EPA Method TO15 Canister Analyzer with High Throughput Screening for Detection of High Concentration Soil Gas Samples Without the Threat of System Contamination

Application Note:

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Abstract

A new technique is available that can warn the TO15 analyst of the presence of high concentration samples before exposure to the trapping system. A totally separate flow path is used to send a very small volume directly to the GCMS, with a screening process that takes as little as 5-7 minutes per sample, allowing 50 or more samples to be screened during normal daytime operations, followed by full TO15 runs during evening hours. The automated system makes only momentary contact with each canister, and fully disconnects and flushes the inlet prior to connection to the next canister to completely eliminate any potential for a "hot" canister to contaminate other samples, as is all too frequent with standard rotary valve based autosamplers. Once screened, analytical volumes as small as 0.1cc or as large as 1000cc can be prepared for analysis, creating a 1 million fold dynamic range when combined with a GCMS calibration over a 100x range. Samples can be arranged in order of increasing concentration to eliminate any carryover concern, or can be diluted to bring concentrations into a safe range for the analyzer.

Handling High Concentration Samples

As the number soil gas and vapor intrusion samples continues to grow, the modern TO15 Laboratory must adapt to handle a wider range of sample concentrations than ever before, from sub-PPBv levels to well into the PPMv range. Classical TO15 systems with rotary valve based autosamplers are subject to contamination and carryover when exposed to concentrations just a few hundred times over reporting limits, yet soil gas samples can approach levels that are millions of times higher than air laboratory method detection limits, creating a real threat to the cleanliness and productivity ofTO15 system.

Handling high concentration samples without carryover requires that the laboratory analytical system follow two very important rules. First, the sample should not come in contact with anything absorptive or adsorptive in the system that can possibly retain enough of the high concentration sample to create a carryover issue. The most absorptive/adsorptive material in any preconcentrator is the trap itself, especially when adsorbents rather than 100% glass beads are used. Therefore, it is very important that THE SCREENING OF SAMPLES COMPLETELY AVOIDS CONTACT WITH ANY ADSORBENT TRAP!! Adsorbents have been known to take literally days to bake out once exposed to very high concentration samples. Equally important is the second rule. System contact with the sample must be as short as possible. All parts of the system are capable of at least some sample penetration and memory effects, even the walls of stainless steel or ceramic lined stainless steel tubing. However, the extent of penetration is directly related to the exposure time. An exposure time of just seconds may require only a few minutes to properly outgas a given flow path, whereas exposure for hours or days may take "hours or days" to completely remove contamination from the deepest recesses. Perhaps the biggest culprit in most flow paths are the plastic

Figure 1 Entech Million Air comprised of the 7200-01 Preconcentrator and 7650-M Robotic Autosampler

rotors found in all rotary valves. If these valves are exposed for just seconds, as is the case with 2 position switching valves in most preconcentrators, then the potential for carryover is low. However, when these rotary stream select valves are used in autosamplers where samples are attached and allowed full contact with lines and valve rotors for up to several days awaiting analysis, the extent of contamination can become quite high with subsequently long clean up times after removal of the high concentration samples. The particular difficulty in this case then becomes the prediction of the level of background that exists in each sample line in a rotary valve based autosampler. Without question, the background level coming out of each rotary valve based autosampler position will be different than the next, as each position has had its own history of low and high concentration samples, making it impossible for a laboratory to even quote reliable MDLs unless these systems never see anything other than ambient air. However, as already stated, soil gas samples concentrations can be millions of times higher than standard TO15 method MDLs. The key then is to verify that samples will not contaminate a system prior to running the samples. This is a catch 22 on most systems where concentrations can only determine after running the samples, and then it's too late.

The problem of longer exposure times and eliminating separate flow paths to each sample have been solved decades ago for TD Tube and Purge & Trap autosamplers by utilizing a single inlet whereby the samples or the inlet are physically moved either on a carrousel or on a robotic X, Y, Z platform to make the analytical system a constant, with only one flow path that all samples must pass through. This one flow path is then immediately flushed to eliminate any memory effects before the sample has a chance to equilibrate with walls, system dead volume, and rotors. Only in this way can a system handle a wider dynamic range of concentrations without carryover and potential intersample leakage and contamination. It is only recently with the availability of Entech's robotic autosamplers that this more analytical approach has been available for TO15 canister analysis.

Entech Million Air and High Concentrated Samples

The Entech Million Air TO15 Analyzer is comprised of the Entech 7200 Preconcentrator and the 7650-M

Robotic Canister Autosampler (Figure 1). This solution obeys both rules of sample engagement, by making only momentary contact with the sample, and by avoiding the 7200 traps altogether when screening samples. During sample screening, a loop valve internal to the 7650-M autosampler is placed inline with the heated transfer line that makes momentary connection with the sample through an Entech Micro QT Valve located on each canister. After a brief 20 second flush of the loop with the sample using a pump to "pull" the sample through the loop, the loop is allowed to come to atmospheric pressure by shutting off the downstream flush valve and by raising the heated transfer line off of the sample. The 1cc volume of the transfer line helps to ensure that the 0.1cc loop receives a full 1 atm of sample prior to injection even if the canister is under partial vacuum. The 7650-M then moves the loop valve in line with the GC Carrier Gas which flushes the sample to the GCMS through the M3 focuser which is kept warm to allow all compounds to immediately pass through (Figure 2). The 7650-M then moves to a flush port to remove any potentially high concentration sample remaining in its heated transfer line. The loop valve in the 7650-M also has a separate Internal Standard loop to allow full quantitative measurements. In those cases, the M3 focuser is cooled down to provide the same point of injection as when samples are preconcentrated in the 7200 traps. M3 focusing is avoided when performing sample screen, as the determination of the approximate concentration does not require co-injection of an Internal Standard.

High Throughput Million Air Screening

Laboratories need to push the maximum quantity of samples through their instruments in order to maximize productivity. Since screening is only semi-quantitative in nature, full separation of compounds becomes unnecessary, especially when you consider that the most common high concentration compounds are far fewer in number than the full TO15 list. The typical offenders are TCE, PCE, and BTEX. In order to maximize the throughput of samples while screening, the GCMS can be operated at an isothermal temperature of 100-160 deg C, depending on the column and the film thickness. Most GC columns will not be adversely effected by a brief exposure to air at these temperatures, yet the compounds mentioned above will be retained just slightly longer than the air peak, allowing the use of a solvent delay to avoid exposure of the filament and EM to a 0.1cc injection of air. Figure 3 shows a typical chromatogram of a 50 PPM sample containing TCE, PCE, and BTEX. These compounds come off of the column within 3-4 minutes on a 30m, 0.25mmID, 0.5um column or in about 5-6 minutes on a 60m, 0.32mmID, 1um film column, allowing the entire run time to be only 5-7 minutes.

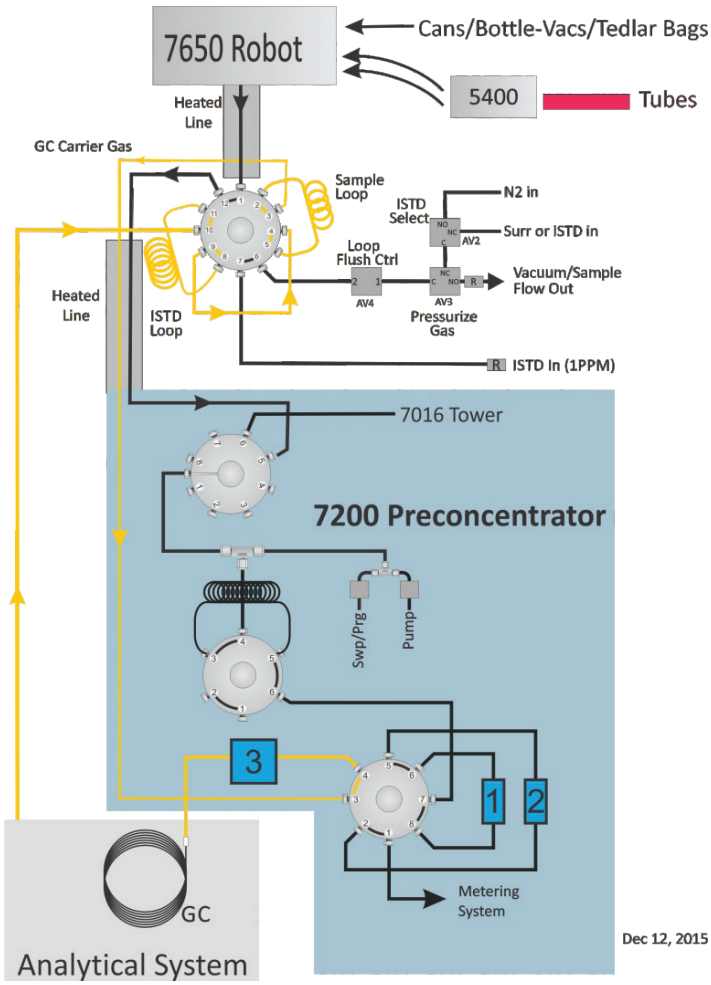

Figure 2 Entech Million Air showing separate flow path for delivering sample loop to GCMS when screening high concentration samples

Since the method is run isothermally, the GCMS becomes ready for the next injection within seconds of the end of the previous sample injection. It is recommended that the GC oven equilibration time be set to 0 min to reduce the cycle time, as the oven is isothermal and does not need time to equilibrate. Figure 4 shows the reproducibility of multiple injections of a 50 PPMv standard.

Figure 5 shows a loop injection blank run immediately after the 50 PPM standard. The short duration exposure to the high concentration sample eliminates the massive carryover that would have resulted on a standard rotary valve autosampler where the sample would have hours or days to absorb into the walls and rotors.

Figure 6 shows a blank run through the trapping system after the loop blank. After running a series of high concentration samples, it is recommended to perform a short system backout before returning to run low level samples. However, a much longer bakeout would be necessary had a 50PPM sample been accidently run as an ambient air sample.

Figures 7 shows the 7650-M with a 6L Canister tray which allows six 6L canisters to be blank tested directly. The small male Micro QT Valve shown in Figure 8 can be used on any canister valve that accepts a 1/4" tube connection to allow it to be run directly. Entech 6L Silonite canisters can also use a Micro QT valve directly, avoiding the need for an expensive intermediate packless valve. Running six 6L samples unattended doesn't seem too terribly impressive, but the short run times allows 6 canisters to be placed onto the system every 35 to 45 minutes,

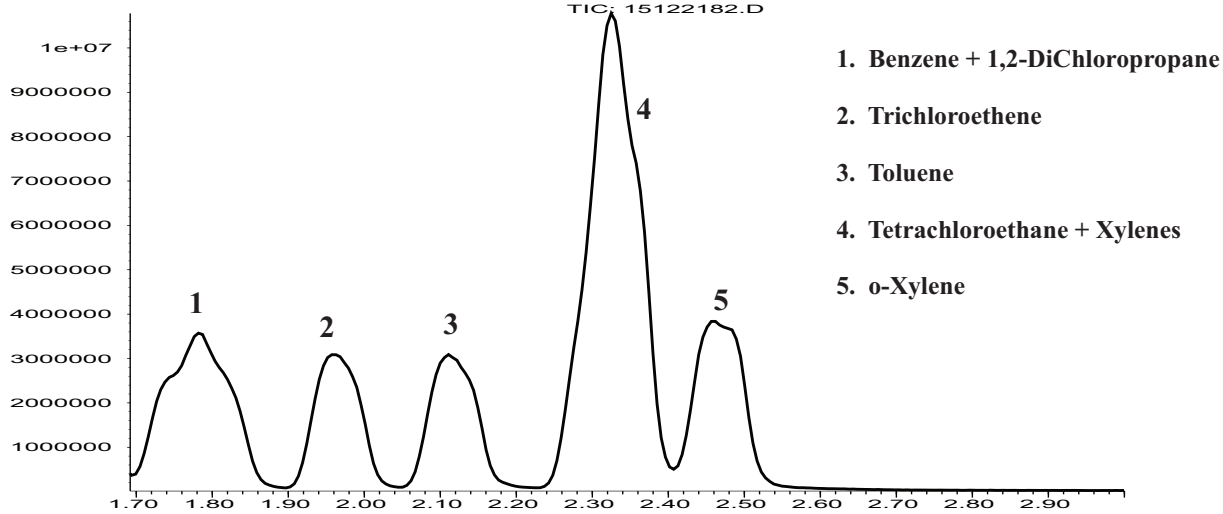

Figure 3 *Fast Screening run of a 50,000 PPBv standard (50 PPMv) containing TCE, PCE, and BTEX. Injections are occuring every 6 minutes allowing over 50 samples to be screened during an 8 hour day.*

	Screening Reproducibility			
	RF1	RF2	RF3	%RSD
Benzene	7.69	9.14	8.52	8.6
Trichloroethene	3.45	4.17	3.84	9.5
Toluene	8.46	9.59	9.12	6.3
Tetrachloroethene	3.00	3.38	3.28	6.1
Xylenes	1.25	1.4	1.31	5.7

Figure 4 *Reproducibility of screening injections of a 50 PPMv Standard containing TCE, PCE, and BTEX.*

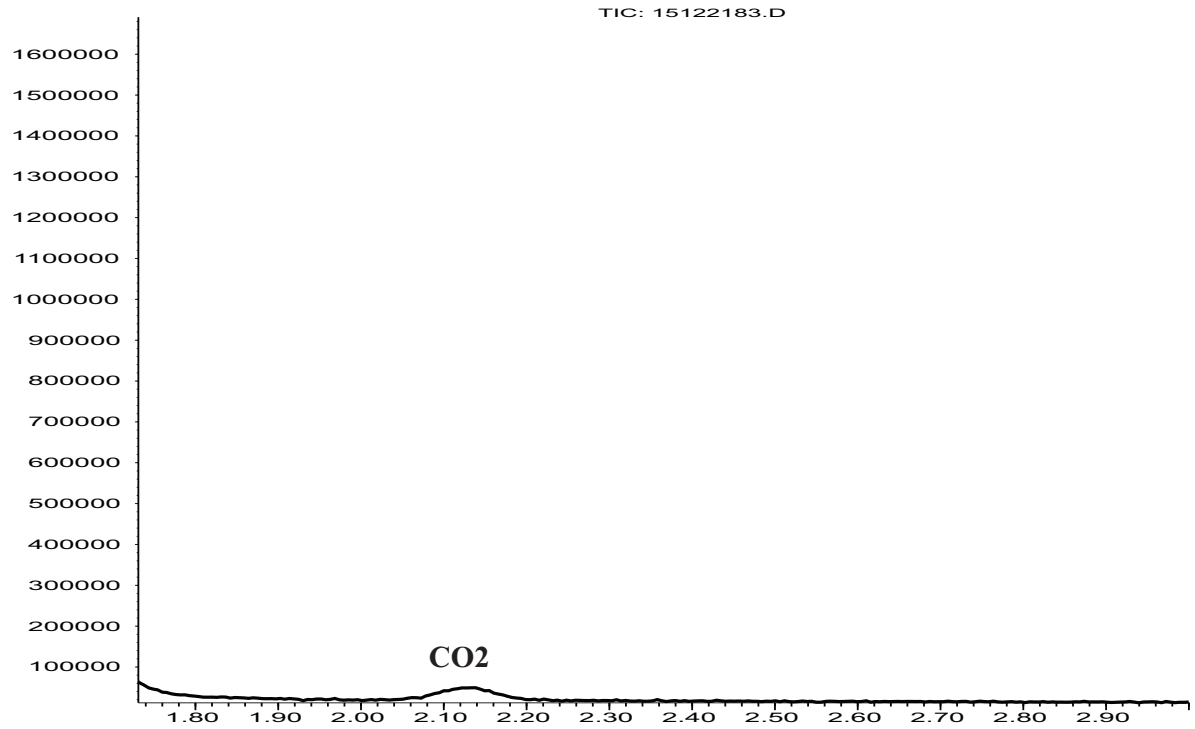

Figure 5 *Blank immediately following a 50 PPM standard injection*

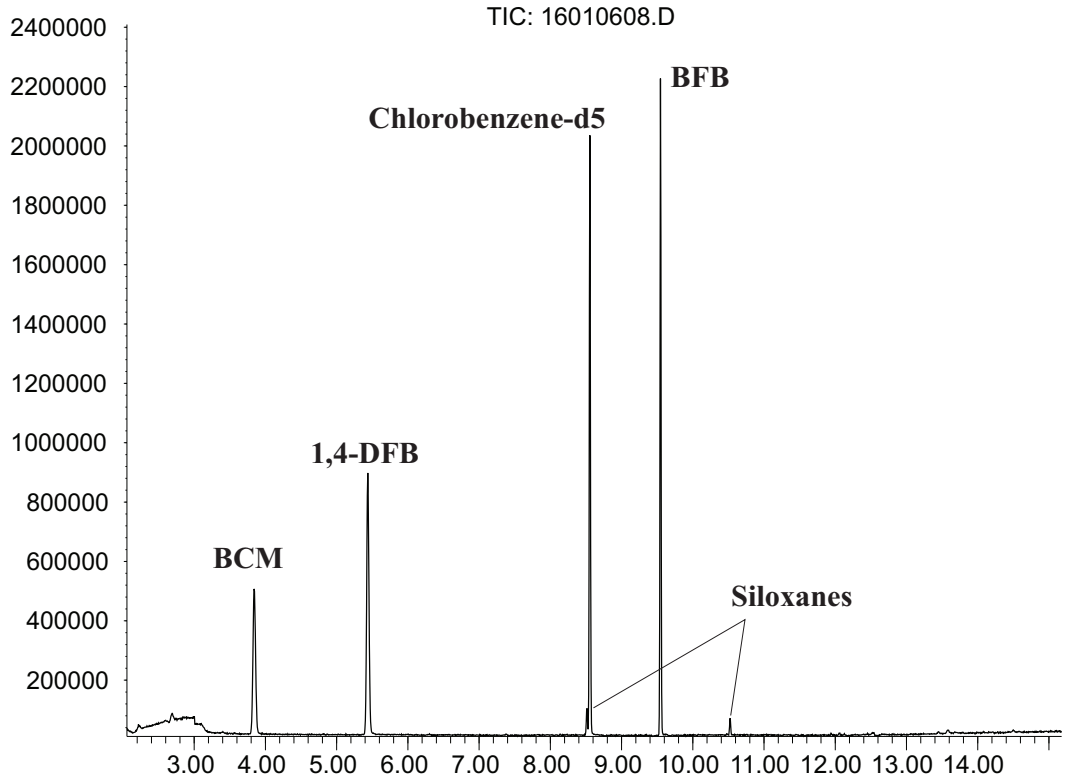

Figure 6 *200cc Blank following high concentration screening showing primarily just the 4 Internal Standards. Concentrations of previous high concentration compounds were below 0.07 PPBv in the first blank*

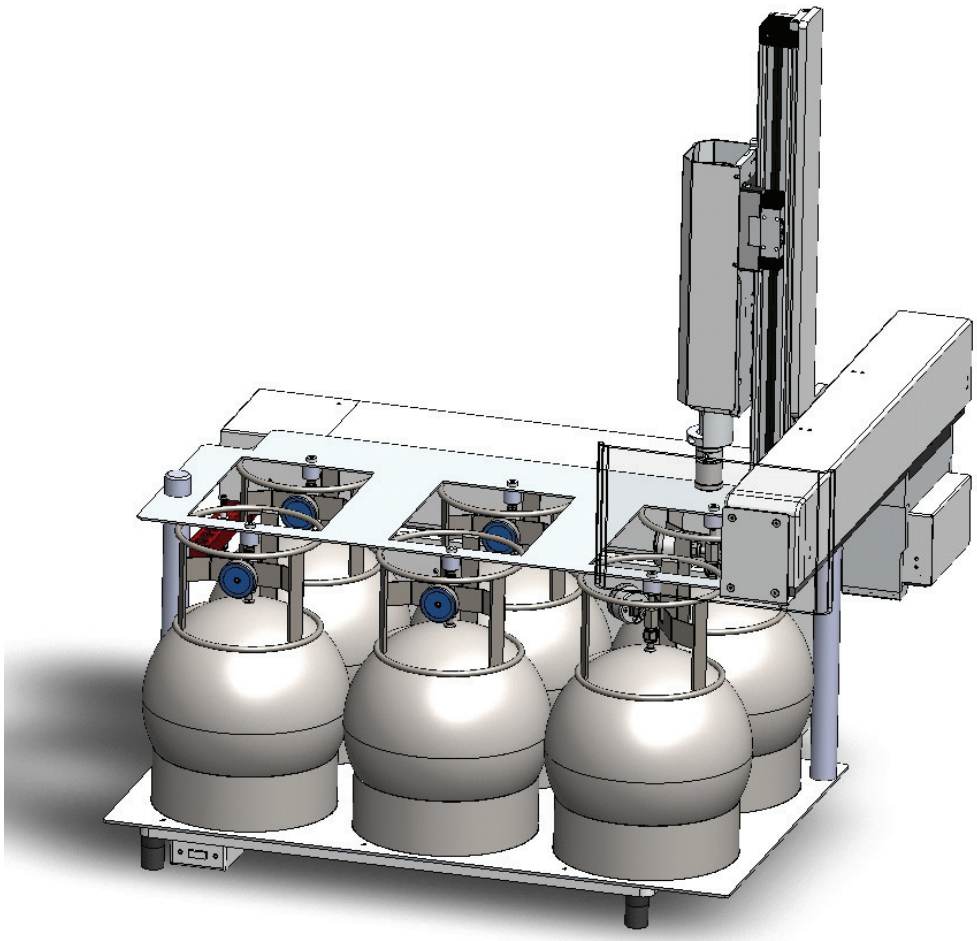

Figure 7 *6L Canisters with quick alignment bracket to properly position them for screening or full TO15 Analysis*

Figure 8 *Attaching the Micro QT Valve shown (PN: MQT-TS400) allows any 6L canister to be analyzed or screened using the Entech Million Air System.*

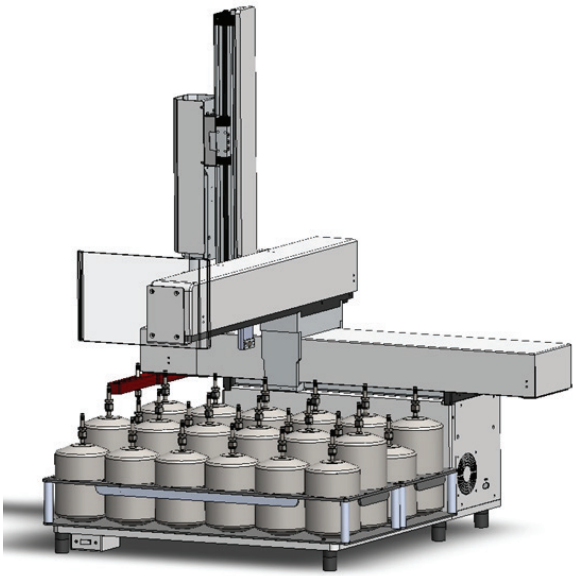

Figure 9 *7650-M configured to analyze twenty four 1 to 1.4L MiniCans or Bottle-Vacs.*

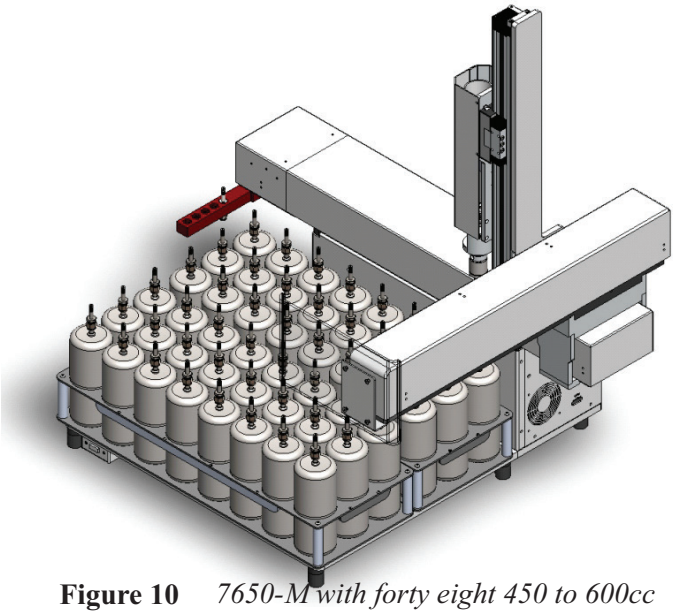

Figure 10 *7650-M with forty eight 450 to 600cc MiniCans*

allowing over 50 to be analyzed by the end of the day. High concentration 6L canisters may require a dilution prior to analysis, and if so they can be diluted into smaller canisters or Bottle-Vacs allowing more to be run unattended overnight. Expansion ports are also available to run 6L canisters off to the side, but care must be taken to only attach canisters that have been demonstrated to be at low concentrations, otherwise the potential for inconsistent blank levels may occur just like with rotary valve autosamplers.

Figures 9 and 10 show how the use of smaller canisters from 450cc to 1.4L can greatly increase the number of samples run unattended through the Million Air system. Many SOPs are calling for 1-1.4L canisters for the collection of soil gas, as this smaller volume provides plenty of sample for the analysis, while making it easier to fill the canister without exceeding the volume of equilibrated soil gas available. Using 1-1.4L MiniCans, the 7650-M can run 24 samples unattended without having to use expansion ports and static connections. Dropping the sample container size down to 450-600cc allows 48 to be accessed directly by the robotic 7650-M, and further dropping the size down to the Entech 50cc MiniCan allows up to 172 samples to be run unattended.

Summary

The Entech Million Air has been demonstrated to allow high concentration samples to be screened without risking contamination of either the preconcentrator or autosampler. The complete intersample isolation and short term connection to the analytical system prevents the memory effects or direct leakage of one canister into another which is a potential problem with all rotary valve based autosamplers. Risk of trap contamination is eliminated by completely avoiding contact with the traps by delivering a 0.1cc volume of sample directly into the GC Carrier Gas stream, thereby bypassing the trapping system altogether. Once samples are screened, the Million Air system can also perform an analytical analysis of the samples using a volume of 0.1cc or 1cc via loop injection, or by preconcentrating 10-1000cc of sample using the 7200's Electronic Volume Control described in Application Note 2015-01. Such a wide dynamic range of volumes allows all but the most concentrated samples to be analyzed without prior dilution once they have been screened to determine the ideal volume to run. In some cases, the presence

of high concentration compounds does not prevent the need to still analyze for lower levels species, so overloading with high concentration analytes may be required to still reach required MDLs for remaining compounds, but at least the avoidance of extremely high concentration samples can be elected. Finally, when relative concentrations are determine by the described screening technique, the laboratory can elect to run the lower level samples first so that subsequent higher concentration samples would not contribute a significant bias to remaining samples. Afterwards, the system can be baked out and blank tested before running additional low level samples. Only with screening and the use of a multi-sample, single inlet solution can such a strategy be performed to maximize both laboratory productivity and analytical accuracy.

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