GEL
problem solved

The GEL Group INC

Environmental | Geophysical | Laboratory Analysis

Sample and Analysis Protocol For ^{14}C in Gaseous Effluents

Jim Holtzclaw, Ph.D., CIH

June 28, 2010

20th Annual RETS–REMP Workshop

San Jose, California

^{14}C COMPOUNDS OF INTEREST

- Organic Carbon Gases – primary form for PWRs
  - $^{14}CH_4$ and other hydrocarbons
- Inorganic Carbon Gases – primary form for BWRs
  - $^{14}CO_2$, ^{14}CO not formed in appreciable quantities
- Particulate Carbon
  - Carbonate, bicarbonate, incorporated in debris

SAMPLE MATRICES

- Air
- Potentially high moisture
- Limited oxygen at some locations
- % levels of hydrogen at some locations
- ^{14}C activities can vary by factor of 10^6 between locations
- Wide range of gas flow rates and pressure at sample locations

ANALYTICAL PROTOCOL REQUIREMENTS

- Differentiate between organic, inorganic, and particulate ^{14}C
- Accommodate wide range of sample activities
- Separate ^{14}C from other interferences
- Handle flammable, low oxygen atmospheres
- Employ practical sample times and gas volumes

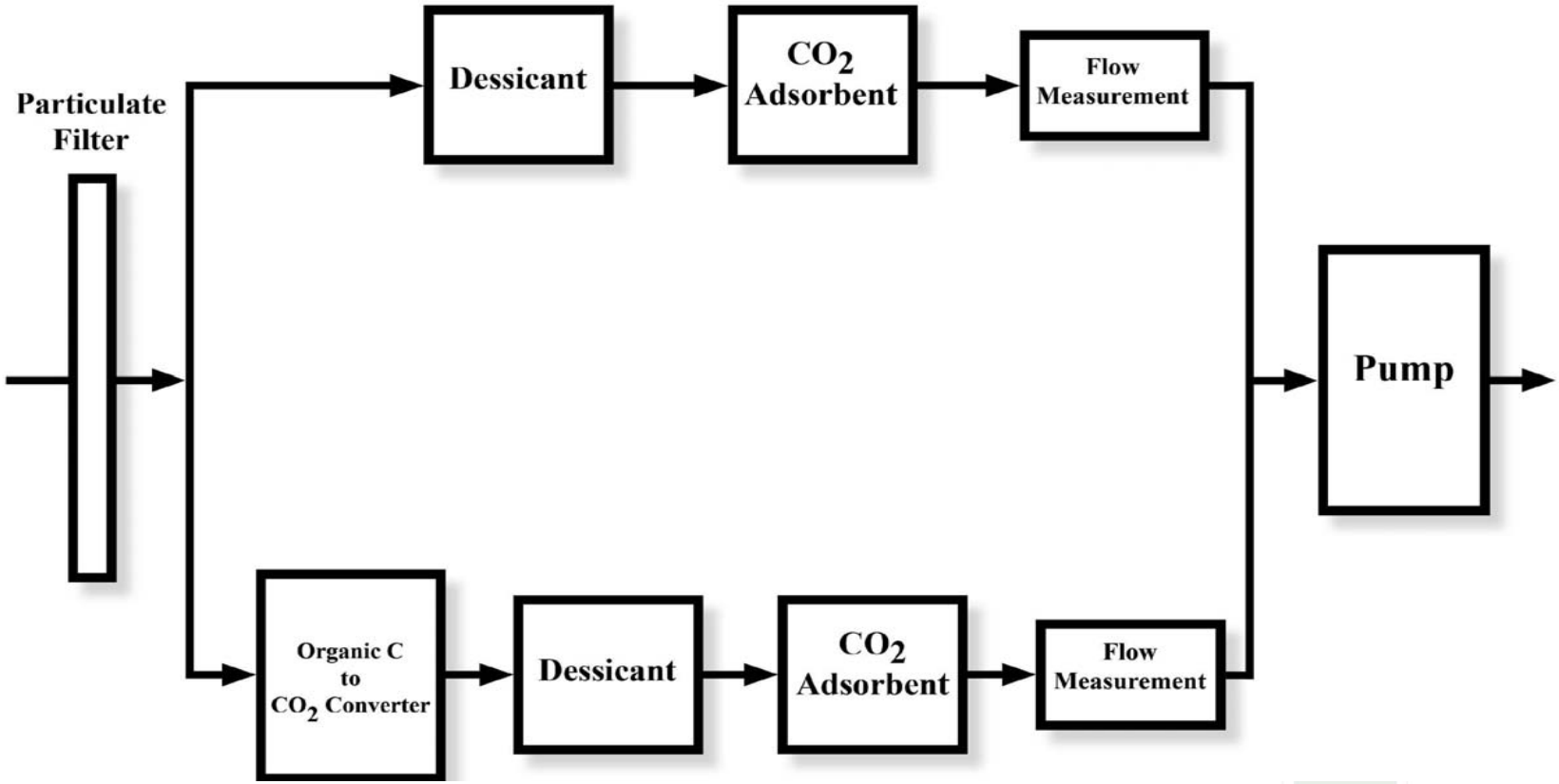
ANALYTICAL PROTOCOL REQUIREMENTS

- Accommodate differences in sample flow, sample pressure
- Adaptable to differences in process interface hardware
- Employ hardware that can be reliably and conveniently transported to and returned from facilities

PRIOR STUDIES

- Thompson – 1978
  - Combustion/mol sieve/cryo-trap/LSC
- Kunz – 1985
  - Combustion/Ascarite/cryo-trap/gas proportional counter
- IAEA – 2004
  - Review including combustion/NaOH soln/LSC
- Magnusson – 2008
  - Combustion/NaOH soln/LSC

SAMPLE COLLECTION SYSTEM



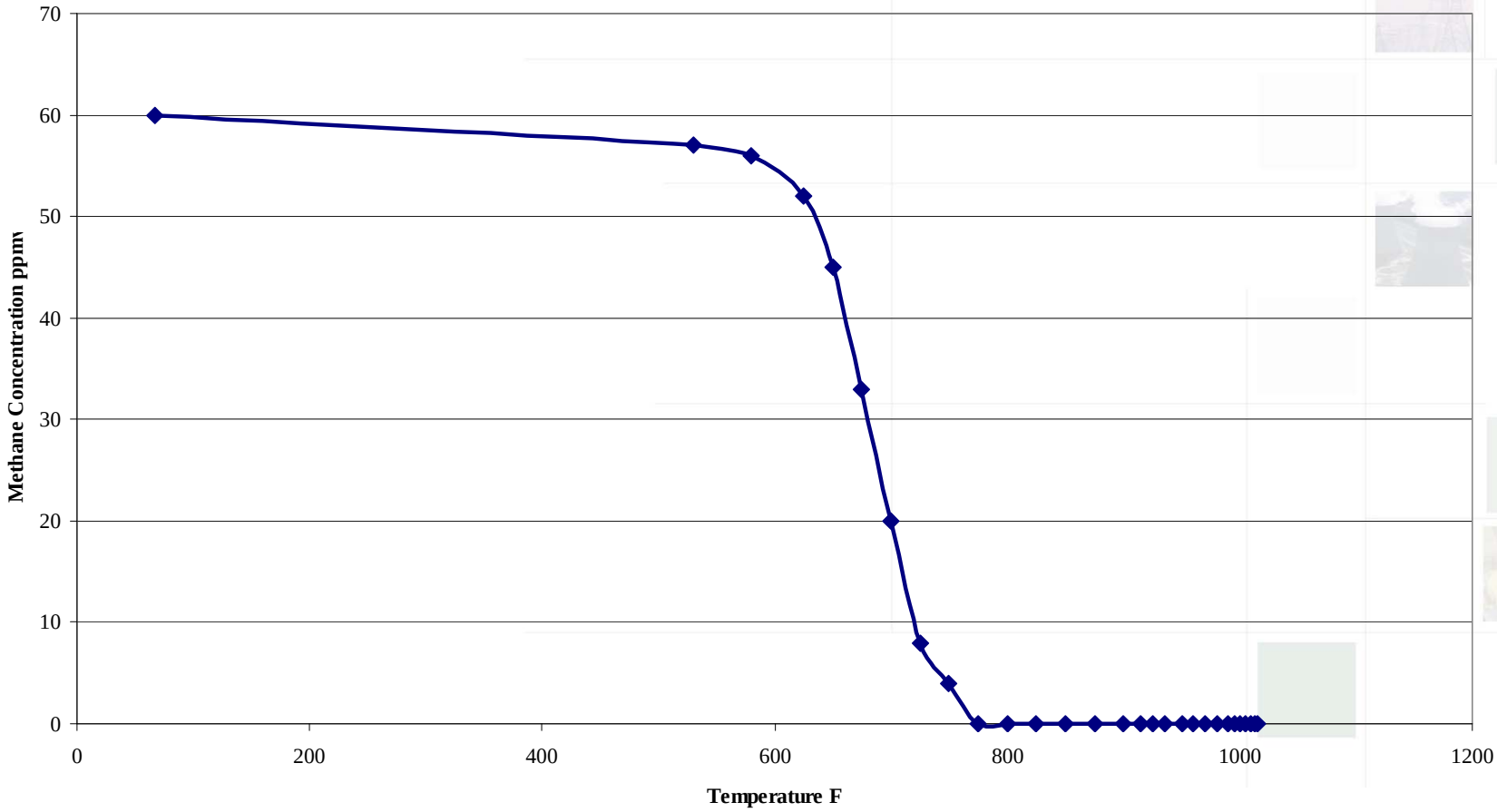
CHEMICAL REACTIONS

- CO_2 Adsorption
  - $CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$
  - $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$
- CO_2 Desorption
  - $NaHCO_3 + HNO_3 \longrightarrow NaNO_3 + H_2CO_3$
  - $H_2CO_3 \longrightarrow H_2O + CO_2$

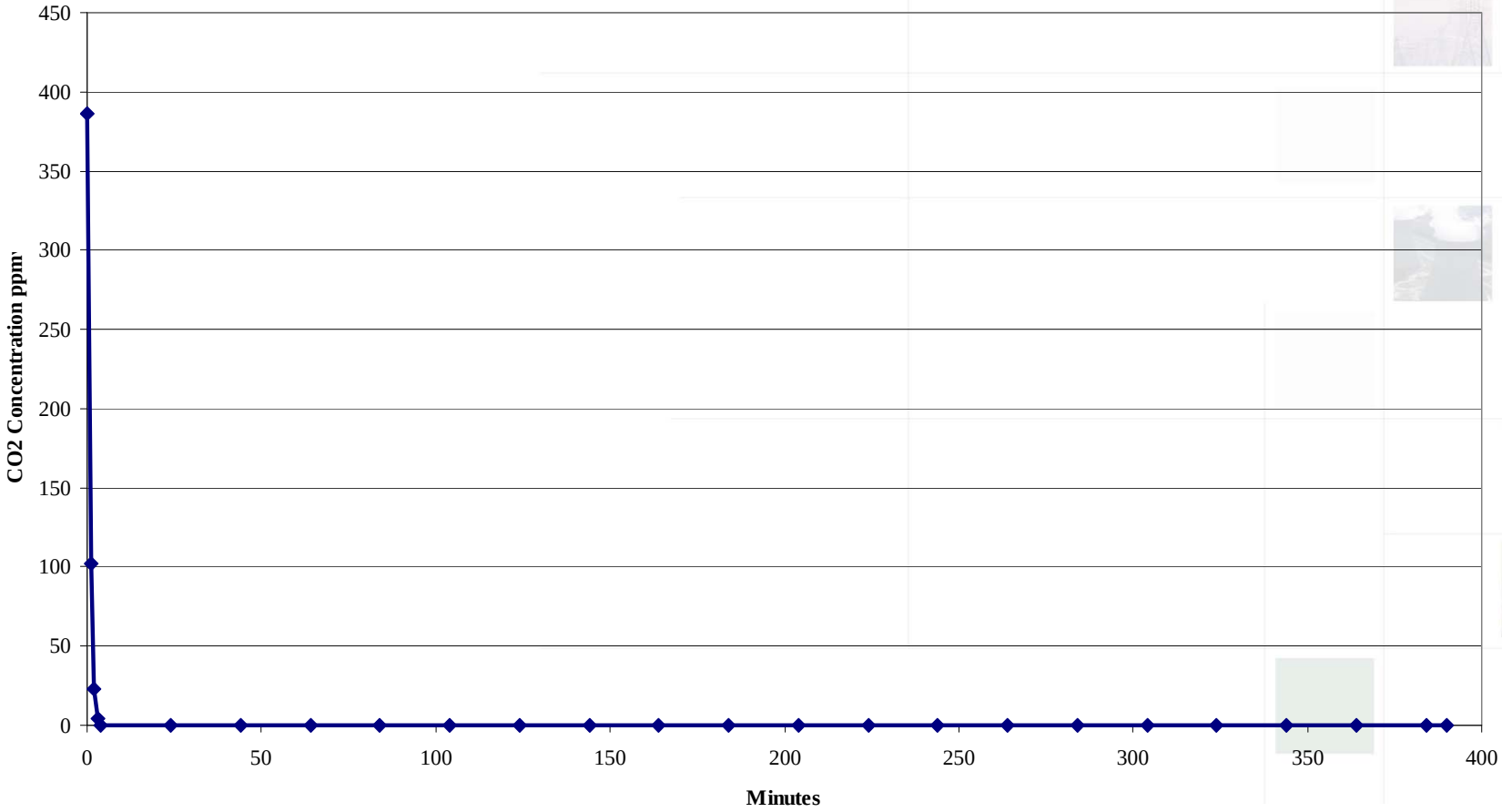
CHEMICAL REACTIONS

- Combustion
  - $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

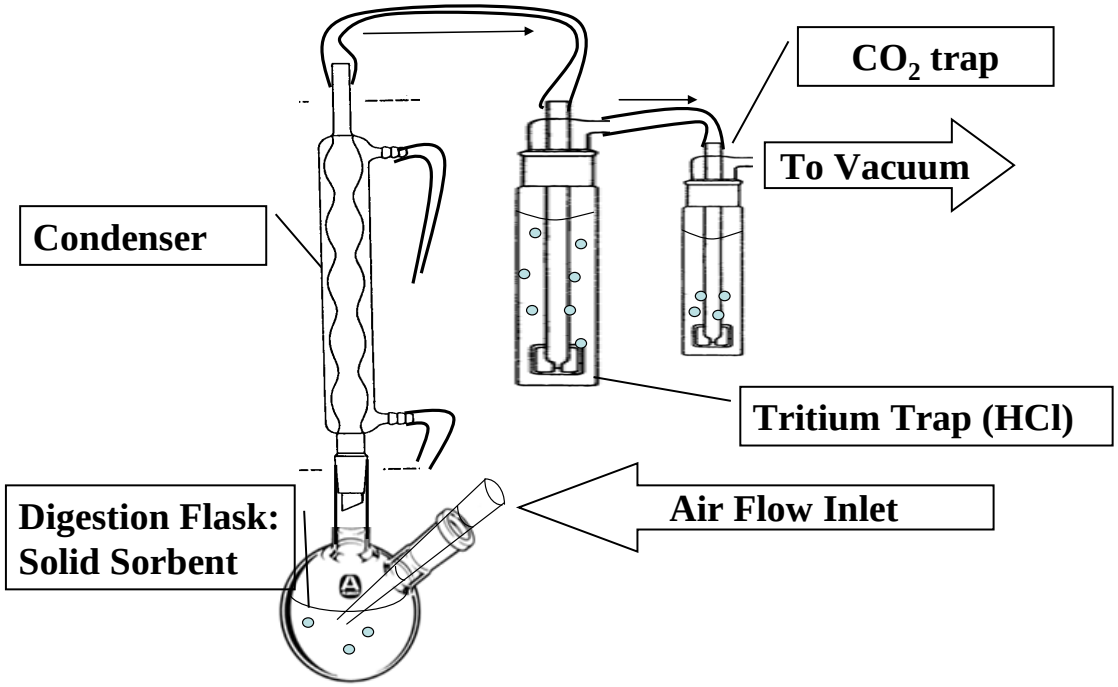
METHANE COMBUSTION EFFICIENCY 2 LPM



CO_2 ADSORPTION EFFICIENCY 1LPM



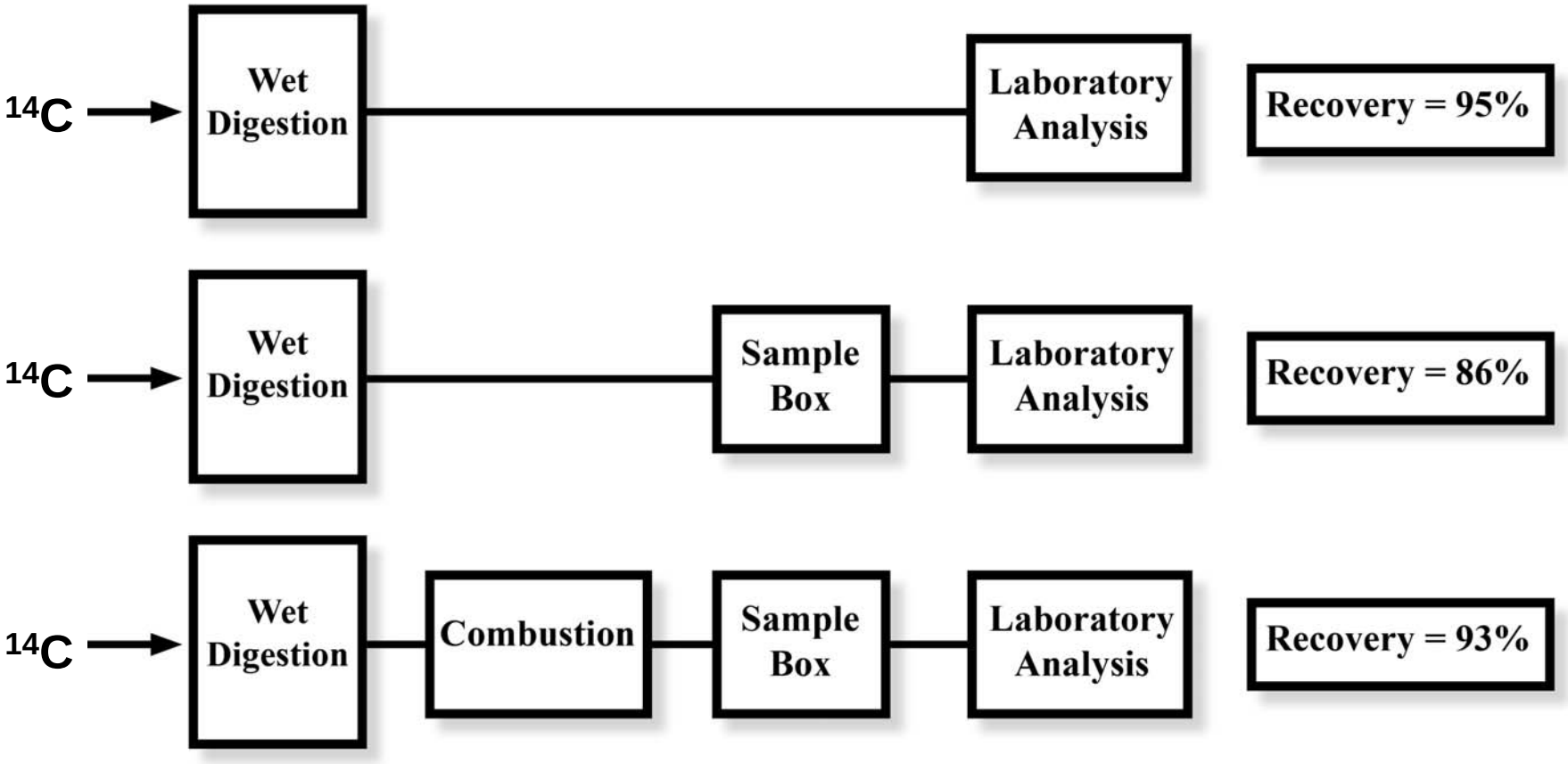
^{14}C LABORATORY DISTILLATION APPARATUS



VALIDATION OF SAMPLE ANALYSIS PROTOCOL

- Method Blank
  - 0.042 pCi/L (4.2 x10^{-11} uCi/ml)
  - Based on a 2 hour sample at 300 ml/min gas sample flow rate
- LCS
  - 95.1 +/- 3% for spike equivalent to 2.0 pCi/L (2x10^{-9} uCi/ml) (total volume sampled=3.6 x10^{4}ml)

VALIDATION OF SAMPLE COLLECTION AND ANALYSIS PROTOCOL



VALIDATION OF SAMPLE COLLECTION AND ANALYSIS PROTOCOL

LCS

(spiked into flask w/ascarite)

Nominal (pCi/sample)	LCS Recovery %
71.71	99%
71.71	97%
71.71	92%
71.71	94%
71.71	95%
71.71	91%
71.71	96%
71.71	96%
71.71	98%
71.71	91%
Average	95%

VALIDATION OF SAMPLE COLLECTION AND ANALYSIS PROTOCOL

Wet Digestion

Wet Digestion of standard to produce $^{14}CO_2$ in sample gas stream

Nominal (pCi/sample)	LCS Recovery %
10486.49	83%
10486.49	85%
10486.49	82%
71.71	85%
71.71	85%
71.71	85%
717.08	90%
Average	86%

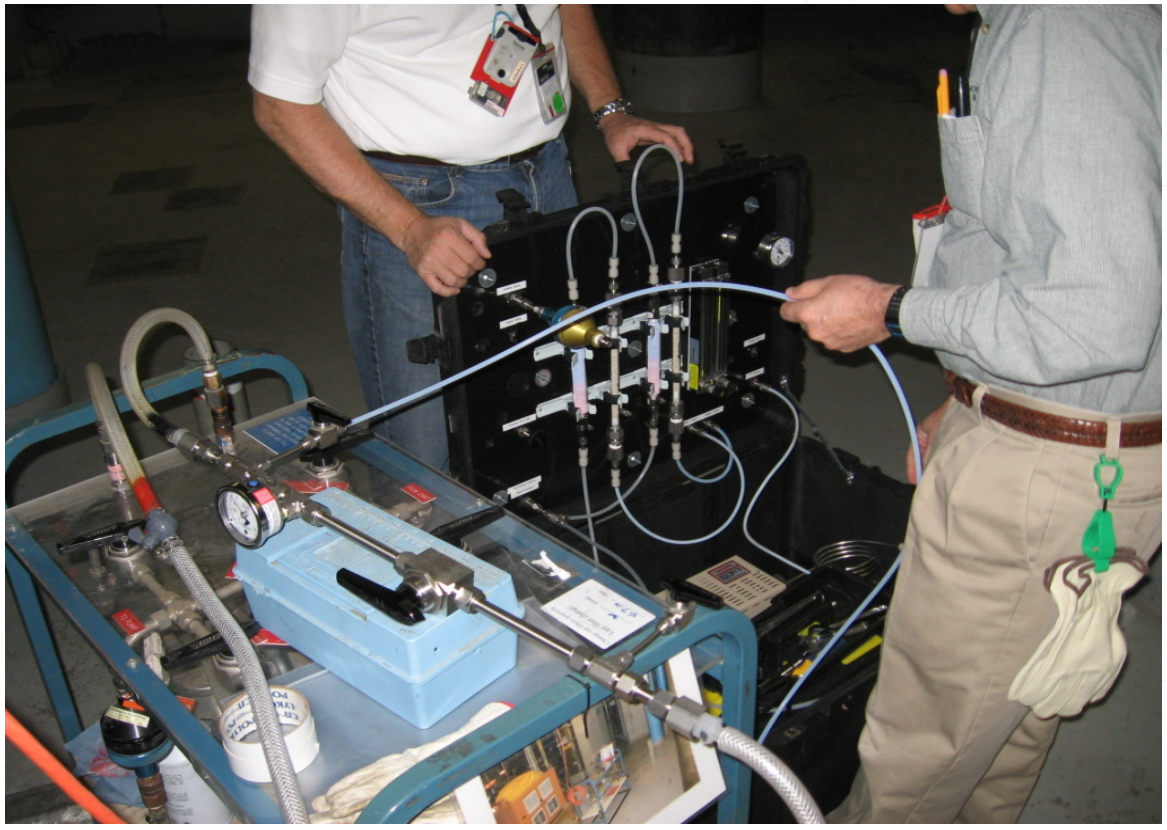
Wet Digestion/Combustion

Wet Digestion of standard followed by combustion to produce $^{14}CO_2$ in sample gas stream

Nominal (pCi/sample)	LCS Recovery %
71.71	99%
71.71	91%
71.71	94%
717.08	92%
717.08	91%
Average	93%

SAMPLE COLLECTION HARDWARE

SAMPLE COLLECTION HARDWARE



EQUIPMENT AND SAMPLE SHIPPING

- Sample box – limited quantity radioactive material
- Sample tubes – contain sodium hydroxide (a hazardous material), excepted quantity

EQUIPMENT PERFORMANCE PARAMETERS

- Carbon to CO_2 Conversion Efficiency>95%
- CO_2 Capture Efficiency>95%
- ^{14}C Measurement Range (to Date) $<7x10^{-11}$ to $5x10^{-3}$ uCi/ml
- Sample Rate (typical, other sample rates can be used) 0.1 - 3 liters per minute
- Power Requirements120V 20 amp
- Sample Collection Interface uses an interface adaptor that can appropriately extract sample gas from plant systems under a wide range of plant gas flow and pressure conditions