

# Preparing Gas Phase Standards from Neat Chemicals to Support Air Monitoring in the Workplace

## Application Note:

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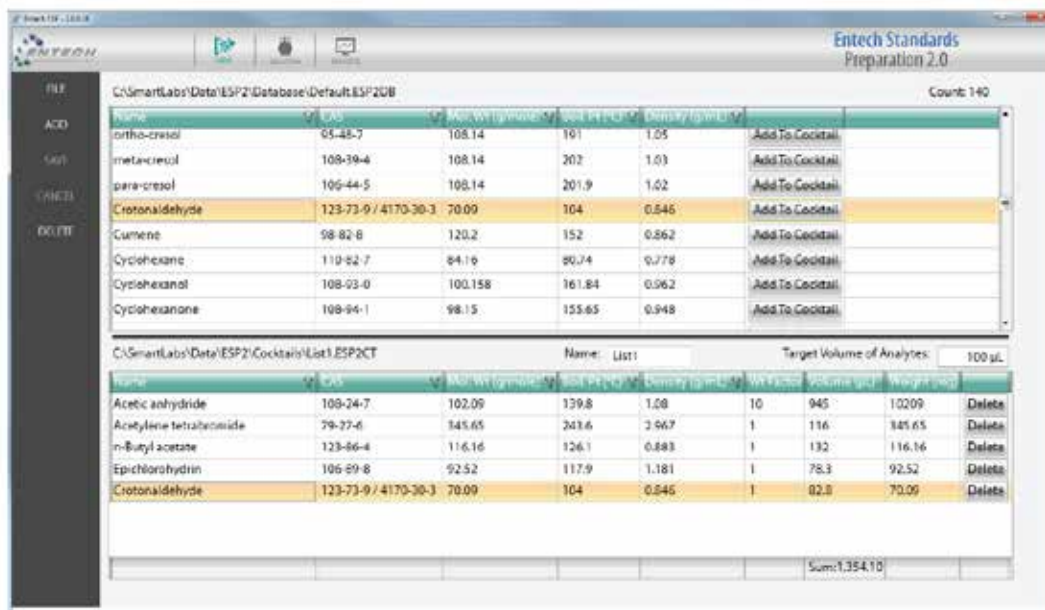
### Abstract

An approach for generating gas phase standards to support air monitoring using the canister technique is presented. A software program called ESP 2.0 performs the calculations to prepare low to high PPMv level standards in canisters and glass Bottle- Vac samplers for the purpose of calibrating GCMS systems and to validate the precision and reliability of GC sample introduction systems. Low cost, neat liquid standards are used to create cocktail mixtures which are then injected into a Silonite coated 6L Canister for creation of high concentration gas phase standards, followed by subsequent dilution into a second canister or Bottle-Vac sampler to make lower concentration standards. Multiple concentrations can be generated to support multi-point calibration curves, such as when calibrating from 5-200% of OSHA PEL levels for analysis of workplace air. To support IH monitoring using HDS Personal Monitors, a Bromofluorotoluene (BFT) standard in helium and a Fluorobenzene ISTD in Nitrogen can be generated in 6L canisters, making it easier for labs to start using this exciting new alternative to badges and tubes. Finally, the ambient air analysis of chemicals not found in commercially available cylinders is supported. Creating a low PPMv standard in a 6L canister creates the initial stock standard for further dilution on an Entech 4700 Precision Diluter when preparing low to sub-PPBv level standards for ambient air methods.

### Introduction

OSHA Permissible Exposure Levels (PELs) typically range from 1 to 1000 PPMv for most compounds, and only drop below 1 PPMv for a very few, select compounds. High pressure cylinder standard mixtures available commercially typically top out at just 1 PPMv in concentration due to the higher pressures and large number of compounds contained in these mixtures (20 to 80+). This creates a problem in calibrating whole air canister methods that must collect and measure concentrations into the mid to high PPMv range. Labs are therefore in need of a reliable way to make PPMv range standards at lower pressures where they will be stable for up to a month or more. This can be easily done using highly inert Entech Silonite coated stainless steel canisters by starting with low cost neat compounds. However, the calculations and procedures can be difficult for even experienced air laboratories.

A procedure is described here that takes advantage of a new software package from Entech called ESP 2.0. (Entech Standards Preparation, Ver2.0). Back in the early 1990s, Entech created a software package called ESP that was used successfully to make unique standards when commercially available standards did not exist. This software package has been updated both to support Win7 and higher operating systems, and to better support the new HDS Personal Monitor workplace monitoring technique. HDS Personal monitors are 50cc stainless steel containers with a proprietary Silonite coating that renders the internal surface inert, allowing chemicals to remain at their original concentrations for up to weeks after sampling. The samplers are filled with helium in the laboratory, along with a recovery compound at PPM levels which verifies the inertness of every sampler during every sampling event. The use of helium rather than an initial vacuum in the canister allows these small canisters



**Figure 1** - Entech ESP 2.0 Standards Preparation Software showing the creation of a cocktail mixture from the included database. Additional compounds can be added to the database as needed.

to sample air at a much slower rate, providing a 15 min to 8 hour constant rate sampler with no external flow controller. As helium diffuses out of the sampler, a vacuum is created that simultaneously draws in the surrounding air at a constant rate. Different samplers are available to exchange approximately 35% of the helium with air over a period of 15 min, 1, 2, 4, or 8 hours, during which time the sampling rates remain constant. The BFT in helium needed for these samplers can easily be made by the laboratories, as described in the next section. When returned to the lab, an internal standard can be added to the canister, which can either be the typical 1 PPMv 4 component standard used for TO15 analysis, or a single component standard such as Fluorobenzene in Nitrogen at PPM levels which can be made using the described procedure.

TO15 laboratories are sometimes required to analyze for compounds that are not found in commercially available mixtures. An example is given here that shows the creation of a 1 PPMv stock in a 6L canister that can then be diluted further to low or even sub-PPBv levels using the Entech 4700 Precision Dilution System. This opens up hundreds of additional compounds that can be quantified using the TO15 technique. As always, working with another laboratory and sharing separately prepared standards for testing calibration accuracy is necessary for added reliability and quality assurance.

## Creating a liquid cocktail Mixture

The ESP 2.0 software allows the creation of a liquid cocktail mixture consisting of 1 to 100 different neat chemicals as obtained from suppliers such as Sigma-Aldrich. Figure 1 shows the database / cocktail creation page which allows selected compounds to be transferred into the cocktail list below. The database can easily be expanded to include chemicals not found in the supplied database by selecting ADD and then SAVE once the new entries have been added. A "target volume of analyte" is chosen to create a rough estimate of the amount to use for each chemical, and 100ul is the default. This value can either be increased or decreased to change the total volume of the liquid mixture, or cocktail, in the vial. The program then calculates the true volume and weight to transfer so that every compound has the same number of moles transferred. When a Weighting Factor greater than 1 is used, the number of moles transferred is multiplied by this factor. In the example in Figure 1, the goal is to make a standard that is 10x higher in Acetic Anhydride than for the other compounds. Therefore, Acetic Anhydride is given a Weighting Factor of 10 while other compounds have 1 as their Weighting Factor. When the final standard is created, Acetic Anhydride will be 10x higher in concentration. This allows standards to be made that are relevant to the toxicity of the compound, and therefore to its Permissible Exposure Limits. Standards can then be made that range from

0.05 - 2 x the PELs for each compound, to provide the ideal monitoring range for each. This is even more important when using GCMS rather than GC/FID, as a mass spectrometer does not have as large of a linear range as an FID, so standard concentrations must be tailored on an individual compound basis. Of course, this is ultimately dictated by what is required in the OSHA, NIOSH, or EPA methods.

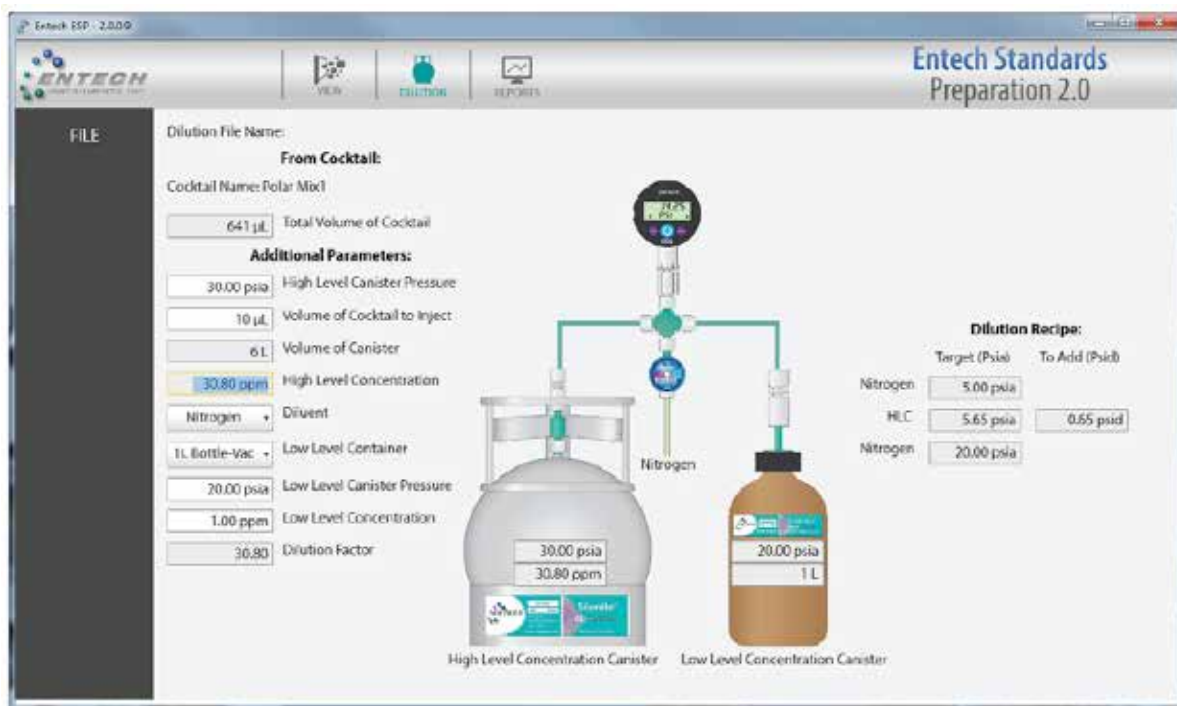
When making the cocktails, use syringes with the appropriate volume range. Never try to measure less than 10% of a syringes total volume, as the error will be too great. That is, it would be better to use a 250ul or 500ul syringe to transfer 100ul than a 1cc syringe. Once you have made up the cocktail in the software, you can increase or decrease the Target Volume of Analyte to make calculated volumes in the cocktail better for your available syringes. The weight for each compound is also given in case some of the neat compounds are solids. It is recommended that you put the compounds into the vial from highest to lowest boiling points, to reduce the potential for evaporative losses. Keep the cocktail in a freezer if possible during storage, both to reduce evaporative loss, and to reduce the potential for chemical reactions. SAVE the cocktail when done, then move to the DILUTION page. If you are returning to

make a dilution calculation to an existing cocktail, just LOAD the saved cocktail and then move directly to the DILUTION page.

## Creating Gas Phase Standards

Figure 2 shows the DILUTION page in ESP 2.0. During dilutions, a liquid volume of cocktail will be injected directly through the stem of a 6L canister by first filling the canister with high purity nitrogen or helium to 2-4 psig (16-18 psia), and then removing the valve and quickly injecting the liquid standard through the stem followed by replacement of the valve. The amount of room air that will get into the canister has been found to be less than 0.1% when done within 20-30 seconds, so there is no chance for any significant contamination. The valve is quickly replaced and the canister is pressurized to the final pressure as calculated by the ESP software. After a period of 2-3 hours for equilibration, the standard is ready for further dilution into a second canister or Bottle-Vac.

When performing the calculations, first enter in all parameters that are fixed, such as the volume of the high concentration canister, the volume of the secondary low concentration canister, and then expected final pressures. Pressures can be adjusted



**Figure 2** - Entech ESP 2.0 Dilutions showing high and low concentration canisters and dilution parameters using the low cost Entech Digital Dilution System (DDS).

to optimize some of the other parameters, such as transfer volumes, so these can be changed as appropriate. Also, remember that a regulator can be placed onto a final canister for actual usage to lower its pressure. When filling into glass bottles, the software sets the maximum pressure to about 7 psig, which is about 22 psi absolute. The Entech Digital Dilution System used for the dilutions has a maximum pressure of 50 psi absolute, or about 35 psig. The digital dilution system is accurate for dilutions up to about 100 fold, so keep this in mind when creating a target concentration for the higher concentration canister. If you are making a separate canister or Bottle-Vac concentration for each point on your curve (as is needed for HDS Personal Monitor method calibration), then you'll want to create a concentration in your first High Concentration Canisters that is equal to your high level point. Keep in mind that the concentrations reported in the software are those for compounds with a weighting factor of 1. In our example where Acetic Anhydride was given a weighting factor of 10, the concentration of Acetic Anhydride will be 10x higher than that shown. The final compounds and their concentrations will be shown accurately on the REPORT page.

Once filling in all necessary parameters, the Dilution recipe for the Digital Dilution System shown in the graphic will appear on the right. To maintain good accuracy, a pressure increase when adding the high concentration standard of 0.5 psid or greater is recommended to prevent measurement errors from becoming too large. Under high vacuum, the DDS is less accurate, so a nominal amount of diluent nitrogen or helium of about 5 psia should be first introduced to bring the gauge into a more accurate range before adding the standard. The pressures are shown both in absolute terms (psia), and for the standard transfer in differential pressure (psid), or pressure to add.

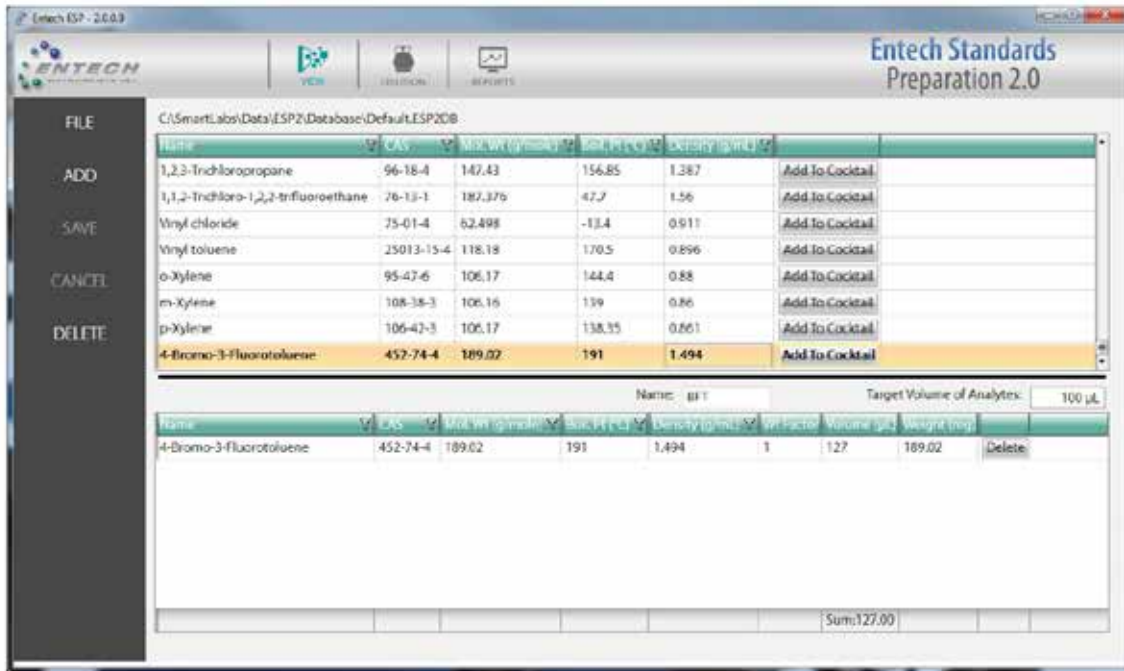
## **Making BFT in Helium Standards**

HDS Personal Monitors are charged with helium which effectively creates a "helium driven pump" that pulls the air sample in as helium diffuses out. To ensure that each Silonite coated monitor is completely inert, a surrogate can be included with the helium. Bromofluorotoluene has been chosen as the normal surrogate to show sampler inertness by demonstrating

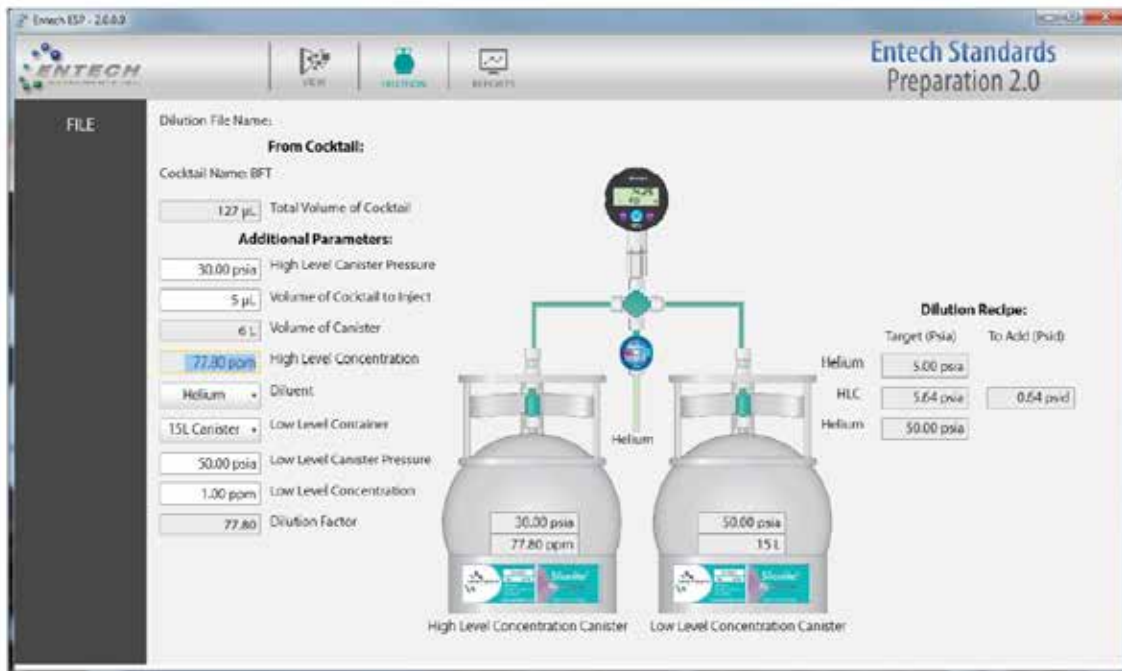
its recovery up to weeks after spiking it into the sampler. However, it's important to realize that any compound can be introduced as a surrogate, including stable isotopes of the compounds to be monitored for even greater certainty in the results when collecting difficult compounds. The following procedure can be used for any surrogate compounds that are available as neat liquids. If the neat chemical is a solid, use 1.00 as its density, and the number of ul to "inject" will then become the number of mg to weigh into the vial.

Figure 3 shows the cocktail page with just 4-Bromo-3-Fluorotoluene (BFT). When making a single component cocktail, there is no reason to actually deliver that chemical to a "cocktailvial". Instead, just move on to the DILUTION page and then use the appropriate syringe to draw the amount needed right out of the neat standard bottle for transfer into the first canister. Be sure to set the weighting factor to 1 so that the concentration calculated in the DILUTION page will be the same as the final concentration of the surrogate in the canister.

Figure 4 shows the DILUTION page when making up the BFT in helium. In the calculations shown, a 5ul injection results in a 77.8 PPMv standard in the high concentration canister. Remember that this canister must be initially filled with UHP helium, then vented before injecting the 5ul BFT standard, and then pressurized to the final pressure of 50 psia with helium. After a minimum 3 hour equilibration (overnight preferable), the dilution into the final canister can be made to create the 1PPM spiking standard that will be used to fill each 50cc HDS Personal Monitor before they go out to the field for sampling. A 15L canister is advantageous here, a sit will allow more HDS monitors to be filled before having to remake the standard. When filling a 15L canister to 50 psia and then regulating it to 20 psia (about 5-6 psig), this will allow over 400 HDS monitors to be filled before having to remake the standard. As quantities of HDS Monitors increases, laboratories may eventually choose to purchase a 1PPMv cylinder of BFT in helium at 2000 psi, allowing perhaps 10,000 samplers to be filled. In the example, a partial pressure of 0.64 psid is transferred from the high concentration canister to the 15L canister, followed by pressurization to 50 psia. Prior to the addition of the 0.64 psid, 5 psi of helium is added, as



**Figure 3** - Cocktail Page when making BFT in Helium. Note that with a single compound, no actual transfer to a separate vial is necessary. Simply withdraw calculated amount to inject into high Level Canister in the Dilution Page (Figure 4).



**Figure 4** - Calculations showing the creation of a 1 PPM BFT standard in Helium. Using a 15L canister for the final 1PPM standard and then regulating this to 5 psig when filling evacuated HDS Personal Monitors should allow this canister to fill over 400 50cc HDS Personal Monitors before having to remake the 1PPM BFT standard.

the DDS gauge is more accurate when not under high vacuum. The final canister should equilibrate for a few hours before use. Regulate the final canister to 4-6 psig when filling each HDS Personal Monitor.

## HDS Internal Standard Preparation

During HDS Personal Monitor Analysis, the Internal Standard is added directly to the HDS Personal Monitor. Prior to this addition, the HDS PM as received from the field is first topped off to 15.00 psia with helium, which is just slightly above atmospheric pressure. This eliminates differences caused by elevation changes between the sampling location and the laboratory. Then, the HDS Personal Monitor is weighed to give an initial mass prior to pulling anything out of the sampler. After the analysis, the sample is evacuated and weighed again to allow the calculation of the actual amount of air collected so that a dilution factor can be determined. It's important to remember that only 25-40% of the helium is displaced during sampling, so the resulting sample has anywhere from 2.5-4x more helium than air. Therefore, the dilution factor must be calculated and multiplied to the final GCMS results to achieve the actual concentration at the sampling site.

Before analysis, the pressure of the HDS PM is raised from 15.00 to 20.00 psia using an Internal Standard, typically at 1PPM. This Internal Standard can either be made using the ESP 2.0 software, or an off the shelf TO15 4 compound Internal Standard can be used, containing Bromochloromethane, 1,4- Difluorobenzene, Chlorobenzene-d5, and Bromofluorobenzene. For laboratories who are also performing TO15, the 4 component TO15 standard makes more sense, as calibrations for many of the analytes required for IH monitoring have already been calibrated for using this ISTD. For "IH Only" labs that are not required to run TO15, a two component standard containing 1,4-Difluorobenzene and BFB makes sense, as including the BFB allows the MS calibration to be checked as needed.

## HDS Method Calibration Standards

Calibrating a GCMS for the analysis of HDS Personal Monitors requires the creation of separate standards for every point on the curve. For a 5 point calibration, 5 different canisters or Bottle-Vacs must be used for each concentration level. When performing

analyses at typical OSHA required monitoring levels, concentrations from 0.1 PPMv to 1000 PPMv will be needed depending on the compounds to be monitored. In this case, the optimum injection volume will be achieved using a 0.25 to 1cc loop. When analyzing compounds with much lower Permissible Exposure Levels (PELs), sample volumes as high as 10-20cc may be required. The Entech 7200/7650-M "Million Air" system can handle any of these volumes quantitatively without any plumbing changes.

Before continuing, it should be noted that making up a separate calibration standard for each level when performing TO15 system calibration is discouraged, because TO15 detection limits requires the preconcentration of several hundred milliliters of sample, which may have anywhere from 5-100% relative humidity. To properly validate these systems for proper water management, it is always recommended to generate a calibration curve with substantially different amounts of water injected, and the best way to do that is to make up just 1 or 2 standards and then take varying amounts out for each point, thereby changing the water load on the analytical system. If a linear calibration is still obtained, then there is no worry about how changing relative humidities in the samples will affect analytical performance. However, with sample volumes of 20cc and less, there isn't enough water to create this same concern. Then, maintaining a constant injection volume from different standard levels becomes the better approach.

When creating calibration standards, look up the allowable exposure levels for each compound. It is typical to analyze from 1/10th to about 2x this amount. When making up the cocktails, choose the compound(s) with the lowest PELs and give them a weighting factor of "1". Then, all other compounds should be normalized off of this. For example, if compound "A" has a PEL of 1PPM and compound "B" has a level of 25 PPMv, then use a weighting factor of 1 for compound A and 25 for compound B, so each will be analyzed in the range required for regulatory purposes. No need to quantify something 100x lower than the reporting limits, or 10x higher. If it's higher, then there is a big problem. If 10x or more lower, then no problem.

NAME	CAS	Weight (g)	Volume (mL)	Concentration (ppm)	Target Volume (µL)	Action
2-Methoxyethyl acetate	110-49-6	118.13	145	1.009		Add To Cocktail
Methyl acetate	79-20-9	74.08	56.9	0.932		Add To Cocktail
Methyl acrylate	96-33-3	86.06	80	0.95		Add To Cocktail
Methyl n-amyloctane	110-43-0	134.18	151	0.8		Add To Cocktail
Methylcyclohexane	108-87-2	98.18	101	0.77		Add To Cocktail
o-Methylcyclohexanone	583-60-8	112.17	162.5	0.924		Add To Cocktail
Methylene chloride	75-09-2	84.93	39.6	1.327		Add To Cocktail
Methyl isobutyl ketone	110-12-3	114.19	145	0.814		Add To Cocktail

NAME	CAS	Weight (g)	Volume (mL)	Concentration (ppm)	Target Volume (µL)	Action
2-Hexanone	501-78-6	100.16	127.6	0.811	1	Delete
Toluene	108-88-2	92.14	111	0.87	10	Delete
Methylene chloride	75-09-2	84.93	39.6	1.327	25	Delete

Figure 5 - Cocktail Standard for HDS Personal Monitoring.

**From Cocktail:**  
 Cocktail Name: List1  
 Cocktail File Name: C:\SmartLab\Data\ESP2\Cocktail:

**Dilution Recipe:**

Target (Psia)	To Add (Psd)
Nitrogen 5.00 psia	
HLC 7.20 psia	2.20 psid
Nitrogen 22.00 psia	

Figure 6 - The amount injected into the first canister can be adjusted to create the required concentration for the high level standard, from which lower levels can be obtained. Note that actual concentrations are found by multiplying the calculated concentrations by the weighting factors. Hence, Toluene's concentration would be 2 PPM x 10WF = 20PPM, or 2x the PELs.

Figures 5 and 6 show the cocktail and the dilution pages for a standard being made up to analyze Methylene chloride, Toluene, and 2-Hexanone. According to the Cal/OSHA listing of PELs, for an 8 hour Time Weighted Average, they are at 25, 10, and 1PPM, respectively. Figure 5 shows a cocktail made up with the appropriate weighting factors being used, so that the resulting standard will cover the appropriate concentration range for each to monitor, namely 5-200% of each of their permissible exposure limits. This cocktail mixture can be saved and recalled for future dilutions. When clicking on DILUTION at the top

of the ESP screen, the dilution page appears, as shown in Figure 6. You can select which kind of container you'd like to make up each calibration standard in, either glass bottles, MiniCans, or 6L cans. A separate dilution needs to be made for each level, roughly 0.05, 0.10, 0.3, 1, and 2x the PELs. For this example, these levels would correspond to 0.05, 0.10, 0.30, 1.0, and 2.0 PPMv. This is best done by making sure the 6L canister that accepts a liquid injection of the cocktail will end up as the high concentration point, 2.0 PPMv in this case. This is easily done by adjusting the amount of cocktail injected and the final pressure of the 6L

Canister(30-50 psia recommended). In the example, 4.7ul of the cocktail has been calculated as the volume to inject into the 6L canister. First clean the canister, fill it with clean nitrogen to a positive pressure, remove the Micro QT Valve, inject the cocktail by inserting the needle through the stem (avoid contact of liquid on stem), replace the Micro QT Valve, and then pressurize with UHP Nitrogen to the pressure set in the dilution calculations.

A secondary dilution is used to achieve the lower concentrations (0.05, 0.1, 0.3, 1x of PELs). You can select a Bottle-Vac, MiniCan, or 6L canister as the receiving container, and you'll need four of these to make these four different levels. Calculate each level one at a time. Figure 6 shows a 0.2 PPMv standard being made from the 2 PPMv 6L canister, which is a 10:1 dilution. When using Bottle-Vacs, the highest allowable pressure is 22 psia, to avoid any potential breakage hazards. The Entech Digital Dilution System as shown on the dilution screen is used to easily transfer the necessary pressure from the higher concentration canister to the lower one. Since the digital pressure sensor is more linear when not at high vacuum, it is recommended to put in about 5 psia of Nitrogen into the receiving canister/Bottle-Vac first. Note all measurements are in ABSOLUTE pressure, so

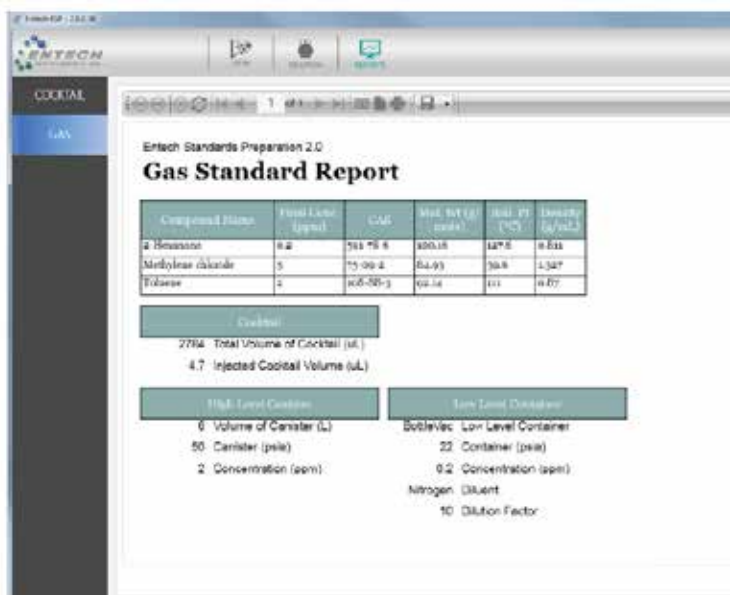
5.0 psi absolute (psia) is still well under atmospheric pressure. Use the TOV-2 control valve to transfer in 5 psia of nitrogen, then the calculated amount needed from the high concentration container (2.2 psid , psi differential), and then top off to final pressure with Nitrogen (22.00 psia in this case). Very easy once you've done a couple. Then, repeat for each of the lower levels.

To calibrate a system used for HDS Personal monitor analysis, simply clean and evacuate 5 HDS Personal Monitors (any range, 15 min to 8 hour), one for each of the 5 different levels, attach each monitor to its respective calibration bottle to pressurize the standard into each HDS Personal Monitor, vent them back down to atmospheric pressure by momentarily opening the valve then closing it, and then perform the same operation on them that you would an actual HDS sample (adjust to 15 psia with helium, then add Internal Standard to 20 psia, then run). That will allow you to create your 5 point calibration curve.

Finally, Figure 7 shows the report that is generated for each dilution. You will have 4 of these reports, because again the high level does not have to be transferred into a second container. Just use the 6L canister for the high level standard directly.

## Summary

A procedure for the creation of custom gas standards has been presented. Entech Standard Preparation Software, Version 2.0 is used to create and maintain a database of neat chemicals, and performs the dilution calculations needed to make PPM to sub-PPM level standards. These standards can be used directly to calibrate GCMS methods where PPM level analyses are performed. In particular, the preparation of standards to support the analysis of HDS Personal Monitors has been described, including the creation of the BFT in Helium standard need to charge the samplers before field sampling. Standard mixtures created by the ESP 2.0 software can also be used with the 4700 Precision Dilution System to make much lower level standards for methods requiring PPB or even sub-PPB level calibrations.



**Figure 7 - Gas Dilution Report for the 0.2PPM Level standard.** Reports can be created for documentation of all dilutions performed. Cocktail reports are shown by clicking on "Cocktails" in the upper left.





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