Excel Spreadsheet Headings

- ID (NIST Identifier)
- Specie (Analyte)
- Balance Gas
- Nominal Concentration
- Batch Size (Number of Cylinders)
- Certification Date (Year and Month)
- Certified value
- Uncertainty
- Factor (Bias between producer and NIST results)

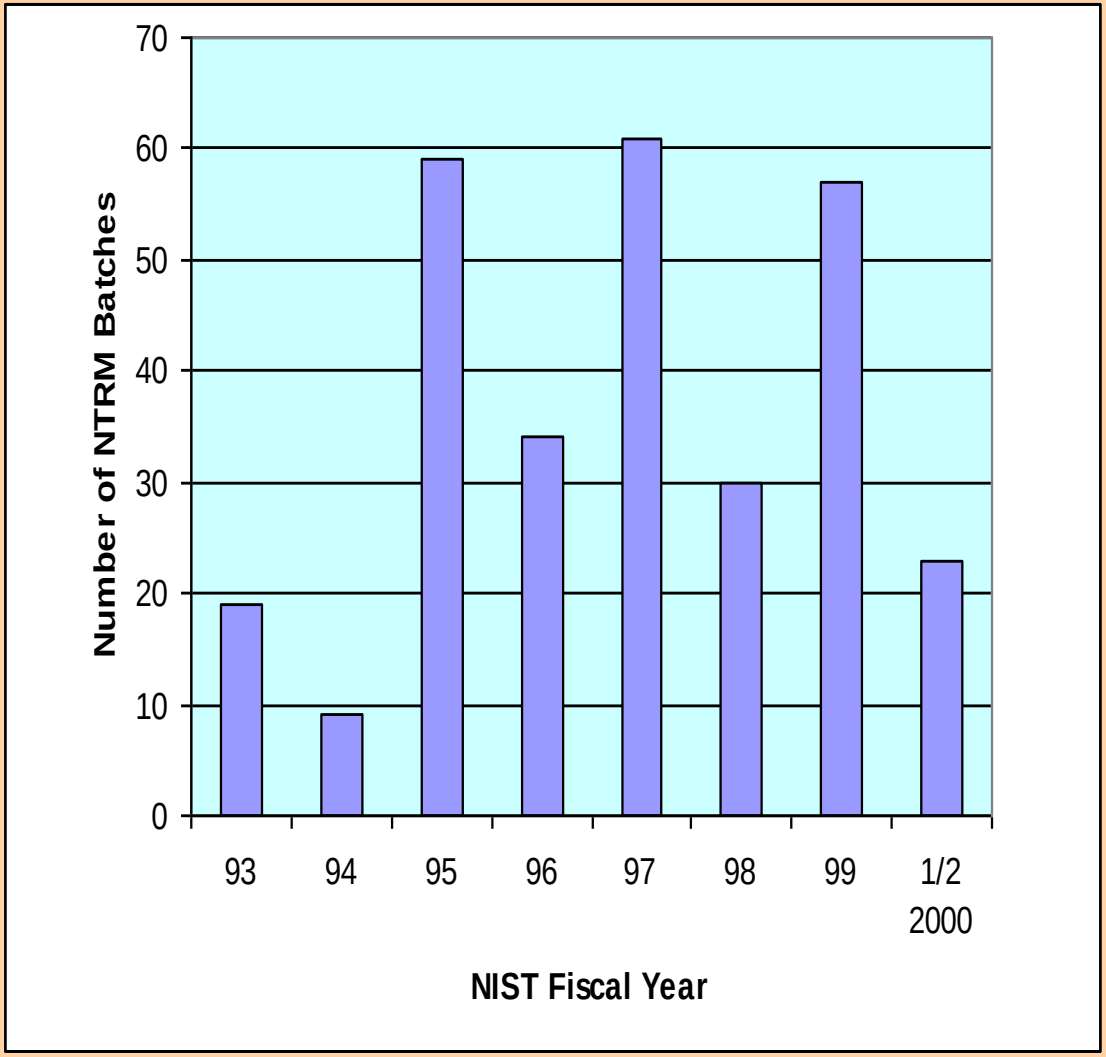
Company Participation by Year

Year	Company Coded											
Y-93	a	b										n=2
Y-94	a											n=1
Y-95	a	b	c	d	e	f						n=6
Y-96	a		c	d	e	f	g	h				n=7
Y-97	a		c	d	e	f	g		j	k		n=8
Y-98	a		c	d	e	f	g	h	j	k		n=9
Y-99	a		c	d			g		j			n=5
Y-00 1/2	a		c	d	e			h				n=5

Companies Participating in the Gas Mixture NTRM Program

- AGA
- Air Products
- Airgas
- ALAC
- BOC / Airco
- Matheson
- MG
- Praxair / Liquid Carbonic
- Scott
- Spectra

Graph of Number of Gas Mixture NTRM Batches by Year



NTRM Batches by Year

93	C3H8	0.0010						
93	CH4	0.0010	0.0010					
93	CO	0.1000	0.1000	0.2500				
93	CO2	2.5000	7.0000	14.0000				
93	NO	0.0500	0.1000	0.3000				
93	SO2	0.0050	0.0100	0.0260	0.0500	0.1000	0.1500	0.3500
94	C3H8	0.0100						
94	CH4	0.0010						
94	CO	0.0100	0.0250					
94	NO	0.0050	0.0250	0.0500	0.1000			
94	SO2	0.0500						

NTRM Batches by Year

95	CO	0.0010	0.0050	0.0250	0.0500	0.1000	0.2500				
95	CO2	3.5000	5.0000	7.0000	14.0000	18.0000	20.0000				
95	NO	0.0020	0.0020	0.0025	0.0050	0.0085	0.0100	0.0100	0.0175	0.0250	0.0250
		0.0250	0.0250	0.0500	0.0500	0.0500	0.0625	0.0750	0.1000	0.1000	0.1000
		0.1500	0.3000	0.3000							
95	O2	2.0000	2.0000	10.0000	10.0000	21.0000	21.0000				
95	SO2	0.0050	0.0050	0.0100	0.0100	0.0175	0.0260	0.0375	0.0500	0.1000	0.1000
		0.1250	0.1500	0.1500	0.2500	0.3000	0.3200	0.3500	0.3500		
96	CO	0.0050	0.0100	0.0100	0.0250	0.1000	0.2500	0.5000	8.0000		
96	CO2	18.0000	22.0000								
96	NO	0.0020	0.0050	0.0500	0.0875	0.1000	0.1000	0.1000	0.1500	0.3000	
96	NO2	0.0100	0.0500								
96	O2	10.0000	20.0000								
96	SO2	0.0500	0.0500	0.0500	0.0875	0.1000	0.1000	0.1000	0.2000	0.2800	0.3500
		0.3500									

NTRM Batches by Year

97	C3H8	0.0100	0.0100	0.0500	0.0500	0.1200	0.2500				
97	CH4	0.0500									
97	CO	0.0025	0.0025	0.0050	0.0100	0.0250	0.0500	0.1000	0.1000	0.1000	2.0000
		0.0050	0.0250	0.0500	0.1000						
97	CO2	0.5000	0.5000	0.5000	1.0000	1.5000	2.0000	3.0000	4.0000	5.0000	7.0000
		9.0000	11.0000	14.0000	14.0000	16.0000	18.0000	20.0000	20.0000	20.0000	
97	EtOH	0.0100	0.0100	0.0120	0.0220	0.0220					
97	Nat Gas	Multi									
97	NO	0.0020	0.0100	0.1000	0.1000						
97	SO2	0.0050	0.0100	0.0100	0.0100	0.0500	0.0500	0.1000	0.1500	0.1500	0.2500
		0.2500									
98	C3H8	0.0050	0.0300	0.0500							
98	CH4	0.0010									
98	CO	0.0050	0.0050	0.0050	0.0100	0.0100	0.0100	0.0250	0.0250	0.0250	0.0500
		0.0500	0.0500	0.1000	0.2500	0.5000	0.5000	7.0000			
98	CO2	4.0000	7.0000	14.0000	20.0000						
98	NO	0.0050	0.0050	0.0100	0.0100	0.0100	0.0250	0.0500	0.0500	0.1000	0.1500
		0.3000	0.3000	0.3000							
98	O2	2.0000	2.0000	4.5000	5.0000	7.0000	10.0000	10.0000	10.0000	10.0000	12.0000
		15.0000	16.0000	21.0000	21.0000	21.0000	21.0000	21.0000	23.0000	23.0000	24.0000
98	SO2	0.0050	0.0050	0.0100	0.0100	0.0100	0.0250	0.0250	0.0250	0.0500	0.0500
		0.1000	0.1000	0.3500							

NTRM Batches by Year

99	C3H8	0.0003	0.0010	0.0010	0.0100	0.0250	0.0500	0.1000	0.2500	0.2500	0.5000
99	CH4	0.0003	0.0010	0.0050	0.0050	0.0100	0.0210				
99	CO	0.0018	0.0025	0.0025	0.0100	0.0100	0.0250	0.0500	0.1000	0.2500	1.0000
		2.0000	8.0000								
99	CO2	0.1000	3.0000	3.0000	3.5000	5.0000	5.0000	7.0000	14.0000		
99	H2S	0.0025	0.0050	0.0100	0.0250						
99	NO	0.0050	0.0100	0.0250	0.0500	0.0500	0.0500	0.1000	0.1000	0.2800	0.3600
99	O2	0.5000	2.0000	2.0000	12.0000	21.0000					
99	SO2	0.0050	0.2500								

1/2 2000	C3H8	0.0050					
1/2 2000	CO	0.0025	0.1000				
1/2 2000	CO2	1.0000	2.0000	7.0000	18.0000	20.0000	23.0000
1/2 2000	H2S	0.0020	0.0025	0.0300			
1/2 2000	NO	0.0050	0.0100	0.0250	0.0500	0.1000	0.1000
1/2 2000	NOx	0.0100					
1/2 2000	O2	2.0000	10.0000	21.0000	24.0000		

NTRM Batches by Specie and Year

93	C3H8	0.0010									
94	C3H8	0.0100									
97	C3H8	0.0100	0.0100	0.0500	0.0500	0.1200	0.2500				
98	C3H8	0.0050	0.0300	0.0500							
99	C3H8	0.0003	0.0010	0.0010	0.0100	0.0250	0.0500	0.1000	0.2500	0.2500	0.5000
1/2 2000	C3H8	0.0050									
93	CH4	0.0010	0.0010								
94	CH4	0.0010									
97	CH4	0.0500									
98	CH4	0.0010									
99	CH4	0.0003	0.0010	0.0050	0.0050	0.0100	0.0210				
97	EtOH	0.0100	0.0100	0.0120	0.0220	0.0220					
97	Nat Gas	1.0000									

NTRM Batches by Specie and Year

93	CO	0.1000	0.1000	0.2500							
94	CO	0.0100	0.0250								
95	CO	0.0010	0.0050	0.0250	0.0500	0.1000	0.2500				
96	CO	0.0050	0.0100	0.0100	0.0250	0.1000	0.2500	0.5000	8.0000		
97	CO	0.0025	0.0025	0.0050	0.0100	0.0250	0.0500	0.1000	0.1000	0.1000	2.0000
		0.0050	0.0250	0.0500	0.1000						
98	CO	0.0050	0.0050	0.0050	0.0100	0.0100	0.0100	0.0250	0.0250	0.0250	0.0500
		0.0500	0.0500	0.1000	0.2500	0.5000	0.5000	7.0000			
99	CO	0.0018	0.0025	0.0025	0.0100	0.0100	0.0250	0.0500	0.1000	0.2500	1.0000
		2.0000	8.0000								
1/2 2000	CO	0.0025	0.1000								

93	CO2	2.5000	7.0000	14.0000							
95	CO2	3.5000	5.0000	7.0000	14.0000	18.0000	20.0000				
96	CO2	18.0000	22.0000								
97	CO2	0.5000	0.5000	0.5000	1.0000	1.5000	2.0000	3.0000	4.0000	5.0000	7.0000
		9.0000	11.0000	14.0000	14.0000	16.0000	18.0000	20.0000	20.0000	20.0000	
98	CO2	4.0000	7.0000	14.0000	20.0000						
99	CO2	0.1000	3.0000	3.0000	3.5000	5.0000	5.0000	7.0000	14.0000		
1/2 2000	CO2	1.0000	2.0000	7.0000	18.0000	20.0000	23.0000				

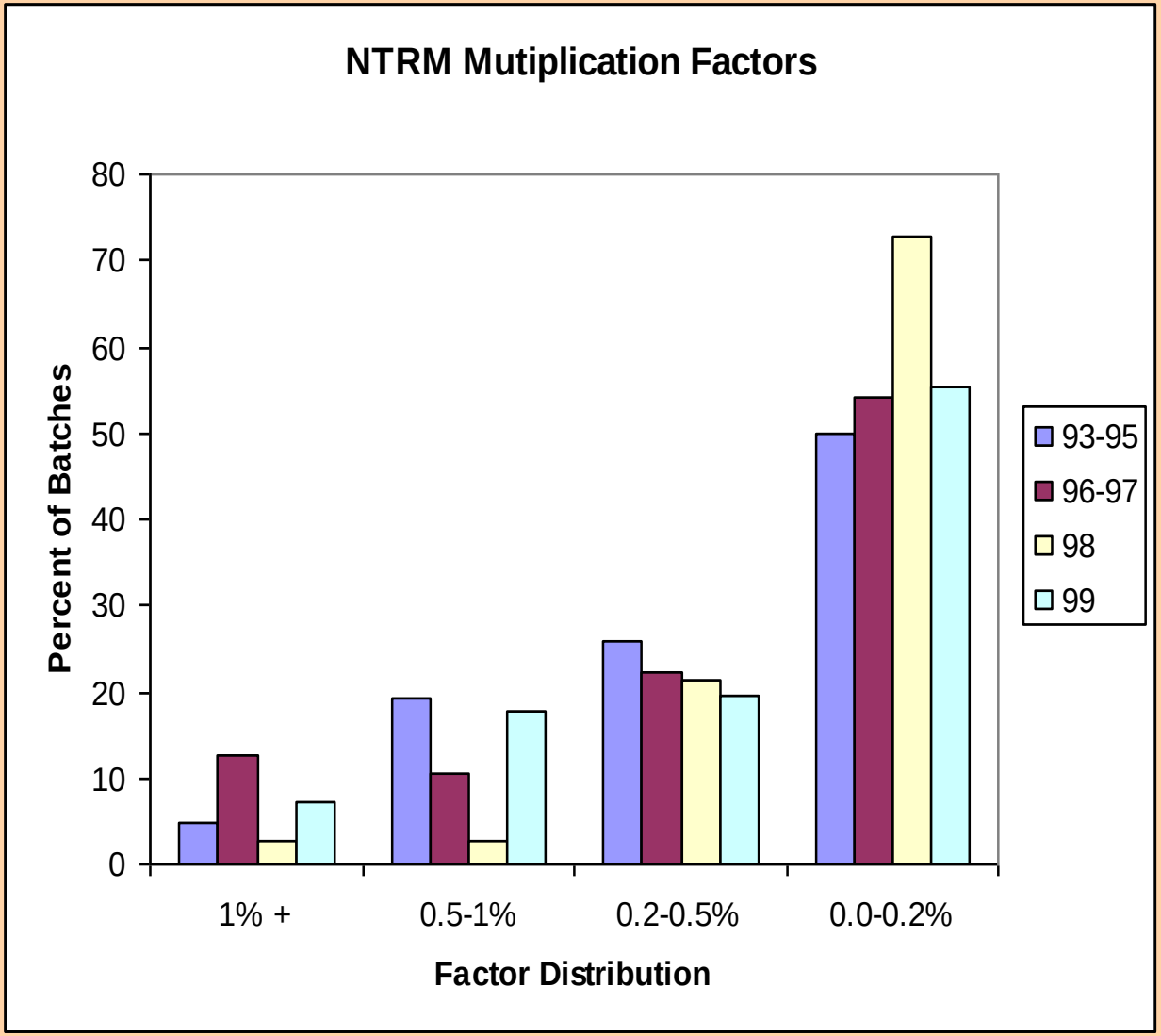
NTRM Batches by Specie and Year

93	NO	0.0500	0.1000	0.3000							
94	NO	0.0050	0.0250	0.0500	0.1000						
95	NO	0.0020	0.0020	0.0025	0.0050	0.0085	0.0100	0.0100	0.0175	0.0250	0.0250
		0.0250	0.0250	0.0500	0.0500	0.0500	0.0625	0.0750	0.1000	0.1000	0.1000
		0.1500	0.3000	0.3000							
96	NO	0.0020	0.0050	0.0500	0.0875	0.1000	0.1000	0.1000	0.1500	0.3000	
97	NO	0.0020	0.0100	0.1000	0.1000						
98	NO	0.0050	0.0050	0.0100	0.0100	0.0100	0.0250	0.0500	0.0500	0.1000	0.1500
		0.3000	0.3000	0.3000							
99	NO	0.0050	0.0100	0.0250	0.0500	0.0500	0.0500	0.1000	0.1000	0.2800	0.3600
1/2 2000	NO	0.0050	0.0100	0.0250	0.0500	0.1000	0.1000				
96	NOx	0.0100	0.0500								
1/2 2000	NOx	0.0100									
95	O2	2.0000	2.0000	10.0000	10.0000	21.0000	21.0000				
96	O2	10.0000	20.0000								
98	O2	2.0000	2.0000	4.5000	5.0000	7.0000	10.0000	10.0000	10.0000	10.0000	12.0000
		15.0000	16.0000	21.0000	21.0000	21.0000	21.0000	21.0000	23.0000	23.0000	24.0000
99	O2	0.5000	2.0000	2.0000	12.0000	21.0000					
1/2 2000	O2	2.0000	10.0000	21.0000	24.0000						

NTRM Batches by Specie and Year

99	H2S	0.0025	0.0050	0.0100	0.0250							
1/2 2000	H2S	0.0020	0.0025	0.0300								
93	SO2	0.0050	0.0100	0.0260	0.0500	0.1000	0.1500	0.3500				
94	SO2	0.0500										
95	SO2	0.0050	0.0050	0.0100	0.0100	0.0175	0.0260	0.0375	0.0500	0.1000	0.1000	0.1250
		0.1500	0.1500	0.2500	0.3000	0.3200	0.3500	0.3500				
96	SO2	0.0500	0.0500	0.0500	0.0875	0.1000	0.1000	0.1000	0.2000	0.2800	0.3500	0.3500
97	SO2	0.0050	0.0100	0.0100	0.0100	0.0500	0.0500	0.1000	0.1500	0.1500	0.2500	0.2500
98	SO2	0.0050	0.0050	0.0100	0.0100	0.0100	0.0250	0.0250	0.0250	0.0500	0.0500	0.1000
		0.1000	0.3500									
99	SO2	0.0050	0.2500									

Measurement of Bias



Continuing Problems

- Straight thread valves
- NO mixtures for NO_2
- Low NO mixtures
- NOx mixtures
- H_2S mixtures
- Hydrocarbon mixtures
  - Analyze BS using GC then homogeneity by GC or THCA
  - Other hydrocarbons
- NIST Primary Standards
- Sufficient standards for producer work

Standards for Producer Analysis

- SRMs
- In certification NTRMs
- PRMs from NMi
- GMIS

If standards other than SRMs or NTRMs are used then information detailing their preparation and verification will have to be supplied

NIST Gripes

- Analyses by Producers
  - Many seem to be done in production facility rather than laboratory
  - Some data resolution done to 1 part in 50 which is 2% whereas we would like to see work done to 0.2%
  - Data reduction does not seem to be sufficiently reviewed
  - Reports are boiler plate rather than specific
  - Report contents could be improved
- Producer Scheduling; planning ahead and sticking to plan

Producer Gripes

- Turnaround time
- Scheduling and sticking to schedule
- Cylinder return
- Conflict resolution

Conflict Resolution

- Most of this results from disagreement between NIST and the producer on the analytical value of batch ie Factor “f” too large
- Past approach
  - NIST would redo the analysis to double check their result
  - This was frequently done at a later time because of slowness of NIST data evaluation
  - NIST would inform Producer of problem only after 2nd analysis which could have been months after 1st analysis
- Current approach
  - NIST reviews NIST data in real time
  - Any re-analysis is done while instrumentation is still set up
  - Producer is informed shortly after QA on NIST results
  - If Producer works to resolve the problem then continues to work with them
  - If Producer does not respond promptly then a report will be issued stating that the batch is not certified “at this time” but giving the Producer the option to resolve conflict and have the batch certified
  - The cost of certification is charged by NIST regardless of outcome

Some Rejected Batches

- NO at 100ppm for high NO_2
- NO at 50ppm for degradation with high NO_2
- SO_2 at 50ppm for inhomogeneity
- NO at 20ppm and below for degradation
  - To date the only batches of NTRMs that have not passed the re-certification tests have been low level NO
- CO at 10ppm
  - Producer said 0.3% spread in batch
  - NIST determined 3% spread
- NO submitted at 100ppm analyzed to be 500ppm
  - Producer could not definitively explain

Uncertainties

- What are the requirements for U's for NTRMs and SRMs?
- Are there regulations?
- Are there EPA requirements?
- Are U's at 0.5% relative needed?
- Are U's at 1% relative sufficiently good?
- Where are U's incorporated in calculations?