Sperian Application Note	Usage and Applications of PID Sensors	Date	August 19, 2008
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Introduction to PID Sensors and VOCs

The photoionization detection (PID) sensor used in the Biosystems PHD6 multigas detector is a broadband sensor primarily designed to detect volatile organic compounds (VOCs), which are carbon containing chemicals that can exist in gaseous form at ambient temperatures. The sensor will also detect certain other toxic gases.

The body of the sensor is made up of a UV lamp, and an electrode stack. Internal electronic circuitry, (an ASIC) is used regulate operation of both the lamp and stack. It is also used to compensate the output signal for environmental conditions. There is also an onboard smart chip used to store information such as serial number, calibration dates, etc.

When the target gas enters the sensor's sensing chamber, the photons emitted from the UV lamp break up the molecule into two ions, one positively charged, one negatively charged. The electric field created by the anode and cathode in the stack attracts the ions, which results in an electric current. This current is then measured by the circuitry in the sensor and a signal is sent to the instrument, reporting the concentration.

The PhD6 PID sensor is designed for use in either diffusion or pump sampling modes. The advantage to use of a pump is generally quicker response and recovery, while for diffusive sampling retention of higher ozone concentrations, generated in the ionization chamber, can act as cleaning agent for VOC residues on electrode & lamp window surfaces.

Linear and Working Ranges

A PID is a broadband detector, with a sensitivity that differs for each VOC. The PID is traditionally calibrated using 100 PPM isobutylene because its sensitivity is near the midpoint of most VOCs, and it is non-toxic, and non-flammable at the low concentrations used for calibration. Being the primary reference, its correction factor (CF) is defined as 1.0. CF's for all photoionizable gases and vapors are calculated based on their sensitivity as compared to isobutylene.

The PID sensor has a linear response up to 2000 PPM for materials with an ionization potential similar to isobutylene (CF~1). Sensitivity decreases when concentrations exceed this value since some of the gas molecules may become shielded from the UV light and fail to ionize. If the instrument will be used in this type of environment, it should be calibrated with a high concentration calibration gas. As a result, readings at the low end may become artificially high.

The PID channel will allow a reading of up to 3000 PPM, since for materials that are less ionizable than isobutylene (CF>1), the linear range may be extended up to this amount. Please consult with Sperian Instrumentation application support at (800) 711-6776 prior to using the Biosystems PHD6 to monitor extremely high concentrations of any gas/vapor.

The PhD6 PID channel may be configured by skilled operators in a way to maximize the working range. To highlight this case consider as a specific example, ammonia (CF = 8.5). If the PID channel is left on an isobutylene setting/scale, the detector subsequently used in an ammonia containing atmosphere could read up to 3,000 PPM. On this scale, therefore, 3,000 PPM IB scale X 8.5 CF = 25,500 PPM ammonia. Theoretically it is possible to read up to 25,500 PPM ammonia, however as stated previously the linear range of the PID sensor is normally 2000 PPM (isobutylene) which would place the linear maximum for ammonia more on the order of 17,000 PPM. Alternately if the PID channel was directly configured for an ammonia scale, then the channel range would be limited to 0-3000 PPM ammonia. It should be kept in mind about the former case that the end user and not the detector would have to apply the correction factor to the displayed value to get the actual level of ammonia and that the alarm setpoints would also have to be adjusted as they would be relevant to isobutylene, not ammonia. Extreme caution must be practiced when using the Biosystems PHD6 in this mode. Failure to do so can cause over-exposure, which can result in serious personal injury or death.

Clamping / Resolution

The VOC display resolution limit of the Biosystems PHD6 with a new, clean PID is 0.1 ppm isobutylene. You must be aware of exposure limit guidelines for extremely toxic gases. Do not use the Biosystems PHD6 in any application where the target gas has an exposure limit below 0.1 ppm (and preferably greater than 0.3 ppm). Failure to do so can cause over-exposure, which can result in serious personal injury or death.

In addition, the Biosystems PHD6 utilizes a clamping mechanism. The standard clamp is 1 ppm for the VOC channel. This means that readings between – 0.9 ppm and + 0.9 ppm are displayed as 0 ppm. This is not a problem with a gas such as isobutylene, whose ceiling alarm is 1800 ppm. But it can be an issue if the alarm is less than 1 ppm. In this case, the Biosystems PHD6 will automatically adjust the clamp to equal the ceiling alarm level. So if the ceiling alarm level for a particular target gas is 0.5 ppm, readings between -0.4 ppm and +0.4 will be displayed as 0 ppm. The PID is active and detecting gas, only the reading is suppressed.

Methane Interference

The PID sensor response to target gases/vapors is measured in laboratory air, with 20.9% oxygen, balance nitrogen. Some gases absorb UV light without causing any PID response (eg methane, ethane). In ambient atmospheres where these gases are present, the measured concentration of target gas will be less than is actually present. Methane absorbs UV strongly, so for accurate measurements in methane containing atmospheres, calibrate with a gas containing the expected methane concentration. 50% LEL methane (2.5% vol.) can reduce the reading by up to 50%.

Gases such as nitrogen and helium do not absorb UV and do not affect PID sensor response.

Cross-Sensitivity with Duo-Tox Sensors

The CO channel of the Duo-Tox sensor used in the PHD6 may exhibit cross-sensitivity to VOCs. When exposed to 100 ppm isobutylene, the CO reading may rise as high as 60 ppm.

Toxic gas sensors often have built-in filters which help prevent this type of cross-sensitivity. Over time, these filters degrade due to age and exposure. In addition, the effectiveness of the filters depends largely on the VOC being detected. Single CO sensors have better filtration for VOCs than Duo-Tox sensors. In fact, a new CO sensor usually will have essentially no cross-interference with 100 ppm isobutylene.

Therefore when an instrument configuration of PID, CO and H2S is necessary, for the best performance, Sperian strongly recommends using separate CO and H2S sensors (p/ns 54-54-01 and 54-54-02) in place of the DuoTox sensor (p/n 54-54-14). Questions regarding specific VOC cross-sensitivity on any toxic gas sensor configurations should be referred to Sperian Instrumentation application support at (800) 711-6776.

Correction Factors

PID sensors are broadband sensors. They will detect many different compounds and few of these compounds will show the same response when detected by the sensor.

The calibration standard for PID sensors is 100 ppm isobutylene. Although the most accurate way to detect VOCs is by calibrating directly to the target gas, most common VOCs have a known correction factor (CF) that can be applied to the sensor reading so that an approximate value can be determined when calibrated to isobutylene.

The PHD 6 has a built in library of CFs for target VOCs. By selecting one of the VOCs in the list, users will cause the instrument to automatically apply the CF for that compound to the sensor reading.

Further, when a compound is selected from the library, the PhD6 PID channel will automatically show a 7 character abbreviation for the scale which has been chosen. Alarms will also be automatically set when a choice is made from the library.

Complex VOC Gas Mixtures

A PID cannot distinguish between different gases in a mixture, and its sensitivity to each gas differs. The displayed reading represents the total concentration of all photoionizable gases present in the sample.

For a VOC mix of known composition, if the total concentration is within the linear range the PID, then it is reasonable to assume that the concentrations are additive without interference between the different VOCs. This additive result is based on each compound's correction factor and can be approximated by:

$$CF(mix) = 1 / [(a/CF(A) + b/CF(B) + c/CF(C)\dots]$$

where CF (mix) is the correction factor for a gas mix containing PID detectable gases A, B, C… , in relative proportions a: b: c…

As an example a paint manufacturer formulates with a mixed solvent containing 25% methyl ethyl ketone, 10% toluene and 65% isopropanol. The questions then become:

1) What is the CF for this mix?

From the formula above, CF(mix) = 1/[(0.25/0.77) + (0.10/0.55) + (0.65/4.35)]
Therefore CF(mix) = 1.52

2) What are the alarm setpoint(s)?

Using a very similar formula to the above:

$$PEL(mix) = 1 / [(a/PEL(A) + b/PEL(B) + c/PEL(C)\dots]$$

Ceiling/Danger PEL = 1/[(0.25/200) + (0.10/300) + (0.65/200)]
Ceiling/Danger PEL = 207 PPM

Similarly PEL(mix) for STEL and TWA would become respectively, 320 PPM and 154 PPM.

3) How can this information be programmed into the PhD6 PID channel?

Through the PhD6 menu select "custom" from the compound library. Into the respective data fields configure the CF value as 1.52, alarm setpoints for Ceiling/Danger as 207 PPM, STEL as 320 PPM and TWA as 154 PPM. In this way the detector can continue to be calibrated with isobutylene and the custom scale will correspond to this solvent mix.

There can be a case where the volatile materials in a mixture are known but their exact proportions are not. For this application we can use the above three materials and simply assume composition is unknown. We can then construct a table to show how the PID would respond at a PEL value as follows:

Material	CF	PEL (TWA) Material	PEL (TWA) Isobutylene Scale
Methyl Ethyl Ketone	0.77	200	260
Toluene	0.51	50	98
Isopropanol	4.35	200	46

It can be seen from the above table that even though isopropanol is only moderately toxic, it is detected least well by the PID sensor operating at10.6 eV (highest CF). Therefore if the TWA alarm setpoint is changed to 46 PPM, then all other vapors should be well below their TWA-PELs. A similar set of calculations can be done for all other PEL types (ceiling & STEL).

PhD6 PID Sensor Compound Library with Correction Factors and Default Alarms

Compound					Alarms - ppm		
Proper Name	CAS No.	Formula	7-Char Abbr.	Correction Factor	Danger/ Ceiling	STEL	TWA
Custom			VOC	1	0	0	0
Acetaldehyde	75-07-0	C_2H_4O	Acetald	4.86	25	150	100
Acetic Anhydride	108-24-7	$C_4H_6O_3$	AcAnhyd	4	5	2	0.5
Acetone	67-64-1	C_3H_6O	Acetone	0.72	500	750	500
Acetophenone	98-86-2	C_8H_8O	Acetoph	0.59	10	30	10
Acrylic Acid	79-10-7	$C_3H_4O_2$	AcrlAcd	2.75	2	6	2
Allyl Alcohol	107-18-6	C_3H_6O	AlylAlc	2.07	2	4	2
Ammonia	7664-41-7	NH_3	NH3-PID	8.5	25	35	25
Amyl Acetate	628-63-7	$C_7H_{14}O_2$	AmylAce	1.8	50	100	50
Amyl Alcohol	75-85-4	$C_5H_{12}O$	AmylAlc	3.2	1200	0	0
Aniline	62-53-3	C_7H_7N	Aniline	0.5	2	6	2
Anisole	100-66-3	C_7H_8O	Anisole	0.47	0	0	0
Benzene	71-43-2	C_6H_6	Benzene	0.5	1	2.5	0.5
Benzaldehyde	100-52-7	C_7H_6O	BenzAld	0.86	2	4	2
Benzyl Alcohol	100-51-6	C_7H_8O	BenzAlc	1.25	10	0	10
Bromobenzene	108-86-1	C_6H_5Br	BromBnz	0.7	500	0	0
Bromoform	75-25-2	$CHBr_3$	MeBr3	2.8	0.5	1.5	0.5
Bromomethane	74-83-9	CH_3Br	MeBr	1.9	1	3	1
Butadiene	106-99-0	C_4H_6	Butdien	0.83	1	5	1
Butoxyethanl,2-	111-76-2	$C_6H_{14}O_2$	Butoxet	1.1	20	60	20
Butanol	71-36-3	$C_4H_{10}O$	Butanol	4.01	50	60	20
Butyl Acetate	123-86-4	$C_6H_{12}O_2$	ButAcet	2.42	150	200	150
Butyl Acrylate	141-32-2	$C_7H_{12}O_2$	ButAcrl	1.5	2	6	2
CarbonDisulfide	75-15-0	CS_2	CS2	1.4	4	12	4
Chlorotrifluoroethylene	79-38-9	C_2ClF_3	C2ClF3	1	5	20	5
Chlorobenzene	108-90-7	C_6H_5Cl	ClBenzn	0.45	10	30	10
Cresols		C_7H_8O	Cresols	1.05	5	15	5
Cumene	98-82-8	C_9H_{12}	Cumene	0.59	50	150	50
Cyclohexane	110-82-7	C_6H_{12}	Cyhexan	1.16	100	300	100
Cyclohexanol	108-93-0	$C_6H_{12}O$	CyHexol	2.91	50	150	50
Cyclohexanone	108-94-1	$C_6H_{10}O$	Cyhexon	1.04	25	50	25
Cyclopentane	287-92-3	C_5H_{10}	Cypentn	4	600	0	600
Decane	124-18-5	$C_{10}H_{22}$	Decane	1.04	800	0	0
Diacetone Alcohol	123-42-2	$C_6H_{12}O_2$	DiacAlc	0.8	50	150	50
Dibromoethane,1,2-	106-93-4	$C_2H_4Br_2$	DiBrEt	2	30	15	20
Dichlorobenzene,1,2-	95-50-1	$C_6H_4Cl_2$	DiClBen	0.5	25	50	25
Dichlororethylene,1,1-	75-35-4	$C_2H_2Cl_2$	DiClEt	0.95	5	15	5
Dichlororethylene,1,2-	107-06-2	$C_2H_4Cl_2$	DiClEt	0.7	200	0	200
Diesel Fuel #1	68334-30-5		Diesel1	0.9	10	0	10
Diesel Fuel #2	68334-30-5		Diesel2	0.75	10	0	10
Diethylamine	109-89-7	$C_4H_{11}N$	DiEtAmn	1	10	25	10

Compound					Alarms - ppm		
Proper Name	**CAS No.**	**Formula**	**7-Char Abbr.**	**Correction Factor**	**Danger/ Ceiling**	**STEL**	**TWA**
Diketene	674-82-8	$C_4H_4O_2$	DiKeten	2.2	1	5	1
Dimethoxymethane	109-87-5	$C_3H_8O_2$	DiMeOMe	1.4	1000	0	1000
Dimethyldisulfide	624-92-0	$C_2H_6S_2$	DiMeDiS	0.23	0.5	0	0.5
Dimethylacetamide	127-19-5	C_4H_9NO	DiMeAct	1.3	10	30	10
Dimethylaniline N,N-	121-69-7	$C_8H_{11}N$	DiMeAnl	0.6	5	10	5
Dimethylformamide	68-12-2	C_3H_7NO	DiMeFrm	0.9	10	30	10
Dioxane, 1,4-	123-91-1	$C_4H_8O_2$	Dioxane	1.5	20	60	20
Divinylbenzene	1321-74-0	$C_{10}H_{10}$	VinStyr	0.4	10	30	10
Epichlorohydrin	106-89-8	C_2H_5ClO	Epiclhn	8	2	0	2
Ethanol	64-17-5	C_2H_6O	Ethanol	8.72	1000	0	1000
Ethanol Amine, 2	141-43-5	C_2H_7NO	EtAlcAm	3	3	6	3
Ethyl Acetate	141-78-6	$C_4H_8O_2$	EtAcet	3.63	400	0	400
Ethyl Acetoacetate	141-97-9	$C_6H_{10}O_3$	EtAcoAc	0.9	1400	0	0
Ethyl Acrylate	140-88-5	$C_5H_8O_2$	EtAcryl	2	5	15	5
Ethyl Ether	60-29-7	$C_4H_{10}O$	EtEther	1.2	400	500	400
Ethyl Mercaptan	75-08-1	C_2H_6S	EtSH	0.7	10	1.5	0.5
Ethylbenzene	100-41-4	C_8H_{10}	EtBenzn	0.54	100	125	100
Ethylene	74-85-1	C_2H_4	Ethene	8	200	600	200
Ethylene Glycol	107-21-1	$C_2H_6O_2$	EtGlycl	20	40	0	0
Ethylene Oxide	75-21-8	C_2H_4O	EtO	15	1	3	1
Furfural	98-01-1	$C_5H_4O_2$	Furfurl	1.39	2	6	2
Gasoline	8006-61-9		Gasolne	1.05	300	500	300
Heptane	142-82-5	C_7H_{16}	Heptane	2.06	400	500	400
Hexane, n-	110-54-3	C_6H_{14}	Hexane	4.2	50	0	50
Hydrogen Sulfide	7783-06-4	H_2S	H2S-PID	4	10	15	10
Indene	95-13-6	C_9H_8	Indene	0.46	10	30	10
Iodoform	75-47-8	CHI_3	Iodform	1.5	0.6	1.8	0.6
Iodomethane	74-99-4	CH_3I	IodMetn	0.4	2	6	2
Isoamyl Acetate	123-92-2	$C_7H_{14}O_2$	IamlAct	1.6	50	100	50
Isobutanol	78-83-1	$C_4H_{10}O$	Ibutanl	3.5	50	150	50
IsobutylAcetate	110-19-0	$C_6H_{12}O_2$	IbtlAct	2.26	150	450	150
Isobutylene	115-11-7	C_4H_8	Ibutyln	1	1800	0	0
Isooctane	540-84-1	C_8H_{18}	Ioctane	1.08	1100	0	0
Isopentane	78-78-4	C_5H_{12}	Ipentan	6	1400	0	0
Isophorone	78-59-1	$C_9H_{14}O$	Iphoron	0.75	5	0	25
Isoprene	78-79-5	C_5H_8	Iprene	0.7	1500	0	50
Isopropanol	67-63-0	C_3H_8O	Ipropnl	4.35	200	400	200
Isopropyl Acetate	108-21-4	$C_5H_{10}O_2$	IplAcet	2.2	100	200	100
Isopropyl Ether	108-20-3	$C_6H_{14}O$	IplEthr	0.8	250	310	250
Isopropylamine	75-31-0	C_3H_9N	Iplamin	0.9	5	10	5
Jet A Fuel			JetA	0.65	34	0	34
Jet B Fuel			JetB	0.75	30	0	30
JP-4 Fuel			JP-4	0.75	30	0	30
JP-5 Fuel			JP-5	0.65	29	0	29

Compound					Alarms - ppm		
Proper Name	**CAS No.**	**Formula**	**7-Char Abbr.**	**Correction Factor**	**Danger/ Ceiling**	**STEL**	**TWA**
JP-8 Fuel			JP-8	0.65	34	0	34
Kerosene	8008-20-6	--	Kerosen	0.83	34	0	34
Ketene	463-51-4	C_2H_2O	Ketene	3	0.5	1.5	0.5
Mesitylene	108-67-8	C_9H_{12}	Mestyln	0.34	25	75	25
Mesityl Oxide	141-79-7	$C_6H_{10}O$	MestylO	0.47	15	25	15
Methacrylic Acid	79-41-4	$C_4H_6O_2$	MeAcryA	2.3	20	60	20
Methoxyethanol l,2-	109-86-4	$C_3H_8O_2$	MeOetnl	2.7	5	15	5
Methoxypropanol l,1-			MeOprnl	3	100	150	100
Methyl Acetate	79-20-9	$C_3H_6O_2$	MeAcet	5.19	200	250	200
Methylacetoacetate	105-45-3	$C_5H_8O_3$	MeAcoAc	1.1	0	0	0
Methyl Acrylate	96-33-3	$C_4H_6O_2$	MeAcryl	3.4	2	6	2
Methyl Benzoate	93-58-3	$C_8H_8O_2$	MeBenzo	0.93	0	0	0
Methyl Benzyl Alcohol	589-18-4	$C_8H_{10}O$	MeBeAlc	0.8	0	0	0
Methyl Ethyl Ketone	78-93-3	C_4H_8O	MEK	0.77	200	300	200
Methyl Isobutyl Ketone	108-10-1	$C_6H_{12}O$	MIBK	0.8	50	75	50
Methyl Mercaptan	74-93-1	CH_4S	MeSH	0.7	0.5	1.5	0.5
Methyl Methacrylate	80-62-6	$C_5H_8O_2$	MMA	1.6	50	100	50
Methyl t-Butyl Ether	1634-04-4	$C_5H_{12}O$	MTBE	0.8	50	150	50
Methylamine	74-89-5	CH_5N	MeAmine	1.4	5	15	5
Methyl Bromide	74-83-9	CH_3Br	MeBr	1.9	1	3	1
Methyl Pyrrolidinone	872-50-4	C_5H_9NO	MePyrrd	0.9	10	0	10
Mineral Spirits	8030-30-6 8032-32-4	--	MinSprt	0.8	100	0	100
Naphtha	8030-30-6 8052-41-3	--	Naphtha	0.8	100	0	100
Naphthalene	91-20-3	$C_{10}H_8$	Naphthl	0.44	10	15	10
Nitric Oxide	10102-43-9	NO	NO-PID	8	25	75	25
Nitrobenzene	98-95-3	$C_6H_5NO_2$	BenzNO2	1.7	1	0	1
Nonane, n-	111-84-2	C_9H_{20}	Nonane	1.27	200	600	200
Octane	111-65-9	C_8H_{18}	Octane	1.59	300	375	300
Pentane, n-	109-66-0	C_5H_{12}	Pentane	7.89	600	750	600
Pentyl Alcohol	71-41-0	$C_5H_{12}O$	PentAlc	3.2	1200	0	0
2-Pentanone	107-87-9	$C_5H_{10}O$	Pentone	0.79	200	250	200
Petrol	8006-61-9		Petrol	1.05	300	500	300
Phenol	108-95-2	C_6H_6O	Phenol	1.2	5	15	5
Phosphine	7803-51-2	PH_3	PH3-PID	2	0.3	1	0.3
Picoline,2-	109-06-8	C_6H_7N	Picolne	0.57	2	5	2
Picoline,3-	108-99-6	C_6H_7N	Picolne	0.9	2	5	2
Pinene, a-& b-	2437-95-8 18172-67-3	$C_{10}H_{16}$	Pinene	0.32	20	60	20
Propanol	71-23-8	C_3H_8O	Propanl	4.8	200	250	200
Propionaldehyde	123-38-6	C_3H_6O	Propald	1.68	20	0	20
Propionic Acid	79-09-4	$C_3H_6O_2$	PropAcd	8	10	30	10
Propyl Acetate	109-60-4	$C_5H_{10}O_2$	PropAct	2.5	200	250	200
Propylene	115-07-01	C_3H_6	Propene	1.4	0	0	0
Propylene Oxide	75-56-9	C_3H_6O	ProplOx	7	20	6	2

Compound					Alarms - ppm		
Proper Name	**CAS No.**	**Formula**	**7-Char Abbr.**	**Correction Factor**	**Danger/ Ceiling**	**STEL**	**TWA**
Pyridine	110-86-1	C_5H_5N	Pyridne	0.75	1	3	1
Styrene	100-42-5	C_8H_8	Styrene	0.44	20	40	20
t-Butyl Alcohol	75-65-0	$C_4H_{10}O$	TB Alc	3.4	100	150	100
t-Butyl Mercaptan	76-66-1	$C_4H_{10}S$	TriBuSH	0.55	0	0	0
t-Butylamine	75-64-9	$C_4H_{11}N$	TBAmine	0.71	0	0	0
Tetrachloroethylene	127-18-4	C_2Cl_4	TetrClE	0.7	25	100	25
Tetrahydrofuran	109-99-9	C_4H_8O	THF	1.55	50	100	50
Thiophene	110-02-1	C_4H_4S	Thiophn	0.47	1500	0	0
Toluene	108-88-3	C_7H_8	Toluene	0.51	300	150	50
Trichlororethylene	79-01-6	C_2HCl_3	TriClE	0.65	200	100	50
Trimethylamine	75-50-3	C_3H_9N	TrMeAmn	0.5	5	15	5
Trimethylbenzene 1,2,3-	526-73-8	C_9H_{12}	TrMeBnz	0.49	25	75	25
Trimethylbenzene,1,2,4-	95-63-6	C_9H_{12}	TrMeBnz	0.43	25	75	25
Trimethylbenzene,1,3,5-	108-67-8	C_9H_{12}	TrMeBnz	0.34	25	75	25
Turpentine Crude		--	TurptnS	1	20	60	20
Turpentine Pure	8006-64-2	--	Turptn	0.45	20	60	20
Vinyl Acetate	108-05-4	$C_4H_6O_2$	VinAcet	1.1	10	15	10
Vinyl Bromide	593-60-2	C_2H_3Br	VinylBr	1	0.5	1.5	0.5
Vinyl Chloride	75-01-4	C_2H_3Cl	VinylCl	2.1	1	3	1
Vinylidene Chloride	75-35-4	$C_2H_2Cl_2$	VindnCl	0.95	5	15	5
Xylene, m-	108-38-3	C_8H_{10}	Xylene	0.44	100	150	100
Xylene, o-	95-47-6	C_8H_{10}	Xylene	0.6	100	150	100
Xylene, p-	106-42-3	C_8H_{10}	Xylene	0.46	100	150	100

Note – An alarm setpoint of zero corresponds to the alarm being disabled. This is because there is no established OSHA PEL (permissable exposure limit) established for these materials.