Calibration Mixtures for Improving Accuracy of Stable Isotope Measurements

Air Liquide
creative oxygen

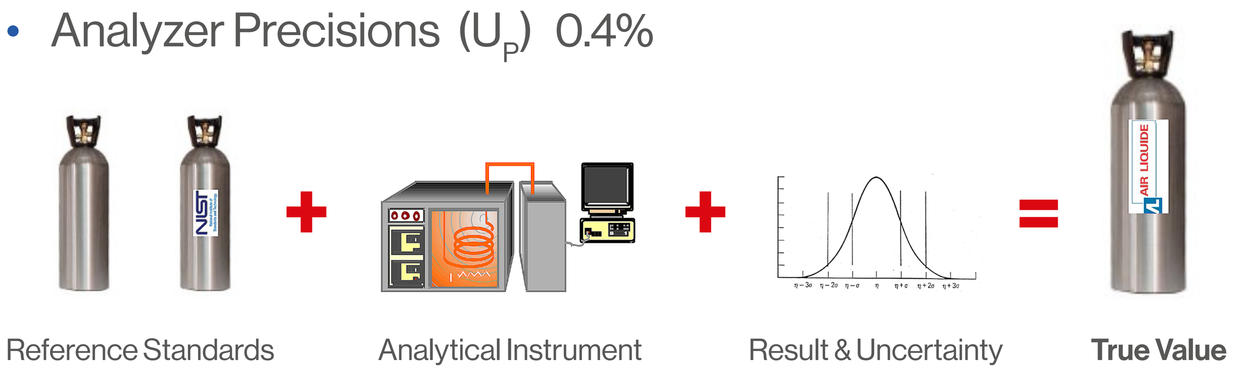
Tracey Jacksier[1], M. C. Matthew[2], Jack de Jong[3]

Errors and Uncertainties

The calibration of an analyser is a measure of the equipment trueness by a **comparison** between the **result on the analyzer** and a **reference material**.

Analytical uncertainty originates from 3 principle sources. The objective is to **minimize** these sources.

- Reference Material (U_S) 1.0%
- Analyzer Calibration (U_C) 0.8%
- Analyzer Precisions (U_P) 0.4%



"Propagation of Error" Calculation.
Accuracy (U_T) = $\pm\sqrt{(1.0)^2 + (0.8)^2 + (0.4)^2}$
Accuracy (U_T) = ± 1.3 %

Achieving an accuracy of less than the reference material is **not possible**.

Isotopic Mixture Production

Does fractionation occur when making batches of identical mixtures?
Do cylinders from the same batch have the same δ values? Consider a mixture made from **$^{15}N_2O$ / $N_2{}^{18}O$**.

	$\delta^{15}N$ avg	$\delta^{15}N$ stdev	$\delta^{18}O$ avg	$\delta^{18}O$ stdev	N
A1	0.063	0.039	-3.143	0.067	15
A2	0.057	0.049	-3.152	0.045	20
A3	0.056	0.042	-3.140	0.064	28
Pooled	0.058	0.043	-3.145	0.059	63

Cylinder filling as a function of manifold and cylinder position vs. Direct filling from mother cylinder.

		$\delta^{13}C$ Methane						$\delta^{2}H$ Methane					
	Cylinder	#1	#2	#3	avg	stdev	RSD	#1	#2	#3	avg	stdev	RSD
Direct 1	519	-40.4	-40.4	-40.5	-40.4	0.06	0.14%	-59	-59	-59	-59	0.00	0%
Direct 2	521	-40.5	-40.5	-40.5	-40.5	0.00	0%	-60	-59	-59	-59.3	0.58	0.97%
Manifold 1	560	-40.5	-40.4	-40.4	-40.4	0.06	0.14%	-58	-58	-58	-58	0.00	0%
Manifold 2	596	-40.4	-40.5	-40.3	-40.4	0.10	0.25%	-59	-60	-59	-59.3	0.58	0.97%
Manifold 3	597	-40.4	-40.4	-40.4	-40.4	0.00	0%	-59	-61	-60	-60	1.00	1.67%
Pooled					-40.4	0.06	0.15%				-59.1	0.83	1.41%

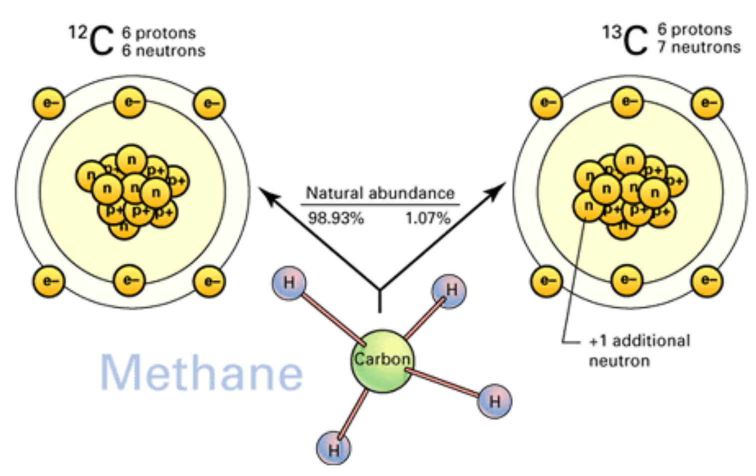
Brian N. Popp, Professor University of Hawaii, SOEST, Department of Geology & Geophysics1680 East-West Road, Honolulu, Hawaii 96822. Note: $\delta^{15}N$ and $\delta^{18}O$ are reported as relative to an internal standard.

Fractionation during cylinder filling **is not** an issue when proprietary filling technologies are utilized.

Adjusting Isotope Ratios

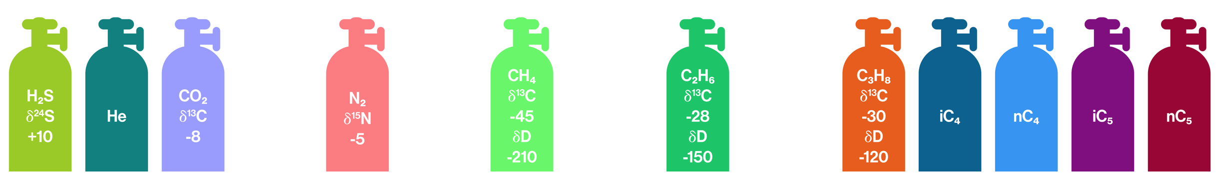
10 different isotopologues: C-H Atomic Permutations

$^{13}CH_4$, $^{13}CDH_3$, $^{13}CD2H_2$, $^{13}CD_3H$, $^{13}CD_4$ / $^{12}CH_4$, $^{12}CDH_3$, $^{12}CD2H_2$, $^{12}CD_3H$, $^{12}CD_4$



Blending Map for an Adjusted Ratio Mixture of Alkanes.

Adjusted source material Std	1	2	3	4	5	6	7	8	9	10	11
	H_2S %	He %	CO_2 %	N_2 %	C_1 %	C_2 %	C_3 %	iC_4 %	nC_4 %	iC_5 %	nC_5 %
Final Composition	2.5 $\delta^{34}S$ +10	0.5	4 $\delta^{13}CO_2$ -8	5 $\delta^{15}N_2$ -5	7 $\delta^{13}C_1$ -45	9 $\delta^{13}C_2$ -28	4 $\delta^{13}C_3$ -30	0.5	1.2	0.3	0.3
					δDC_1 -210	δDC_2 -150	δDC_3 -120				



Summary

- Errors and uncertainties are a combination of several principle sources which need to be minimized to achieve desired accuracy.
- Filling protocols have been developed and demonstrated to discount effects of mixture fractionation during production.
- Custom mixtures can be manufactured in a wide range of concentrations and δ values.

[1] Air Liquide, Delaware Research and Technology Center, 200 GBC Dr., Newark DE 19702 USA. [2] Airgas, 6141 Easton Road, Plumsteadville, PA 18949 USA. [3] Air Liquide, Northwest Europe Expertise Center, Takkebijsters 46-48, 4817 BL Breda, The Netherlands.