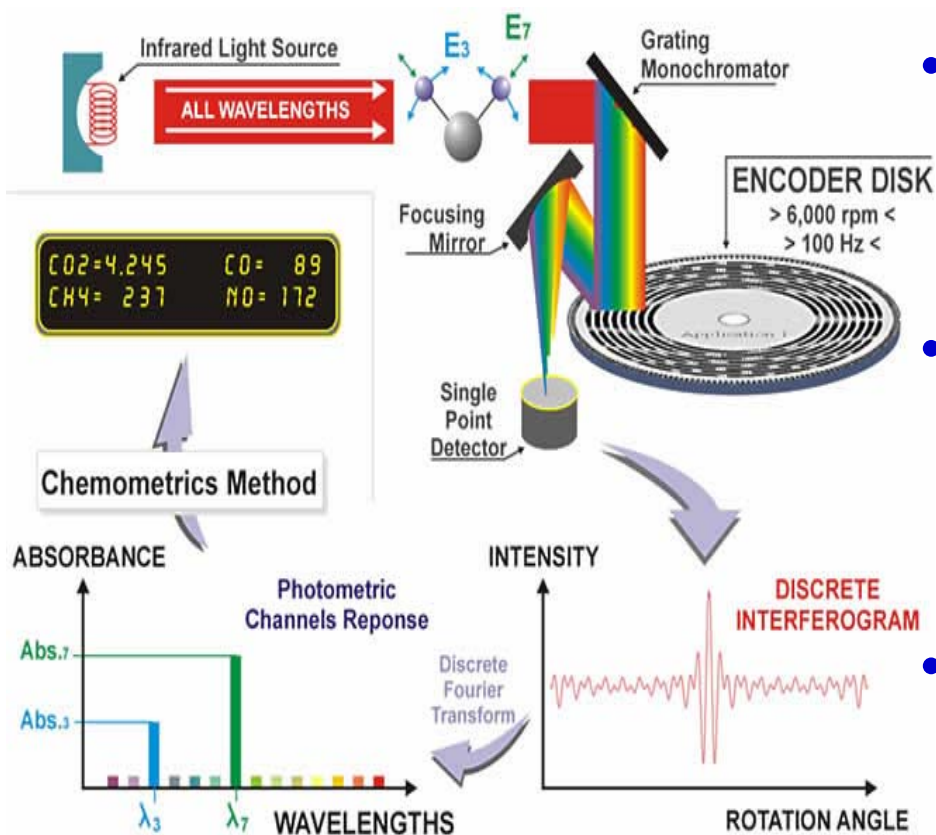
Optical Spectroscopy

- Gases absorb light at different wavelengths
- If the wavelength can be identified the analyte concentration can be calculated
- Based on well known physical principles
- Many methods established
 - Dispersive (UVDOAS)
 - Nondispersive (NDIR, NDUV)
 - FTIR
 - Tunable Diode
- Expensive, Large, Need controlled environment





Miniaturization of Optical Spectroscopy



- Increase feasibility
 - Aiming at reducing cost
 - Ability to operate in more severe environment
 - In-situ measurement
- Cascade Technologies
 - Quantum Cascade Lasers (QCL) for absorption spectroscopy in mid-IR range
 - ppb resolution (in-situ probe sampling)
- Aspectrics “FTIR-on-a-CD”
 - Reduced size
 - Fast sampling rate

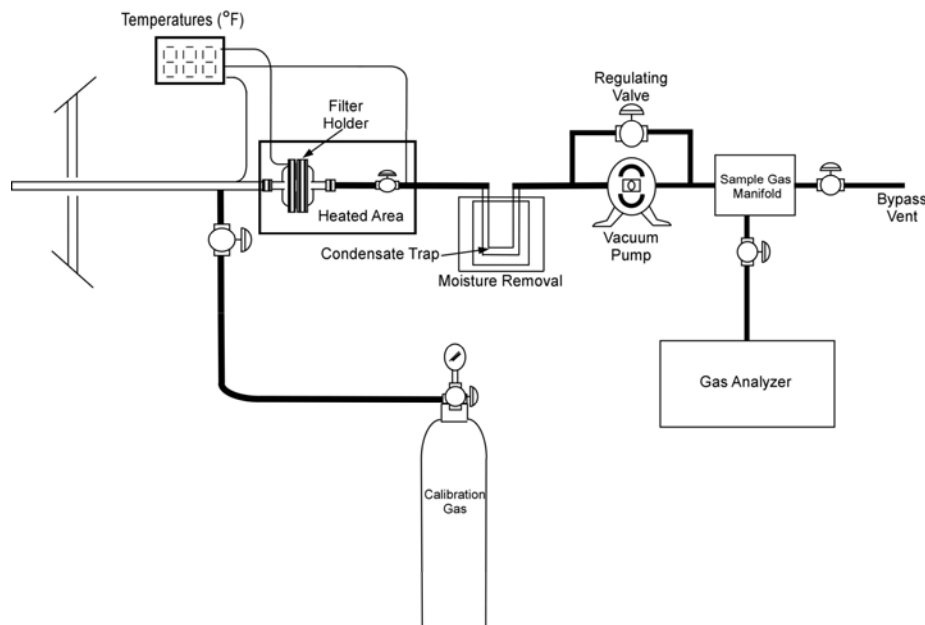
Reference Method Testing

- Low level NO_x
 - More frequently encountered
 - Eye for details in testing
- Performance Specification 2
 - 20% accuracy
 - Drift
- Problems most easily overlooked
 - Quenching
 - Absorption of NO₂
 - Variability of NO₂ converter



Changes to Method 7E

- Chemiluminescence analyzer no longer required
- Span defined as value of high concentration calibration gas
- Dynamic spike added as alternative to interference and bias tests



Sampling Systems

- Siting criteria
- Bias can occur outside of analyzer
 - Sample probe
 - Sample lines
 - Gas Conditioner/Dilution equipment
- When measuring low level NO_x this can account for significant error

Sample Probe

- Materials of Construction
 - Corrosion resistance
 - Reactivity to analytes
- Probe length
 - Breaching depth
 - Potential cold spot
- Filtration
 - Reactivity to analytes
 - Myth of the filter blowback
 - Works well for in-situ filtration
 - Poorly for ex-situ filtration

Sample Lines

- Two kinds
 - Series wound element
 - Parallel heat tape
- Materials
 - Sample transport tube - varieties of Teflon, SS
 - Service tubes - polypropylene, nylon, etc.

Sampling Lines

- Adsorption/absorption
- Relative error increases as the concentration of NO_x decreases
- Heating Teflon lines cannot solve all the problems
 - Must heat above all dewpoints and/or sublimation temps

Condition: Wet Simulated Turbine Exhaust with Ammonia (13% H₂O, 13% O₂, 4% CO₂ + 10 ppm NH₃)

	0.2		1		4.75		8.5	
Avg. Nominal NO Input (ppmd)	0.2		1		4.75		8.5	
Avg. Nominal NO ₂ Input (ppmd)	0.2		1		4.75		1	
Avg. Total NO _x Input (ppmd)	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Stainless Steel Sample Line (25 °C)	+/- 0.04 ppm	9.9%	N/A	N/A	+/- 0.48 ppm	4.9%	N/A	N/A
Teflon Sample Line (107 °C)	+/- 0.03 ppm	7.8%	N/A	N/A	+/- 0.48 ppm	5.0%	N/A	N/A
SilcoSteel Sample Line (107 °C)	+/- 0.05 ppm	11.1%	N/A	N/A	+/- 0.49 ppm	5.1%	N/A	N/A
Stainless Steel Sample Line (175 °C)	+/- 0.06 ppm	13.0%	N/A	N/A	+/- 0.48 ppm	5.0%	N/A	N/A
SilcoSteel Sample Line (175 °C)	+/- 0.05 ppm	11.8%	N/A	N/A	+/- 0.48 ppm	5.0%	N/A	N/A

Gas Conditioning

- Conditioning has error that increases with reducing NO_x concentration
- NO₂ absorbs in water, pH dependent
- Cleanliness more significant factor

Condition: Wet Simulated Turbine Exhaust with Ammonia (13% H₂O, 13% O₂, 4% CO₂ + 10 ppm NH₃)

	0.2		1		4.75		8.5	
	0.2		1		4.75		1	
	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Avg. Nominal NO Input (ppmd)								
Avg. Nominal NO ₂ Input (ppmd)								
Avg. Total NO _x Input (ppmd)								
Permeation Dryer	+/- 0.04 ppm	10.4%	N/A	N/A	+/- 0.56 ppm	5.8%	N/A	N/A
Combination Ambient Condenser/Perm	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Refrigerated Condenser	+/- 0.06 ppm	13.7%	N/A	N/A	+/- 0.54 ppm	5.6%	N/A	N/A
Thermoelectric Chiller	+/- 0.06 ppm	12.8%	N/A	N/A	+/- 0.62 ppm	6.5%	N/A	N/A
Glass Impingers in an Ice Bath	+/- 0.06 ppm	13.1%	N/A	N/A	+/- 0.54 ppm	5.7%	N/A	N/A

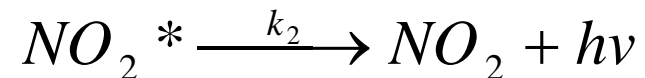
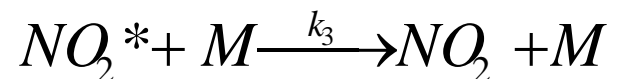
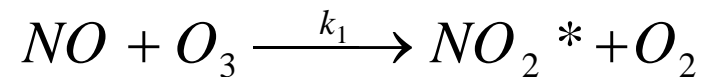
Ref. 7

Protocol Gases

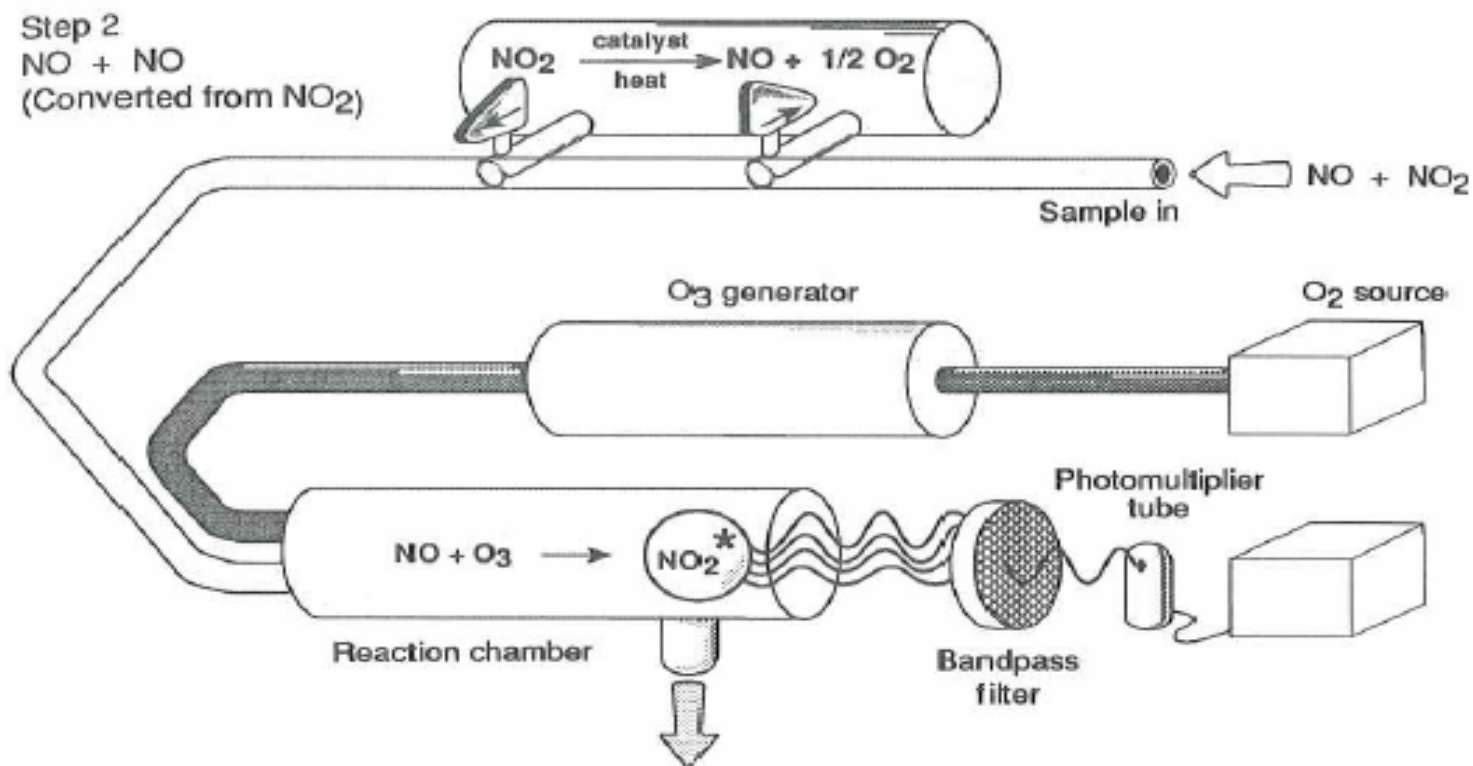
- Low NO_x calibration standard accuracy
 - As of 2002 protocol gas standards are guaranteed to 0.5ppm ±2%
 - 6 month shelf life for NO (<4 ppm)
 - EPA Study - Blind audits

Chemiluminescence

- Oxidation
- Chemiluminescence
- Quenching
 - **M''** refers to any molecular third body that is present in the reaction chamber of the NO_x analyzer.
 - **Non-diatomic or polyatomic molecules are most likely to quench the chemiluminescent reaction.**



Chemiluminescence



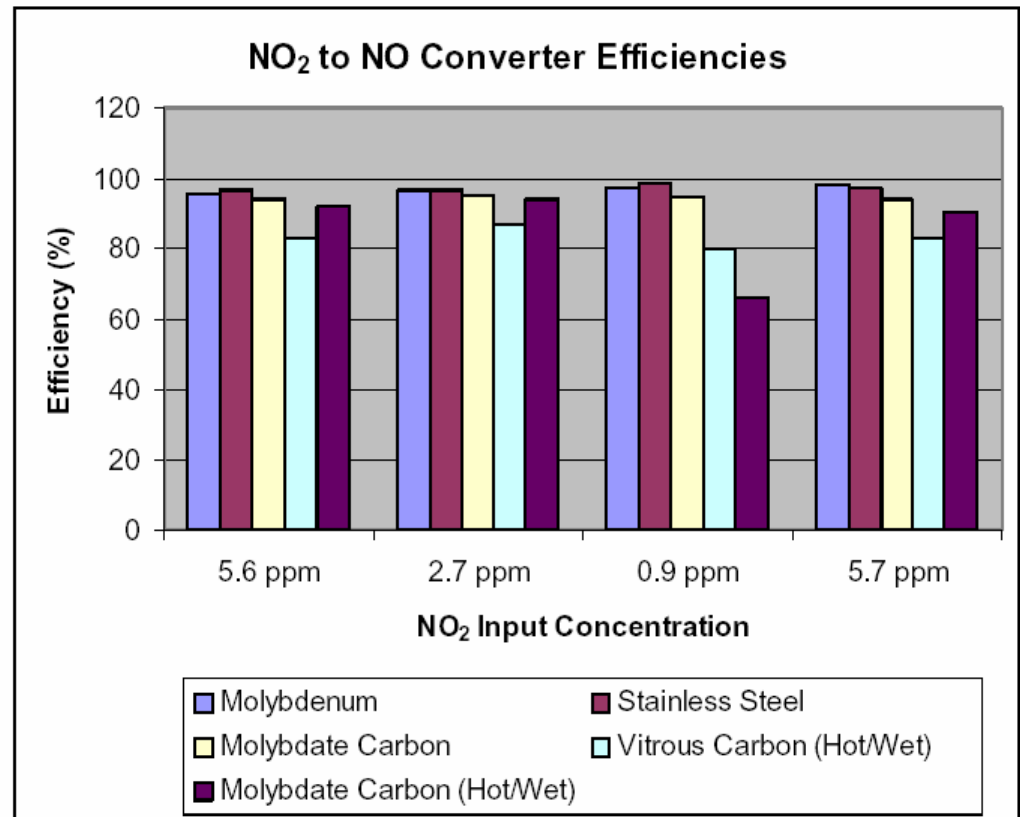
Jahnke, James A., "Continuous Emission Monitoring", Van Nostrand Reinhold, 1993

NO₂ Converters

- Two types
 - Internal analyzer
 - Molybdenum, SS, vitreous carbon
 - External bulk stream
 - Molybdenum, vitreous carbon, molybdate carbon

Converter Efficiency

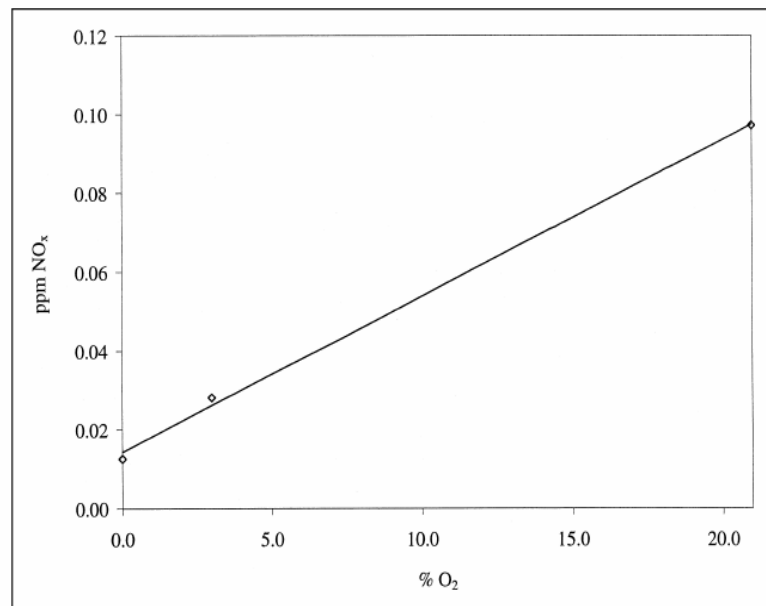
- Factors
 - Flow
 - Poisons
 - Temperature
 - NO₂ concentration



Ref. 7

Chemiluminescence

- Uncertainties
- Systematic Bias
 - Converter efficiency
 - Interferents
 - H₂O
 - CO₂



	% NO ₂ Converted to NO				
	Horiba	CAI	Rosemount	ABB	Siemens
Dry sample with 0% CO ₂	89.6	89.4	95.3	93.9	94.9
Dry sample with 15% CO ₂	88.5	90.3	91.5	92.2	88.8

Gluck et al., J. Air & Waste Manage. Assoc.,
June 2003.

Reliability of Analyzers

- Bias
 - CO₂
 - Absorbs signal
 - NH₃
 - Easily converted to NO at high temperatures
 - Depends on catalyst
 - H₂O
 - Absorbs signal
 - NO₂ is easily soluble

	Range(s) / Min. Detection Conc.	INSTRUMENT BIAS (%) PER INPUT BLEND				AVERAGE CO ₂ BIAS (%)	MOISTURE INTERFERENCE RESPONSE (%)
		80 ppmv NO in 15% CO ₂	25 ppmv NO in 15% CO ₂	25 ppmv NO in 5% CO ₂	NO in N ₂ (MAK Gas Cond)		
NOx Analyzers						<i>per 1% CO₂ in synthetic gas stream</i>	<i>per 1% H₂O in sample gas</i>
EcoPhysics Model 70E	0-500 ppm; four ranges, user selectable / 0.02 ppm	-15.13	-13.01	-3.66	-3.19	-0.87 %	-3.98%
TECO Model 42C	0-50, 100, 200, 500 ppm / 0.40 ppb	-14.38	-10.80	-2.42	-3.75	-0.72%	-4.69%
TECO Model 42C Low Source	0-2 ppm; 0-200 ppm / 0.01 ppm	-9.13	-7.09	-1.97	-0.63	-0.49%	-0.78%
TECO Model 42CHL	0-10, 20, 50, 100, 200, 500, 1000, 2000, 5000ppm / 50 ppb	-5.25	-4.80			-0.34%	

Summary of Chemiluminescence

- CO₂ and moisture quench the chemiluminescence resulting from the reaction between nitric oxide and ozone, causing negative interference. Quenching is a potentially significant source of error in chemiluminescent NO_x analyzers.
- If there is a great difference between the CO₂ content of the calibration gas and that of the measured gas, the measurement is particularly affected.
- The bias introduced by gas conditioners as a result of residual moisture in the gas stream is measurable.
- In order to mitigate errors resulting from CO₂ in the flue gas, the nitric oxide calibration gas should be a three component blend of NO, CO₂, and N₂. The CO₂ content of the calibration gas should be similar (± 2 mole %) to the CO₂ content of the sample gas.

Conclusions

- Some interesting new technologies just on the horizon
- Uncertainties unknown at this time
- Likely cheaper, more sensitive
- Current technologies capable of detection limit around 1 ppm
- Careful design and maintenance of system
- Care in selection of RATA contractor
- ASTM D-7036