The application of EA-IRMS to stable isotope analysis of explosives

Charles Belanger

- Notification of hazardous goods
    - MSDS Sheets
- Receipt of samples
    - Inspection
- Booking in
    - Client notification
    - Assignment of reference and tracking number
    - Labelling of samples with unique reference number
- Sample storage
    - Safety
    - Correct atmosphere (heat, light, moisture)
    - Contamination
    - Security (internal, external)

- Drying, grinding, homogenising where necessary
- Identification of material (where possible)
    - Chemical structure
- Unknown sample screening
    - Analysis of sub-samples to determine CNHOS makeup
    - Approximation of isotope enrichment
    - Calculate required samples size for analysis
        - Sufficient material present?

- Select reference material based on sample material
    - Similar to sample material (best possible)
        - Elemental composition
        - Isotopic enrichment
    - Traceable to primary reference materials
        - Air, PDB, SMOW, CDT
- Select quality control materials
    - Different to sample and reference materials
        - Elemental composition
        - Isotopic composition
    - Calibrated samples
    - Previous samples

Primary Reference Standards

	PDB	SMOW	AIR	CDT
Name	Pee Dee Belemnite	Standard Mean Ocean Water	Nitrogen in Air	Canyon Diablo Triolite
Material	$CaCO_3$	H_2O	N_2	FeS
Isotopes	^{13}C ^{18}O	^{2}H ^{18}O	^{15}N	^{34}S

❖ **Available in small quantities or not at all.**

Secondary Reference Standards: ^{13}C

	NBS-22	***IAEA-CH-6***	***IAEA-CH-7***
Material	Mineral Oil	Sucrose	Polyethylene
Published values	-29.7 ‰	-10.4 ‰	-31.8 ‰

Secondary Reference Standards: ^{15}N

	IAEA-N-1	***IAEA-N-2***	***IAEA-NO-3***
Material	Ammonium Sulphate	Ammonium Sulphate	Potassium Nitrate
Published values	+0.4 ‰	+20.3 ‰	+4.7 ‰

Secondary Reference Standards: ^{34}S

	IAEA-S-1	***IAEA-S-2***	***IAEA-S-3***
Material	Silver Sulphide	Silver Sulphide	Silver Sulphide
Published values	-0.3 ‰	+21.5 ‰	~ -31.4 ‰

Secondary Reference Standards: ^{18}O

	V-SMOW	***IAEA-CH-6***
Material	Water	Sucrose
Published values	0.0 ‰	*+36.4 ‰

Tertiary/Working Reference Standards

- **Available in larger quantities**
- **For day to day analysis**
- **Carefully calibrated and traceable to primary standards**
- **Matrix similar to samples**
- **Isotopic enrichment similar to samples**

ISO ANALYTICAL

LOADING SHEET-Blank

Batch No: 120602A3.BCH

IA Ref No: 020408-4

Client: AB Client Ltd.

Date Prep'd: 11/04/2002

Analyst: A N Other

Analysis Notes	
Nitrogen .SET	
Urea-A .REF	
Nitrogen .SRC	
Sample Wt: 0.8mg	Ref Wt/Vol: 0.3mg
Catalyst: none	Capsules: Tin 8x5
Sample Tray: 123	Reference Tray: 123

Position	Plate	Sample	Wt./Vol.
1	-	Blank	-
2	-	Blank	-
3	-	Blank	-
4	A1	Dummy	0.27
5	A2	Dummy	0.28
6	A3	Reference	0.31
7	C1	Sample-1	0.79
8	C2	Sample-1	0.8
9	C3	Sample-2	0.82
10	C4	Sample-2	0.75
11	C5	Sample-3	0.86
12	C6	Sample-3	0.84
13	C7	Sample-4	0.71
14	C8	Sample-4	0.75
15	A4	Test Urea A	0.28
16	A5	Reference	0.31
17	D1	Sample-5	0.82
18	D2	Sample-5	0.75
19	D3	Sample-6	0.86
20	D4	Sample-6	0.84
21	D5	Sample-7	0.71
22	D6	Sample-7	0.75
23	B1	Test Sample 1	0.35
24	B2	Test Sample 1	0.33
25	A6	Test Urea A	0.3
26	A7	Reference	0.29
27	E1	Sample-8	0.82
28	E2	Sample-8	0.75
29	E3	Sample-9	0.86
30	E4	Sample-9	0.82
31	E5	Sample-10	0.75
32	E6	Sample-10	0.86

Position	Plate	Sample	Wt./Vol.
34	E8	Sample-11	0.82
35	B3	Test Sample 2	0.33
36	B4	Test Sample 2	0.33
37	A8	Test Urea A	0.032
38	A9	Reference	0.27
39			
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48			
49			
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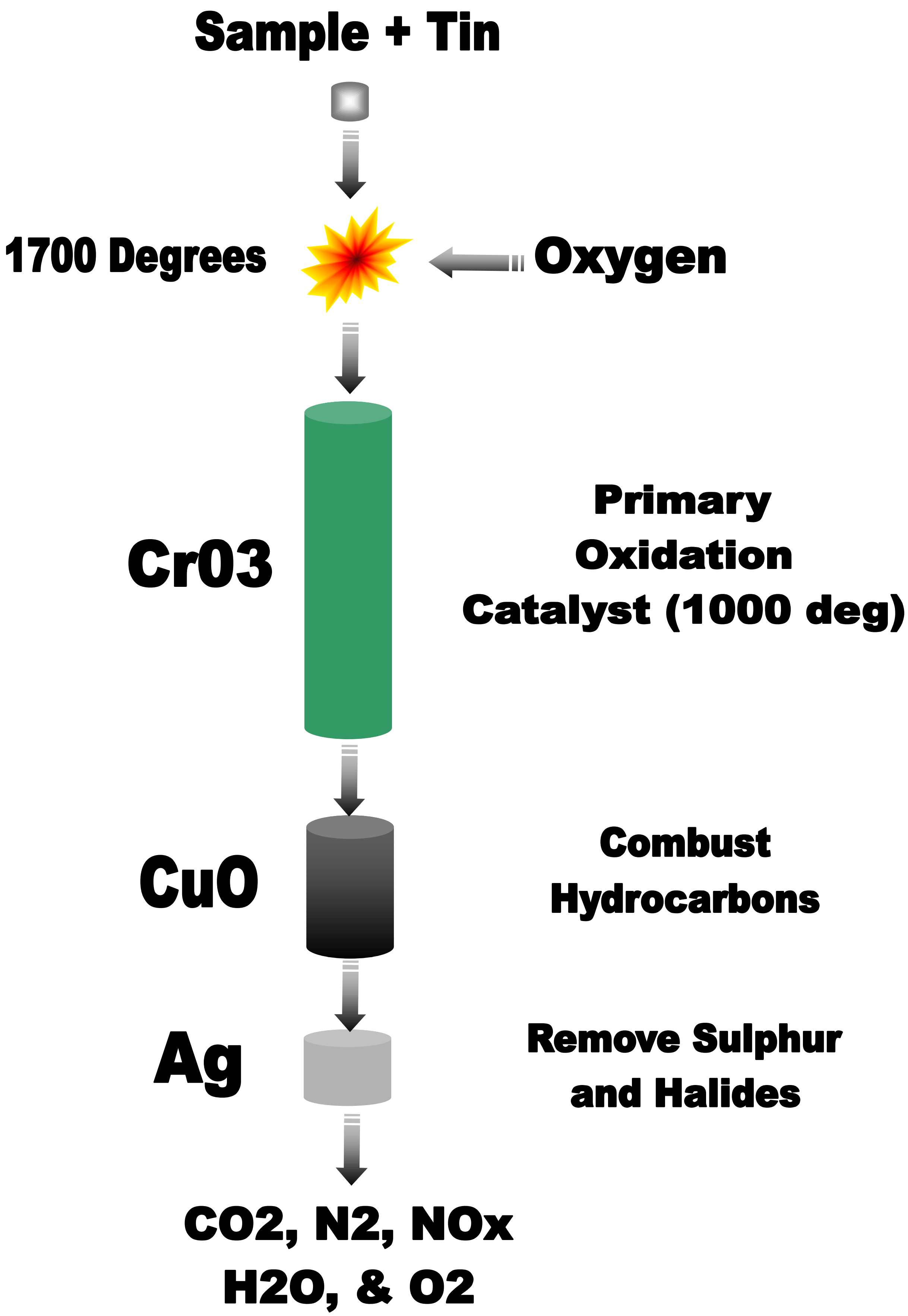
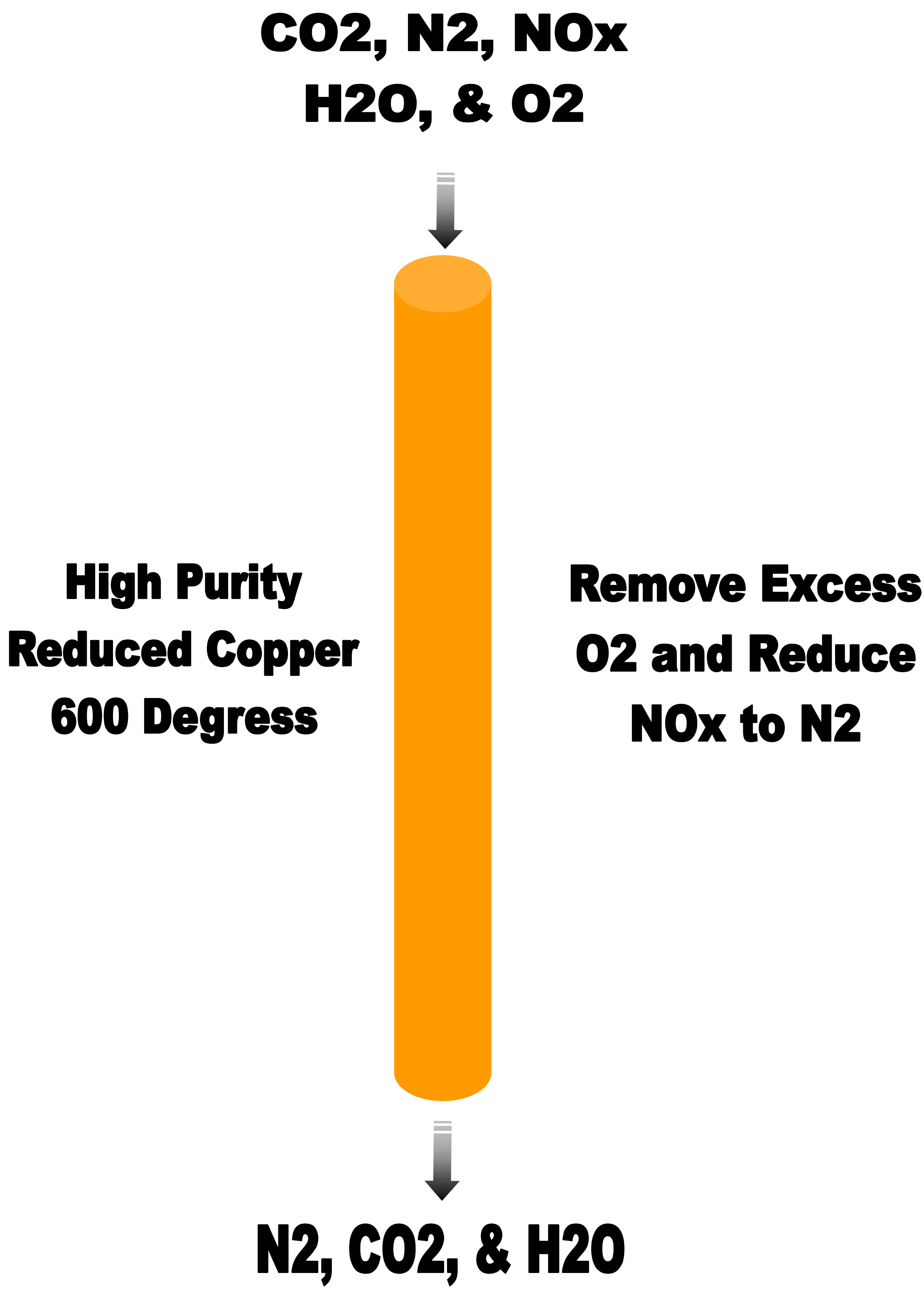
60			
61			
62			
63		6	
64			
65			

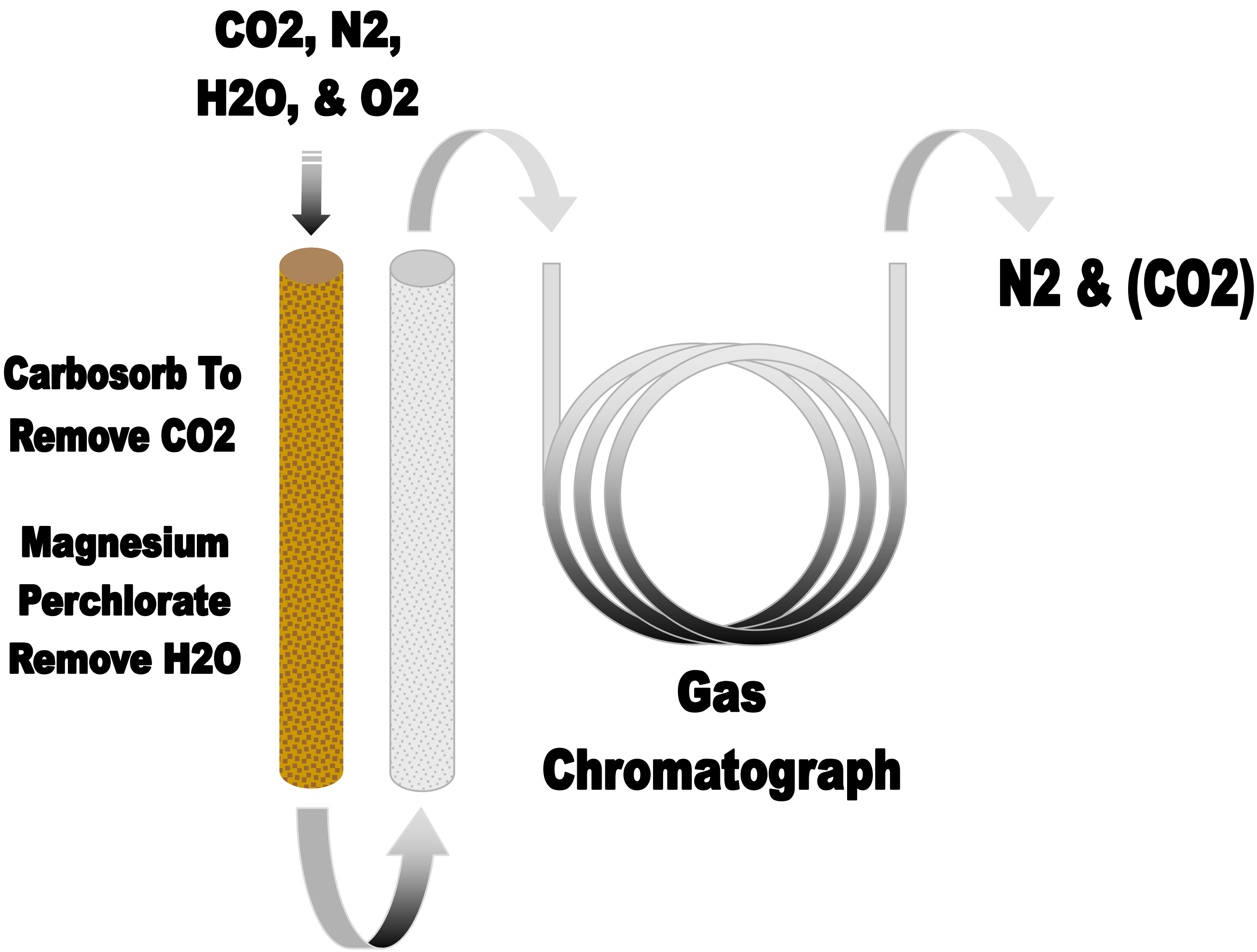
Dumas Combustion

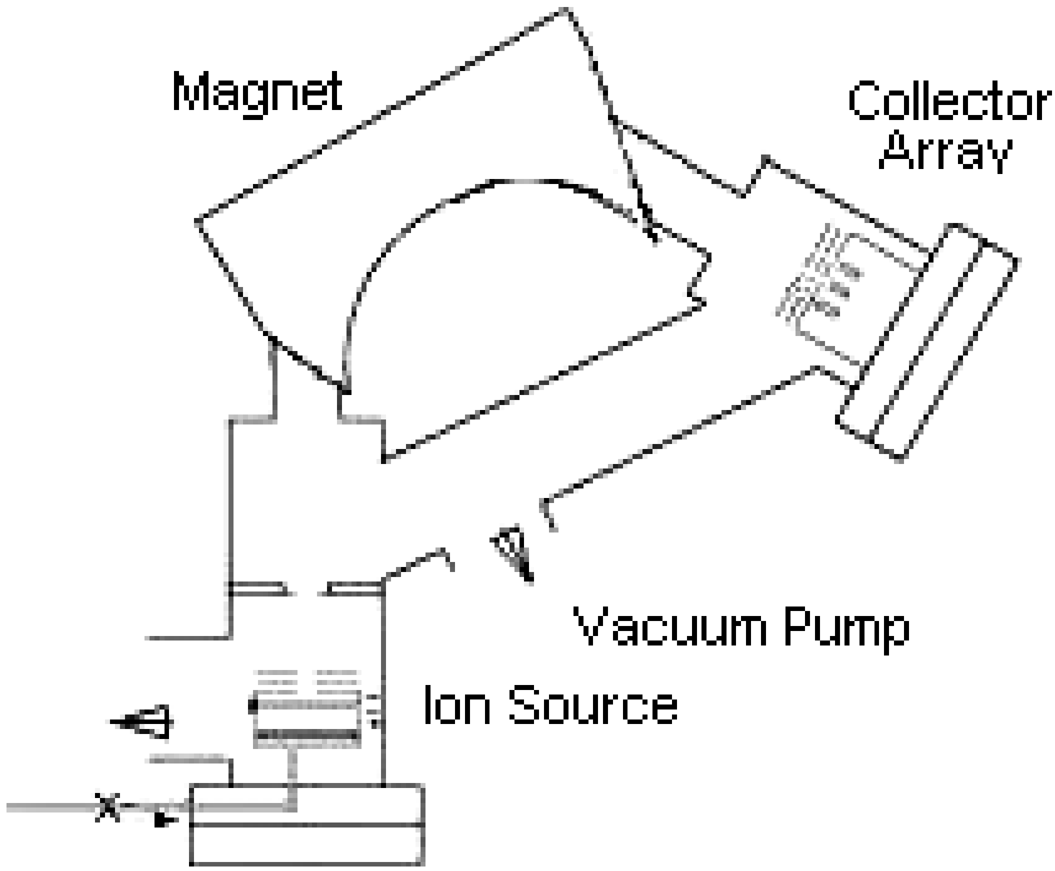


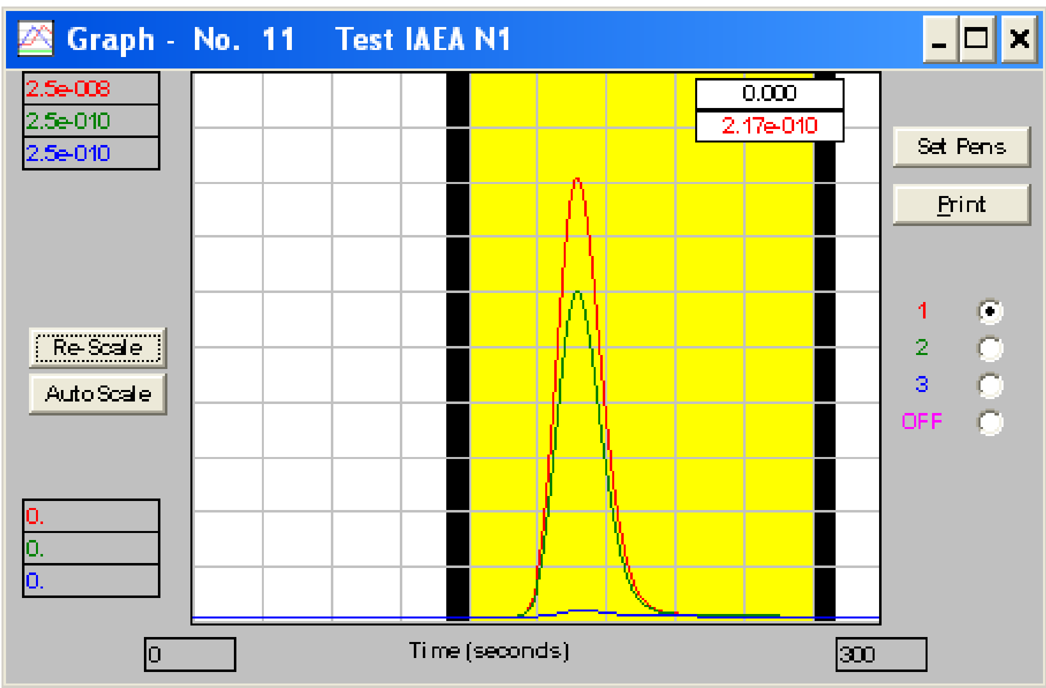
Reduction Stage



Chemical Traps & Chromatography

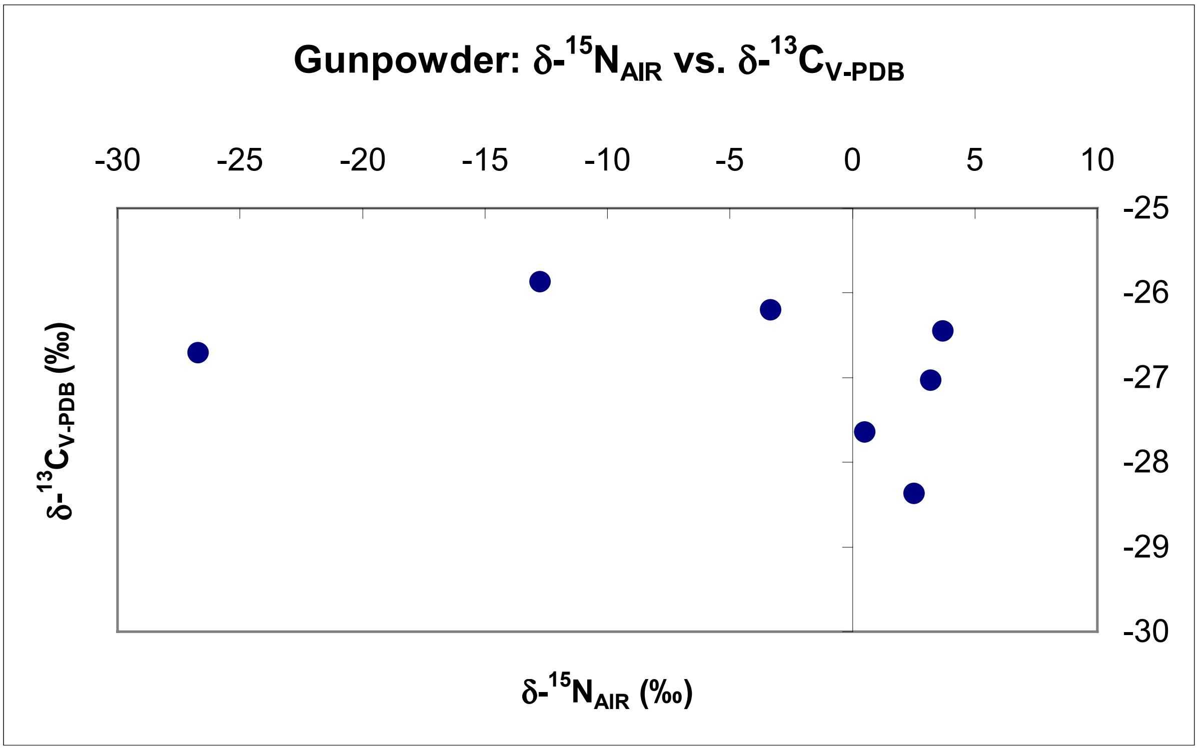



Magnet
Collector Array
Vacuum Pump
Ion Source


Graph - No. 11 Test IAEA N1
2.5e-008
2.5e-010
2.5e-010
0.000
2.17e-010
Set Pens
Print
1
2
3
OFF
Re-Scale
Auto Scale
0.
0.
0.
0
Time (seconds)
300

Material
Ammonium Nitrate
Gunpowder
TNT
Plastic Explosive

Material	Nitrogen-15	Carbon-13
Ammonium Nitrate	Range = 5.4 ‰ n of 7	-
Gunpowder	Range = 30.4 ‰ n of 7	Range = 2.5 ‰ n of 7
TNT	Range = 19.8 ‰ n of 3	Range = 3.1 ‰ n of 3
Plastic Explosive	Range = 14.0 ‰ n of 4	Range = 10.1 ‰ n of 4



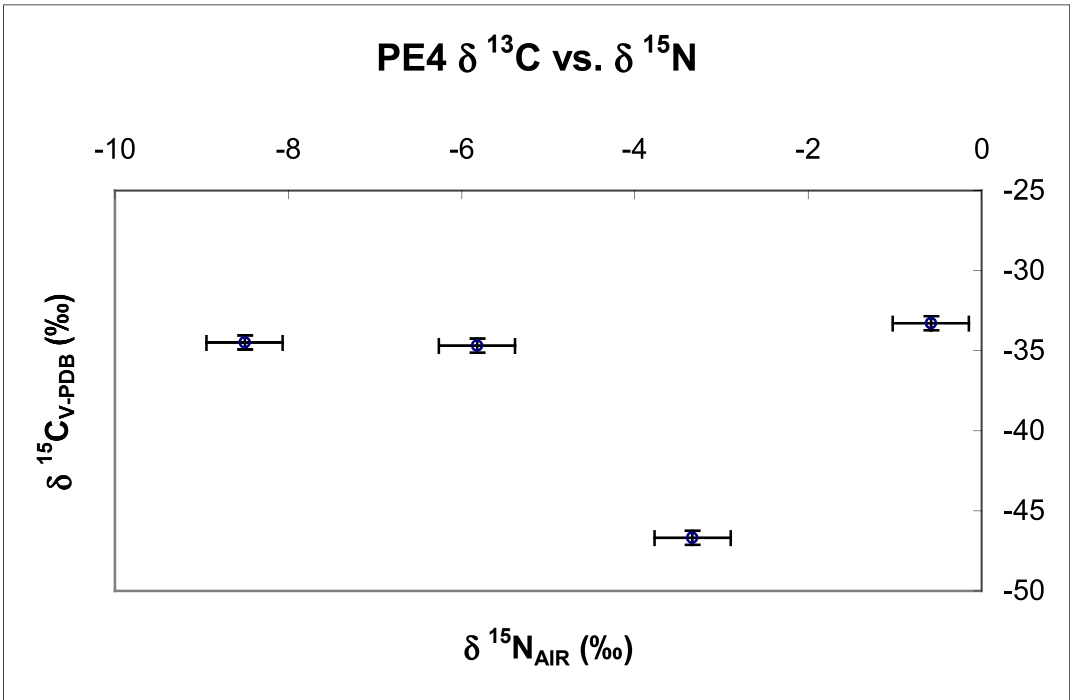
Blind Study: PE4

Sample ID	Mean δ-$^{15}N_{AIR}$ (‰) n of 6	1sd (‰) n of 6	Mean δ-$^{13}C_{V\text{-}PDB}$ (‰) n of 6	1sd (‰) n of 6
Ref: 1	-8.50	0.13	-34.48	0.23
Ref: 2	-3.34	*0.64*	-46.67	*0.50*
Ref: 3	-5.82	0.09	-34.68	0.13
Ref: 4	-0.59	0.14	-33.28	0.09
Ref: X	-5.81	0.08	-34.79	0.14
	mean 1sd =	0.22	mean 1sd =	0.22
	mean 2sd =	0.44	mean 2sd =	0.44

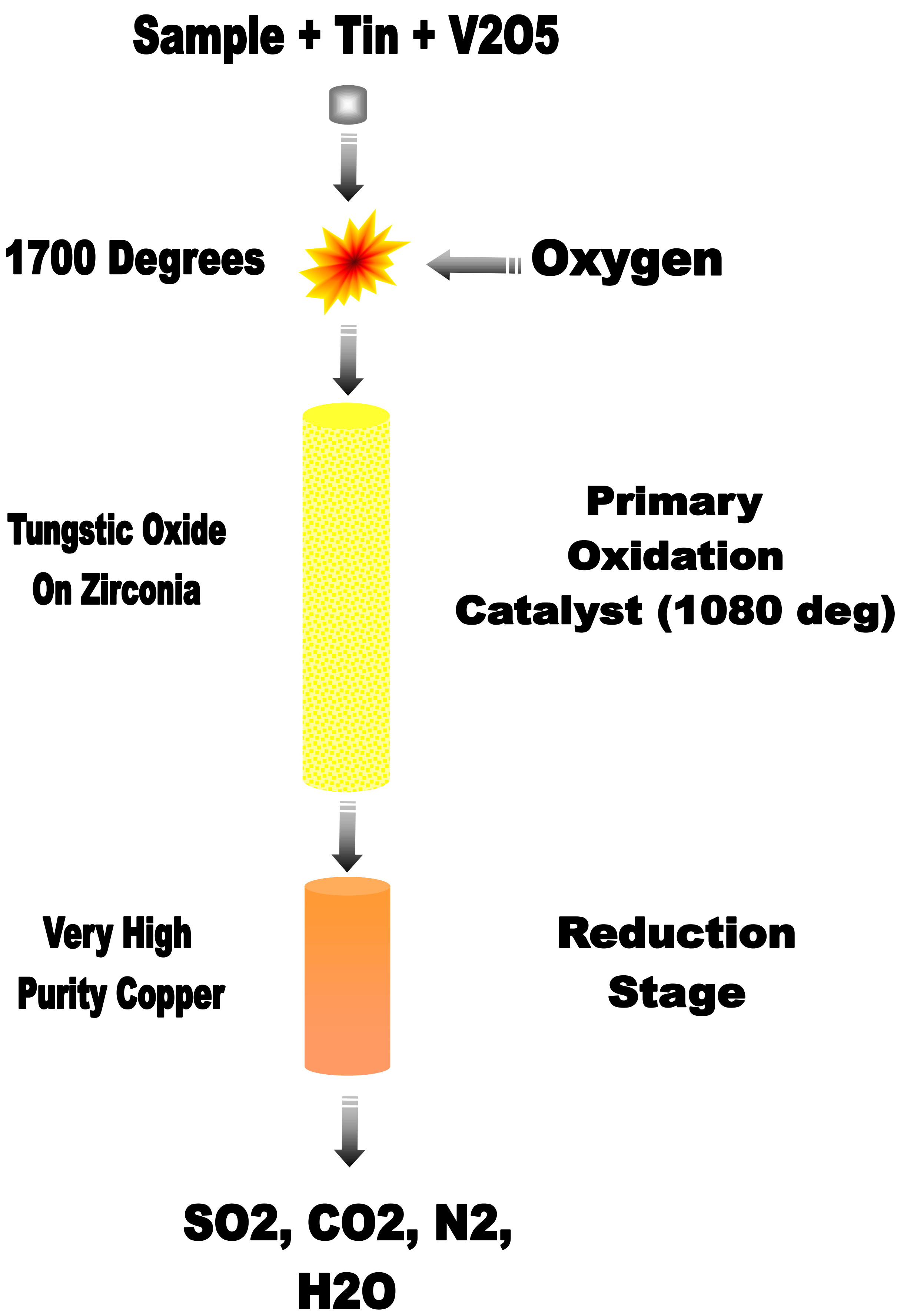
Determination of Sample 'X'

Is sample x within 2sd of the sample?

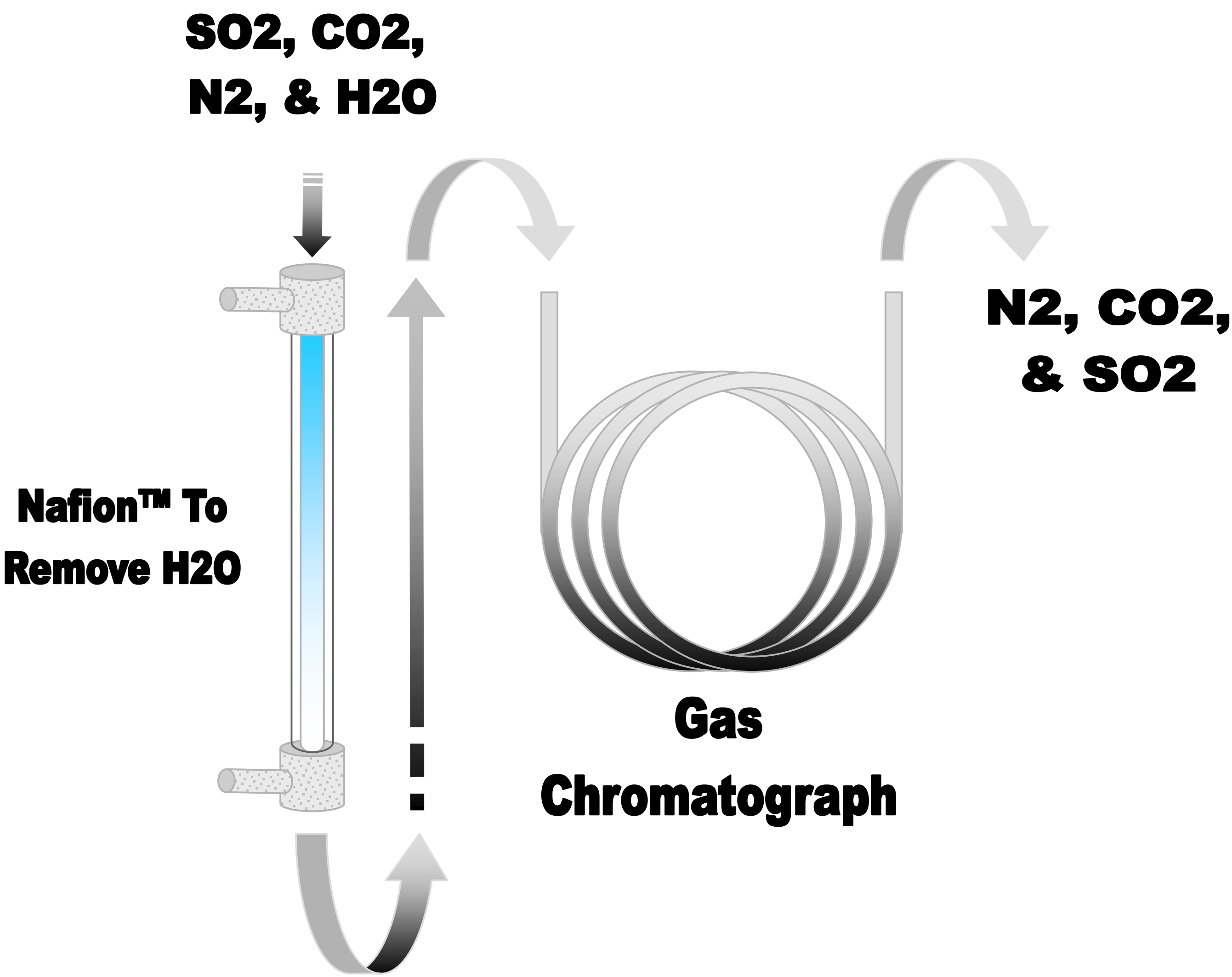
ID	δ-^{15}N < 2sd	δ-^{15}N < 2sd
Ref: 1	No	**Yes**
Ref: 2	No	No
Ref: 3	**Yes**	**Yes**
Ref: 4	No	No



Sulphur Combustion



Water Removal
& Chromatography

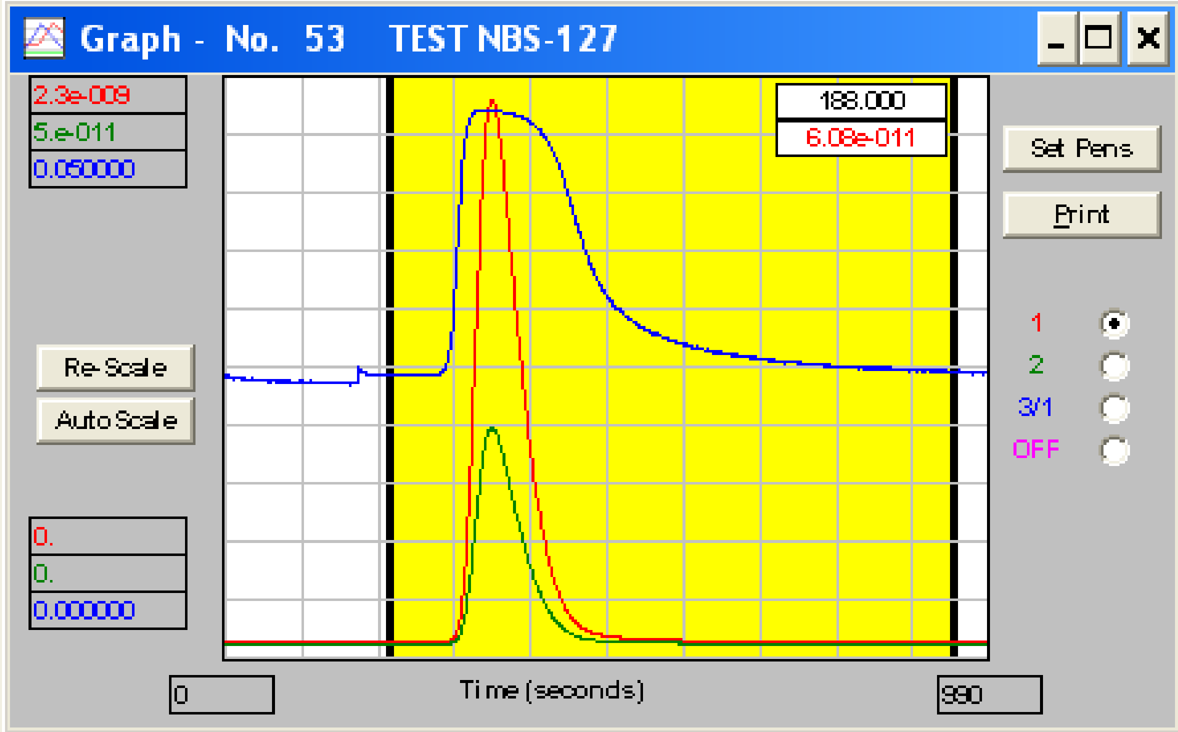


Factors effecting $\delta\ ^{34}S$ measurements

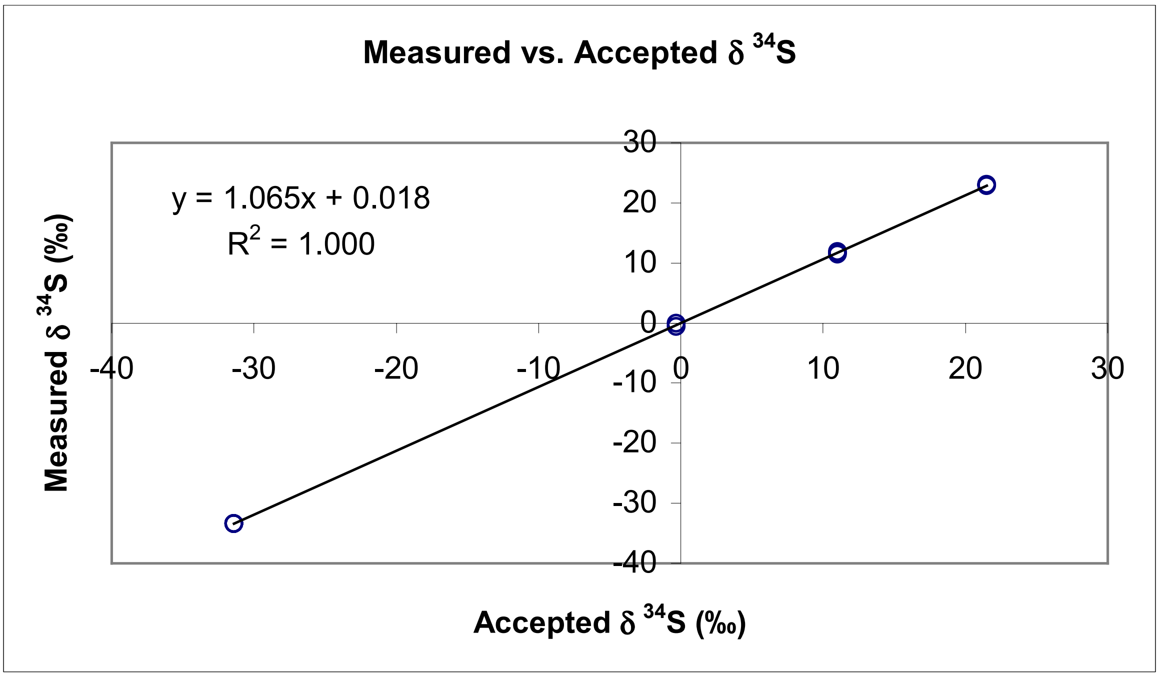
- Carbon dioxide interference
  - In general, high carbon content and low sulphur content
  - Chromatographically, CO_2 will elute before SO_2
  - What you don't see <u>can</u> hurt you
- Chromatographic 'tailing'
  - SO_2 chromatographic peaks tend to have long 'tailing' period
- Oxygen-18 interference
  - $^{32}S^{16}O_2 = {}^{32}S + {}^{16}O + {}^{16}O = 64$
  - $^{34}S^{16}O_2 = \underline{^{34}S} + {}^{16}O + {}^{16}O = 66$
  - $^{32}S^{18}O_2 = {}^{32}S + \underline{^{18}O} + {}^{16}O = 66 \leftarrow$
  - Various oxygen sources
    - V_2O_5, Sample, O_2 pulse, catalyst

Overcoming these factors

- CO_2 interference solved by diverting
  - Physical diversion of eluting CO_2 peak to atmosphere using automated valves
  - Improved results, reduced source pressure
- Integration of entire peak elution period
  - Amplification dependent on mass collected.
  - Integration of SO2 peak allowing for <u>all</u> ion beams to reach baseline values.
- Oxygen-18 Correction
  - Analysis of a range of accepted/traceable standards.
  - Correction curve generated.
  - Samples and QC standards corrected.
  - Oxygen-18 Correction
- Applications limited to sulphur bearing samples
  - Gunpowder

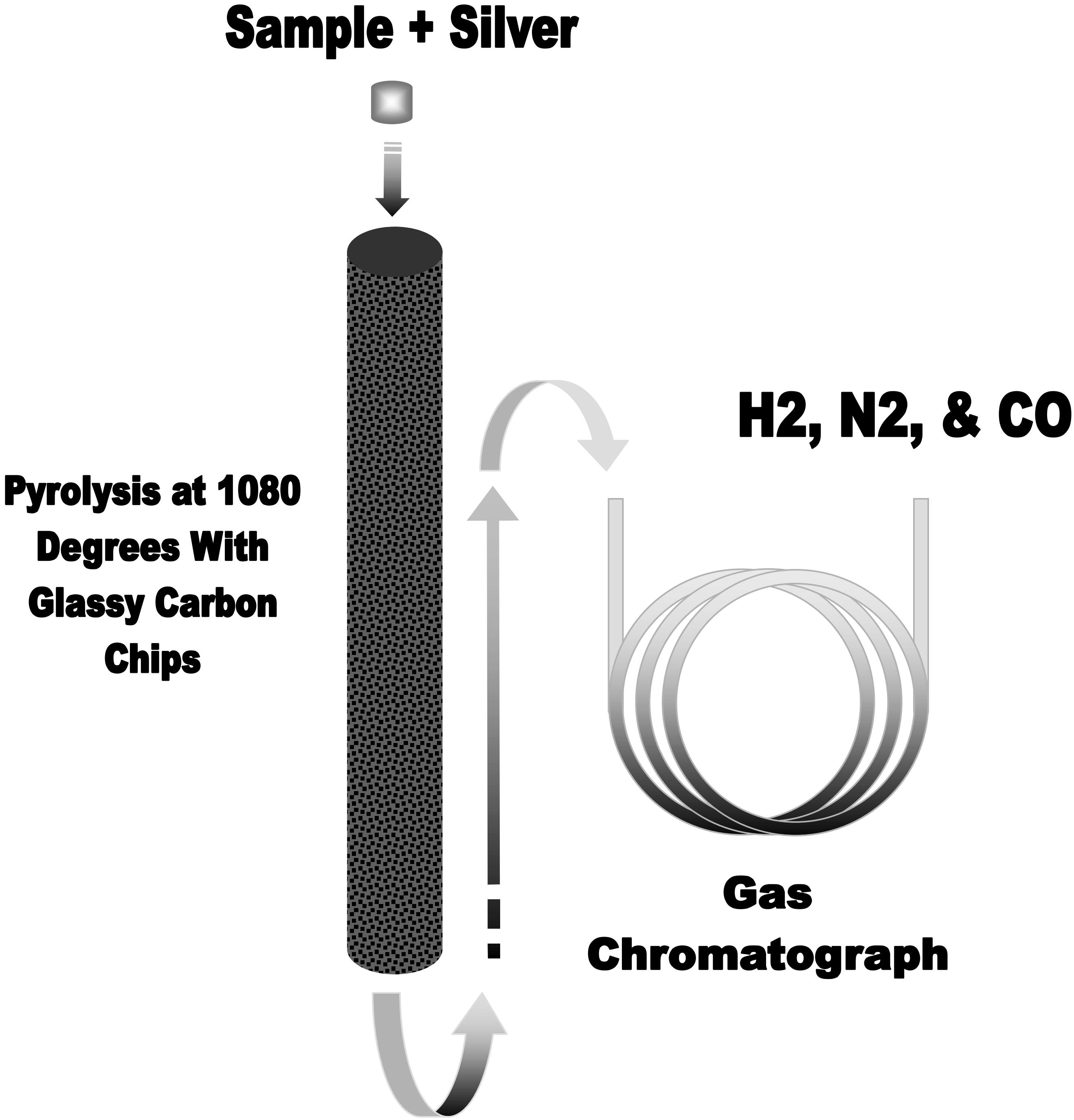


Graph - No. 53 TEST NBS-127
2.3e-009
5.e-011
0.050000
188.000
6.08e-011
Set Pens
Print
Re-Scale
Auto Scale
1
2
3/1
OFF
0.
0.
0.000000
0
Time (seconds)
990



Measured vs. Accepted δ 34S
y = 1.065x + 0.018
R2 = 1.000
Measured δ 34S (‰)
Accepted δ 34S (‰)

Oxygen-18 Pyrolysis



Oxygen-18 Analysis by Pyrolysis (total conversion)

- Samples in CHNOS matrix thermally converted to H_2, CO, N_2 with elemental S deposition.
- Oxygen-18 determined by isotope ratio measurement of CO (masses 28, 29, and 30)
- CO resolved from N2 and H2 by packed molecular sieve 5A GC column
- Ensure total or near total conversion
- Sample preparation
  - Ensure stability
  - Keep dry!
  - Silver capsules

Oxygen-18 Analysis of RDX and Nitro-glycerine

- Conversion rates to CO tested using ‘standard’ pyrolysis set-up
- RDX conversion to CO found to be ~65%
- NG conversion to CO found to be ~79%
- Both RDX and NG found to have high standard deviations of analysis and day-to-day variation.
- New method required.

Modified pyrolysis technique

- RDX conversion rate improved to ~97%
- NG conversion rate improved to ~100%
- ‘Typical’ standard deviation of analysis of 0.4 ‰ n of 6
- Day-to-day results consistent

Modified Pyrolysis