PHILIS ANALYTICAL METHODS FOR THE ANALYSIS OF CHEMICAL WARFARE (CWAS) AND FUTURE GENERATION AGENTS (FGAS) IN ENVIRONMENTAL SAMPLES

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INTRODUCTION

BACKGROUND:

Trace level detection limits are required for clean confirmational analysis of chemical warfare agents to meet US Army Public Health Command (USAPHC) – Chemical Agent Health Based Standards and Guidelines.To meet the detection limit requirements two techniques were investigated by PHILIS utilizing GC/TOF and UPLC/MS/MS.

OBJECTIVE:

Presentation of current analytical method capabilities with detection limit and data quality objective information that are utilized by PHILIS for the determination of chemical agents (A-230, 232, and 234, GB, GD, HD, GF and VX by GC-TOF Mass Spectrometry (GCMS-TOF) and UPLC/MSMS.

METHODS:

Analytical analysis performed via GC/TOF and UPLC/MS/MS.

RESULTS:

The results range from sub parts per billion ppb for GC/TOF to low parts per trillion (ppt) for UPLC/MSMS. Sample preparation via UPLC is significantly less time consuming than for GC/TOF (30 min. total/ 1.5 hours total), because UPLC/MSMS does not require concentration during sample preparation. UPLC/MSMS reporting limits are approximately 100X lower than GC/TOF. PHILIS can deliver low level reporting limits to support evaluation of contamination that is less than established remediation civilian clean levels.

CONCLUSIONS:

The analysis of agent compounds by GC/TOF and UPLC/MS/MS by the methods outlined in this poster provides qualitative (with confirmation) and quantitative (with increased sensitivity) data at levels that satisfy established remediation criteria.

REFERENCES:

Lawrence Livermore National Laboratory, "LC/MS/MS Methods and Information for NTA [FGA] and Phosphonic Acids" Dr. Dreyer. Dr Koester. 2020.

Chemical Agent Health-Based Standards and Guidelines Summary Table 2: Criteria for Water, Soil, Waste, as of July 2011.

Footnotes:

1.) Environmental Protection Agency. *2016.* "Analytical Protocol for Cyclohexyl Sarin, Sarin, Soman and Sulfur Mustard Using Gas Chromatography/Mass Spectrometry". *EPA/600/R/115 . September 2016.*

2.) Environmental Protection Agency. *2016.* "Analytical Protocol for VX Using Gas Chromatography/Mass Spectrometry". *EPA/600/R/116 . September 2016.*

3.) CSS. 2018. *SOP L-A-602 Analysis of CWAs in Air, Sect. 12.1, Rev. 0.*

METHOD

Equipment

- GC-TOFMS: Agilent 7890/ LECO Pegasus BT (low resolution TOF)
- Thermal Desorption System: Markes Unity Xr
- UPLC/MS/MS: Vanquish/ Altis TSQ
- Desorption Tube: Markes #C2-CAXX-5138 (PAH)

Safety

All procedures performed in accordance with CSS-Inc. PHILIS Laboratory Safety and Chemical Hygiene Plan , Rev6 2022

METHOD

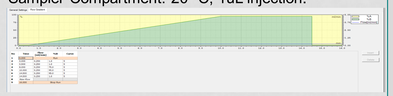
Parameters

GC/TOF

Primary Column: Restek Rxi-5Sil 30m x 250um x 0.25um
Temperature Program: 40 °C for 0.75 min; 30C/min, to 130 °C; 40C/min, to 240 °C, 25C/min, to 315 °C.
Inlet pulse pressure: 30 psi
Inlet pulse duration: 0.75 min.
Inlet purge time: 0.75 min.
Inlet purge flow: 30 mL/min.
Liner: 2mm straight
Flow: 1.2 mL/min.

UPLC/MS/MS

Column: Waters Aquity UPLC HSS T3 1.8um, 2.1 x 150 mm (part # 186003540)
Column Compartment: 40 °C, Forced Air. Pre-heater, 40 °C
Sampler Compartment: 20 °C, 1uL injection.



VX	4	6	268.175	86.208	26.44	265.668	59	
A230	6	8.5	195.2	74.125	14.18	87.483	44	
A230	6	8.5	195.2	122.042	15.99	87.483	44	TRUE
A232	6	8.5	211.2	97.06	30.02	87.483	51	
A234	6	8.5	225.21	74.065	20.5	87.483	62	
A234	6	8.5	225.21	197.196	13.72	87.483	62	TRUE
Triphenyl-d15 Phosphate	10	12	342.175	222.113	28.17	265.668	153	

Method development

- GC/TOF methods were performed in accordance with the Analytical Protocol for Cyclohexyl Sarin, Sarin, Soman and Sulfur Mustard Using Gas Chromatography/Mass Spectrometry and Analytical Protocol for VX Using Gas Chromatography/Mass Spectrometry
- Optimization of gas chromatography parameters to achieve maximum sensitivity, optimum chromatographic resolution and minimum run time.
- SRM's were optimized for sensitivity via direct infusion. Ion source parameters and mobile phases selections were based on previous work accomplished by Dr. Mark Dreyer and Dr. Carolyn Koester of LLNL.

Procedure

- **GC-TOFMS**
  - Liquids – 35mL sample: 8.8g $NaCl_2$ extracted with 2mL $MeCl_2$ without concentration.
  - Solids – 10g sample: 2.5g Na2SO4/ 5 extracted with 25mL $MeCl_2$ and concentrated to 1mL.
  - Wipes – wipe extracted with 15mL $MeCl_2$
- **UPLC/MS/MS**
  - Liquids – 2mL of sample filtered through a 0.2um PTFE filter – then 100uL of MeOH passed through the filter for a final volume of 2.1mL
  - Solids – 5g sample weighed into a 40mL containing 5-10 3mm glass beads. 5mL of a 5% MeOH/water solution added to the vial. Vial vortexed on high for 30 seconds – then, placed on shaker table for 15 min. at 1500 rpm. 5% MeOH/water extract then filtered through a 25mm, 0.22um PVDF filter.
  - Wipes – sample extracted in a 40mL with 15mL of a 5% MeOH/water (100% MeOH for VX) solution on a shaker table at 1500 rpm for 15 min. Supernatant was decanted and filtered through a 25mm 0.22um PVDF filter. Final volume – 15 mL.

RESULTS

Method Detection Limit Study

Soman (GD)	0.184	0.214	0.00371
Cyclohexyl sarin (GF)	0.253	0.178	0.00546
A-230	0.651	0.244	0.0431
A-232	0.475	0.593	0.0236
A-234	0.317	0.815	0.0156
A232	0.007823	0.00362	0.00004605

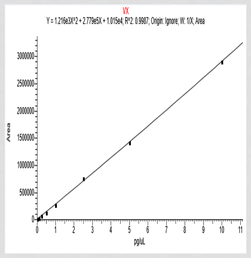
Precision and Accuracy Study

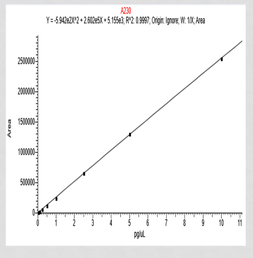
50/25pg on column liq; 50/20/10pg soil; 100/50 PG WIPE

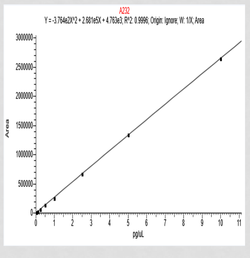
Soman (GD)	96.9	1.55	55.2	14.6	95.5	6.9
Cyclohexyl sarin (GF)	92.5	1.8	57.6	5.7	76.7	5
A230	81.3	10.2	76	2.6	62.2	7.1
A234	73.9	5.2	64.9	7.6	50.3	10.6
A232	101	10.7	143	5.08	102	22.1

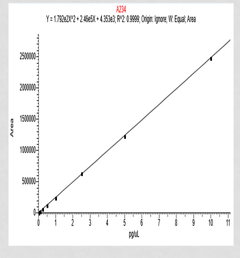
UPLCMSMS CALIBRATIONS

•VX •A230 •A232 •A234

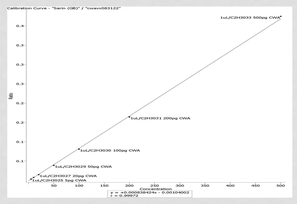


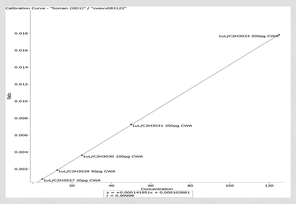


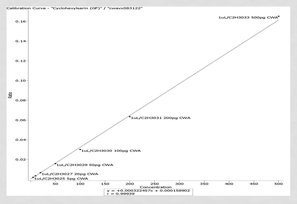


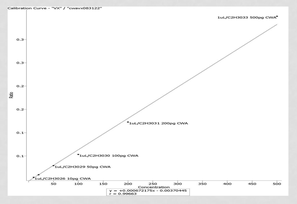


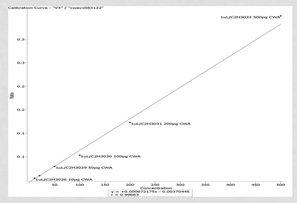
GC-TOF CALIBRATIONS

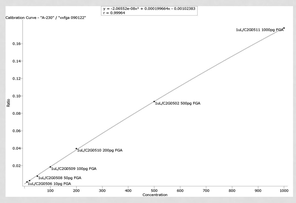


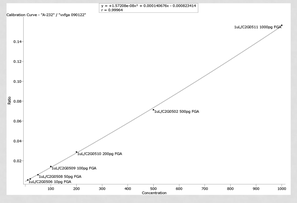


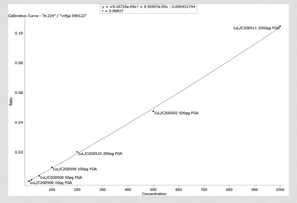












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