Near Real Time Liquid Analysis for Explosive Destructive System

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We are Working to Decrease the Process Time of EDS

**One approach is to develop an on-board, near-real-time liquid analyzer (NRT-LA)**

– EDS effluent is not drained until analysis confirms that the agent is destroyed
– Manual sample collection, transport and analysis takes an hour or more
– First sample at one hour is almost always non-detect

An NRT-LA will have several benefits

– Allow continuous monitoring of treatment
– Save time spent collecting and analyzing samples
– Reduce operator workload collecting samples
– Improve safety by eliminating handling of samples

Challenges to be addressed

– Functional while EDS vessel is operational/rotating
– Background matrix in EDS may be quite complex
– Detection sensitivity (sufficient to determine treatment threshold)
– Residual HD must be determined, not just hydrolysis or degradation products

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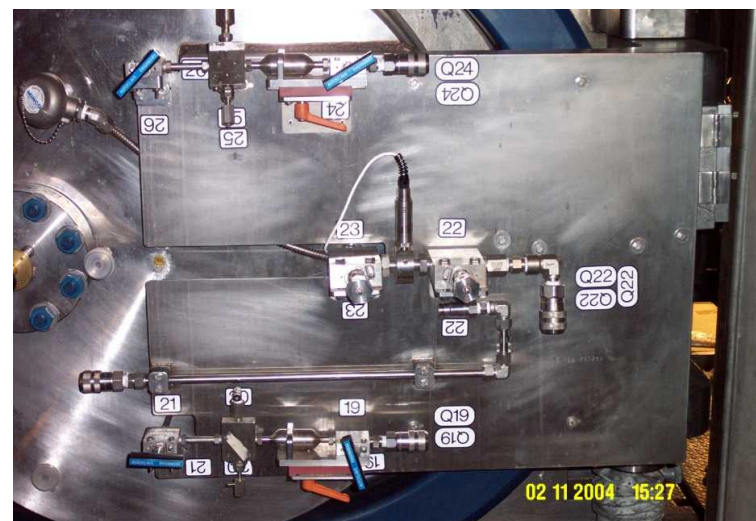
Incorporating an On-board Chemical Analysis System into EDS

Mount Capillary electrophoresis-based analysis system on the EDS

Automatically collect and analyze samples at regular intervals (5 to 7 minutes)

- Filter and prepare sample as needed
- Separate using capillary electrophoresis
- Detect peaks using COTS UV detector
- Analyze data to detect and quantify agent peaks

Drain vessel when destruction target is reached

- Effluent remains under engineering control

Collect final sample for laboratory RCRA analysis

- On-line analyzer is for process control only; verification of agent destruction will still require laboratory analysis
- EDS processing can continue while sample is analyzed

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Previous Year's Development Status: Demonstrated Proof of Concept with Agent
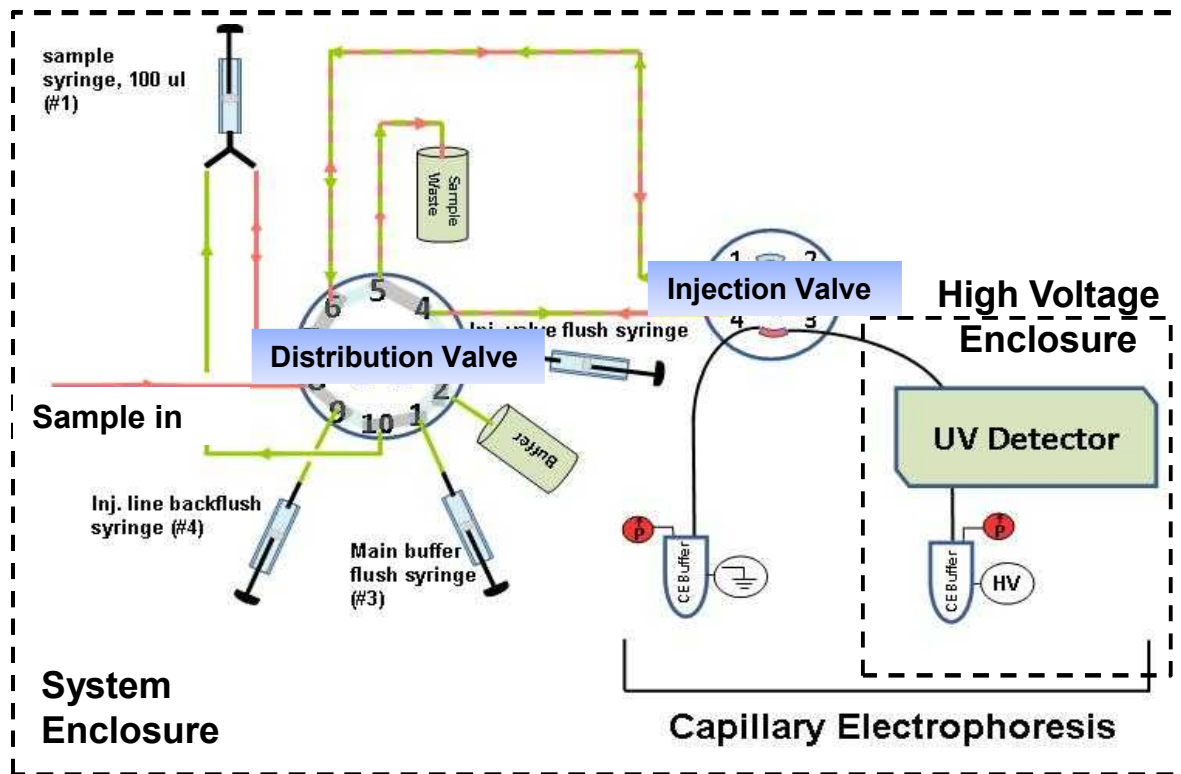
- **Separation methods were developed for mustard and Lewisite class**
- **Bench top prototype (1st generation)**
  - Assembled and tested at ECBC (Dec 09)
  - Demonstrated proof of concept
  - Observed decrease in mustard (HD) peak with corresponding increase of thiodiethanol (TDE) due to hydrolysis
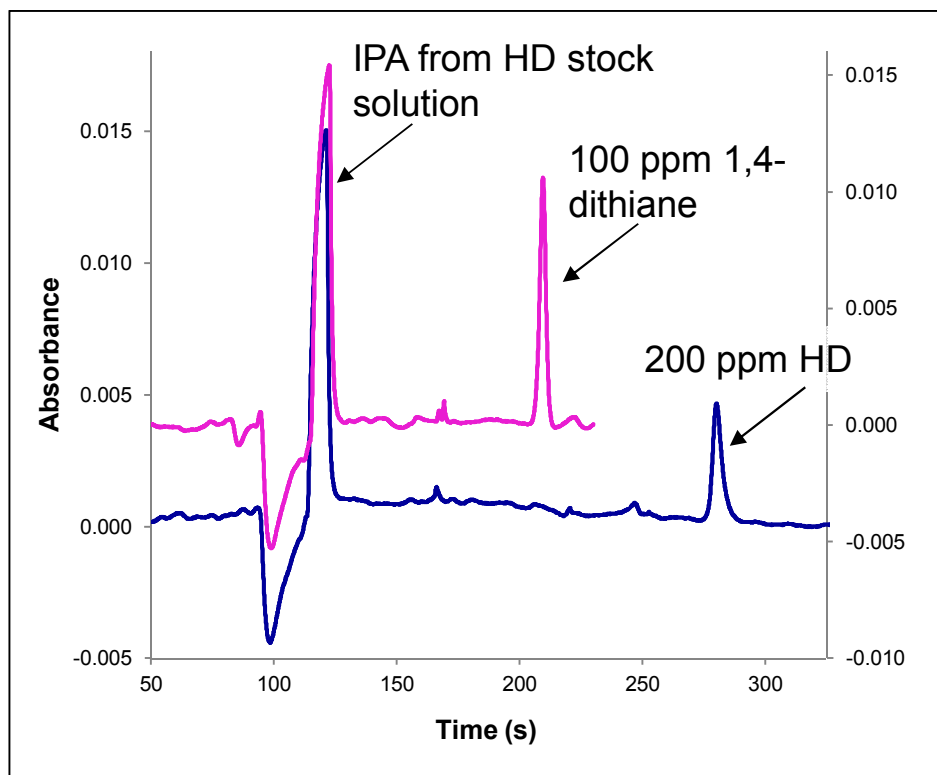
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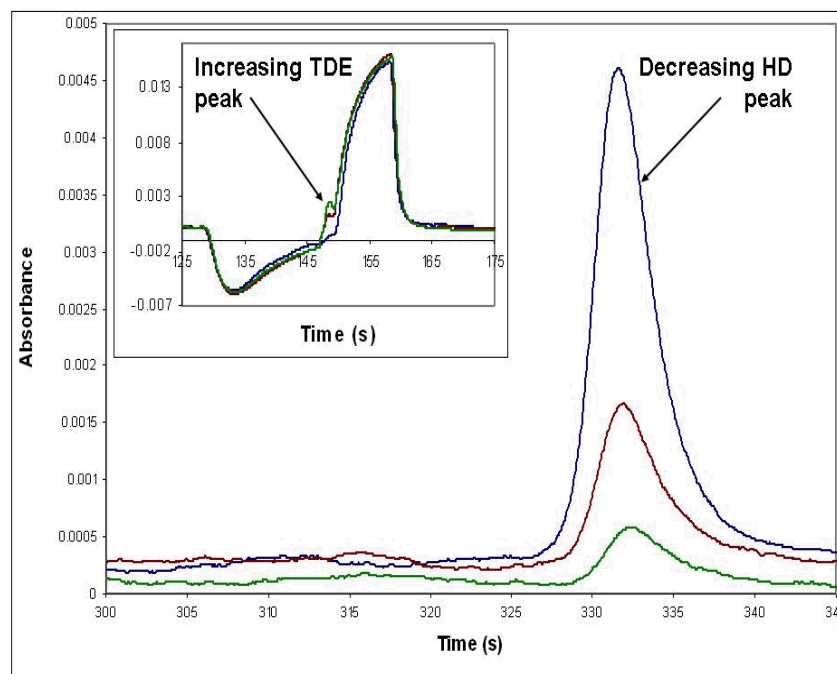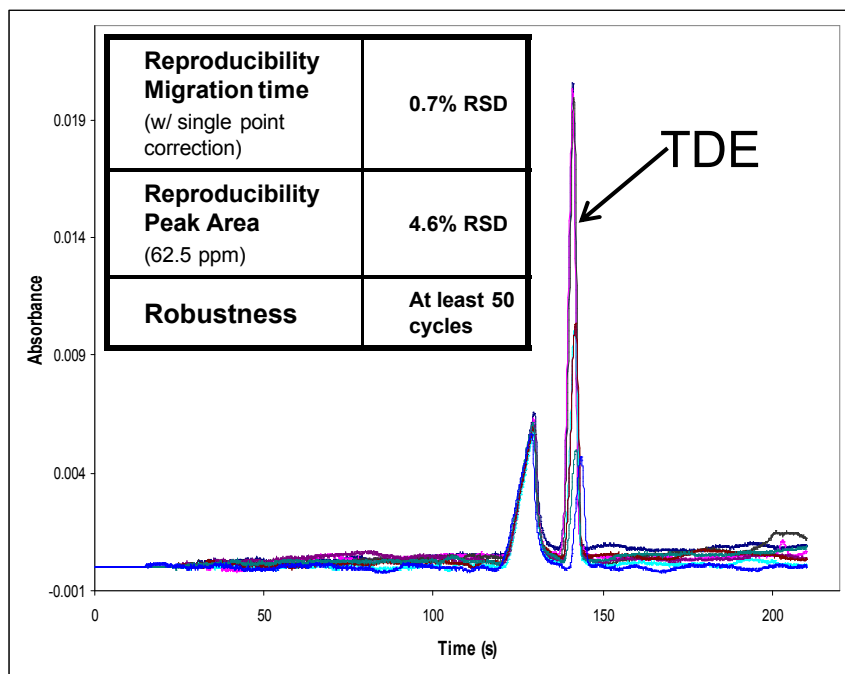
Current Effort is Geared to a Prototype for Testing on the EDS Vessel

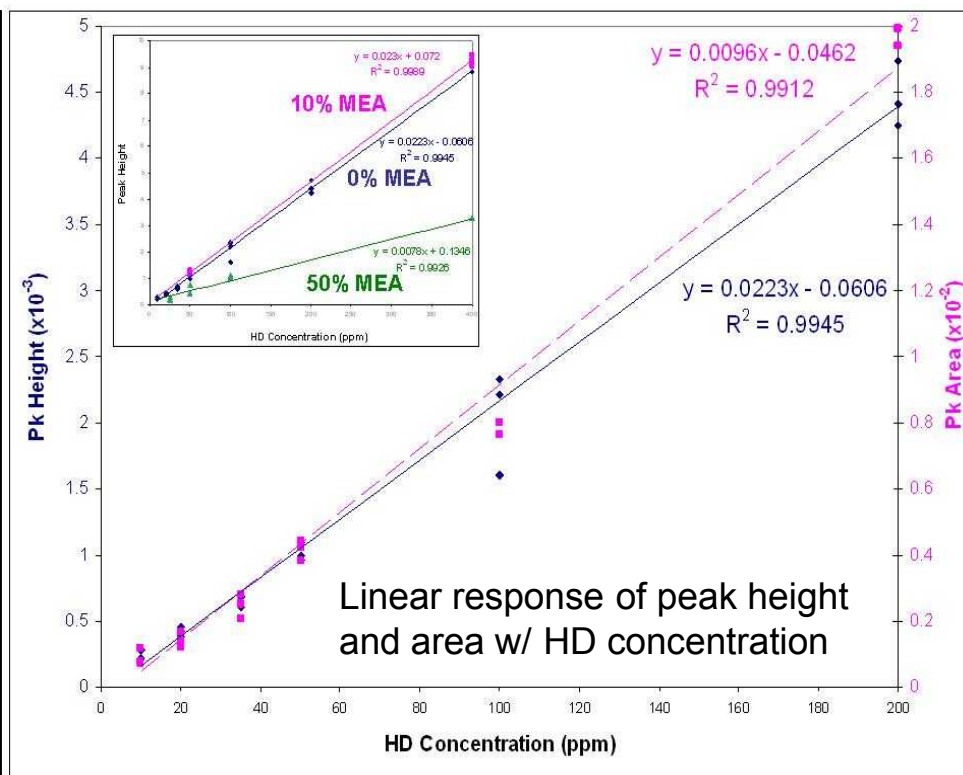**Development and testing of a 2nd generation prototype**

- Refined the hardware design based on proof of concept testing carried out at ECBC
- Tested with agent at ECBC (late May 2010)
- Determined detection/quantitation limits in more realistic sample matrices
- Demonstrated significant level of integration and automation

# Agent Testing with Mustard Shows Good Resolution and Quantitation

IPA from HD stock solution

100 ppm 1,4-dithiane

200 ppm HD

*IPA (isopropyl alcohol)

$y = 0.023x + 0.072$
$R^2 = 0.9989$

10% MEA

$y = 0.0223x - 0.0606$
$R^2 = 0.9945$

0% MEA

$y = 0.0078x + 0.1346$
$R^2 = 0.9925$

50% MEA

$y = 0.0096x - 0.0462$
$R^2 = 0.9912$

$y = 0.0223x - 0.0606$
$R^2 = 0.9945$

Linear response of peak height and area w/ HD concentration

Quantitation Limit of HD in aqueous samples is ~10ppm

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Agent Testing with Mustard Shows Sufficient Sensitivity in Neutralent
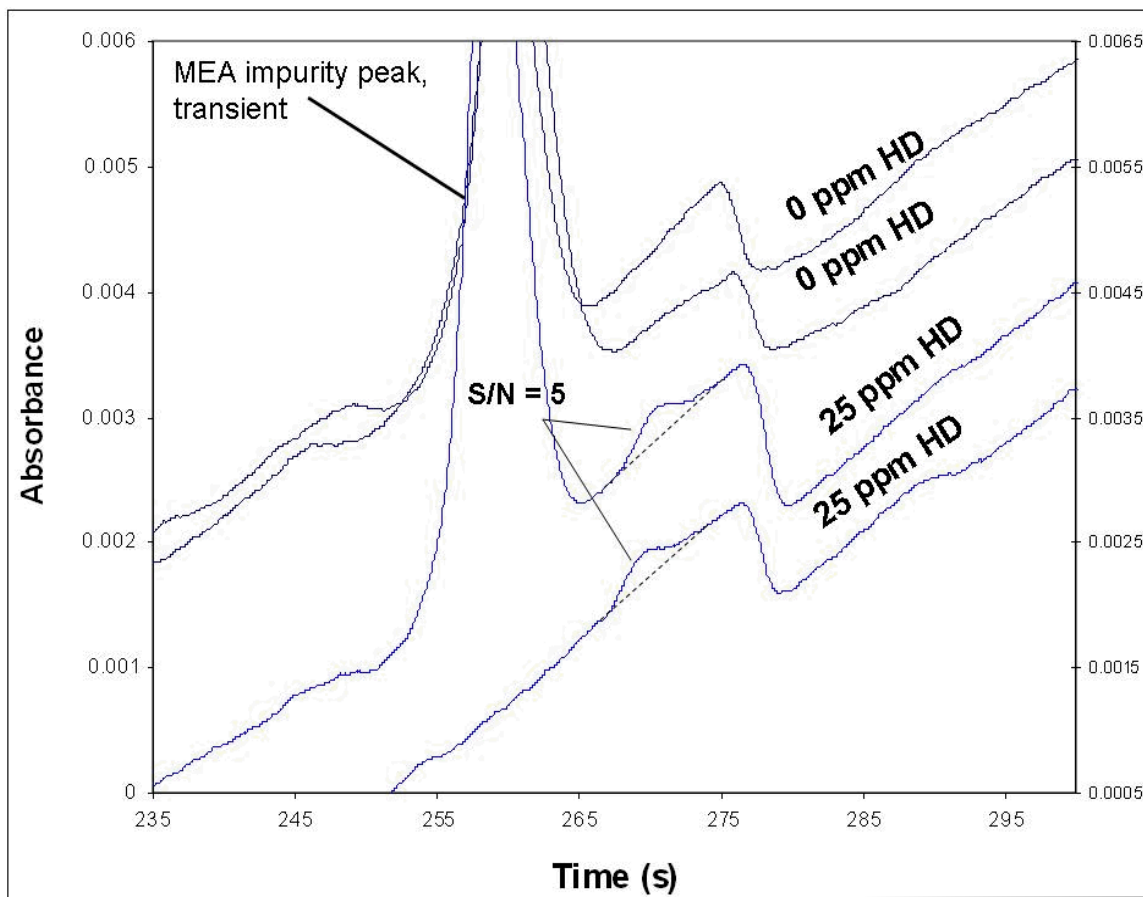
Quantitation limit (S/N ratio of 5) of HD in 50% MEA is ~25 ppm
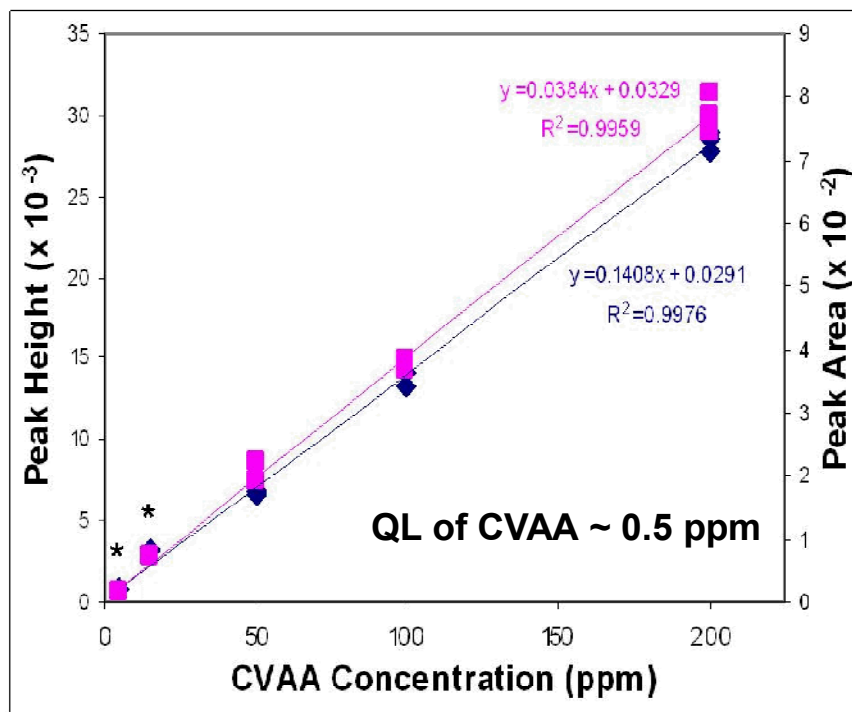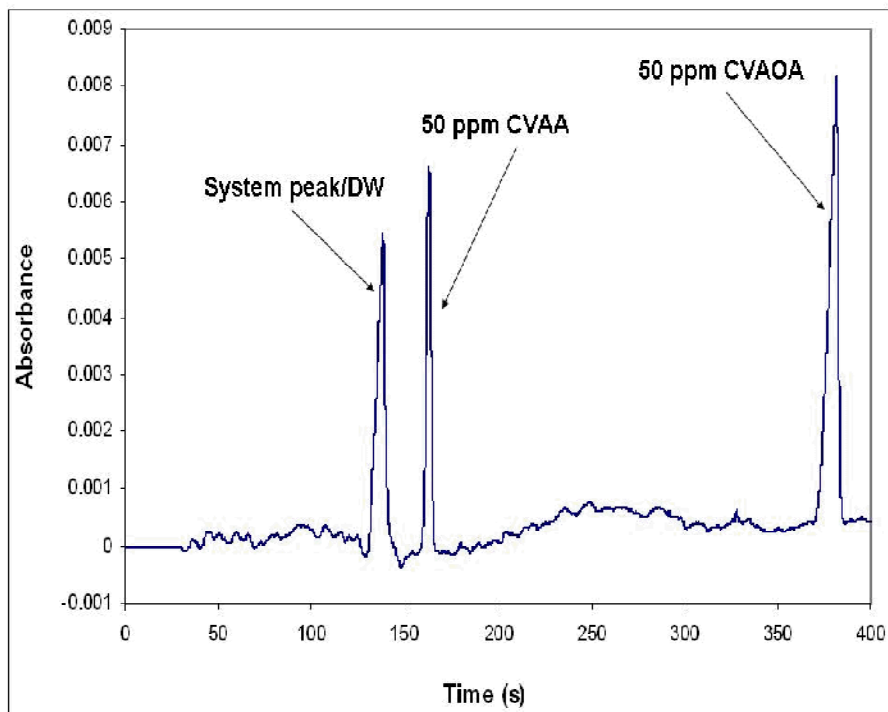
• in 90% MEA: 35 ppm

Replicate injections of 25 ppm HD in 50% MEA

Peak Height (x 10⁻³)	Peak Area (x 10⁻³)
0.2267	0.6943
0.2807	0.8154
0.2141	0.6003
0.1800	0.3622
<0.23 ± 0.04>	**<0.6 ± 0.2>**

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NRT-LA Method is also Suitable for Lewisite Agent Class

Hydrolysis of Lewisite ($t_{1/2}$ ~1 minute) is too rapid to detect directly

- Detection is of CVAA (2-chlorovinyl arsenous acid), also a blister agent
- Comparable to current state-of-the-art GC methods that derivatize Lewisite/CVAA and do not discriminate between the two
- Detection of CVAA not impacted by presence of Lewisite neutralent
- Identical hardware & reagents were used

$y = 0.0384x + 0.0329$
$R^2 = 0.9959$

$y = 0.1408x + 0.0291$
$R^2 = 0.9976$

QL of CVAA ~ 0.5 ppm

*CVAOA (2-chlorovinyl arsonic acid)

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Current Development Status: Prototype Ready for Testing on the EDS Vessel

3rd Generation Prototype

– Mounted on EDS vessel (shakedown testing underway)

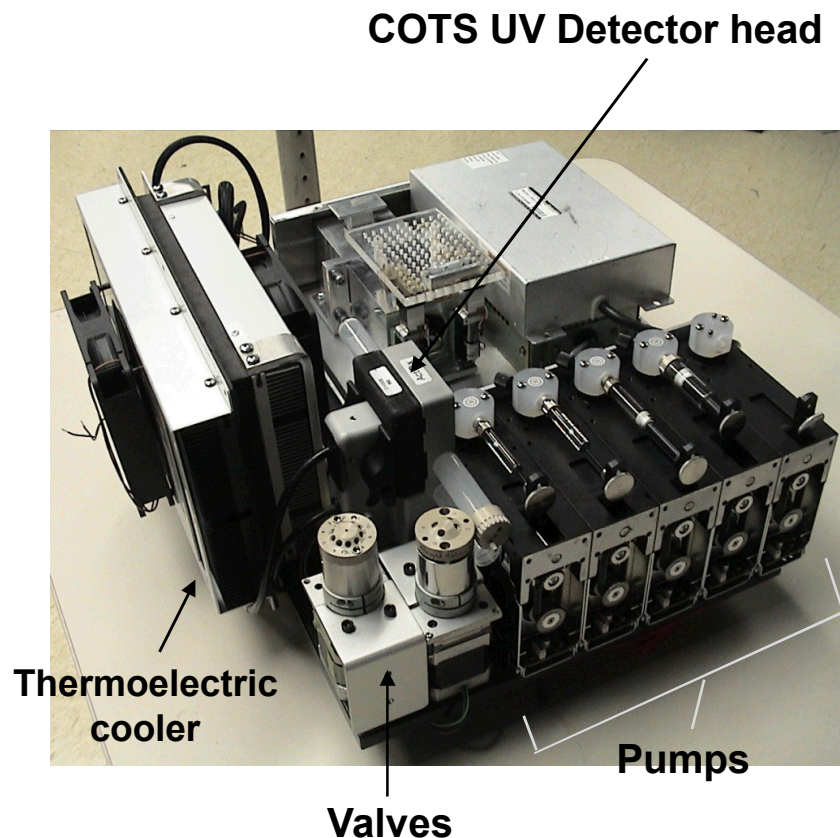– Fluid, data and electrical connections made to EDS vessel

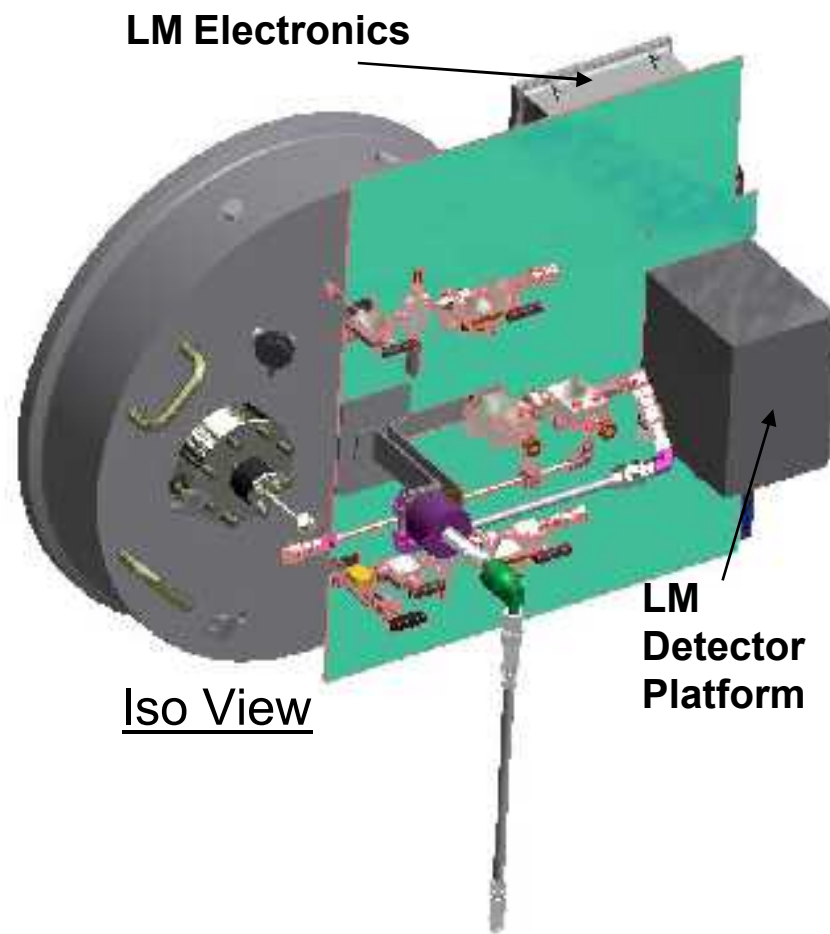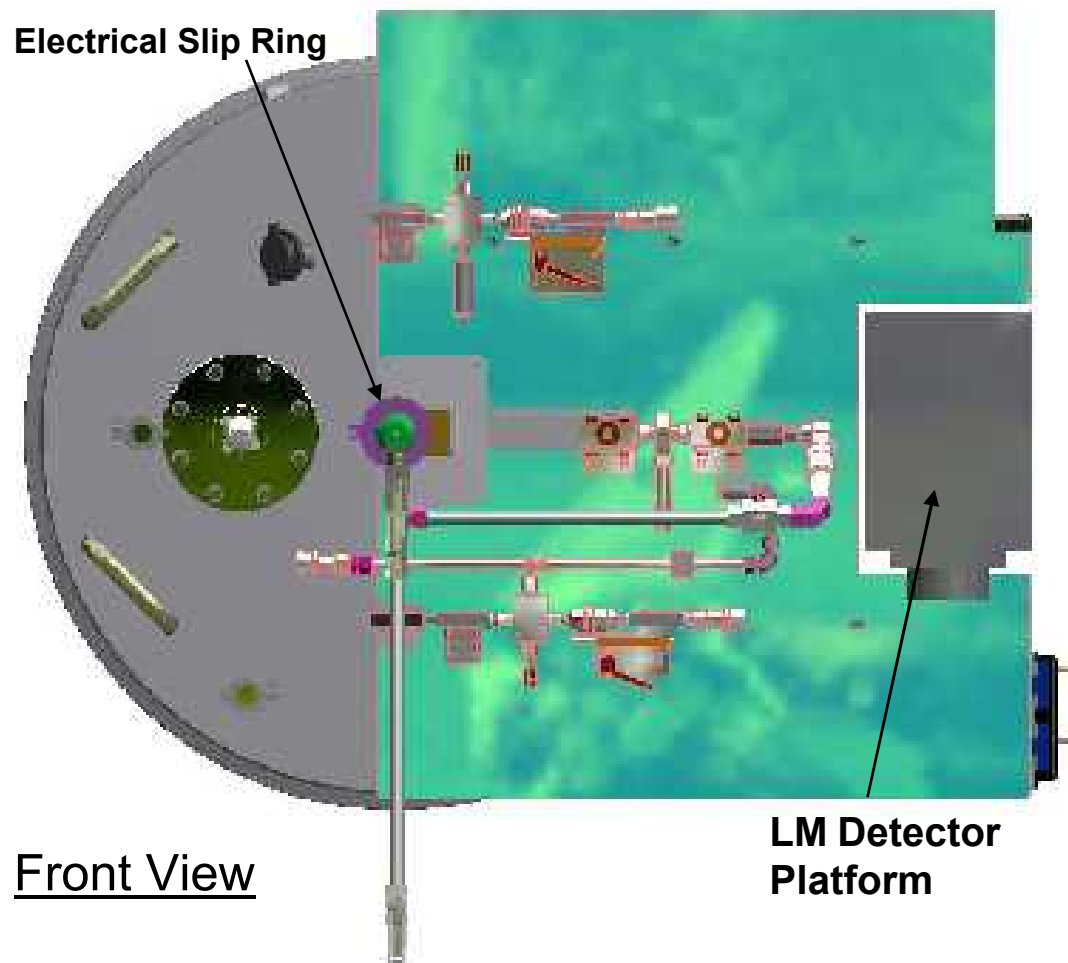**Operational testing on EDS at APGEA scheduled for this summer**

COTS UV Detector head

Thermoelectric cooler

Valves

Pumps

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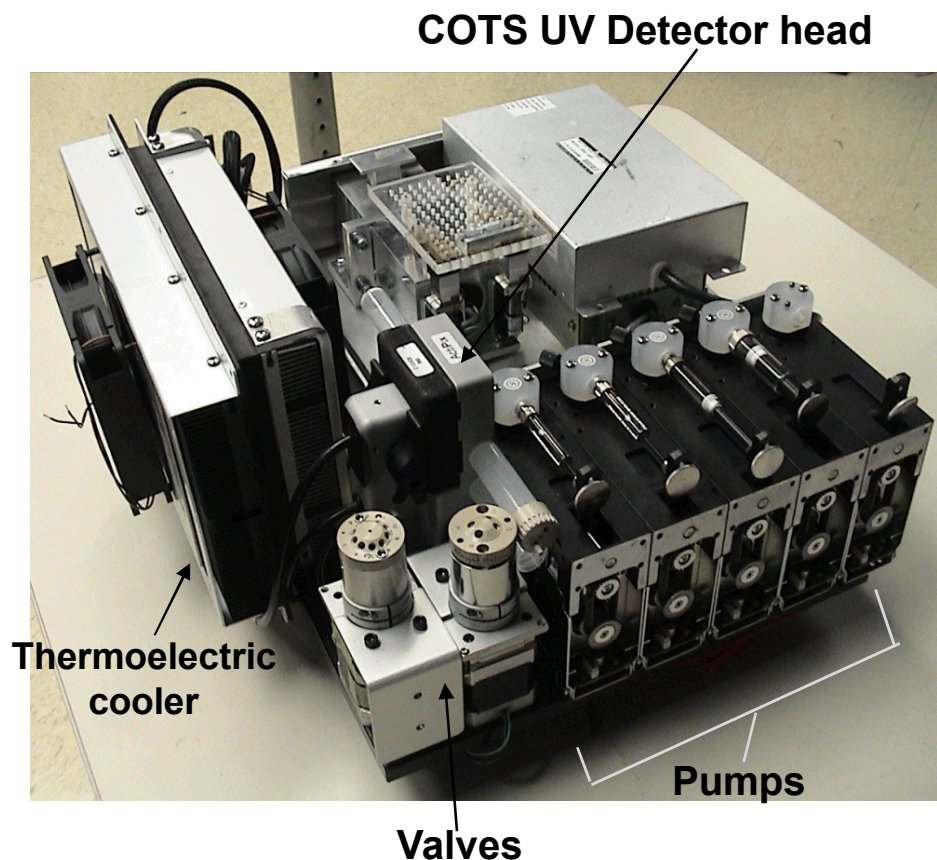
3rd Generation Prototype was Designed to Mount onto EDS

Attributes/Features

- **Builds on the same analysis platform**
- **Can collect & analyze multiple samples during first hour of processing time**
  - Minimizes manual intervention required to take a sample (PPE)
- **Integrated sample collection tube with the door valve manifold**
  - Maintaining chemical agent containment and pressure safety
  - Wastes contained & flushed back into treatment vessel between analyses
- **Operation During Rotation**
  - Orientation independence of analysis platform
  - Orientation sensing to ensure sampling when port is submerged
  - Slip ring electrical connections to supply electrical power
- **Automated operation w/ wireless communication interface to computer**
- **Pressure transducers to monitor system pressure**
- **Temperature controlled**
- **Same hardware can be adapted to other agent classes**

COTS UV Detector head

Thermoelectric cooler

Valves

Pumps

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CAD Illustration of 3rd Generation Prototype Mounted on P2

Electrical Slip Ring

LM Electronics

LM Detector Platform

LM Detector Platform

Front View

Iso View

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Additional Potential Applications of a NRT-LA

NRT-LA is a generic analysis tool that is suitable for a wide range of chemical analyses

- **Other Chemical agents**
  - CE is versatile: can tune to any number of agents (nerve agents, explosives)
  - pH, viscosity, voltage/polarity, buffer additives
  - Capillary length/chip based separations
- **Underwater or ocean burial sites**
  - Current technology is further miniaturizable, suitable for seagoing vessel or submersible operation
    - Remote sampling w/ analysis on nearby vessel/submersible OR analysis done at sample collection site
  - Can sample fluids and pre-concentrate agents out of fluid for injection (e.g. sea water)
    - Dilute samples can be concentrated
    - Locate leaking munitions

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