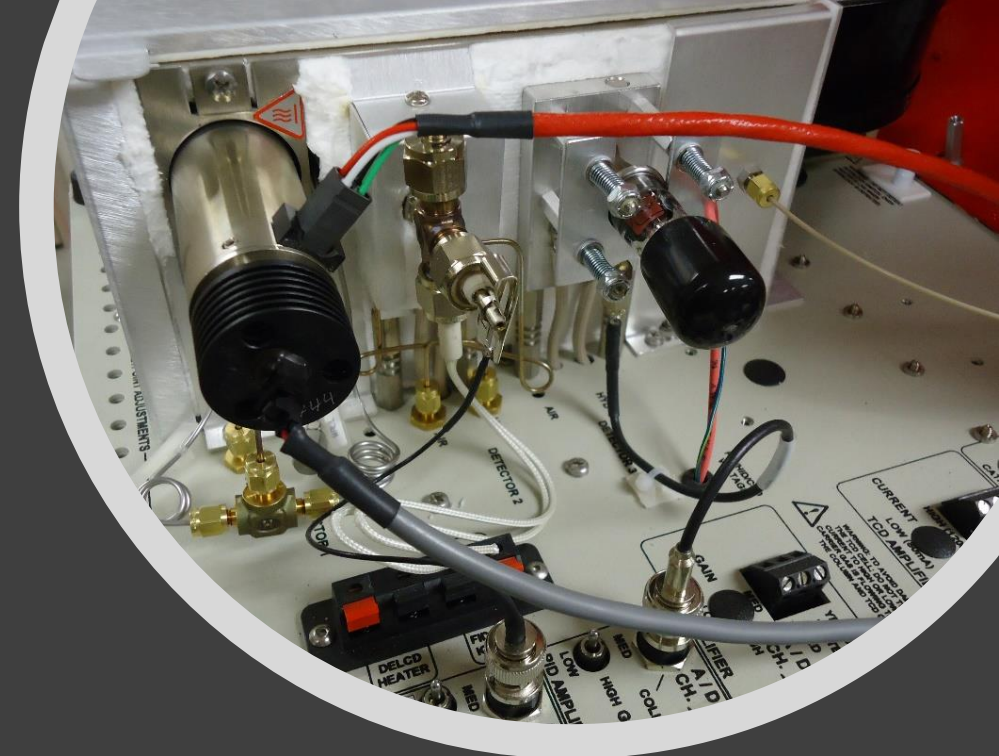


# MIP Detector System

Gas Phase Detectors – XSD, FID, PID  
Mounted on the GC under the red hood

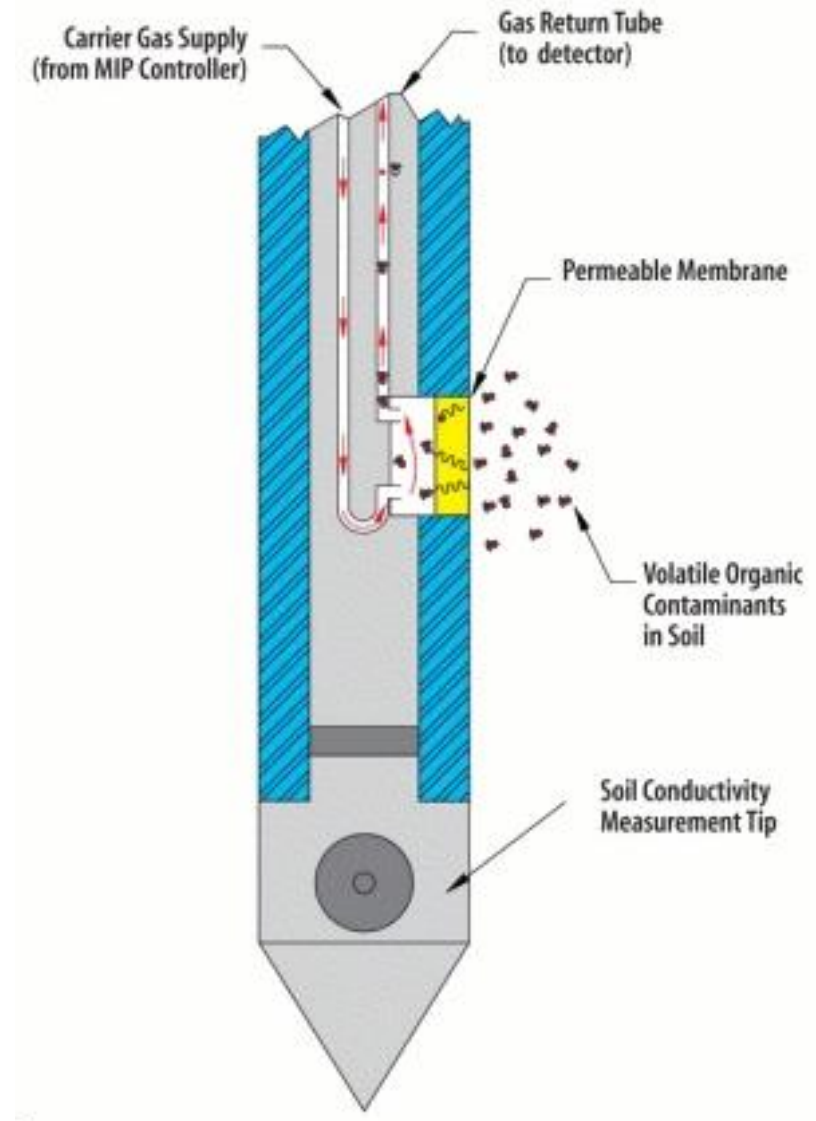
Gas Chromatograph (GC)  
XSD Controller

April 2020



# MIP Theory of Operation

Under a concentration gradient VOCs move across the membrane via diffusion and then are transported to a series of detectors at the surface in an inert carrier gas that continuously sweeps past the membrane.





PID

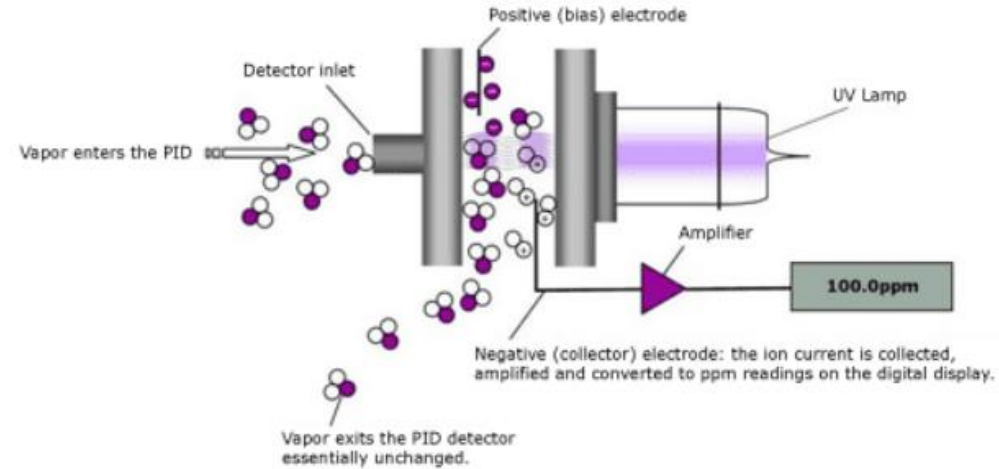
Photo Ionization  
Detector

---

Geoprobe



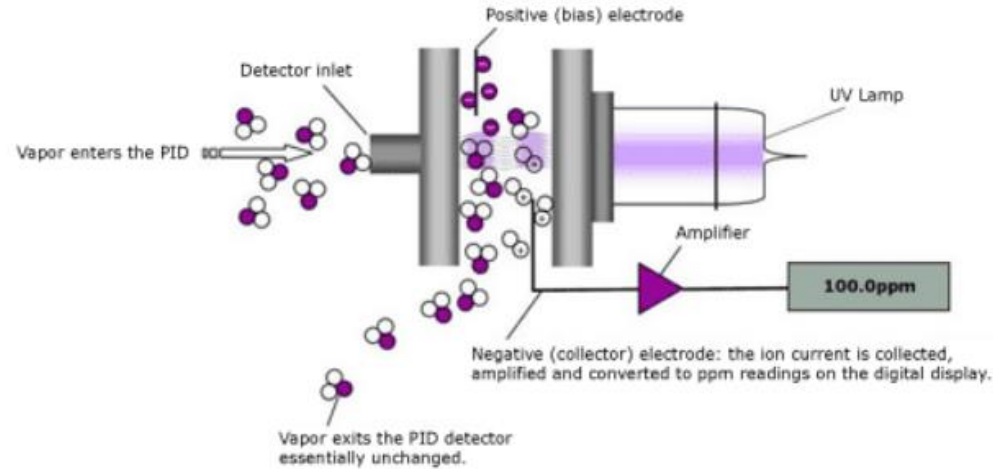
# Operating Principle



## Photoionization Detector (PID)

The carrier gas stream flows through the detectors ionization chamber where it is continuously irradiated with high energy ultraviolet light. When compounds are present that have a lower ionization potential than the irradiating energy (10.6eV) they are ionized. The ions that are formed are drawn to a collector electrode, which produces an ion current proportional to its compound mass. The resulting current is amplified, and the output signal is received by the MIP controller for log generation.

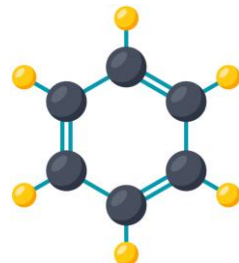
# Operating Principle



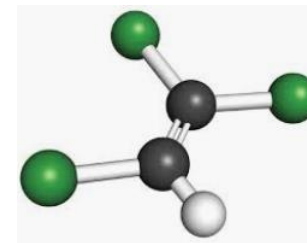
## Photoionization Detector (PID)

An ultraviolet lamp, typically in the 10.6eV range, is used in this detector. The compounds that will ionize under that energy are aromatic and carbon double bonds (petroleum and chlorinated solvents such as trichloroethylene). Aliphatic or straight chain hydrocarbon, the resulting compounds of petroleum weathering, and single bonded halogenated solvents have higher ionization potentials than this and will not be detected by the PID. The PID is a non-destructive detector and is usually configured as the initial detector in a series.

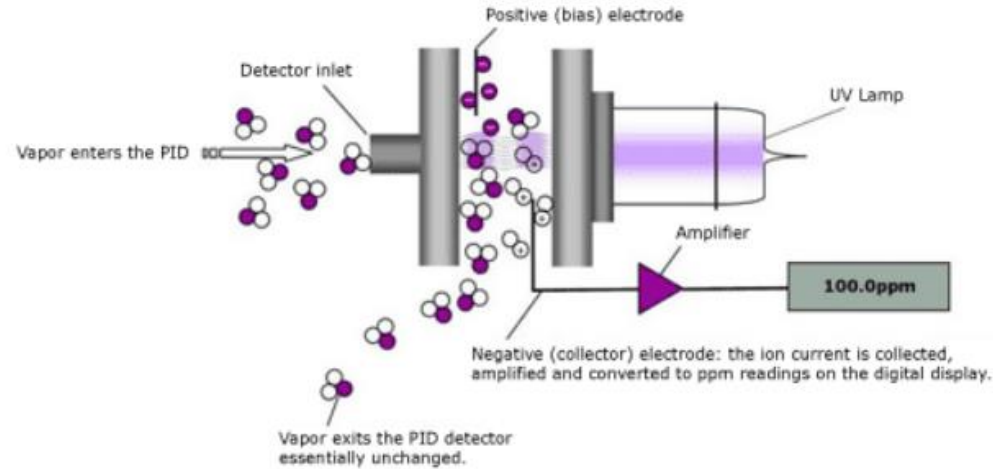
Benzene  
IP = 9.25eV



Trichloroethylene  
IP = 9.45eV



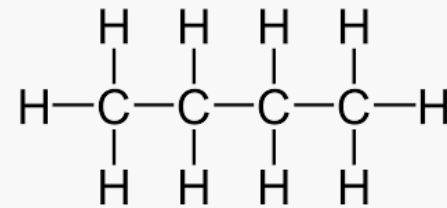
# Operating Principle



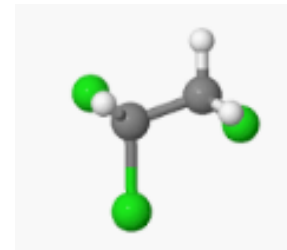
## Photoionization Detector (PID)

An ultraviolet lamp, typically in the 10.6eV range, is used in this detector. The compounds that will ionize under that energy are aromatic and carbon double bonds (petroleum and chlorinated solvents such as trichloroethylene). Aliphatic or straight chain hydrocarbon, the resulting compounds of petroleum weathering, and single bonded halogenated solvents have higher ionization potentials than this and will not be detected by the PID. The PID is a non-destructive detector and is usually configured as the initial detector in a series.

Butane  
IP = 11.2eV



1,1,2 - Trichloroethane  
IP = 11.0eV





FID

# Flame Ionization Detector

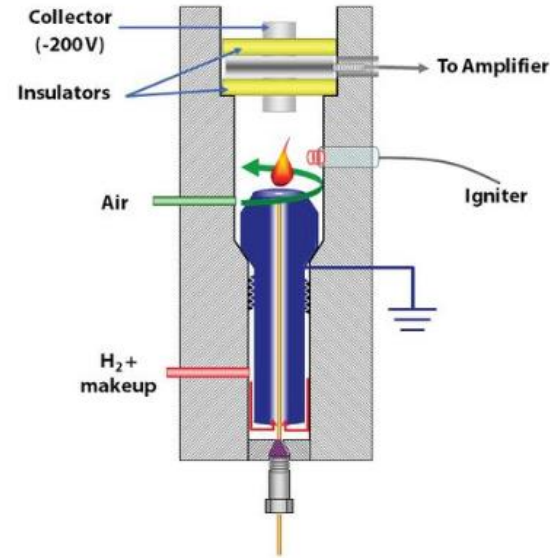
---

Geoprobe



# Operating Principle

## Flame Ionization Detector (FID)



Analytes in the MIP carrier gas stream are combusted in a hydrogen flame, creating positive ions and electrons. The positive ions are attracted to the negatively-biased collector while the (negatively charged) electrons are repelled toward the jet.

The ionized products are past through an electrode which creates a current which is converted to a voltage signal and outputted to the MIP controller for log generation. The voltage output is directly proportional to the amount of mass of carbon-based molecules in the carrier gas. The FID output signal voltage is mass dependent. The FID is a destructive detector and is typically in series behind the PID or configured as a stand-alone detector.





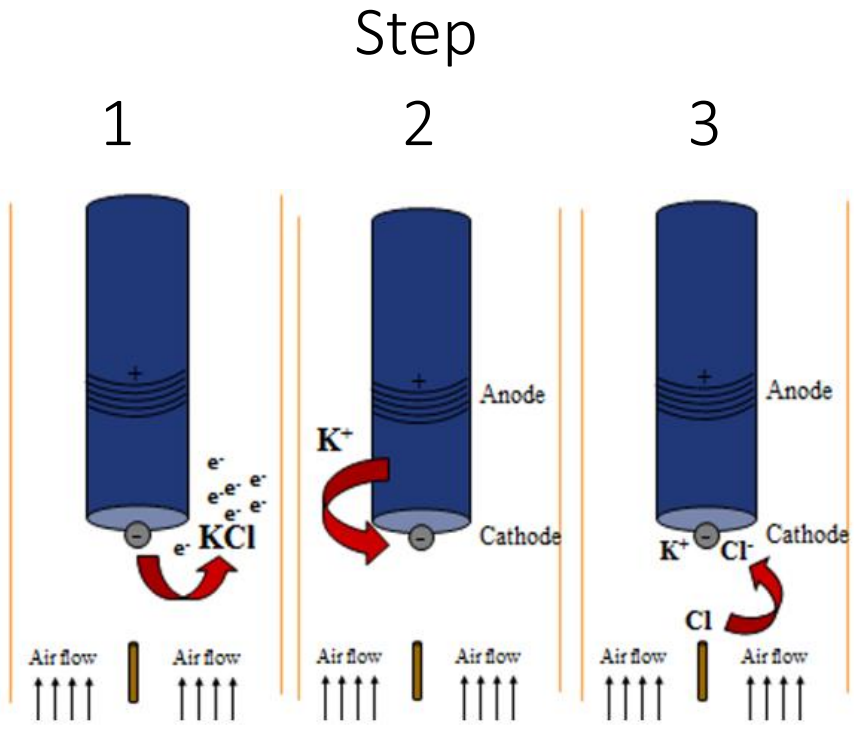
XSD

Halogen Specific  
Detector

---

Geoprobe

A close-up photograph of an XSD Halogen Specific Detector. The detector is a cylindrical metal component with a series of horizontal cooling fins on its right side. It is mounted on a metal plate. A black connector with four wires (red, green, black, and white) is attached to the top. A black cable is plugged into the right side of the detector. The background is a blurred red and white striped pattern.



### Operating Principle

## Halogen Specific Detector (XSD)

The reactor is operated in an oxidative mode, pyrolyzing the effluent from the MIP carrier gas. This oxidative pyrolysis efficiently converts compounds containing halogens to their oxidation products and free halogen atoms.

The cathodic surface is activated by neutralization of alkali ions emitted from the anodic surface. The adsorption and reaction of free chlorine atoms with this alkali-sensitized cathodic surface yields an increased thermionic emission comprised of free electrons and halogen ions.

The total current is measured by the electrometer and converted to a 0-1 V output signal.

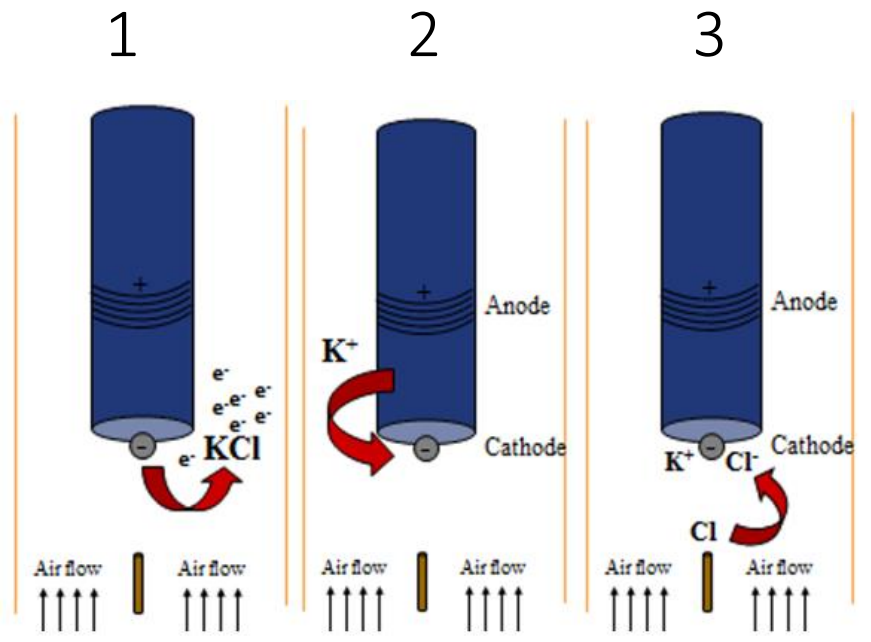


# Halogen Specific Detector (XSD)

The presence of oxygen in the reactor serves to oxidize the analytes and liberate the halogen atoms from their parent molecules. This oxidation process serves to make the response of the XSD largely independent of the type of molecule (e.g. straight chain hydrocarbon, aromatic hydrocarbon, etc.).

The response of the XSD is flow rate dependent, and corresponds to the residence time of the analyte within the detector volume---the higher the total flow rate, the less time the analyte has to adsorb on the cathodic surface and generate a response, i.e. the emission of electrons (measured as a current, and constitutes the 'signal'). Bottom line, the response is nearly inversely proportional to the total gas flow rate through the detector.

Step

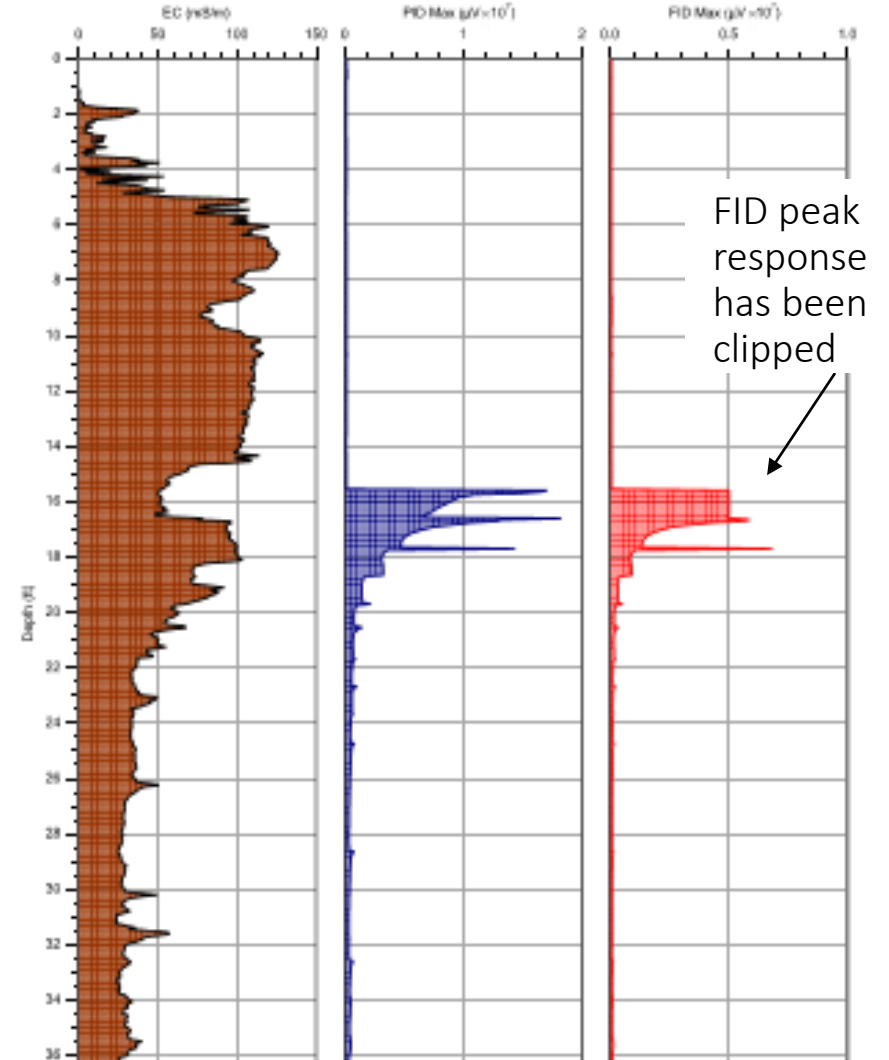


## Operating Principle

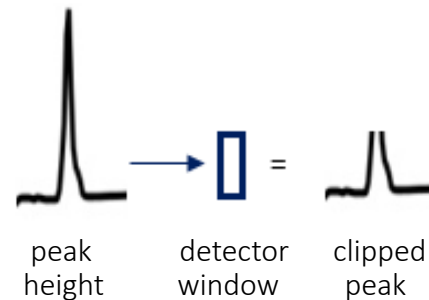


Gas chromatograph detectors have a signal output window height limit that they cannot go above. When a peak does go above this it appears to “clip” as shown above.

The log above shows how the FID had its response “clipped” at the 5V level which is the maximum window height on SRI detectors. The PID and FID should have matching Peak shapes throughout the log.

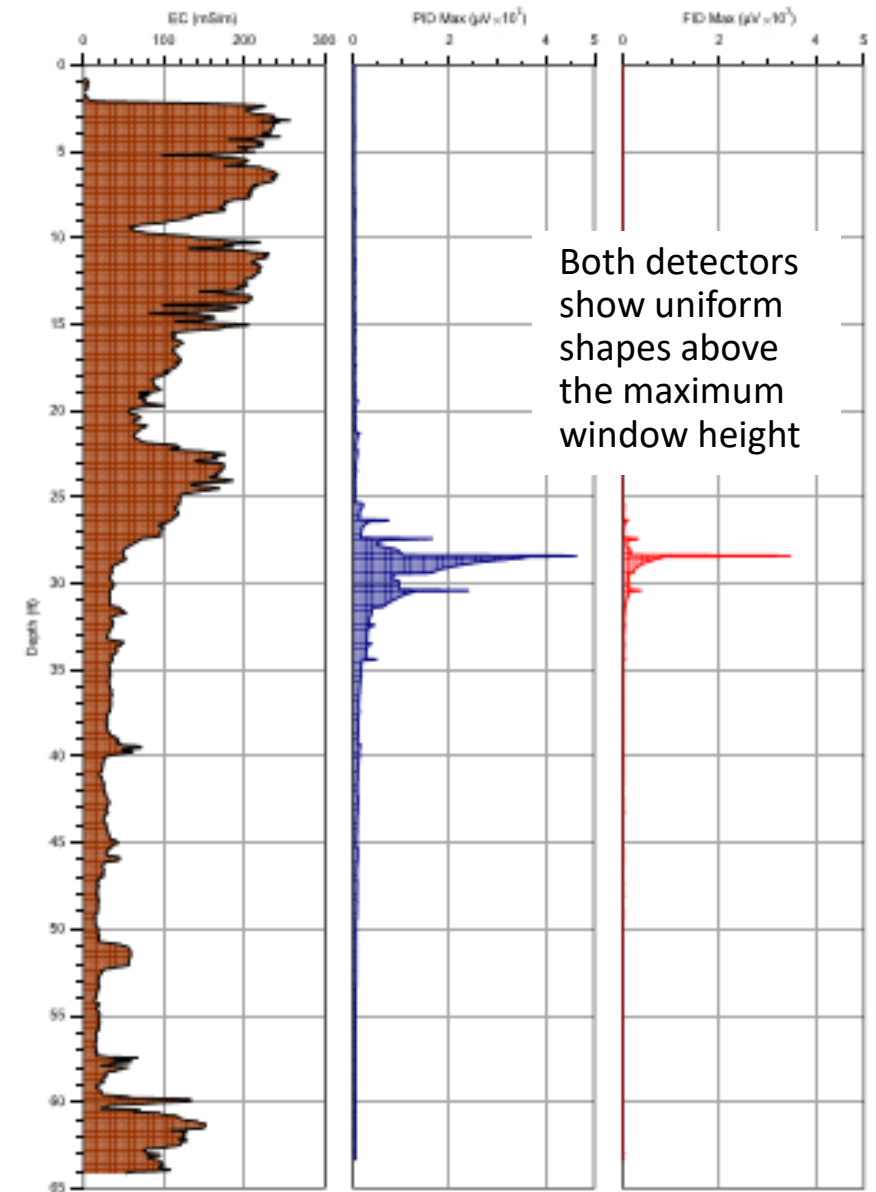


## MIP Detector Gain Adjustments

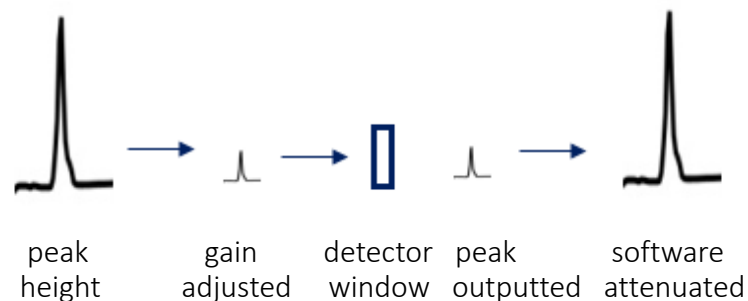


To avoid peak “clipping” the detector gain can be adjusted down by the operator. This divides the detector signal by some factor – 10 for example.

Now the response will fit within the output limits of the instrument. Once the signal is divided at the detector the operator then will increase the corresponding detector attenuation in the software. This detector attenuation (10 in this case) will multiply the detector signal back to its original height for reporting.



## MIP Detector Gain Adjustments

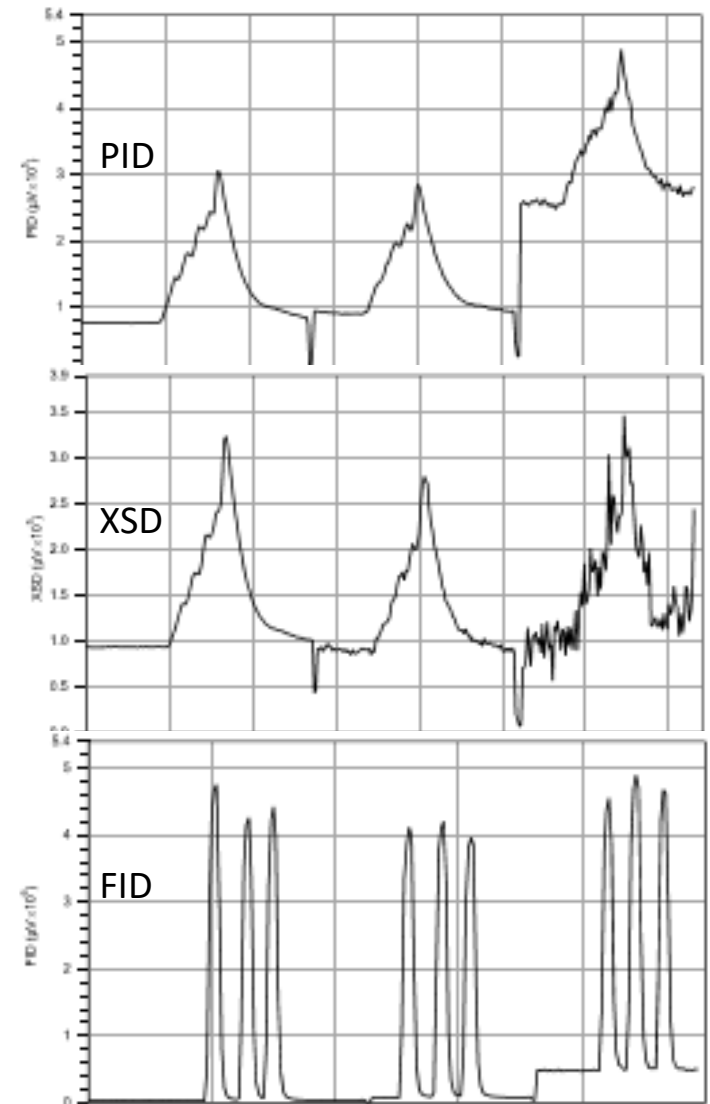


This is an example of a test of the detector gain adjustments.

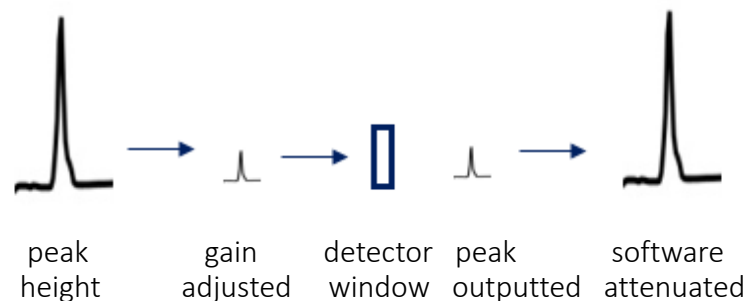
The PID & XSD are tested with ~40ppm TCE. The FID is tested with a 5 sec. butane exposure. Each test run was performed in High, Medium and Low gain setting with the corresponding attenuation values.

Operating in a lower gain setting should not reduce a detector's ability to respond at a consistent level for a given concentration.

Operating in a lower gain setting can increase baseline noise at low contaminant concentrations



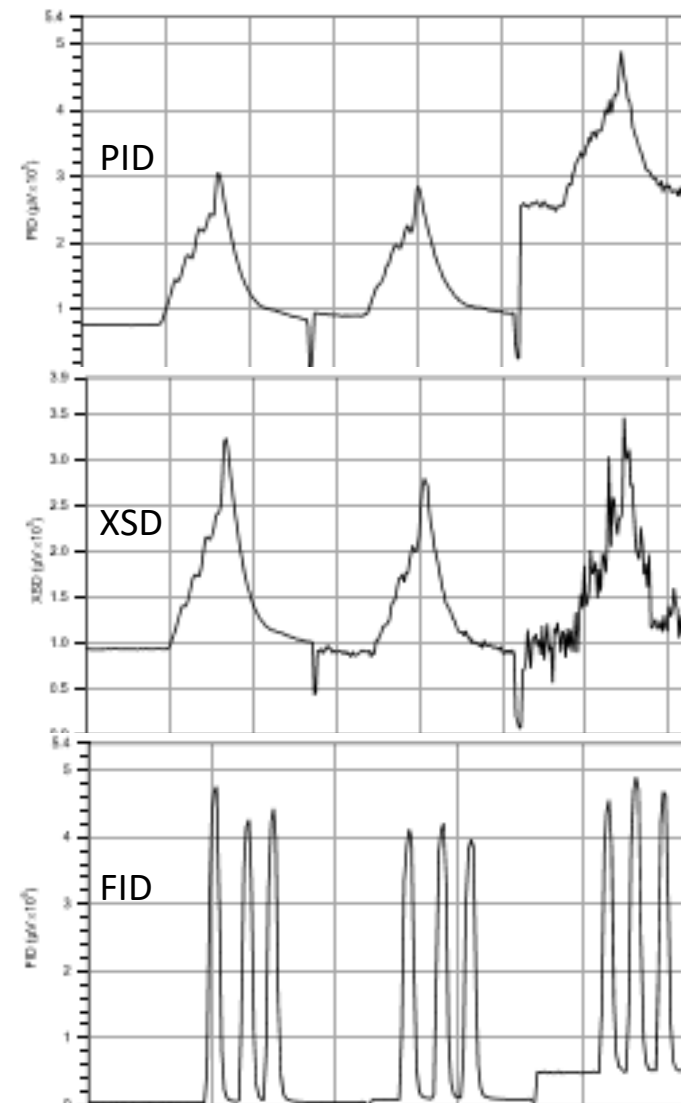
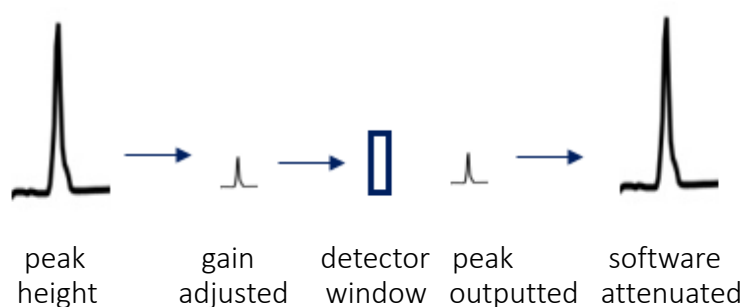
## MIP Detector Gain Adjustments



## Gain Adjustment Test on the SRI PID and FID and the OI XSD.

Detector	Gain Setting	Software Attenuation
PID	High	1
	Medium	10
	Low	100
FID	High	1
	Medium	20
	Low	200
XSD	High	1
	Medium	10
	Low	100

### MIP Detector Gain Adjustments



# MIP Analyte List – Common Environmental Contaminants

Not all Encompassing

Chemical Compound:	Boiling Point	Molecular Weight	Density	Ionization Potential	Solubility in Water	Vapor Pressure	Analytes		
	(°C)	(g/mol)	(g/mL)	(eV)	g/L	kPa @ ~25C	Detected By		
							PID*	FID**	XSD
Methane	-161	16.0	.657 g/L	12.61	0.02		n	y	n
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	47.7	187.4	1.564	11.78	0.17	285mm Hg	n	y	y
Vinyl Chloride (Chloroethene)	-13.0	62.5	0.910	10.00	2.7	2580mm Hg	y	y	y
Acetone	56.5	58.1	0.790	9.69	Miscible	30.6	y	y	n
1,1-Dichloroethene	32.0	97.0	1.213	9.65	0.04%		y	y	y
Methylene Chloride (Dichloromethane)	40.0	84.9	1.327	11.35	17.5	57.3	n	y	y
tert butylmethyl ether (MTBE)	55.2	88.2	0.740	9.24	42.0		y	y	n
trans-1,2-Dichloroethene	47.5	97.0	1.260	9.66			y	y	y
1,1-Dichloroethane	57.2	96.7	1.213	11.06	0.6%	182mm Hg	n	y	y
cis-1,2-Dichloroethene	60.3	97.0	1.280	9.65			y	y	y
Chloroform	61.0	119.4	1.480	11.37	8.1	25.9	n	y	y
1,1,1-Trichloroethane	74.0	133.4	1.320	11.25	0.4%	100mm Hg	n	y	y
Carbon tetrachloride	76.7	153.8	1.809	11.28	0.8	11.9	n	y	y
Benzene	80.1	78.1	0.879	9.25	1.8	12.7	y	y	n
1,2-Dichloroethane	83.7	99.0	1.253	11.04	8.7		n	y	y
Trichloroethylene	87.0	131.4	1.460	9.45	1.3	58mm Hg	y	y	y
1,2-Dichloropropane	96.0	113.0	1.156	10.87	2.6	40mm Hg	n	y	y
Toluene	110.6	92.1	0.867	8.82	0.5	2.8	y	y	n
1,1,2-Trichloroethane	115.0	133.4	1.435	11.00	0.4%	19mm Hg	n	y	y
Tetrachloroethylene	121.1	165.8	1.622	9.32	0.15	14mm Hg	y	y	y
Chlorobenzene	131.0	112.6	1.110	9.07	0.5	9mm Hg	y	y	y
Ethylbenzene	136.0	106.2	0.860	8.76			y	y	n
m, p-Xylene	138.5	106.2	0.860	8.50	insoluble	9mm Hg	y	y	n

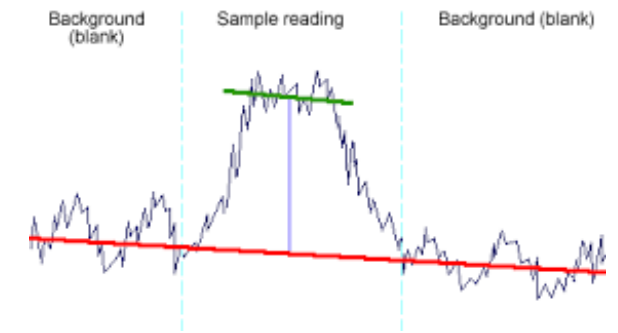
Here is an example list of compounds that are dateable by MIP. This list has many of the pertinent physical properties of the compounds and also indicates which detector they would be detected by. It is based upon an EPA 8021 list. There is a extensive list on the Geoprobe website under MIP/Technical documents.





# MIP Detection Limits (Standard Configuration) 10PSI (70kPa) with a 150ft (45m) Peek TL

	PID	FID	XSD
Methane	N/A	0.25-2.5%	N/A
Benzene	0.25-2.5	2.5-25	N/A
Toluene	0.4-4.0	4.0-40	N/A
PCE/TCE	0.25-2.5	2.5-25	0.20-2.0
Chloroform/TCA	0.25-2.5	2.5-25	0.2-2.0
Vinyl Chloride	0.5-5.0	5.0-50	0.5-5.0

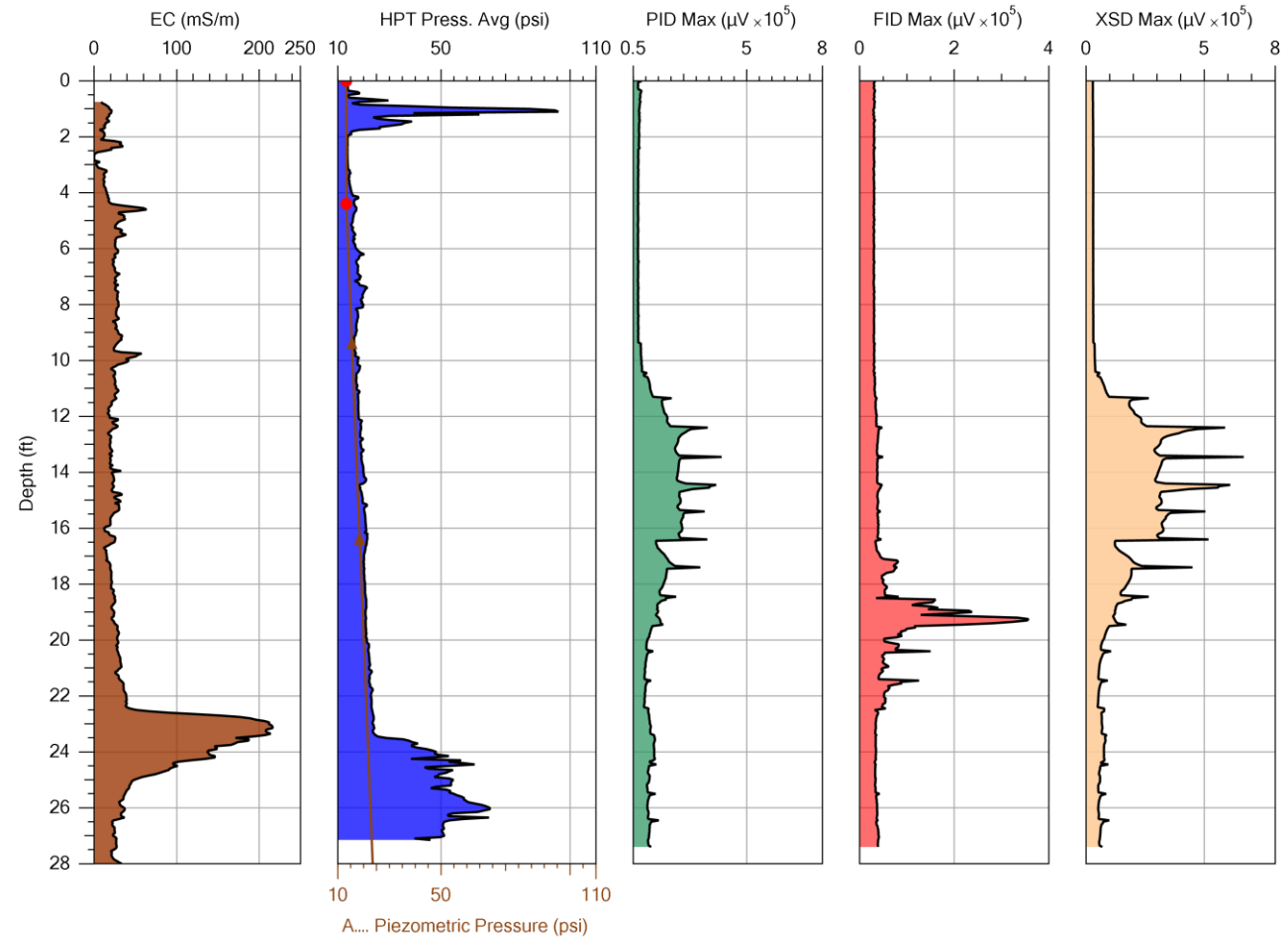


Detection Limit is defined as signal that is 3x higher than base line noise

\*PID response based upon ionization potential (IP). If a compound's IP is  $\leq$  PID lamp eV ( $\sim 10.6$ ) then it can be detected.



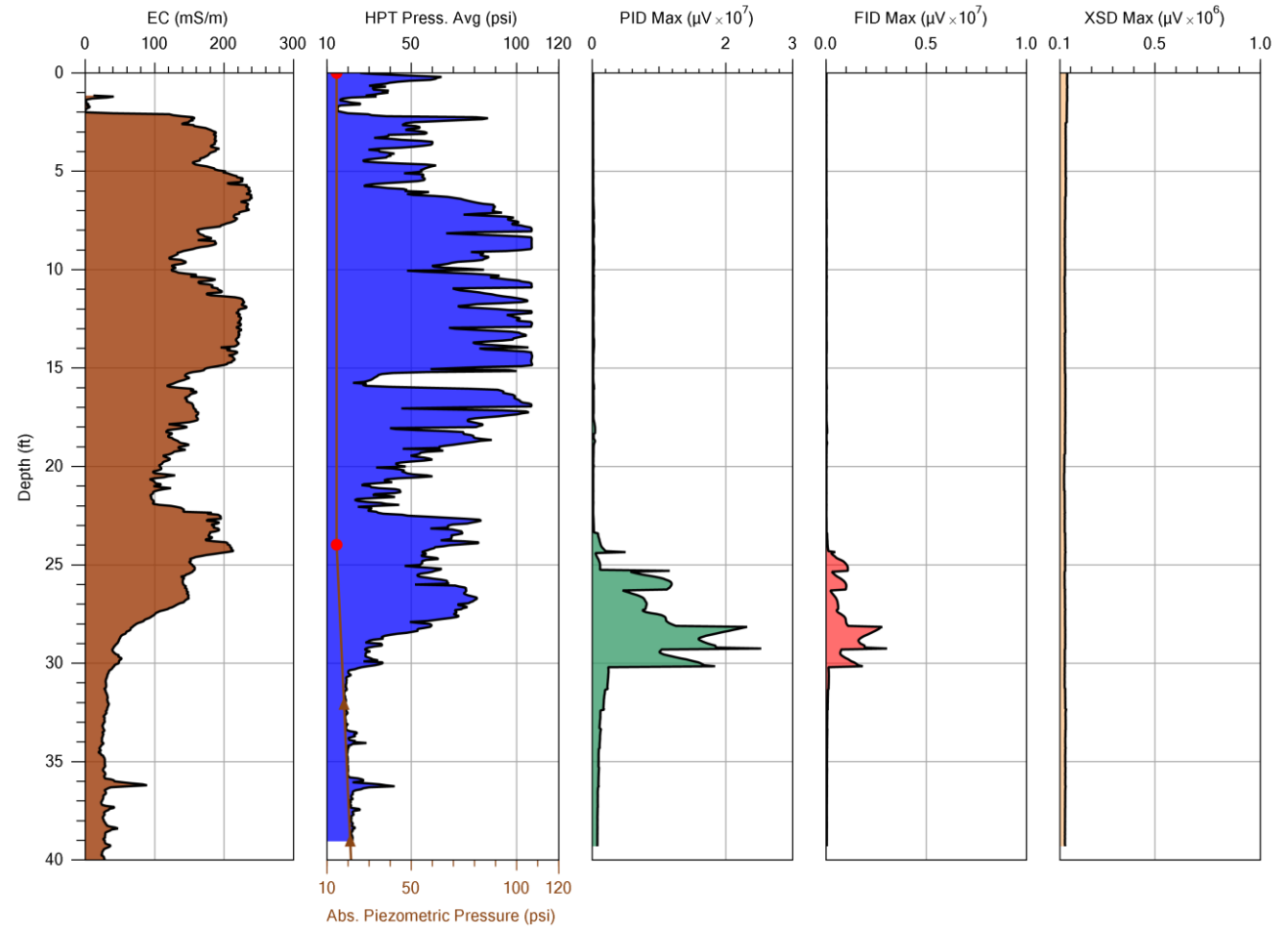
# MIHPT Logs



Detector interpretation of this log shows similar readings between the PID and XSD which means that there are halogenated compounds that are double bonded ( $\text{IP} < \text{PID excitation voltage}$ ). We can also see that profile in the FID above the larger FID response. That larger FID response is not seen on either the PID or XSD so it has a higher IP and is non halogenated – probably methane. These responses are all seen in a low EC/HPT pressure indicating it is a highly permeable zone. This is in a mobile coarse-grained aquifer.



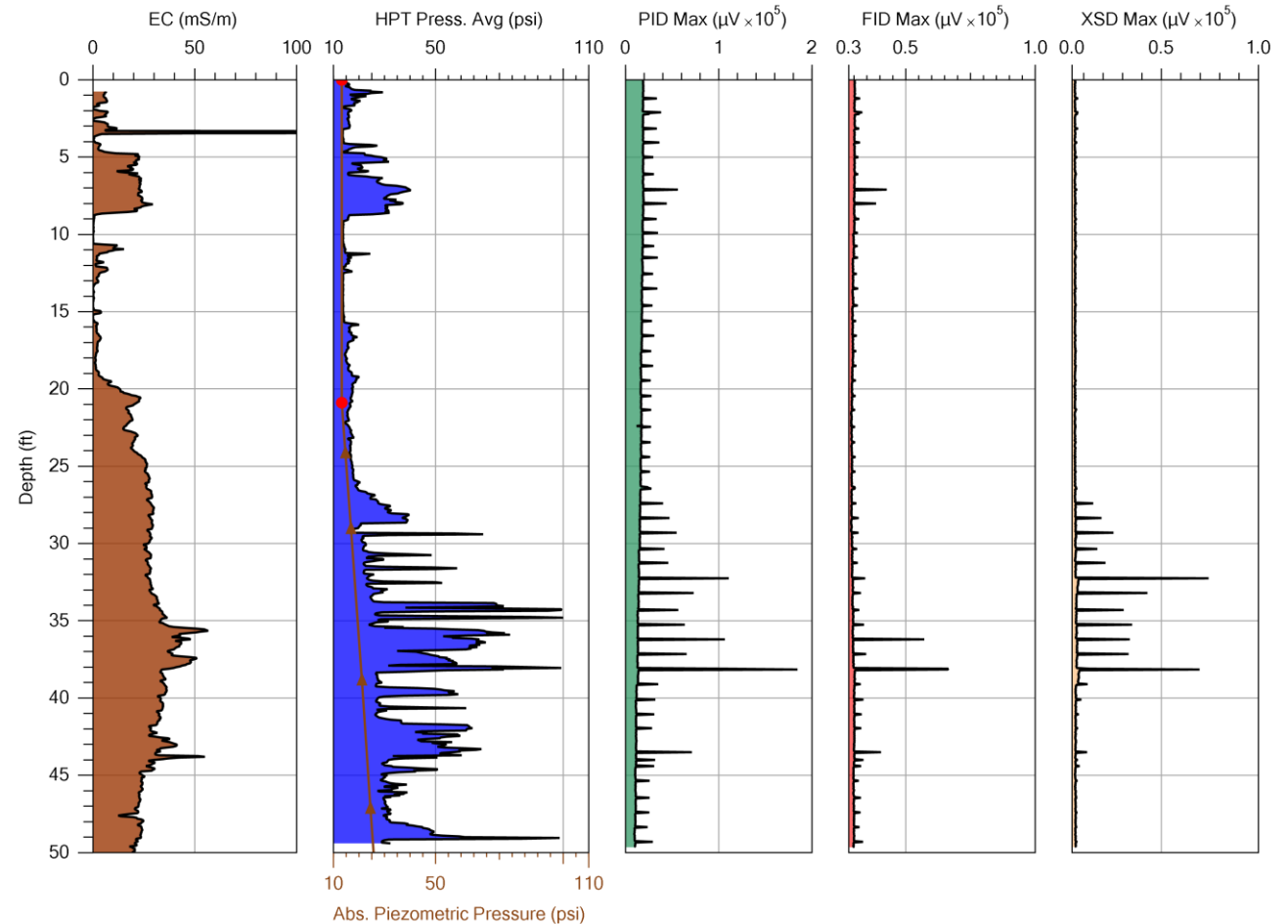
# MIHPT Logs



In this log we have similar readings on the PID and FID with no XSD response. This means that there are no halogenated compounds. With the PID and FID responding it is likely petroleum hydrocarbons. It could also be compounds such as MTBE or ketones such as Acetone or MEK which are present in certain aerosols. These responses are all seen in the higher EC/HPT pressure indicating it is a low permeable zone. This is predominantly in a contaminant storage zone within the aquifer and could slowly diffuse over time into the coarse grained material.



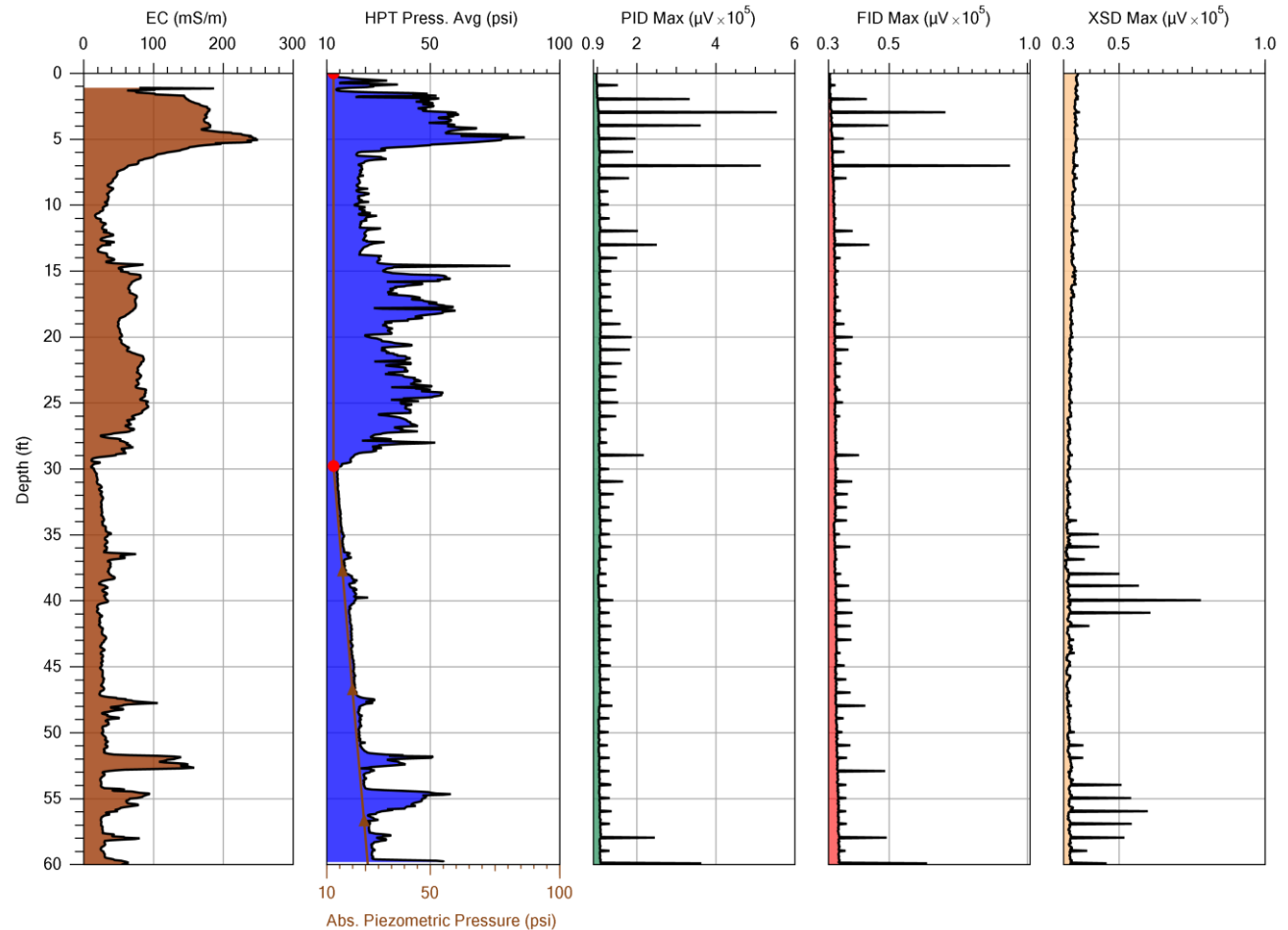
# MIHPT Logs



This is a low level MIHPT Log. We will read it the same as a standard MIP log however the responses come across in spikes. Between 5-10ft we have similar readings on the PID and FID with no XSD response. This again means that there are no halogenated compounds and it is likely petroleum hydrocarbons near the surface. Below 25ft in this log there are comparable PID and XSD responses as well as FID. These must be halogenated and have IP < the PID lamp excitation energy. This could be a compound such as PCE or TCE. These responses occur where there is intermixed sand-silt layers based upon the EC-HPT data.



# MIHPT Logs



In this low level MIHPT log, we again have surface PID-FID response with no XSD response so likely petroleum hydrocarbons. These responses occur where there is slightly lower permeability perhaps a sandy-silt or silty-clay based upon EC-HPT data. Starting at 35ft there are 2 separate XSD response zones 35-42ft and 51-60ft bgs. There is little response on the PID so these halogenated compounds must have an IP > the PID lamp excitation energy which is commonly single bonded chlorinated. At this location groundwater samples were taken from these deeper zones and sent to a laboratory for identification. The upper zone from 35-42ft was primarily 1,2-Dichloroethane and the lower zone from 51-60ft was comprised of a mix of carbon tetrachloride and chloroform. All of these compounds have ionization potentials above the PID lamp energy of 10.6eV.

