Report on Sandia National Laboratories Micro Chemical Analysis System for Simultaneous Detection of CW Agents at STEL Levels

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Overall Goal of Project

Build a system capable of analyzing for, separating and identifying multiple agents (GB, HD, and others-possibly VX and phosgene) at below STEL concentrations
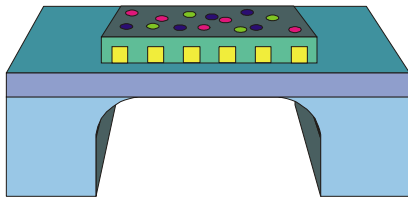
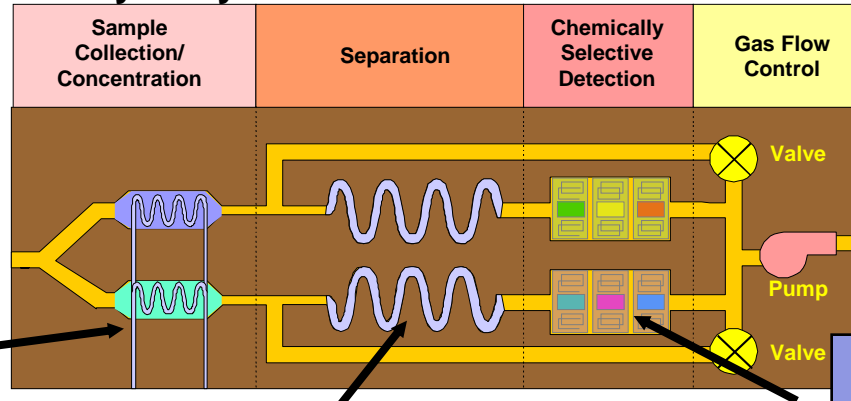| Agent	Mol Wt.	mg/m³	Level	PPM (million)	PPB (billion)	PPT (trillion)
GB	140.09	0.0001	STEL	0.0000175	0.0175	17.45
HD	159.07	0.003	STEL	0.000461	0.461	461.12

Other Requirements for CMA are:
- Portability

- Fast response time (15 minutes or less)

- Internal check system

- Low/no maintenance (known requirements)

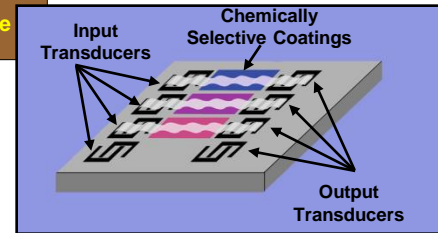# Field Portable, Hand-held Chemical Analysis System (Review)

**A hand-held, gas-phase chemical analysis system that uses three microfabricated analysis stages**
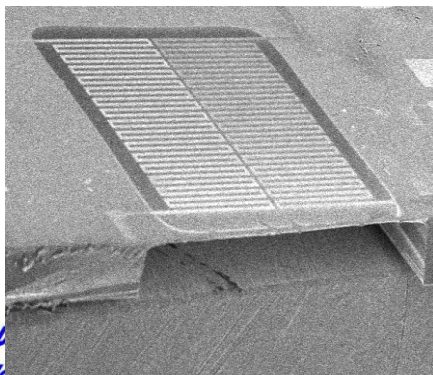

| Sample Collection/ Concentration | Separation | Chemically Selective Detection | Gas Flow Control |

Preconcentrator accumulates species of interest

Gas Chromatograph separates species in time

Acoustic Sensors provide sensitive detection

SAW Array

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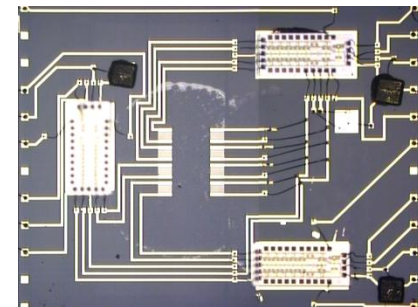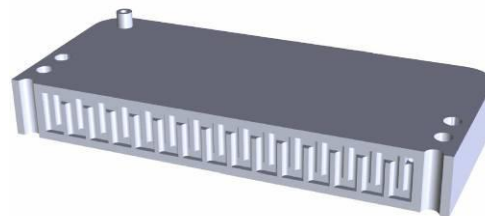
January 2010 Testing Results
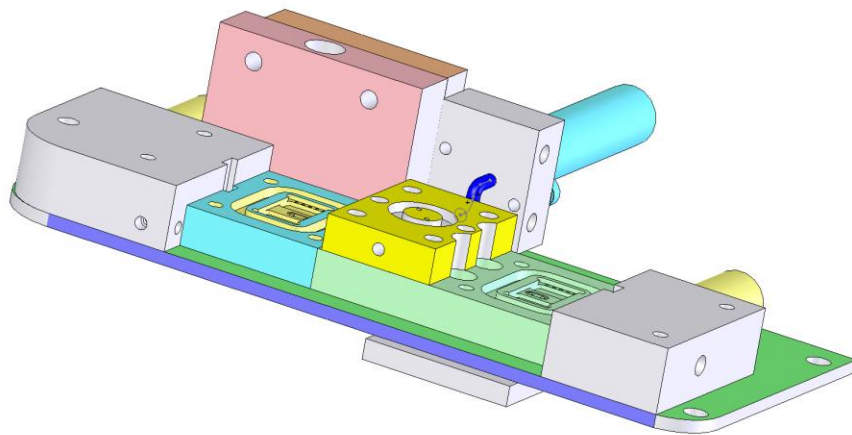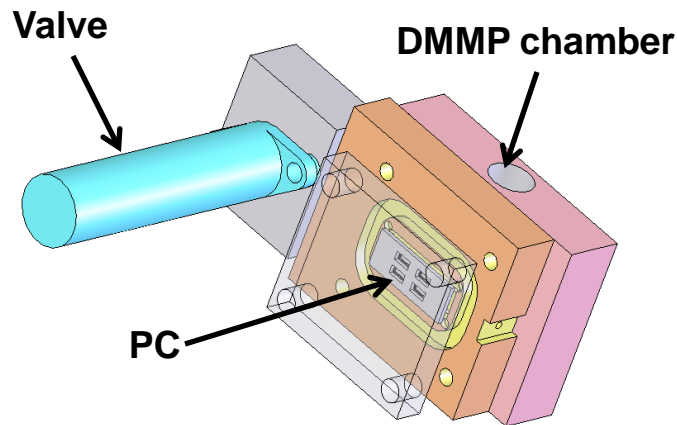
Testing performed at ECBC in January 2010:
- Performance was measured against GB, HD and VX
- Analysis was performed against each agent separately (there was no capability to deliver multiple agents simultaneously)
- Residual agent was present in most tests
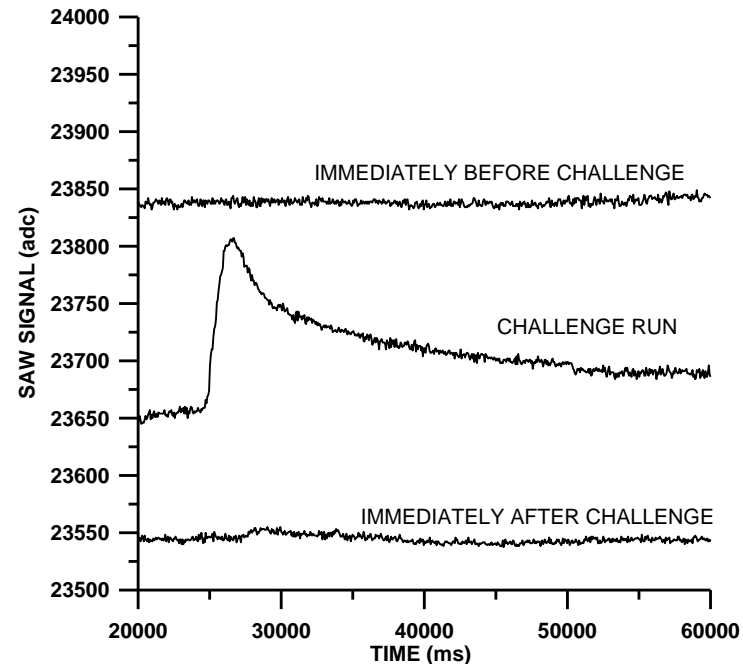
Measured three performance characteristics:
- Limit of detection (LoD)
- Three point calibration curve (R2 performance of minimum 0.99)
- Precision and accuracy across eight tests (repeatability of below 25%)

Agent	Collection Time (sec)	Concentration (pptv)	Peak Height (A/D counts)	Estimated LoD (ppt)	STEL Concentration
GB	600	1300	13781	28.3	17.45
HD	600	3080	2130	434	461.12
VX	150	1280	308752	1.24	0.914

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Internal Check for Monitoring State of Health of System
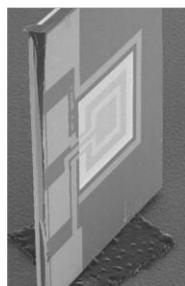
Valve

DMMP chamber

PC

No residual DMMP remains on the PC after each fire

IMMEDIATELY BEFORE CHALLENGE

CHALLENGE RUN

IMMEDIATELY AFTER CHALLENGE

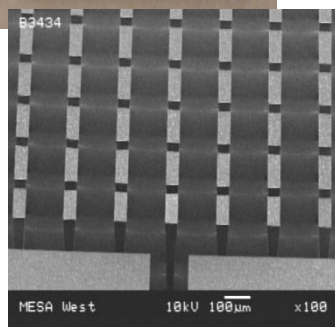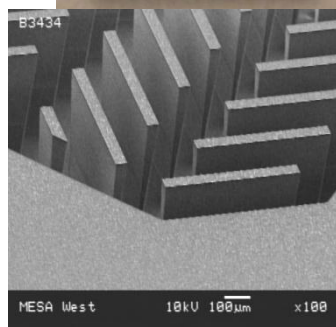SAW SIGNAL (adc) vs TIME (ms)

Can expect up to 360 test cycles before DMMP concentration drops substantially
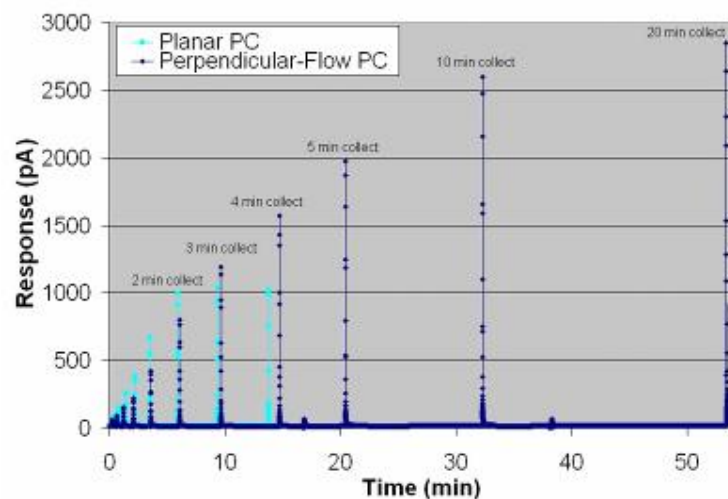
Preconcentrator
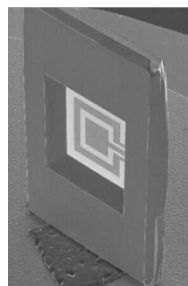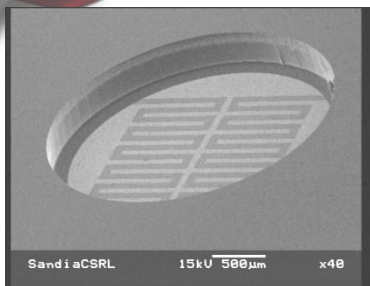
**Hot Plate (Planar) Designs - Heater element on SiN membrane**

3-D PC Designs – Rapid heating with increased surface area for collecting more volatile species

Selective collection and preconcentration of compounds of interest while ignoring interferents based on coating materials used
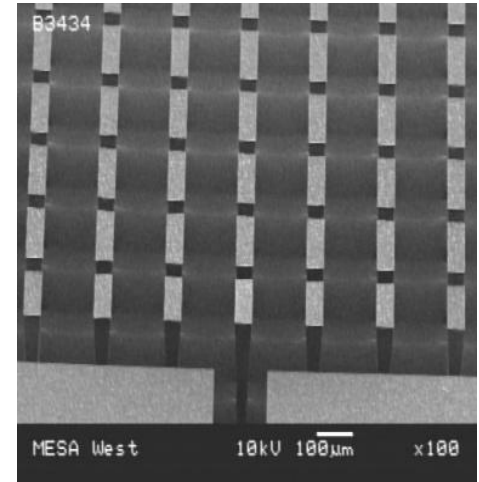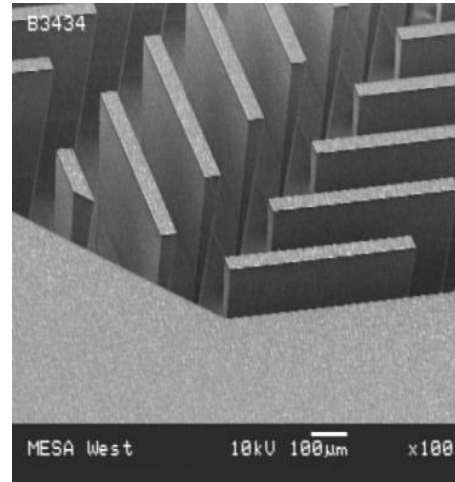

• **Short collection time for rapid identification or**
• **Longer collection time for forensics application**

High Surface Area PC to Achieve Required Level LOD Capability
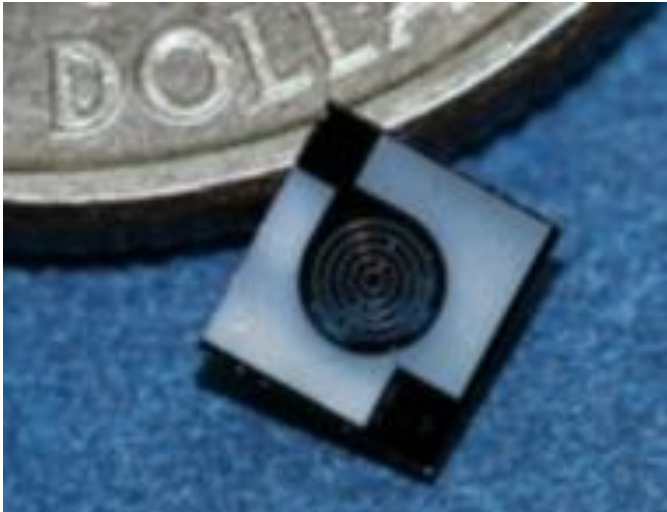
3D PC with aluminum heater

Tortuous path PC's

- Perpendicular flow PC (3D-PC) has much higher analyte capture efficiency than planar PC (50% or more)
- Use of 3D-PC allows for sampling much larger volume
- Can use stacked PC design, using 2 or more PC's for even higher sampling efficiency
- Used in January 2010 test

- Tortuous path PC's provide very high surface area for capturing analytes
- Tested in laboratory setting with surrogates as comparison to 3D-PC

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High Surface Area PC to Achieve Required Level LOD Capability
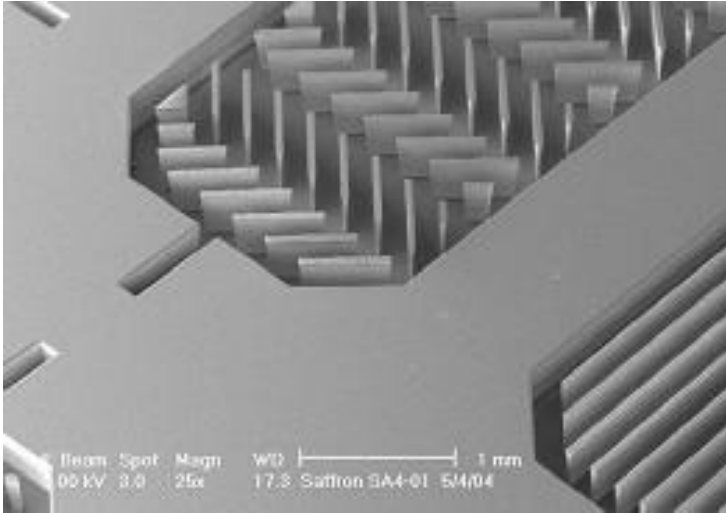
Tortuous path preconcentrator (TPPC)
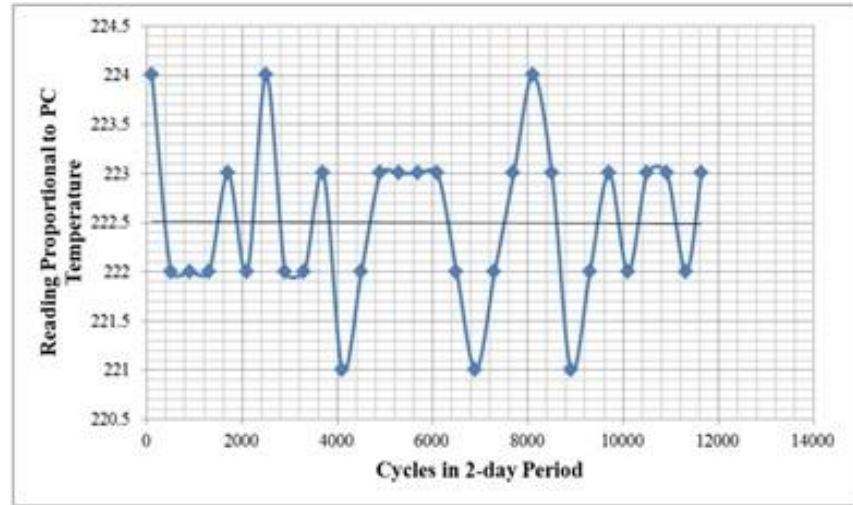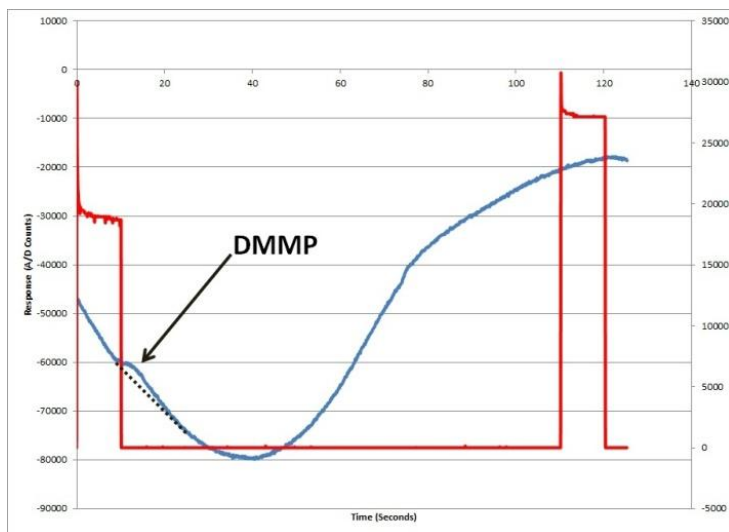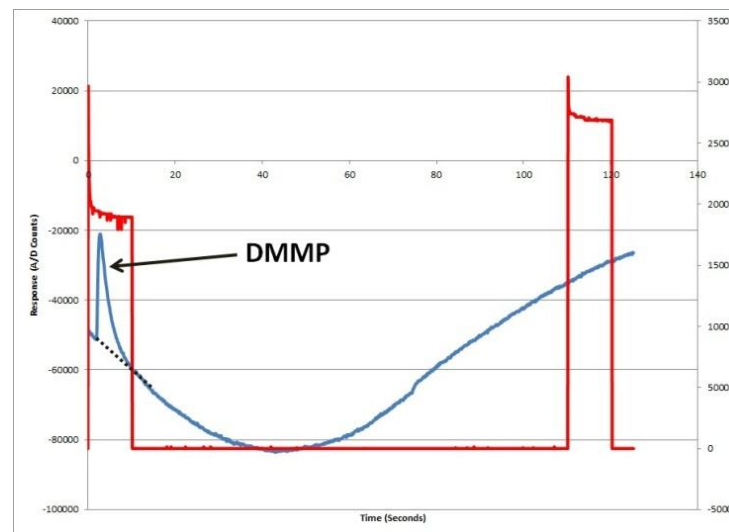

Ion implanted heater performance on TPPC

- TPPC's use ion implanted heaters
- Heaters are extremely reliable, no failure even after more than 10000 cycles
- Note the temperature variation on TPPC is only from 221 ˚C to 224 ˚C
- TPPC's used in September test at Sandia with DMMP and MES

New GC Columns for Separation

DMMP detection with column
fabricated in nickel using LIGA

DMMP detection on column
fabricated in steel and passivated

- Nickel surface in the LIGA columns interacts with analyte (cannot be easily passivated)
- Stainless steel (316) columns can be passivated, using CVD process (similar to sulfinert passivation), prior to coating
- Passivation tremendously improves performance of column, leading to lower retention time and much sharper peaks with much smaller tails

SAW Performance Enhancement
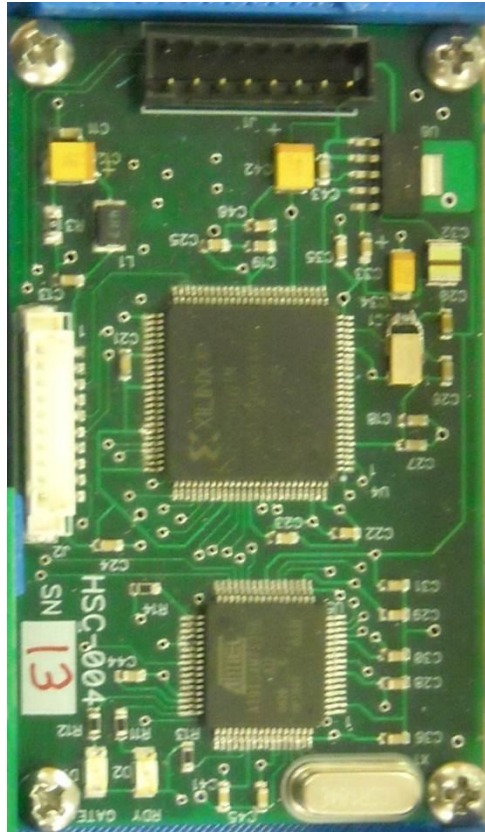
Frequency counting circuit (shown installed in next slide)

SAW response is normally recorded based on the sinusoidal change observed from the change in phase of the SAW. Issues with phase detection are:

➢ **Sensor drift into low sensitivity region (crest or trough), SAW response decreases**

➢ **Dithering can move response out of low sensitivity region; difficult to do on the field**

➢ **One needs to detect both positive and negative peaks when looking at phase change; results in more complicated software**

Frequency change is only in one direction

➢ **New SAWs are compatible (cleaning issue-remember previous slide)**

➢ **September 2010 test at Sandia demonstrated almost same sensitivity range**

➢ **Agent testing needed to determine which is better, phase change or frequency counting**

New System Package

A is the gas module
B is the frequency counting circuit
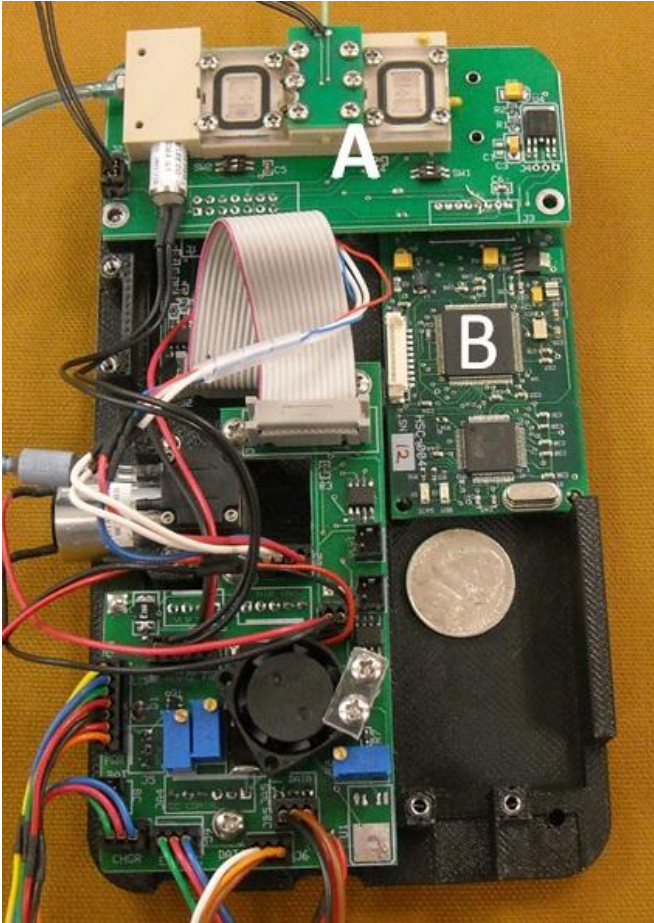
New system package contains:

- New electronics board (24 bit processing)
- New power distribution board
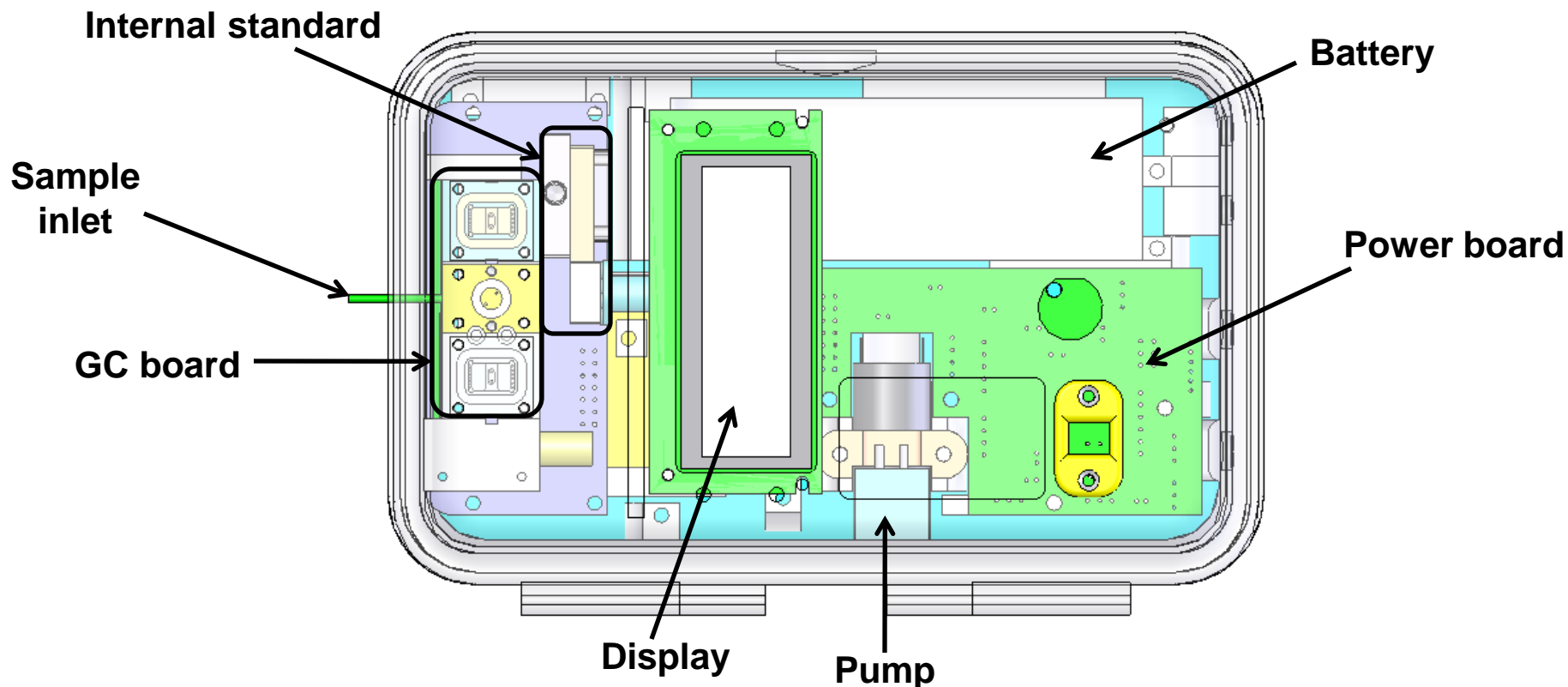- Frequency counting board for SAW
- New GC module

Entire system still fits in the original package box (dimensions are still 7" x 5" x 2")
> still easily portable and battery operable if needed

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New Package

Internal standard

Battery

Sample inlet

Power board

GC board

Display
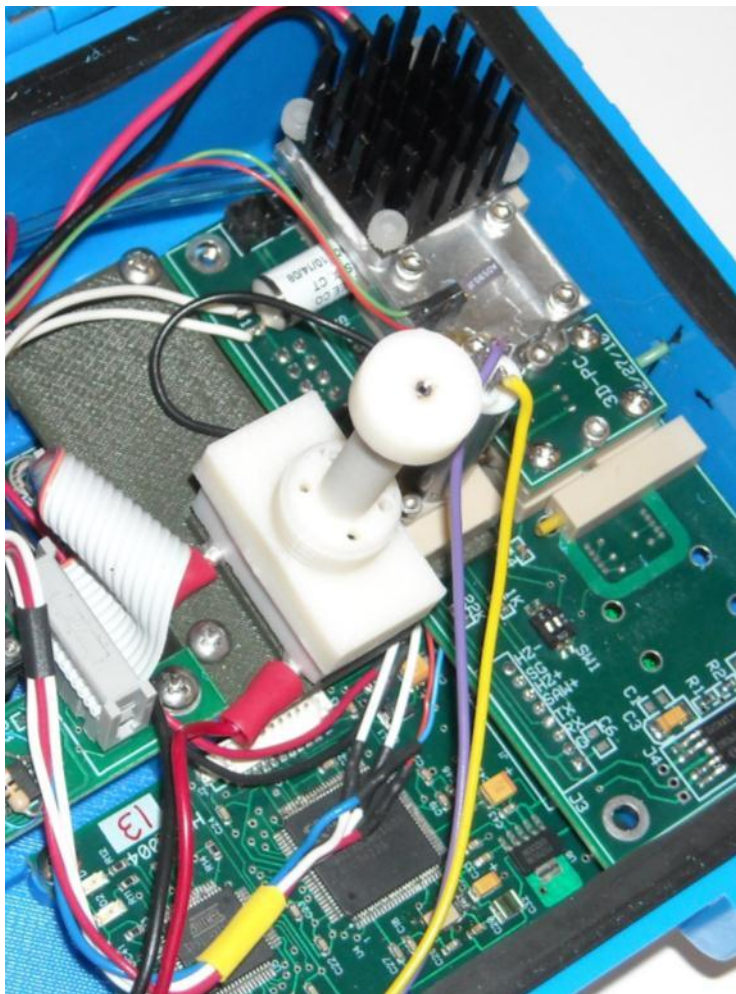
Pump

- **Full package size is still 5x7x2 inch**
- **Power will be provided through 120V although battery capability is still available**
- **Data will be collected through laptop/desktop computer although 4 line display is still functional**
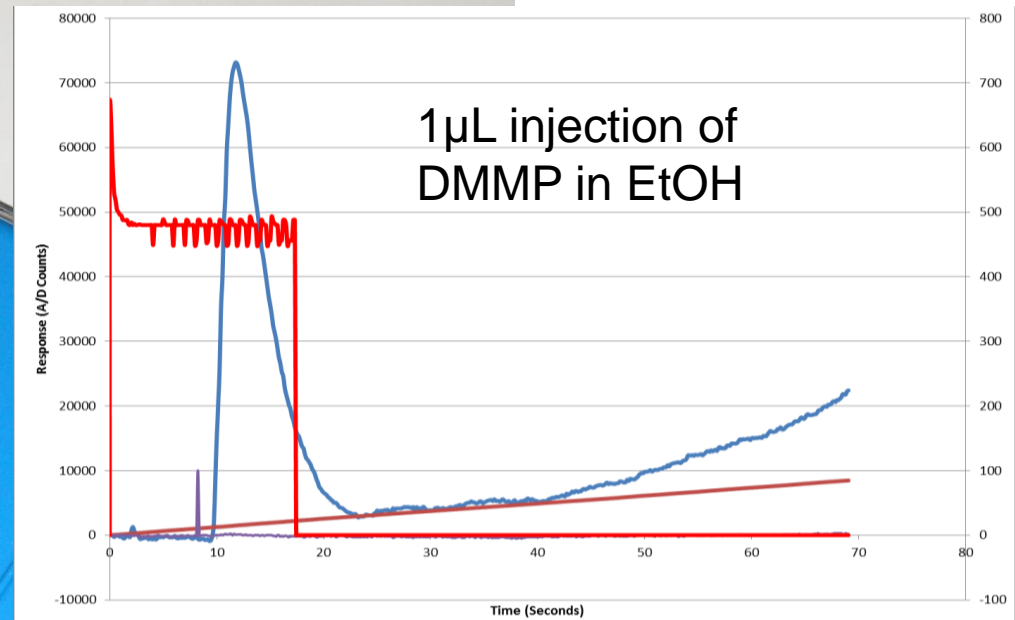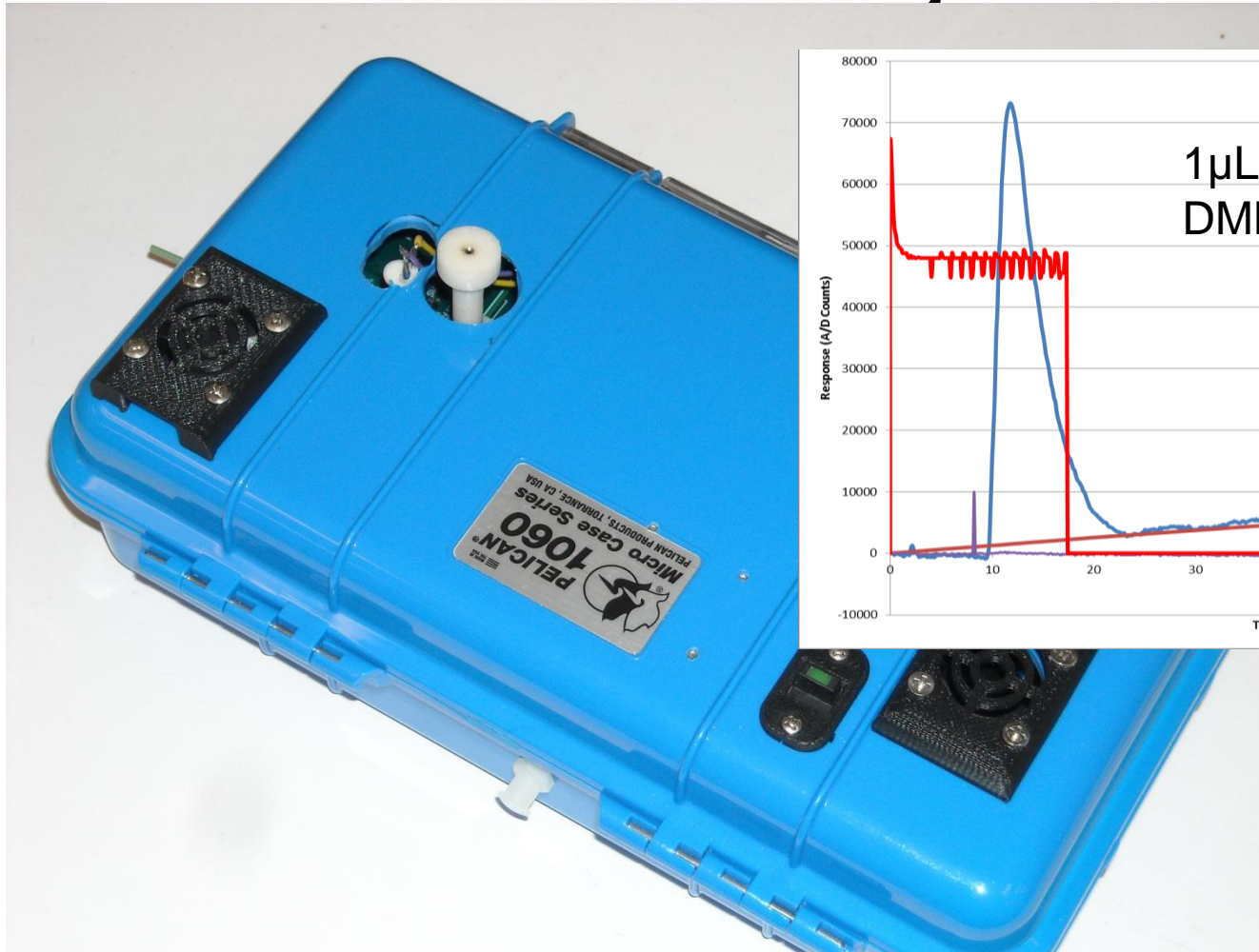
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Liquid Injection Port

Syringe Guide for Injection Port

Vaporization Stage of Injection Port
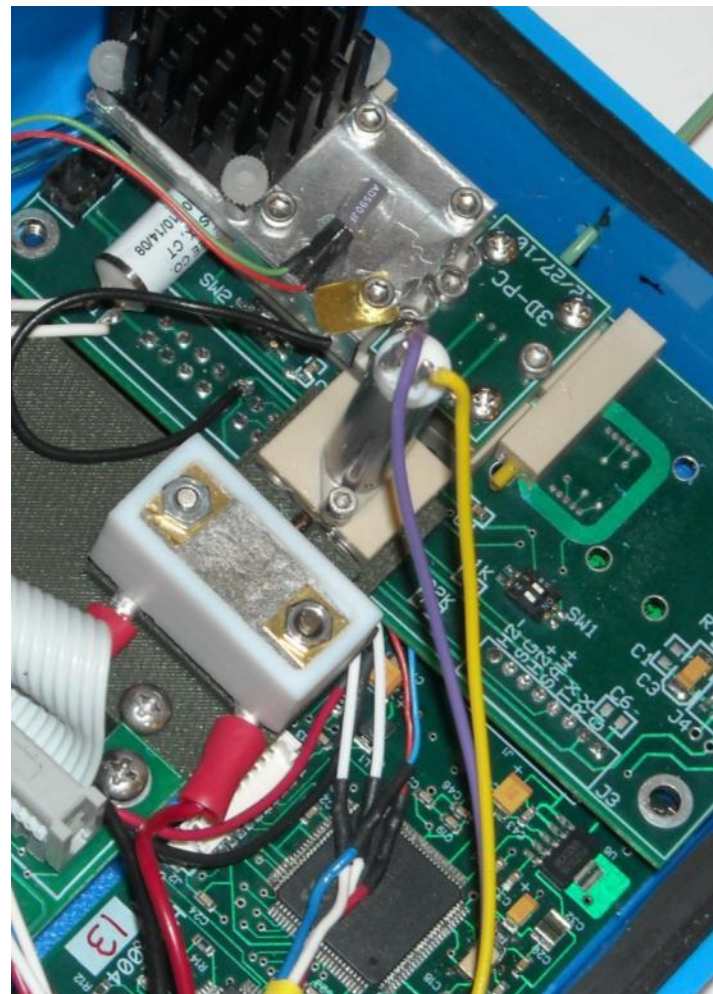
Multi-Agent Analyzer with Injection Port

1µL injection of DMMP in EtOH

System Performance- September 2010 at Sandia

- Performance was measured against DMMP (Surrogate for GB) and MES (surrogate for HD)
- Sandia's vapor system delivers DMMP at 247 ppt and MES at 2000 ppt

- Collection time was limited to 10 minutes for both analytes
- Frequency counting was used for SAW measurement

| Analyte	Collection Time (sec)	Concentration (pptv)	Standard Deveiation (pptv)	Estimated LoD (ppt)
DMMP	600	247	2.1	6.5
MES	600	2000.	50.48	170.

System Performance
February 2011 at ECBC

- Performance was measured against GB and HD at ECBC, February 2011
  - ➤Goal was to determine system LOD against low agent concentration
  - ➤Compared January 2010 system with one containing latest modifications (new columns, frequency counting, modified connections within GC module)

- Testing conditions:
  - ➤Analytes tested simultaneously
  - ➤Collection time was limited to 10 minutes

Agent	Collection Time (sec)	Lowest Concentration Delivered (pptv)	Peak Height (A/D counts)	MDL (3.14*.STDEV) (ppt)	STEL Concentration (ppt)
GB	600	104, 88.3	2387, 3238	10.6, 12.6	17.45
HD	600	98.1, 136	3031, 3031	40.6, 55.5	461.12

Sample Chromatograms
February 2011 at ECBC
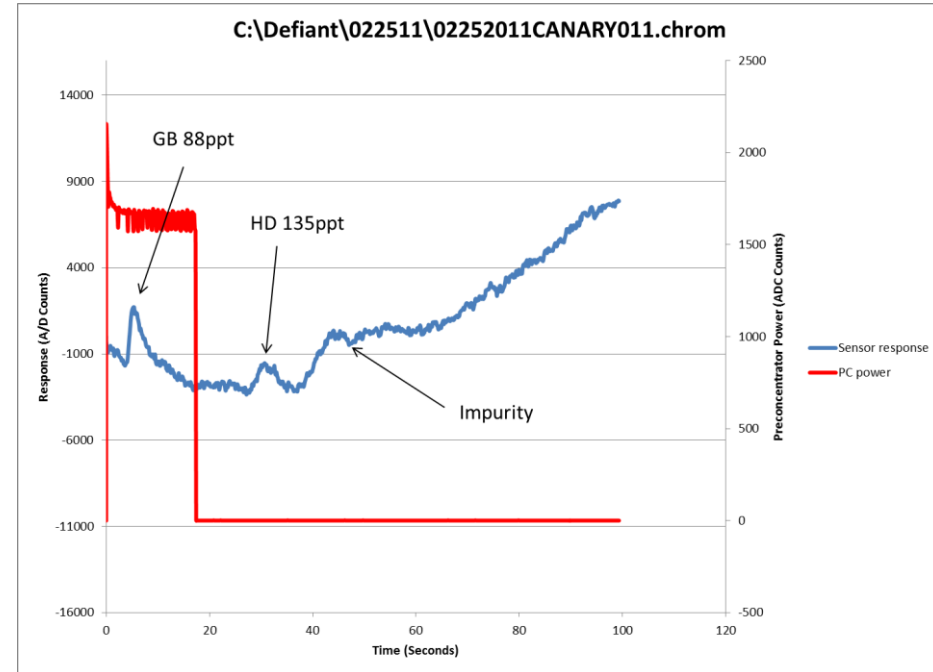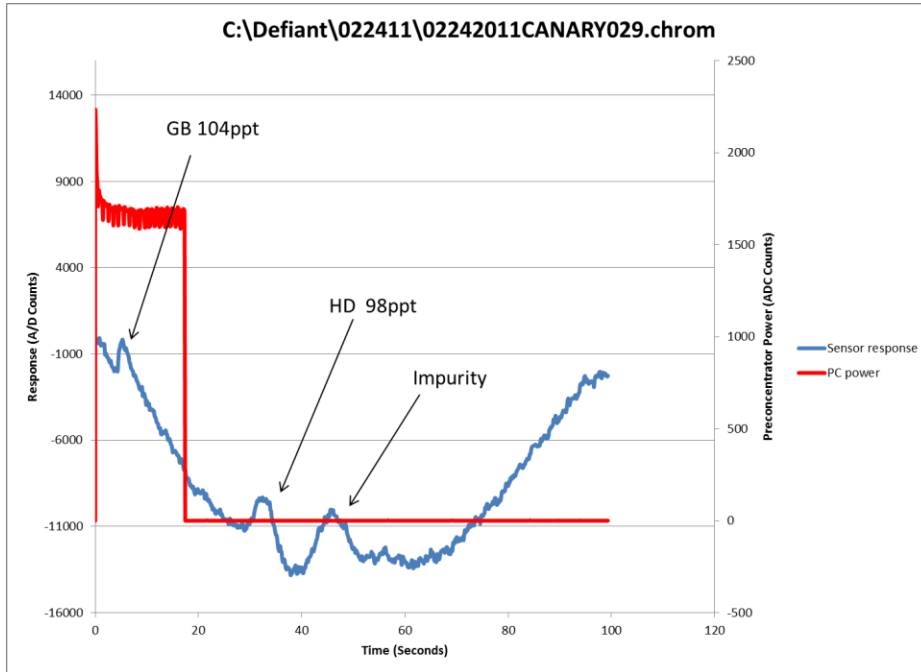
Conclusions

So far:
- 2011 system with new modifications performs significantly better than 2010 system
- Able to simultaneously detect GB and HD at very low concentrations
- Able to baseline separate GB and HD (and identify interferent/impurity present in agent)
- LOD concentrations are well below STEL levels
- Frequency counting does not provide improvement over phase detection (SAW)
- 3D-PC performs better than tortuous path PC

2011 work to be performed:
- Continue improvement in LOD
- Develop front-end liquid injector source for testing system state-of-health with agent
- Test system performance against compounds used in neutralization of agents in the EDS