Tech Note: Operation and optimization of the Halogen Specific Detector (XSD)
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FAQ: How does the Halogen Specific Detector (XSD™) operate? Can it be optimized?

Principle of Operation:

The XSD is only responsive to halogenated molecules in the carrier gas stream making it a highly beneficial detector to operate in mixed waste contaminant plumes. The halogen atoms that the XSD is sensitive to include Bromine, Chlorine and Fluorine.

The model 5360 XSD's reactor assembly is operated in an oxidative state that converts halogenated organics into free halogen atoms. These halogen atoms are adsorbed onto the activated platinum surface of the detector probe assembly resulting in an increase thermionic emission. This emission current comprised of free electrons, negative and positive ions provides a corresponding voltage that is measured via an electrometer circuit in the detector controller. The detector controller then outputs the signal to a data handling device such as Geoprobe MIP controller and FC or FI data acquisition system.

Operating features of the OI Analytical Model 5360 Halogen Specific Detector (XSD™) include:

- Simple design provides enhanced reliability and compound reproducibility to other chlorinated detectors.
- Linear range >4 orders of magnitude.
- Easy to operate and is field repairable.
- Produces no radioactive emission.
- Eliminates the need for disposal of used organic solvents associated with other halogen selective detectors, such as the electrolytic conductivity detector (ELCD).
- Installed either as a stand-alone detector or in tandem with the Model 4430 Photo-ionization Detector (PID).
- Requires only air as a makeup gas to operate.

Fig. 1: XSD reactor and controller

The XSD (Figure 1) can be configured either as a stand-alone detector or mounted in tandem off of the exhaust of an OI Analytical PID. Either way, when operating 3 detectors on the MIP-GC, the XSD will receive approximately 50% of the typical 40ml/min MIP carrier flow. The XSD has reactor core temperature settings of 800, 900, 1,000 or 1,100^{o}C. The higher the temperature the more sensitive the detector will be. The higher the reactor temperature the shorter the life of the XSD's 2 main expendable components: the reactor core and the probe assembly.

Expected MIP-XSD Responses:

The MIP-GC system typically is configured with 3 detectors – PID, FID and XSD and the trunkline carrier gas is usually split approximately 50-50 between the destructive XSD & FID detectors. This configuration produces an XSD signal of approximately 15,000µV for 1ppm of TCE in water at atmospheric pressure (Figure 2) during a MIP response test. This is considered a typical and useful response. Most of the detector systems that have been configured for MIP use have produced XSD responses for TCE in the 10,000 – 25,000µV/ppm range with a 50% carrier flow rate. Occasionally detectors have produced initial TCE responses of 50,000µV/ppm or better with a 50% carrier flow rate. The reason for the differences in responses is likely due to slightly higher temperatures in the reactor core. The reactor core is heated to the set temperature and has an accuracy of $\pm$ 50^{o}C.

Typical XSD configuration and MIP response test parameters:

- Split flow (50%) receiving 20ml/min carrier gas.
- Reactor core temperature set at 1,100^{o}C
- 45 second exposure time of the membrane
- Response test using 500mL water spiked with TCE.

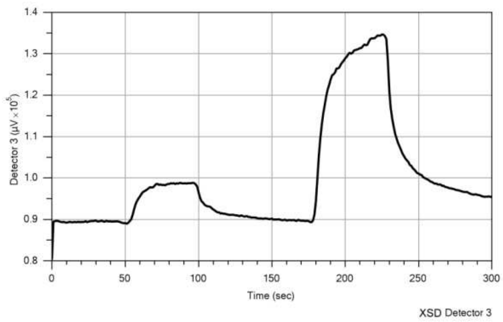

Fig. 2: Typical XSD TCE response at 1ppm and 5ppm using 50% flow from the PID

Optimizing the XSD response for low level detection:

If a MIP operator needs to delineate a chlorinated plume in the sub ppm range there are ways of enhancing the XSD's response. Improved chlorinated responses will be seen with:

- High XSD temperature setting – 1,100^{o}C
- New XSD probe assembly and reactor core
- Provide 100% carrier flow into XSD reactor cell
- Reduce flow/system pressure – usually the quickest rate with the best response is 20ml/min.

To receive the most sensitivity from your XSD it must be operated with a reactor core temperature setting of 1,100^{o}C. This will provide for the most complete reaction of the halogenated components in the carrier gas stream. Overall detector response will be reduced by 30-40% with each step down in reactor temperature. If the MIP system will be used to map chlorinated source areas it is recommended to operate the XSD at a lower (less sensitive) temperature. By operating at a lower temperature it will provide the MIP operator a higher linear range to work with and minimize detector saturation. The reduced response levels should not be an issue in source areas.

Another way to improve the signal response of the XSD, as with any gas phase detector, is to make sure that it is receiving full flow of the carrier gas. Typical XSD configuration would split the carrier flow inside the GC oven between the XSD and other destructive detectors such as the FID. For the greatest sensitivity, direct 100% of the carrier flow into the XSD reactor chamber and then reduce the overall trunkline carrier gas flow to 20ml/min.

Reducing the carrier flow rate of the system from 40ml/min to 30 or 20ml/min will increase the detectors ability to complete the conversion and adsorption of the halogen compounds onto the platinum probe surface. A lower carrier flow rate in the trunkline system also will reduce the pressure behind the membrane which will provide some improved PID and FID due to a more efficient chemical diffusion across the membrane resulting in higher chemical concentrations in the carrier gas stream. This higher concentration along with a lower carrier flow rate through the chamber improves the completeness of the reaction within the XSD reaction chamber (See figures 3 and 4). You can lower the system pressure in the following ways:

- Use a shorter trunkline. Using a 100' instead of a 150' will reduce the pressure by about 1/3.
- Lower the carrier flow from 40ml/min to 30ml/min or 20ml/min.
- Use a SS heated trunkline. This trunkline has a larger ID in the SS gas line which will reduce the system pressure. A 150' Peek tubing trunkline pressure will be approximately 12psi. A 150' SS heated trunkline will have a pressure of approximately 5psi unheated and 6.5PSI heated to 100°C.

Over time, the XSD probe assembly will lose sensitivity. The reactor core will also eventually need to be replaced. These components have a life to them and the more they are operated and the hotter the temperature they are set to the shorter the life span. Expect to replace the XSD reactor core and probe assembly approximately every 10-24 months depending on usage. For this reason, if an operator is going to perform a MIP investigation on a petroleum site where there is no concern for chlorinated detection they may choose to not operate the XSD on that job.

Low level MIP-XSD Response Results for Trichloroethylene (TCE)

MIP System Setup and parameters:

- 150' SS trunkline –unheated
- Flow = 21ml/min = 3.1PSI = Trip time of 115 seconds for TCE
- SRI GC Configured PID-XSD = 100% Flow
- XSD = 1,100°C, Attenuation = 1X, Air Flow = 20ml/min
- New Membrane
- Response test levels were 10, 25, 50, 100, 250 & 500µg/L (ppb).

Run ID: Low Level 5 Date: 6/16/2010

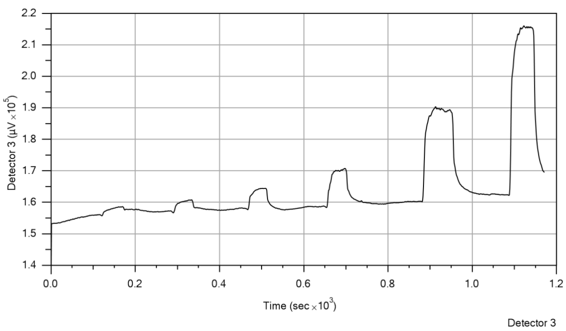

Fig 3: MIP-XSD response test for 10 to 500µg/l standards

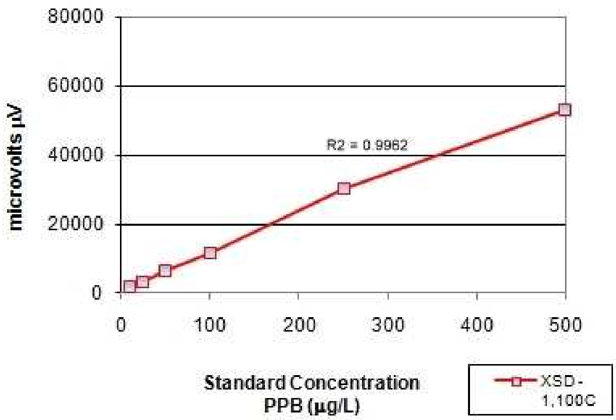

Fig 4: Response curve of LL5: XSD response over baseline

Table 1 shows XSD response levels for 1ppm of TCE using different carrier flow rates but keeping reactor temp at 1,100°C, attenuation setting of 1x and 100% flow to the detector.

Flow (ml/min)	XSD Response (µV)	PSI	Trip Time (sec)
41	40,000	5.8	65
31	55,000	4.5	83
21	105,000	3.1	115

Table 1: XSD response versus flow rate with constant temperature setting of 1,100°C in reactor core

The XSD response level performance is affected by carrier flow rate, reactor temperature and compound class.

Other detectors such as the PID and FID also will see a slight increase in response when trunkline flow rates are dropped but not because of increased ionization of the compounds. Increased signal seen on a PID or FID in a MIP system when flows are reduced commonly are due to the lower pressure at the membrane which will allow for more efficient chemical diffusion across the membrane resulting in a higher concentration of compound in the carrier gas stream.

Conclusion

When provided with an opportunity to map out a solvent plume, a MIP operator has many detectors he could turn to: Electron capture detector (ECD), dry electrolytic conductivity detector (DELCD), electrolytic conductivity detector (ELCD/HALL), photo-ionization detector (PID) and flame-ionization detector (FID). All of these detectors have the ability to detect halogenated compounds. The ECD, XSD, DELCD and ELCD are selective to only the halogenated compounds so they perform best in mixed fuel and solvent plumes. The DELCD and ELCD can be difficult to maintain so they operate with consistency.

In the arena of detectors available for use on halogenated site investigations, the XSD is a very viable, easy to interpret, user friendly option for MIP operators. When compared to the ECD, likely the most common chlorinated detector coupled with the MIP tool, the XSD is a good alternative. It has a wider working linear range, highly sensitive to a wider range of chlorinated solvents. It does not take a long time for the detector baseline to stabilize even after long periods of downtime. When maintenance is needed, it is easy for an operator to make the necessary changes, even in the field, provided the needed components are on hand. Detection levels with typical configuration, receiving 50% flow of a 40ml/min trunkline flow rate, of 250µg/l TCE can be expected. After detector optimization TCE delineation of ≤100µg/l can be achieved. Because of the XSD's ease of operation, it is expected to see this detector more widely used and accepted in the coming years of MIP site investigation.