Field Screening Method Developed Testing GRO and DRO in Drinking Water for U.S. Navy Jet Fuel Site in Hawaii

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2021 Red Hill Fuel Leak, Pearl Harbor, Hawaii

27,000 gallons of JP-5 jet fuel leaked into nearby aquifer, the water supply serving base.

Thousands of homes were affected, hundreds of people reported getting sick.

U.S. Navy built 20 huge underground fuel tanks from 1940 to 1943. 250-million-gallon capacity, largest UST site in the world.

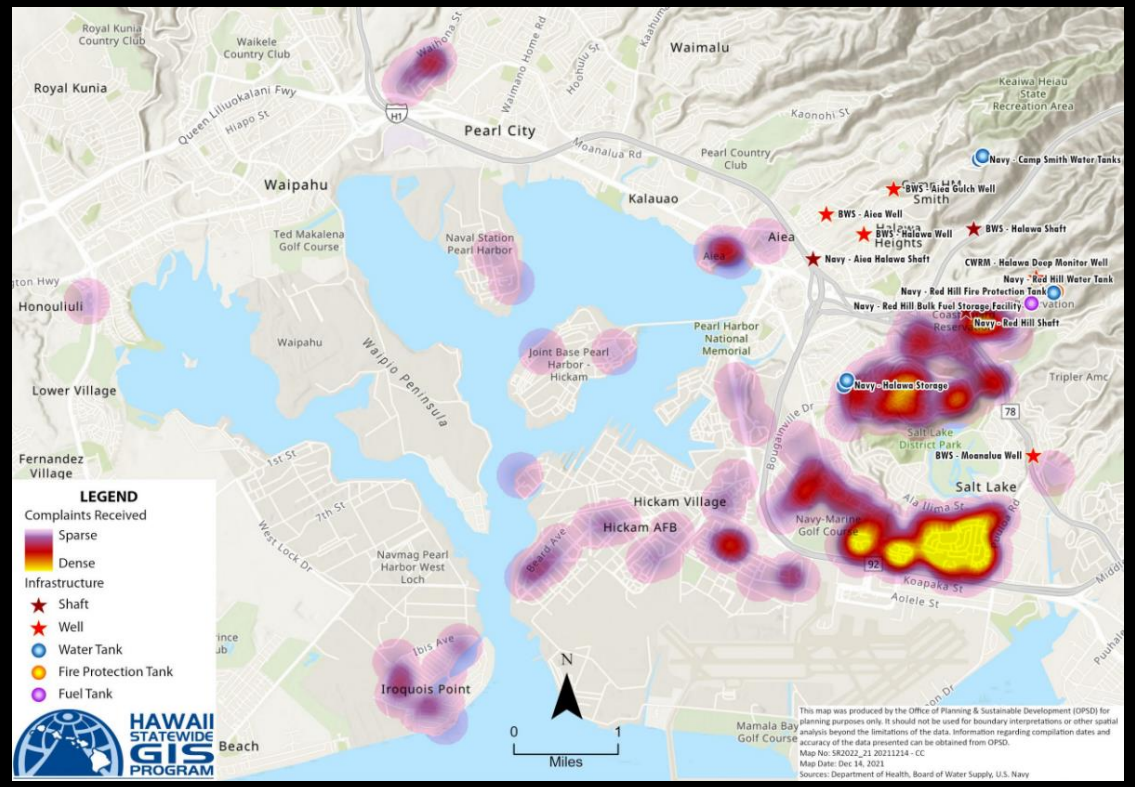
U.S. Navy Needed a Fast, Accurate Screening Tool

Navy's contractor AECOM recommended Sitelab UVF-Trilogy analyzer

To date, 9 instruments have been sold, used by 4 different contractors

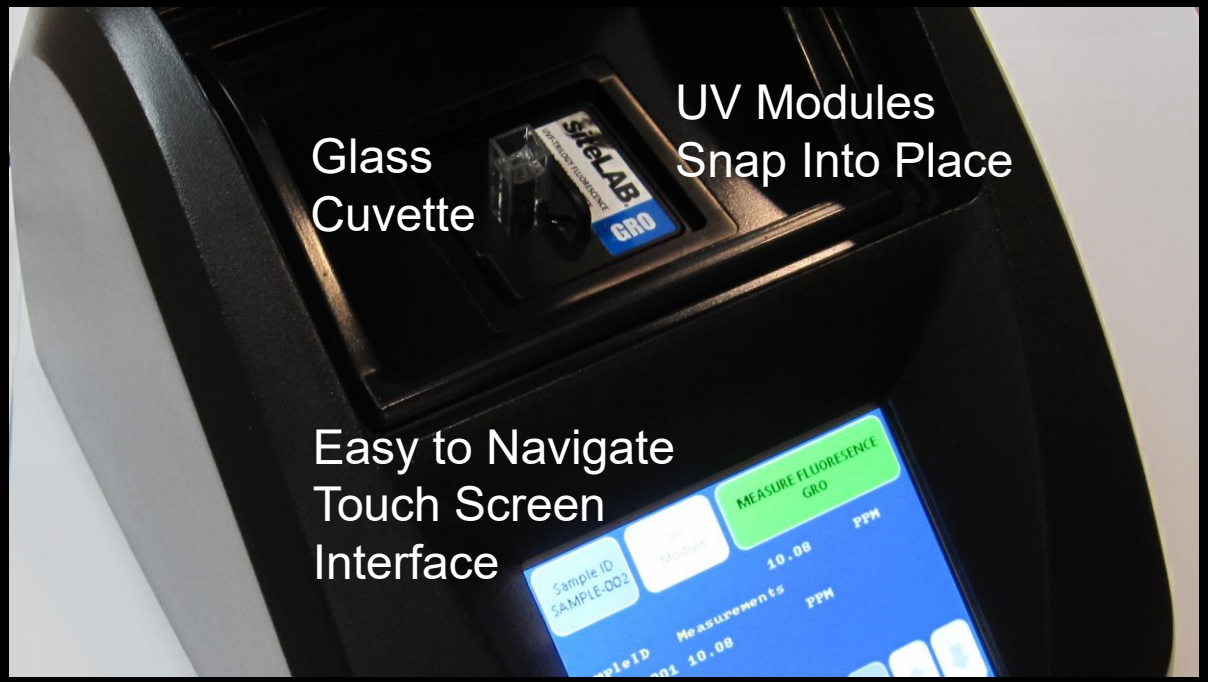
Site has since been defueled, but monitoring and remediation efforts continue to this day

Select samples are sent off-site to certified labs for confirmation analysis



Complaints map shows extent of spill

Portable Ultraviolet Fluorescence (UVF) Analyzer



UVF-Trilogy is factory calibrated
Instrument does not drift – ever!

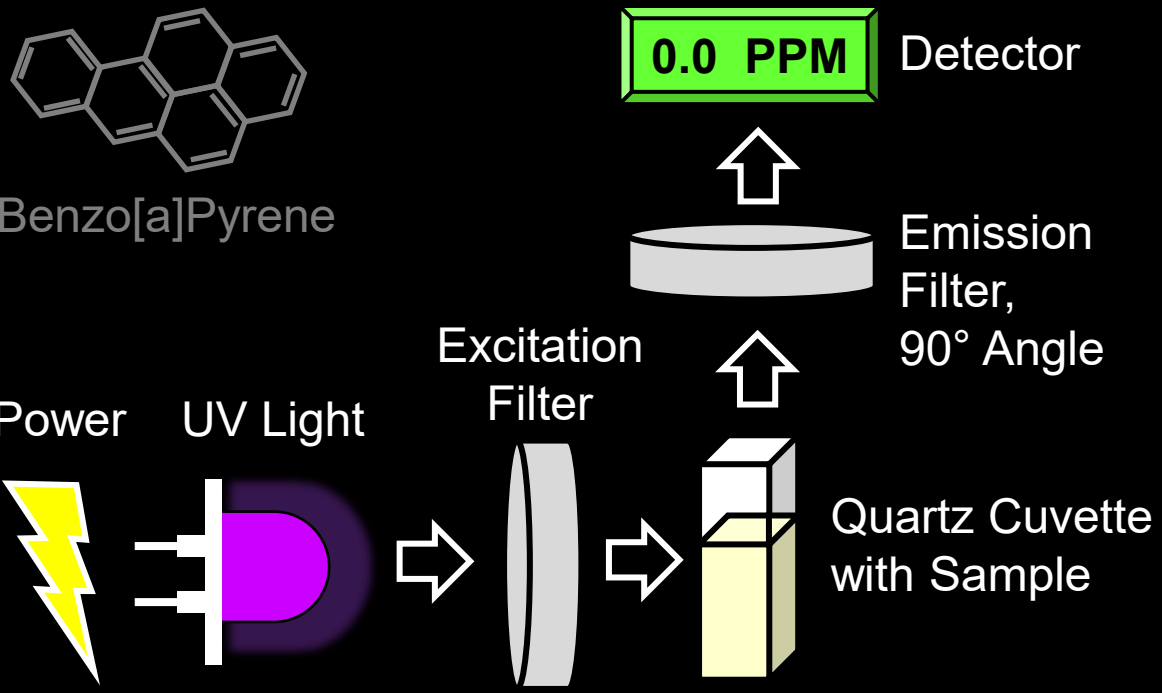
Sitelab UVF-Trilogy detects a wide range of petroleum contaminants; gasoline, diesel, crude oils, PAHs and more

Highly sensitive to aromatic hydrocarbons

Method uses hexane for water analysis and methanol for soil analysis

Fluorescence UV Modules fitted with UV LED light, excitation and emission optics

How Fluorescence Works



Detector converts voltage as Raw Fluorescence Units (RFU) to concentration. 6 second measurement time.

Limitations Using UVF?

Does not detect one compound from another, they co-fluoresce

Does not detect aliphatic hydrocarbons

Can exhibit fluorescence ‘quenching’ in highly contaminated soils or coal tars

Limited regulatory acceptance, but…

UVF methods submitted to U.S. EPA SW-846 program in 2024 for approval

UV Modules Used For Testing Refined Hydrocarbons

Module	Excitation	Emission	Hydrocarbons Detected and Test Name
GRO	254 nm	270-290 nm	C6-C10 Range Gasoline Range Organics
EDRO	254 nm	300-400 nm	C10-C36 Range Extended Diesel Range Organics

What's in Jet Fuel? Made with kerosene, contains aromatic hydrocarbons in both ranges, but is mostly aliphatic.

UVF-Trilogy Calibration Kits Used for Analysis

1. GRO Standards

Sitelab CAL-025H
Supplied in Hexane

Conc.	RFU (Voltage)
Blank	19
0.5 ppm	25
1 ppm	34
3 ppm	58
5 ppm	81
10 ppm	136

Linear, $R^2 = 0.999$

2. EDRO Standards

Sitelab CAL-042H
Supplied in Hexane

Conc.	RFU (Voltage)
Blank	14
0.1 ppm	103
0.5 ppm	412
1 ppm	781
3 ppm	2,224
5 ppm	3,670

Linear, $R^2 = 1.00$

GRO Response Testing Monoaromatic Compounds

Hydrocarbons Tested	Response (%)
Benzene, C6	28
Toluene, C7	114
Ethylbenzene, C8	82
m-Xylene, C8	98
o-Xylene, C8	125
p-Xylene, C8	180
1,3,5-Trimethylbenzene, C9	140
Naphthalene, C10 (2-rings)	0

Fluorescence varies due to size and shape of each molecule

Compare to 100% Response using Sitelab GRO Calibration

Samples tested using Sitelab CAL-025M calibration kit in methanol (used for soils)

CRMs supplied in methanol by AccuStandard

EDRO Response Testing Polyaromatic Compounds

Hydrocarbons Tested	Response (%)
Benzene, C6 (1-ring)	0.1
Naphthalene, C10	84
2-Methylnapthalene, C11	160
Phenanthrene, C14	900
Anthracene, C14	1,280
Benzo[k]Fluoranthene, C20	230
Benzo[a]Pyrene, C20	122
Dibenz[a,h]Anthracene, C22	12

Fluorescence varies due to size and shape of each molecule

Compare to 100% Response using Sitelab EDRO Calibration

Samples tested using Sitelab CAL-042M calibration kit in methanol (used for soils)

CRMs supplied in methanol by AccuStandard

Fluorescence Response Comparing Fuels and Oils

Light to Heavy Petroleum Products at 100 ppm	GRO Response (%)		EDRO Response (%)	
JP-5 Jet Fuel	18	← 5.5X Lower	4.5	← 22X Lower
JET-A Jet Fuel	25		5.0	
Gasoline, Regular 87 Octane	27		0.8	
Highway Diesel, Ultra-Low Sulfur	30		18	
No. 2 Fuel Oil	25		70	
No. 4 Fuel Oil	16		160	
No. 6 Fuel Oil	8		270	

Gas and diesel collected from retail station. CRMS provided by AccuStandard.

Accuracy Testing GRO in Water Proficiency Sample

Calibrations in Hexane: Water Samples using ERA 762	Result µg/L	Certified Value µg/L	Recovery %
1. Sitelab GRO Standard	1,010	2,210	46%
2. ERA 762 GRO Standard	2,030	2,210	92%
3. Weathered Gasoline Standard	1,615	2,210	73%
4. Fresh Gasoline, 87 Octane	3,840	2,210	174%
vs. Study Mean Result	2,380	2,210	108%
PT Performance Acceptance Limits		815 – 3,890	

→ Products contain 50% weathered gasoline

Sitelab GRO made with BTEX, contains no aliphatics

Accuracy Testing DRO in Water Proficiency Samples

Calibrations in Hexane: Water Samples using ERA 764	Result µg/L	Certified Value µg/L	Recovery %
1. Sitelab EDRO Standard	209	1,770	12%
2. ERA DRO Standard	1,756	1,770	99%
vs. Study Mean Result	1,250	1,770	71%
Water Samples using NSI QC-115			
1. Sitelab EDRO Standard	275	1,880	15%
2. NSI DRO Standard	1,925	1,880	102%
vs. Study Mean Result	1,300	1,880	69%

ERA and NSI products made with ultra-low sulfur diesel fuels

Sitelab EDRO made with weathered diesel fuel, contains more aromatics

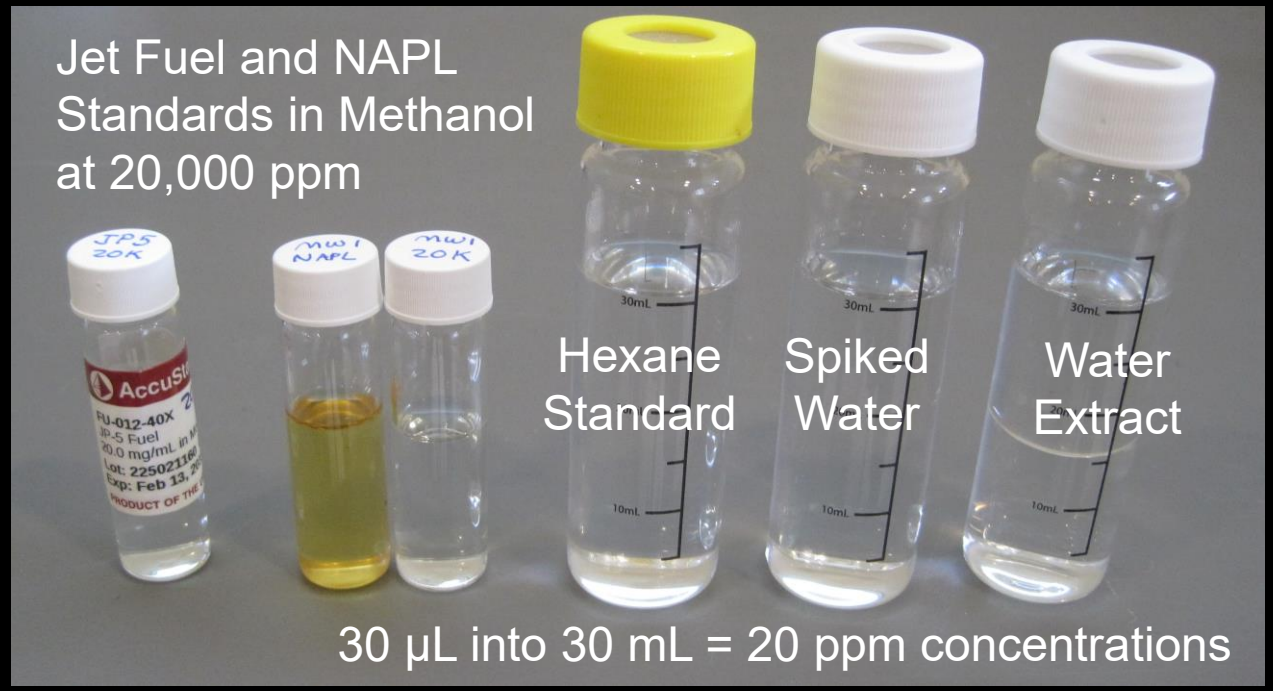
Performance Studies Testing Jet Fuels in Water

Jet fuel standards and NAPLs collected from monitoring wells used for analysis

Analyzer calibrated to GRO, EDRO plus JP-5 jet fuel using 1-point calibrations

Water samples extracted and tested 24 hours after preparation

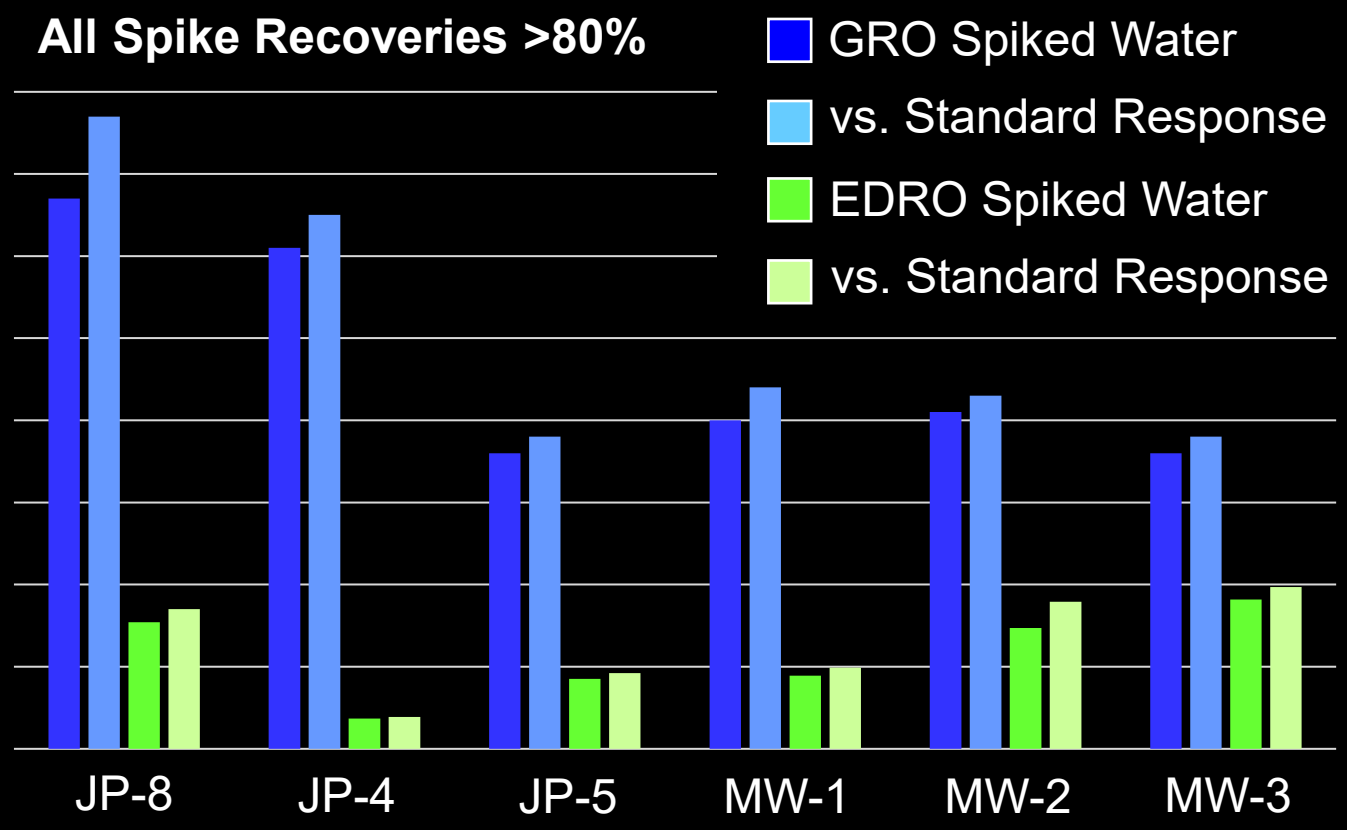
Water samples also tested without solvent extraction for comparison



Methanol standards used to spike water samples and prepare hexane standards for analysis

Water Spiked at 20 mg/L with Jet Fuels and NAPLs

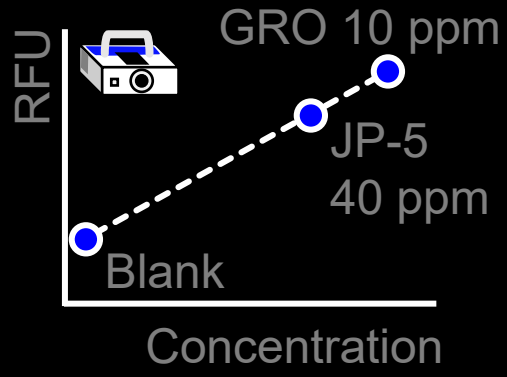
	GRO Results		EDRO Results	
Jet Fuel CRMs	Water mg/L	Standard Response	Water mg/L	Standard Response
JP-8	6.7	7.7	1.54	1.70
JP-4	6.1	6.5	0.37	0.39
JP-5	3.6	3.8	0.85	0.92
NAPLs from Naval Air Station, Adak, Alaska				
MW-1	4.2	4.4	0.88	0.99
MW-2	4.1	4.3	1.47	1.79
MW-3	3.6	3.8	1.82	1.97

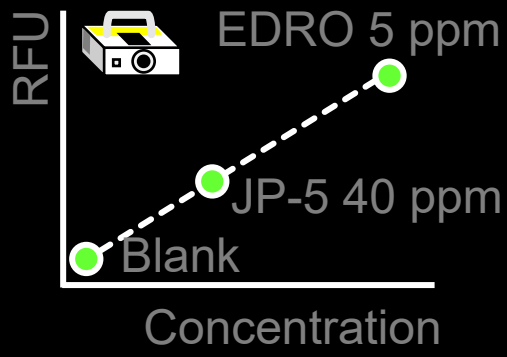


Spiked Water Results using JP-5 Calibrations

Samples Spiked at 20 mg/L	Analyzer Calibrated to JP-5 using GRO UV Module			Analyzer Calibrated to JP-5 using EDRO UV Module		
	Water mg/L	Standard Response	Recovery %	Water mg/L	Standard Response	Recovery %
JP-8 Jet Fuel	35	40	88%	34	37	92%
JP-4 Jet Fuel	32	35	91%	8.1	8.6	95%
JP-5 Jet Fuel	19	20	95%	19	20	95%
NAPL MW-1	21	23	91%	20	22	91%
NAPL MW-2	21	23	96%	32	39	82%
NAPL MW-3	19	20	95%	40	44	93%

Results are accurate using both UV Modules





Water Results With and Without Hexane Extraction

Samples Spiked at 20 mg/L	Analyzer Calibrated to JP-5 using GRO UV Module			Analyzer Calibrated to JP-5 using EDRO UV Module		
	Without Extraction mg/L	With Extraction mg/L	Ratio	Without Extraction mg/L	With Extraction mg/L	Ratio
JP-8 Jet Fuel	36	35	1.0	134	34	3.9
JP-4 Jet Fuel	41	32	1.3	35	8.1	4.3
JP-5 Jet Fuel	20	19	1.1	100	19	4.8
NAPL MW-1	32	21	1.5	73	20	3.7
NAPL MW-2	19	22	0.9	106	32	3.3
NAPL MW-3	15	19	0.8	99	40	2.5

Samples tested 30 minutes after preparation

Mimics oil-in-water fluorometers and submersible probes

Performance Testing Soils from Westover AFB Site

Results in mg/Kg	UVF GRO	Lab Total VPH	UVF EDRO	Lab Total EPH		UVF TPH	Lab TPH	RPD
Soil 1	6	8	1	<0.4	→ Add Fractions Together	7	8	15%
Soil 2	4,760	1,100	680	4,400		5,440	5,500	1%
Soil 3	6,270	4,200	700	5,000		6,970	9,200	28%
Soil 4	7,797	6,500	950	6,700		8,747	13,200	41%
Soil 5	9,763	3,900	1,175	7,000		10,938	10,900	0.4%
Soil 6	16,380	6,000	1,800	12,000		18,180	18,000	1%

GRO Results are Higher

EDRO Results are Lower

Results Close to MADEP VPH + EPH

Samples extracted and analyzed in methanol

Water Sample Extraction Procedure is Fast & Easy

Samples prepared using 40 mL glass VOA vials with 5 mL graduations. Everyone should use them!

15 mL of water is poured into vial

15 mL of hexane is added to vial using squirt bottle

Extract is shaken for two minutes, allowed to settle and then analyzed. This creates a 1:1 Extract

Vials perform same compared to using bigger size bottles, but are less expensive and less wasteful!

Samples Tested using GRO and EDRO Calibrations

Pour sample extract into cuvette, place into analyzer with UV Module inserted and press measure

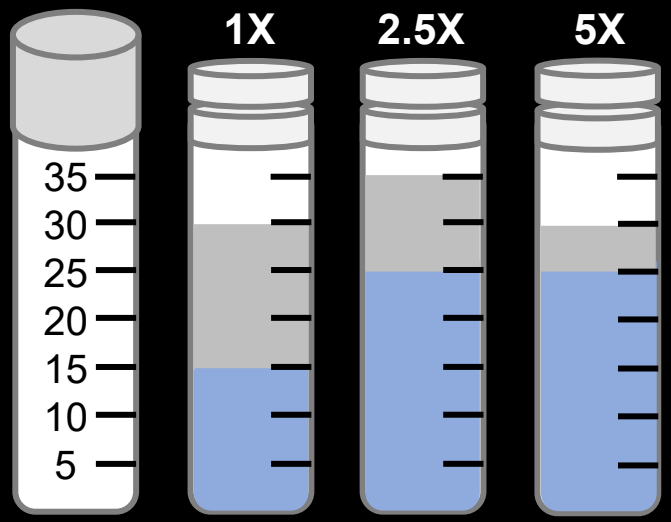
Swap out Module and test extract again

Perform calibration checks, confirm minimum detection limits are accurate:

GRO = 0.5 ppm (500 µg/L)

EDRO = 0.1 ppm (100 µg/L)

Detect Low PPB Levels in Concentrated Extracts



Water	Solvent	Ratio	GRO Reporting Limit	EDRO Reporting Limit
15 mL	15 mL	1X	500 µg/L	100 µg/L
25 mL	10 mL	2.5X	200 µg/L	40 µg/L
25 mL	5 mL	5X	100 µg/L	20 µg/L

Use vials to prepare concentrated extracts, cuvette only needs 2 mL for measurement.

Divide sample readings by ratio to report lower concentrations

QC Tests using JP-5 Laboratory Control Samples

Sitelab CAL-JP5-LCS
Developed for Navy project

Supplied in hexane, 30 mL each per vial. Standards are reusable with 6-month shelf life

Product used to check UVF-Trilogy performance

Acceptance Criteria	GRO Range	EDRO Range
40 ppm High Standard	6.0 – 8.0 ppm	1.4 – 1.9 ppm
20 ppm Middle Standard	3.0 – 3.8 ppm	0.6 – 1.0 ppm
4 ppm Low Standard	0.5 – 0.9 ppm	0.13 – 0.17 ppm

Readings within these ranges confirms detection of JP-5 jet fuel is linear and valid

QC Tests in Solvent Blanks

GRO Blank Readings

PPM	RFU (Voltage)
0.00	19
0.14	22
-0.40	17
0.05	20
-0.00	19

<20% RSD Limit

Concentrations bounce, RFUs more repeatable

EDRO Blank Readings

PPM	RFU (Voltage)
0.00	14
0.01	18
-0.00	11
0.00	15
-0.00	14

<20% RSD Limit

Concentrations more stable, close to zero

Use HPLC grade hexane only!

Use solvent resistant FEP-lined squirt bottle to avoid phthalate contamination

Red Hill Project on U.S. Dept. of Defense Website

A Naval Facilities Engineering Systems Command contractor tests a water sample in 2022.

U.S. Navy is working closely with the Hawaii Department of Health, U.S. Environmental Protection Agency and the U.S. Army to restore safe drinking water to Joint Base Pearl Harbor-Hickam housing communities through sampling and flushing, and the recovery of the Red Hill Well.

U.S. Dept. of Defense Visual Information Distribution Service: www.dvidshub.net

CBS Featured Story on 60 Minutes

April 18, 2024 Episode: Crisis at Pearl Harbor

UVF-Trilogy Featured in Video... for 10 Seconds!

This show has great history of site in WWII and interviews with families who got sick

The End, Thank You

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