Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion to Indoor Air Using Quantitative Passive Diffusive-Adsorptive Sampling Techniques

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Study Team

Organization	Name	Role
Geosyntec Consultants, Inc. Guelph (Canada)	Todd McAlary Hester Groenevelt	Overall project direction & reporting
US EPA Labs, Las Vegas (NV)	Brian Schumacher John Nocerino	Experimental Design & Statistics
Arizona State University (AZ)	Paul Johnson	Practicality for Vapor Intrusion Sites
University of Waterloo (Canada)	Tadeusz Gorecki Suresh Seethapathy	PDMS Membrane Sampler
Cranfield University (UK)	Derrick Crump	ATD Passive and Active Samplers
Fondazione Salvatore Maugeri (Italy)	Paolo Sacco	Radiello Samplers
Columbia Analytical Services (CA)	Michael Tuday Cuji	High Conc. Laboratory Testing Ultra II™ samplers & canisters
Air Toxics Limited (CA)	Heidi Hayes Stephen Disher	Low Conc. Laboratory Testing ATD Passive and Active Samplers

Rationale

- Quantitative passive sampling is not “familiar” to regulators
- No head-to-head studies to date between methods
  - Capabilities and limitations will probably vary between methods
  - Limitations may be overcome with different adsorbent media, of which there are many
- Applicability to soil gas monitoring is unknown
  - Potential “Starvation Effect” from low face velocity
- Detailed costing information is needed

We know quantitative passive sampling will work in many cases, but a comparative study is needed to demonstrate whether there is a preferred method, and demonstrate comparison to conventional methods (TO-15 and TO-17)

Summa Canisters/TO-15

Summa Canisters/TO-15

- Each canister costs ~$1,000 if damaged
- Time-consuming to clean and certify
- Bulky to ship
- Potential for leaks
- Samples usually <24 hours duration
- Multi-step procedures – requires training
- High visibility, not very discrete
- Costs for VOC analysis: ~$250 to $400 ea.
  - Plus canister rental: $50
  - Plus flow controller rental: $25
  - Plus shipping, plus fittings, etc., etc.

ATD Tubes/TO-17

- Air is pumped at a fixed rate through a tube filled with adsorbent media for a fixed time. Measure the mass on the tube, and calculate the concentration

ATD Tubes/TO-17

- Industry standard for industrial hygiene research and National Air Toxics Assessment
- Higher level of training required
  - Selection of adsorbent(s), flow rate, duration
- Power required
- Pumps have some variability in operation
- Nevertheless, this is the analytical method used for calibration of TO-15. Very accurate and precise, with ability to achieve low part-per-trillion reporting limits

Temporal Variability

- www.epa.gov/radon
  - Preferred duration >3 days
  - Some methods collect samples over 1 year

- Long-term average concentrations are more representative for risk assessment
  - Short-term variability just leads to requests for more monitoring with no real benefit

Quantitative Passive Samplers

$$\left(\frac{M}{t}\right) = D\frac{A}{L_m}\left(C_{ma} - C_{ms}\right)$$

M = Amount of analyte collected by the sorbent

D = Diffusion coefficient

A = Area of membrane

C_{ma} = Concentration of the analyte "on" the membrane surface in contact with air

C_{ms} = Concentration of the analyte "on" the membrane surface in contact with the sorbent

t = Sampling time

L_m = Membrane thickness

Simplifies to:

$$C_0 = \frac{kM}{t}$$

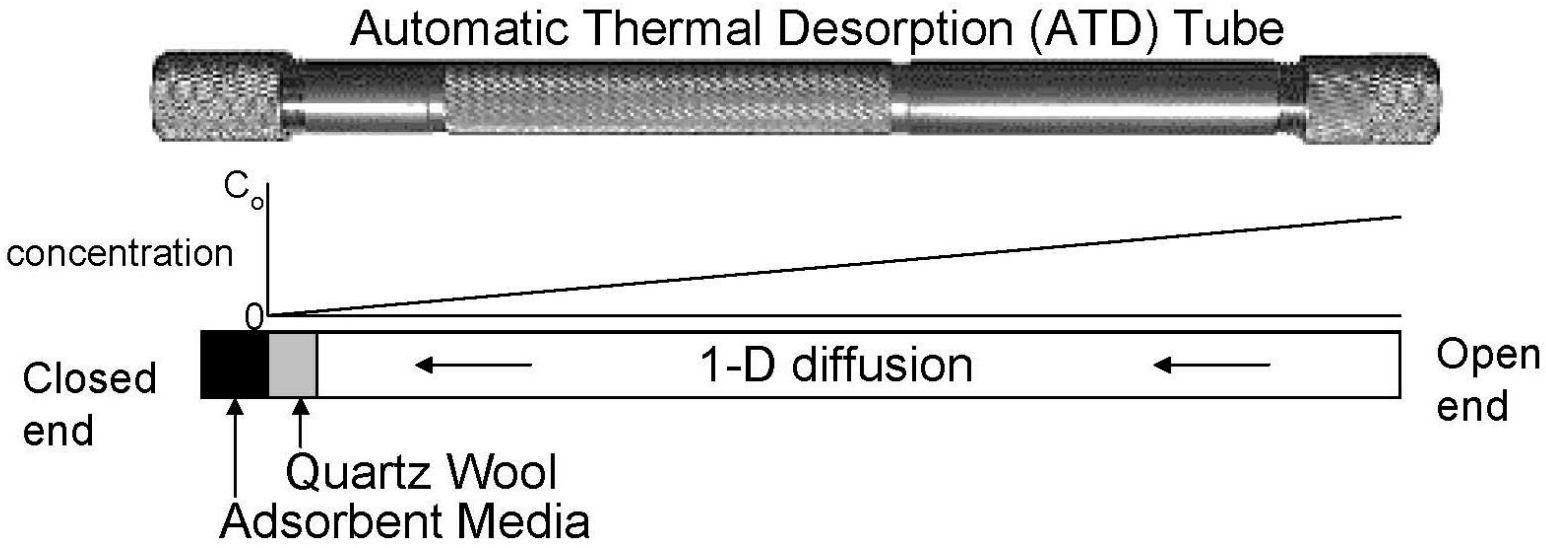
Each sampler has a fixed uptake rate (k) for each chemical, so the average concentration (Co) can be calculated from the mass (M) adsorbed over time (t)

SKC Ultra II Badge

Sorbent media vial

- Used for many years in Industrial Hygiene
- Recently improved for lower reporting limits

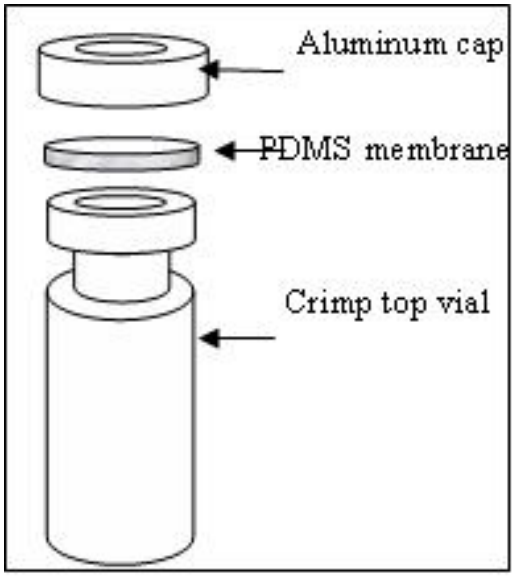
ATD Tube Sampler



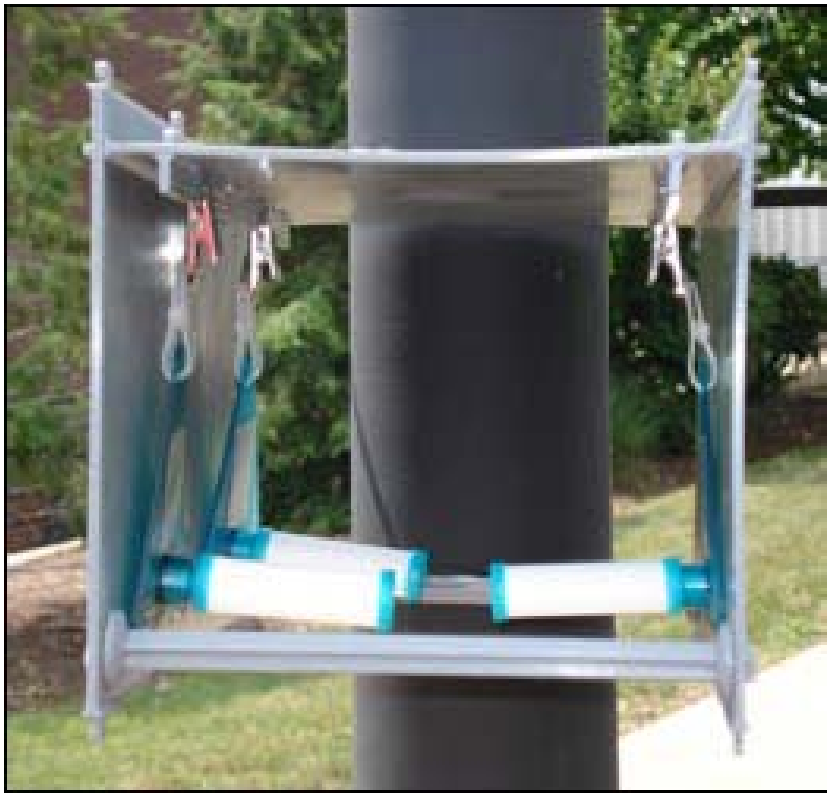
- Simplifies procedure for analysis, simply take off the caps, and put the ATD tube on the auto-injector for analysis via EPA Method TO-17

PDMS Sampler

- Poly(dimethylsiloxane) (PDMS) is the material used to coat GC columns
- Uptake rate is proportional to elution time (well known)



Radiello Sampler



- Radial design increases uptake rate for lower reporting limits

Differences between Samplers

- Medium of Uptake
  - Porous plate, Air Column, Membrane
- Method of Analysis
  - thermal vs chemical desorption
- Uptake rates
  - 0.5 to 80 mL/min (sensitivity vs starvation)
- Size
  - <1 to > 5 cm diameter
- Adsorbent
  - Anasorb 747, Carbopack X and B, Tenax TA
- Cost

Experimental Variables

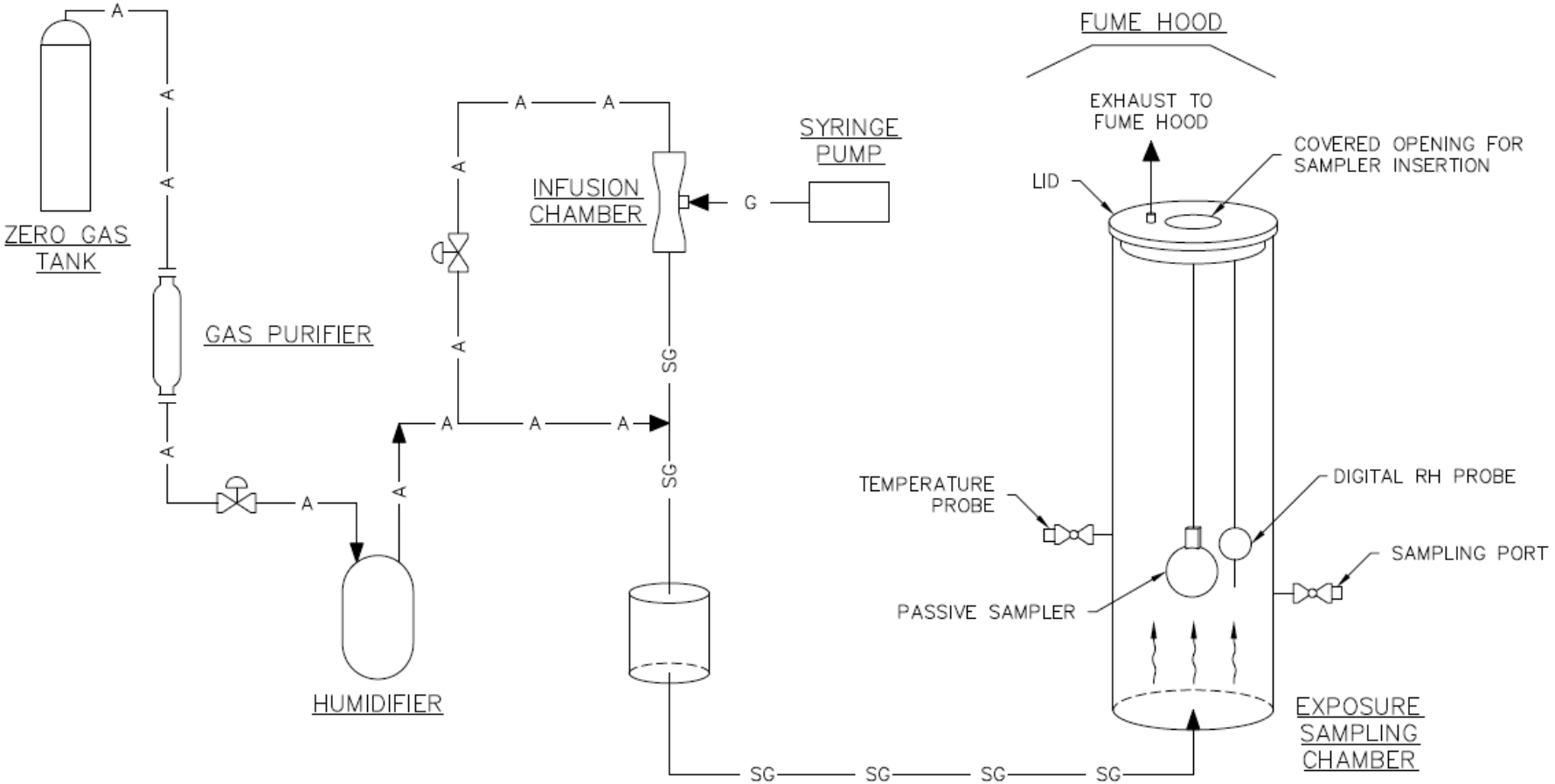
Factor	Units	Values
Concentration	ppb	1, 50, 100, 1000, 10000, 100000
Temperature	°C	15, 20, 25
Gas Flow Velocity	Cm/min	1, 10, 1100, 2200
Sampling Duration	days	30 min, 1, 4, 7
Relative Humidity	%	30, 60, 90

10 Target compounds

Analyte	OSWER indoor conc. at 10^{-6} risk (ppb)	Vapour pressure (atm)	Water solubility (g/l)
1,1,1-Trichloroethane	400	0.16	1.33
1,2,4-Trimethylbenzene	1.2	0.00197	0.0708
1,2-Dichloroethane	0.023	0.107	8.52
2-Butanone (MEK)	340	0.1026	~ 256
Benzene	0.10	0.125	1.75
Carbon tetrachloride	0.026	0.148	0.793
Naphthalene	0.57	0.000117	0.031
n-Hexane	57	0.197	0.0128
Tetrachloroethene	0.12	0.0242	0.2
Trichloroethene	0.22	0.0948	1.1

Selected to span a range of compounds of interest for vapor intrusion studies

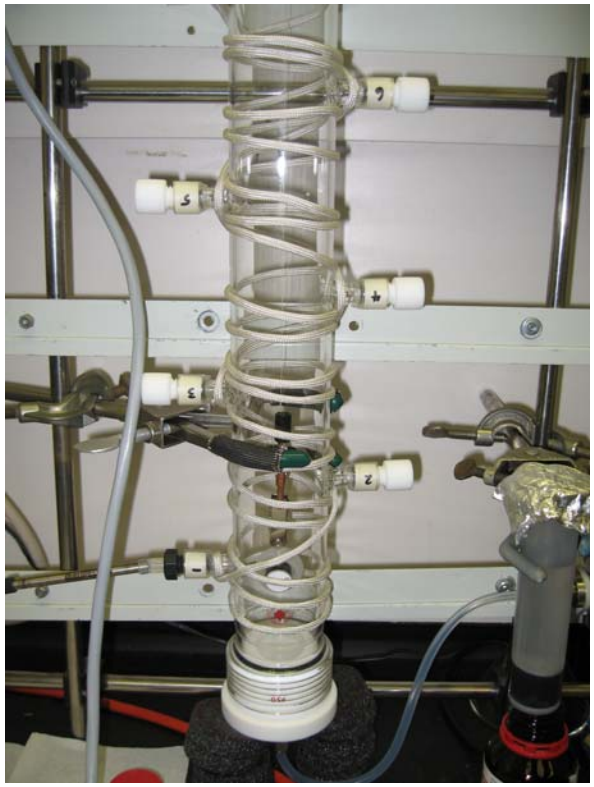
High Concentration Tests (CAS)



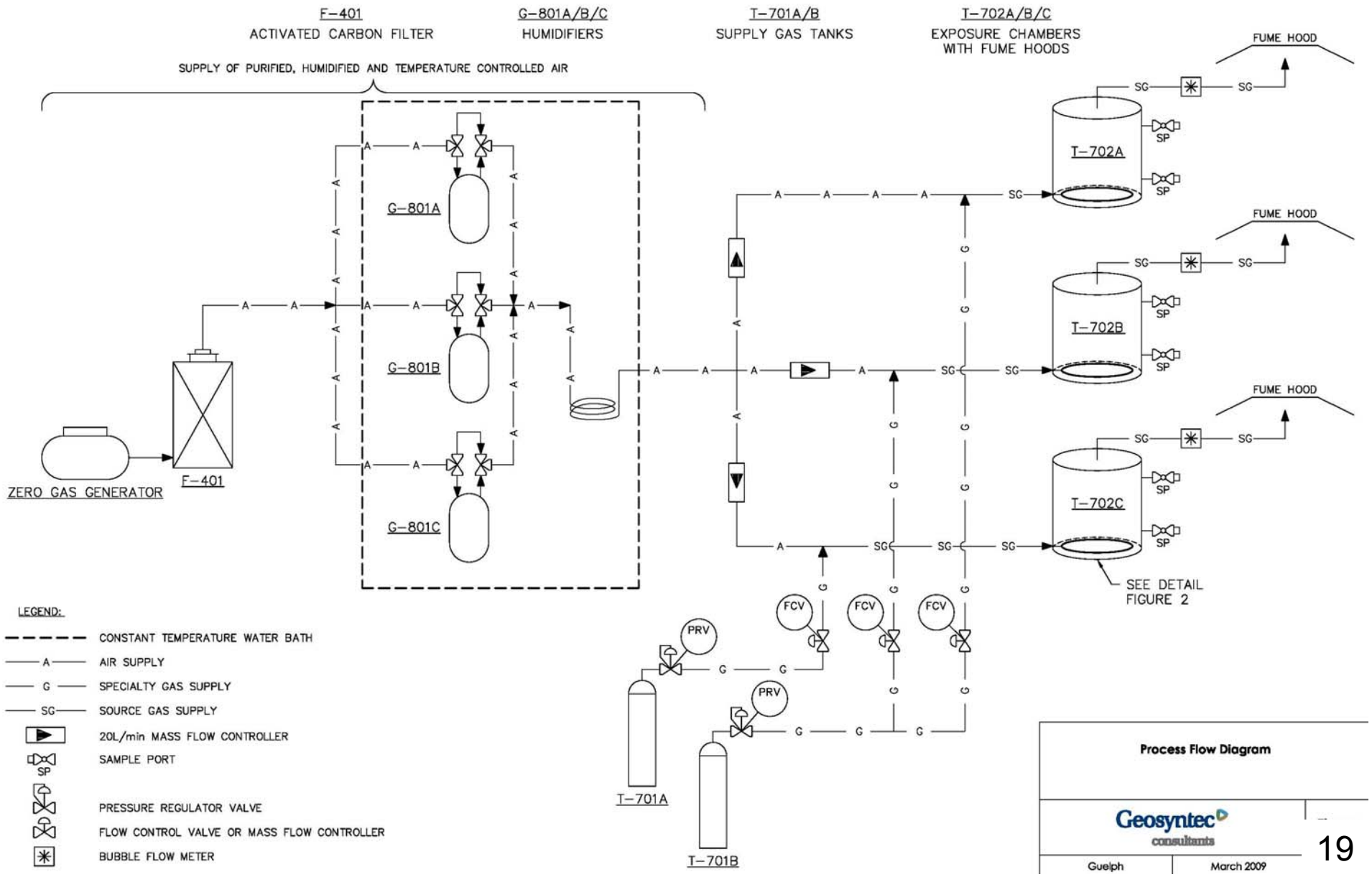
High Concentration Tests (CAS)

(To mimic soil gas conditions)

Concentration : 1, 10, and 100 ppmv
Temperature: ambient
Humidity: 90-100%
Face velocity: very low ($5x10^{-5}$ m/s)
Exposure time: 30 minutes



Low Concentration Tests (Air Toxics)



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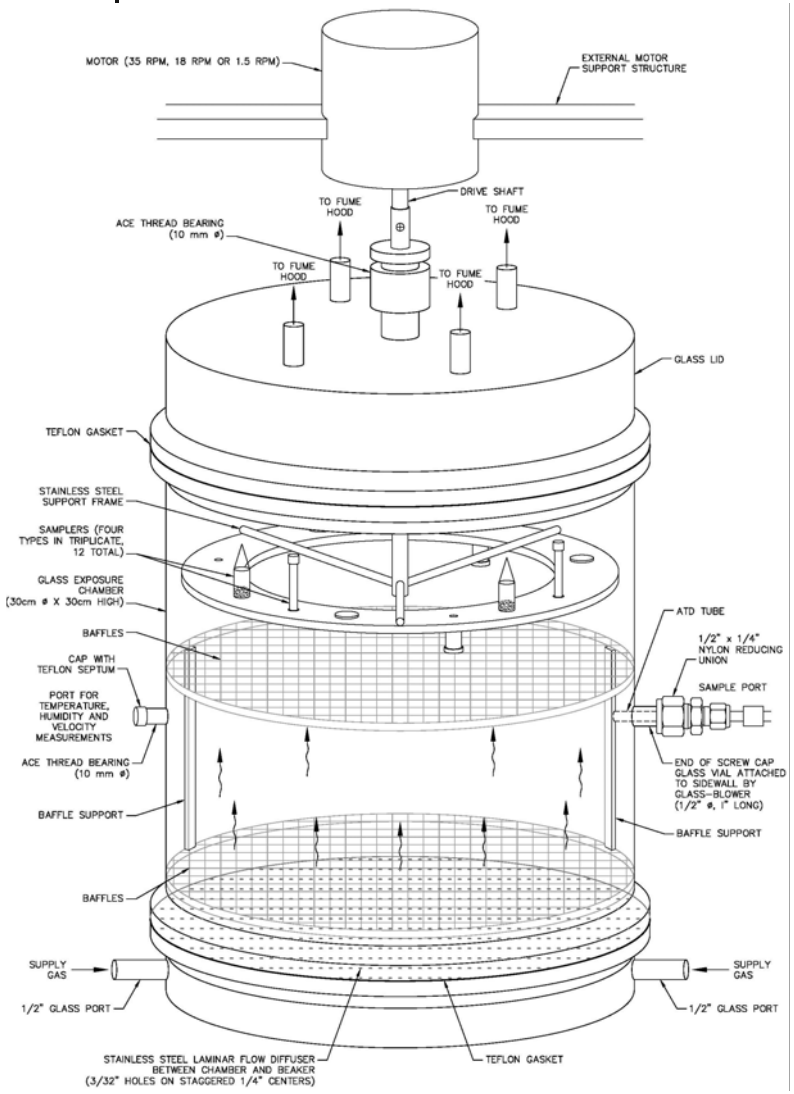

Experimental Design

- Brian Schumacher and John Nocerino of EPA Research Labs in Las Vegas will use Design-Expert 7.1.1 by the Stat-Ease group (http://www.statease.com/) and strategies outlined by Deming and Morgan (1987).
- Familiarity Testing
  - Set-up controlled conditions and demonstrate method
- 1-Way ANOVA Test
  - Five tests under identical conditions
- Two-Level Fractional-Factorial Test
  - Change multiple factors to test sensitivity
- Information from each successive step being used to refine the design of the subsequent steps.

Two-level Fractional Factorial Testing

C:\Program Files\DX7\ESTCPTest2.dx7 - Design-Expert 7.1.1

File Edit View Display Options Design Tools Help

Select	Std	Run	Factor 1 A:Concentration ppb	Factor 2 B:Temperature deg C	Factor 3 C:Gas Flow Velocity m/hr	Factor 4 D:Sampling Duration Days	Factor 5 E:Relative Humidity %	Response 1 Recovery1 %
	13	1	1.00	15.00	0.40	7.00	90.00	
	12	2	10000.00	30.00	0.00	7.00	30.00	
	4	3	10000.00	30.00	0.00	1.00	90.00	
	2	4	10000.00	15.00	0.00	1.00	30.00	
	9	5	1.00	15.00	0.00	7.00	30.00	
	6	6	10000.00	15.00	0.40	1.00	90.00	
	17	7	5000.50	22.50	0.20	4.00	60.00	
	14	8	10000.00	15.00	0.40	7.00	30.00	
	18	9	5000.50	22.50	0.20	4.00	60.00	
	3	10	1.00	30.00	0.00	1.00	30.00	
	7	11	1.00	30.00	0.40	1.00	90.00	
	20	12	5000.50	22.50	0.20	4.00	60.00	
	15	13	1.00	30.00	0.40	7.00	30.00	
	1	14	1.00	15.00	0.00	1.00	90.00	
	11	15	1.00	30.00	0.00	7.00	90.00	
	21	16	5000.50	22.50	0.20	4.00	60.00	
	19	17	5000.50	22.50	0.20	4.00	60.00	
	16	18	10000.00	30.00	0.40	7.00	90.00	
	10	19	10000.00	15.00	0.00	7.00	90.00	
	8	20	10000.00	30.00	0.40	1.00	30.00	

For Help, press F1 NUM

Field Testing

- Multiple media (indoor air, soil gas, sub-slab gas)
- Range of chemicals and geologic materials (site-specific)
- Method development required for soil gas sampling
- Three rounds planned:
  - demonstrate reproducibility
  - allow improvements in field applications during program
  - collect sufficient data to support statistical analysis
- Currently considering Hill AFB and Vandenberg

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