Extremely Wide Concentration Ranges for Toxic Analytes in Air with Lotus Consulting TO15 Analyzer and Scion SQ Mass Spectrometer

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INTRODUCTION

USEPA released their Second Edition Compendium Method TO-15[1] in 1999 for measure of toxic organics in ambient air, and listed a target linear range of 0.5 nmol/mol (ppbV) to 20 nmol/mol (ppbV), and expected detection limits as less than 0.2 nmol/mol of targeted VOCs, for a dynamic concentration range of 100. These restrictions had been imposed by limitations in available analytical hardware at the time the method was finalized. In addition, this procedure lists mandated requirements for the initial calibration.

Since the release of this protocol, other assessments of toxics in vapor samples routinely reference this method of analysis, often to requirements well outside the original target performance of the standard method, including measurement of volatile toxic organic compounds from landfills, dairy farms, digester gas, stack emissions, indoor air and soil gas. For example, California Human Health Screening Levels (CHHSL)[2] for residential indoor vapor intrusion require a dynamic concentration range for listed target analytes from Carbon Tetrachloride (0.0095 nmol/mol) to 1,1,1-Trichloroethane (420 nmol/mol), for a dynamic range of 44,210. Others, such as Illinois Tiered Approach to Corrective Action Objectives (TACO)[3] mandate reporting levels for residential soil gases from 1.6 nmol/mol for 1,2-Dichloropropane to 316,000 nmol/mol for acetone, for a dynamic range of 197,500. And Environmental Screening Levels, Tier 1 - Soil Gas for San Francisco Bay Regional Water Quality Control Board lists their concentration range for Indoor Air Screening Levels for Residential Land Use[4] from 0.0013 nmol/mol for 1,2-dibromo-3-chloropropane to 339 nmol/mol for 2-butanone, for a dynamic range of 260,769. Most frequently these levels are set based on health effects of the chemicals, rather than limitations in the analytical process to generate accurate results.

Many “high performance” single quadrupole mass spectrometers achieve a limited calibration range possibly of up to 1,000. However, in order to measure the wide range mandated by these regulations, the sample may be required to run multiple times after sample dilutions, to bring sample concentrations into the operating range of the measuring system. Alternatively, the sample must be prescreened by flame ionization detector to determine the sampling conditions needed to subsequently measure concentrations with a mass spectrometer system.[5] However, missing in any screening method is positive identification of the reported compound that is provided by using mass spectrometry.

EXPERIMENTAL METHODS

Calibration Standards

Working TO-15 standards are generated from a 1 µmol/mol (ppmV) standard from Restek (Bellefonte, Pa) and serially diluted into working standards ranging from 0.01 nmol/mol to 100 nmol/mol with a Lotus Consulting Pressure Station Model PS-1 (Long Beach, Ca). See Table I.

Table I. Serial Dilution Parameters for Calibration Standards

Starting Concentration	Aliquot (psiA)	Final Pressure (psiA)	Final Concentration
1,000 nmol/mol	5.00	50.00	100 nmol/mol
100 nmol/mol	5.00	50.00	10 nmol/mol
10 nmol/mol	5.00	50.00	1 nmol/mol
1 nmol/mol	5.00	50.00	0.1 nmol/mol
0.1 nmol/mol	5.00	50.00	0.01 nmol/mol

Standard Loadings with Mass Flow Controller

The instrument includes a mass flow controller (Sierra Instruments, Model 840, Monterey, Ca) for sample loading with low level analytes. A sample pressure regulator is installed just after the automated sampler to provide a consistent sample pressure for the mass flow controller. Sample is first allowed to flow into the pathway without trapping to flush all samples lines with the new sample. After a typical two-minute delay, the sample is then directed into a hydrophobic mixed-bed adsorbent trap maintained just above ambient temperature, at a flow rate of 50 ml/mim. Sample volume loaded onto the trap becomes a product of mass flow controller flow rate and time allowed for trapping.[6] This allows loading volumes from 5 ml to 300 ml by simply altering this time interval.

Conveniently, a multi-point calibration series can be accomplished by altering the time of sample loading and/or the sample flow rate. Table II illustrates a typical setup to perform this task. Data plotted in Figures 1-3 are generated from such a procedure.

Chromatographic Conditions for TO-15 Measurements

Scion SQ Single Quadrupole Mass Spectrometer (Scion Instruments, Austin, Tx) is used to demonstrate a very useful capability to perform accurate measurements over a very wide concentration range, using its patented Extended Dynamic Range (EDR™) feature.[7] This operation senses the level of the ion signal at the detector for every scan, and then adjusts the detector voltage and the perceived gain in order to keep the signal output at the optimum level for detection. Also, its off-access source and detector dramatically reduce signal background generated from neutrals and photons during the source ionization process. These effectively improve the performance for low level analytes with increased voltage, while still allowing larger peaks to be within the operating range and not overload the detector response by adjustment of the voltage as the scan proceeds across the top of the eluting peak. Analytical results are presented showing a concentration range approaching six orders of magnitude.

Table II. Operating Settings for Generation of Multi-Point Calibration Levels

Calibration Level	Working Standard (nmol/mol)	Dilution Factor	Sampling Time (minutes)	Sample Loading Volume (ml)	Standard Concentration (nmol/mol)	Dynamic Range
1	0.01	30	0.2	10	0.000333	1
2	0.01	12	0.5	25	0.000833	2.5
3	0.1	60	0.1	5	0.00167	5
4	0.1	30	0.2	10	0.00333	10
5	0.01	2	3	150	0.005	16.7
6	0.1	6	0.5	25	0.0167	50
7	0.1	2	3	150	0.05	167
8	0.1	1	6	300	0.1	333
9	1	3	1	50	0.33	1,000
10	1	2	3	150	0.5	1,667
11	1	1	6	300	1	3,333
12	10	3	1	50	3.33	10,000
13	10	2	3	150	5	16,667
14	10	1	6	300	10	33,333
15	100	0.5	3	150	50	166,667
16	100	1	6	300	100	333,333

Analytical measurements are performed with a Scion 456 Gas Chromatograph (GC) equipped with a Scion SQ Prime Mass Spectrometer (MS). Results are computed and reported using Scion MS Workstation Version 8.2. This GC/MS system is modified by Lotus Consulting (Long Beach, Ca) into Air Scion to perform conventional canister sampling, and automated, online measurements of ambient air, landfill gas and digester gas streams, with provisions for sampling from Tedlar bags. A multi-position stream selector valve is included to provide automated, unattended switching between sample, blank and standard streams. To prevent possible condensation of analytes in the interconnecting lines after the sample attachment, all lines are heated to a minimum of 90 ºC. Valving is accomplished with Valco series C_WE valves, with universal electric actuators (Valco Instruments, Houston, Tx). Mass flow controlled loading of typically 300 ml sample is set up to dose into a multi-bed, hydrophobic adsorbent trap held initially at near ambient temperature. Water, methane, carbon dioxide and carbon monoxide are allowed to pass on through to vent. After the sample is loaded and flushed with nitrogen, the contents are passed on to a cryofocus trap to reduce the effective analyte concentration. This trap contents are isolated while the cryofocus trap heated up. Then the full trap contents are injected into the analytical column.

Concentrator Parameters

Adsorbent Trap: multi-layer hydrophobic mixed bed
    Initial Temperature: +55 °C, hold 9.10 minutes
    Temperature Ramp: +200 °C/min
    Temperature: +202 °C, hold 51.30 minutes

Cryofocus Trap: 90 µl empty trapping
    Initial Temperature: +79 °C, hold 2.60 minutes
    Temperature Ramp: -200 °C/min
    Temperature: -146 °C, hold 8.10 minutes
    Temperature Ramp: +200 °C/min
    Temperature: +202 °C, hold 48.40 minutes

Trapping time: variable as needed from 0.1 min. to 6 min.

Mass Flow Controller Flow Rate: 50 ml/min

Water (150 µL) is added to all evacuated canisters to generate a final relative humidity level inside of about 30%, to deactivate polar surfaces inside the canister and to preserve target analytes, especially polar ones.

Internal Standards

Compounds: Bromochloromethane, Chlorobenzene-d5, 1,4-Difluorobenzene

Source: Restek (Bellefonte, Pa), P/N 34408, 1 µmol/mol each compound

Concentration: 100 nmol/mol (10 times dilution of 1 µmol/mol) loaded with a 1 ml loop, 0.333 nmol/mol with sample volume of 300 ml.

Column Conditions

Column: Restek, Rxi-5Sil MS, 30 m, 0.32 mm ID, 1 µ film

Column Flow: 2.0 ml/min with EFC Type 25, constant flow mode, splitless, no splitter installed

Column Temperature Program:
    Initial Temperature: +50 °C, hold 0.00 minutes
    Temperature Ramp: -100 °C/minute to 0 °C, hold 11.10 minutes
    Temperature Ramp: 5 °C/minute to +50 °C, hold 0.00 minutes
    Temperature Ramp: 8 °C/minute to +150 °C, hold 0.00 minutes
    Temperature Ramp: 25 °C/minute to +220 °C, hold 0.10 minutes

Mass Spectrometer

Source: EI
Filament Emission Current: 80 µA
Electron Energy: -70 eV
Source Temperature: 200 °C
Transfer Line Temperature: 170 °C
Manifold Temperature: 40 °C
Selected Ions Monitoring (SIM)
Extended Dynamic Range (EDR™) activated

RESULTS AND DISCUSSIONS

Toluene is selected in the discussion to be representative of the full range of analytes targets in this examination of an ability to achieve a very wide dynamic concentration range. “Toluene is believed to be the most prevalent hydrocarbon in the troposphere. Its dispersion is largely dependent upon meteorological conditions and its atmospheric reactivity. Reaction with hydroxyl radicals in the troposphere represents the principal mechanism by which toluene is removed. In winter, the lifetime of toluene can be several months; in summer, several days. Together with other emitted pollutants associated with smog production, toluene may contribute significantly to the causation of smog.”[8] As toluene is very pervasive in our atmosphere, special efforts are presented to minimize contributions from blanks and analytical interferences in achieving measurement of low concentrations in samples. These assessments make toluene an important target for this evaluation.

Figure 1. Cartesian Calibration Plot for Toluene

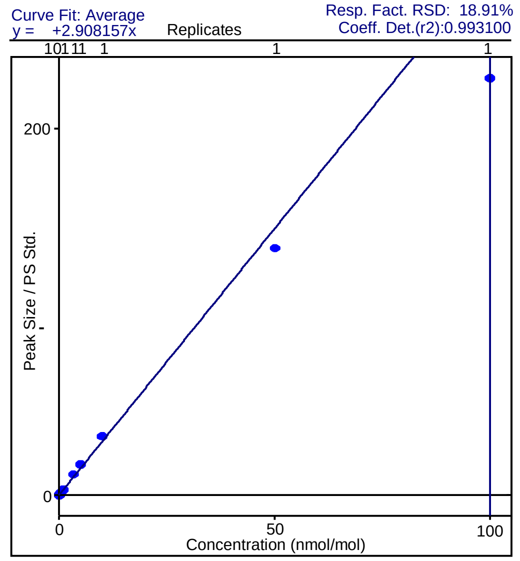
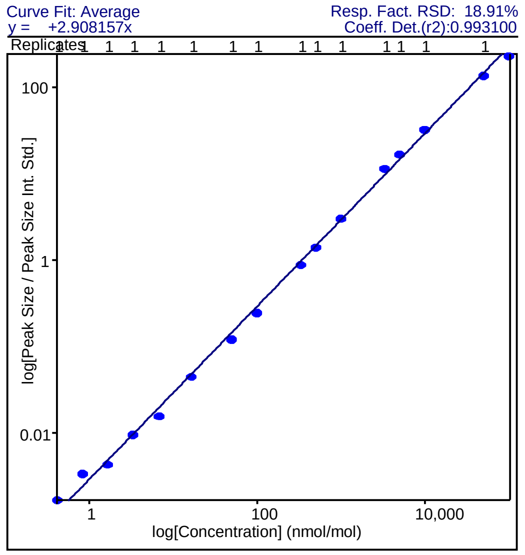


Figure 2. log-log Calibration Plot for Toluene



Conventional Cartesian (x-y) plots of area versus concentration (Figure 1), normally employed with most data workstations, work well with very narrow concentration ranges, but suffer in adequate display of low concentrations when the concentration range is over a factor of 100, especially when using 16 calibration levels. An available display of log[area] versus log[concentration] (Figure 2) provides better visibility of the calibration points over a larger range, but variations from the average response factor remain hard to discern. Table III lists deviations for each calibration point from linearity for data displayed in Figures 1 and 2. These variations are not obvious from these displayed plots.

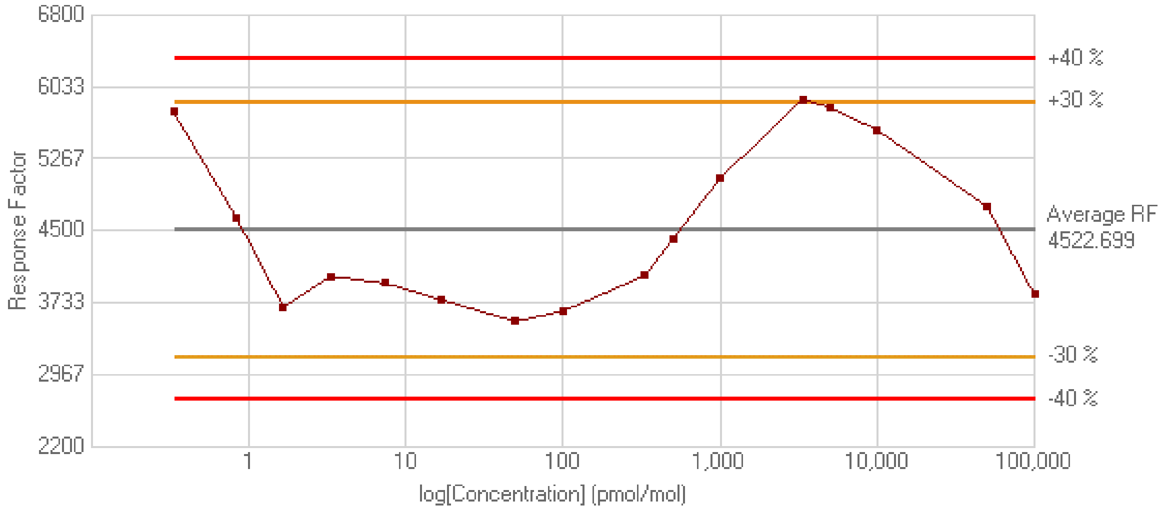
Table III. Deviations from Linearity for Calibration Plot for Toluene

Concentration Level (nmol/mol)	% Deviation	Concentration Level (nmol/mol)	% Deviation
0.00033	+27.42	0.33	-11.02
0.00083	+2.72	0.5	-2.44
0.00167	-18.49	1	+11.92
0.0033	-11.21	3.33	**+30.49**
0.005	-12.85	5	+28.54
0.012	-16.67	10	+23.21
0.05	-21.83	50	+5.71
0.1	-19.39	100	-15.55

A better approach for handling very wide concentration ranges is to plot response factors for each level versus log[concentration] (Figure 3). Perfect linearity is demonstrated by "constant" response factors over a given concentration range. This presentation permits concentrations over many orders of magnitude to be plotted, along with an indication of linearity over the range, visually displayed over huge concentration ranges demonstrated by consistent response factors. It shows how well the data fits into a target tolerance band. A special program, RF Plots (Lotus Consulting, Long Beach, Ca), has been developed to automatically generate these plots from operations in the data collection and processing.

Figure 3 displays a plot of relative response factors versus log[concentration] for toluene, covering a range from 0.33 pmol/mol to 100 nmol/mol, for a dynamic range of in excess of 333,333. This plot allows easy visualization of deviations from linearity over a very wide concentration range. Only one point (3.33 nmol/mol) exceeds to 30% guideline, but is within the tolerance for one deviate point under 40%.

Figure 3. Calibration Plot of Relative Response Factor versus log[Concentration] for Toluene.



The EPA Method TO15 protocol specifies that an acceptable range must possess a relative standard deviation for response factors over the proposed concentration range of less than 30% for each analyte, with two exceptions to 40%.[9] When response factor results are displayed in this new graph style and most of the response factors are consistent with each other, the computation of relative response factor tolerance can allow a wildly deviate value and still remain within the tight method criterion. A display of response factors versus log[concentration] readily demonstrates concentration levels that fit within the requirement, and clearly indicates levels that do not fit consistency. The Lotus Consulting RF Plots program allows the operator to manually opt out of levels that are wildly deviate from the requisite requirements, and recomputes and displays the new average response factors. The dynamic range becomes very easily defined from these plots. This new average response value can then be manually entered into the appropriate calibration table in the Workstation method to then compute the correct results for unknowns over the newly defined linear range. Figures 4 and 5 illustrate the ability of the Extended Dynamic Range (EDR) in the Scion SQ Mass Spectrometer to accurately measure a very wide dynamic range, from fmol/mol to nmol/mol, or over 300,000, without altering operating conditions.

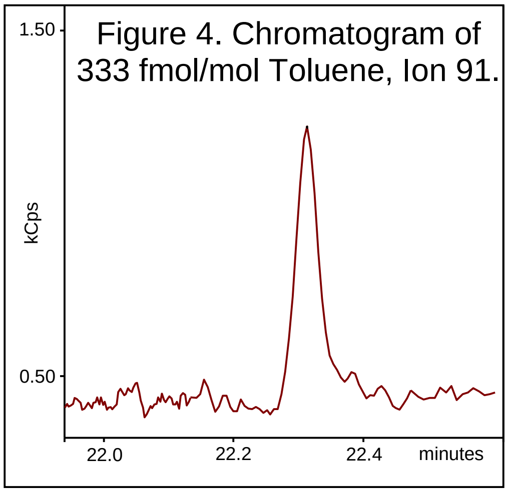


Figure 4. Chromatogram of 333 fmol/mol Toluene, Ion 91.

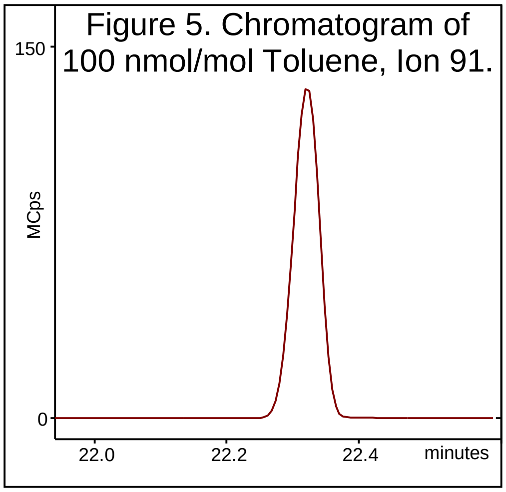


Figure 5. Chromatogram of 100 nmol/mol Toluene, Ion 91.

Blanks

Modern spectrometers can now readily measure trace analytes into the fmol/mol concentration range. This level puts a major stress on achieving very clean method blanks with the background adding to the analyte peak count and yielding inaccurate concentrations, due to severe deviations from linearity at the low end. Extreme efforts are required to eliminate all target compounds from every supply gas needed for the instrumentation, including high purity supply gases (>99.9999%), nitrogen purge supplied from headspace liquid nitrogen, chromatographic-grade stainless steel tubing for supply gases,[10] appropriate in-line filters, cryo-cleansing of purge flows, disuse of liquid “leak detector”, and filtering of outgassing of polymer materials evolved from pneumatic controllers. Another contamination source involves cleanliness of canisters, with often acetone, hexane and diethyl ether being pervasive, even after thorough cleaning processes. New canisters must be dedicated to low level measurements. And the workspace for these air measurements must remain well isolated from any exposure to solvents, especially ones involving solvent extractions, to keep these solvent vapors at an extremely low ambient concentration, especially around sample processing, including instrumentation.

A common practice is to add 150 µL of liquid water into empty six-liter standard and sample canisters, after careful cleaning, to provide a thin layer of water on possible active sites inside the canisters and prevent retention of polar analytes on the inside surface. This addition effectively creates a relative humidity of about 30% inside the canister at 25 °C and one atmosphere. Even after these measures are undertaken, careful checks on all canisters is required to ensure that blanks come up with minimal contributions of low level analytes from blanks and system components, such as unswept volumes, active sites in traps and interconnecting tubing, polymeric surfaces in contact with sample, and native backgrounds from columns, especially from contaminant releases from repetitive temperature cycling.

Figure 6 illustrates typical performance of a very clean system for toluene. Sample is generated from headspace of liquid nitrogen. Detected concentration is equivalent to <0.088 pmol/mol.

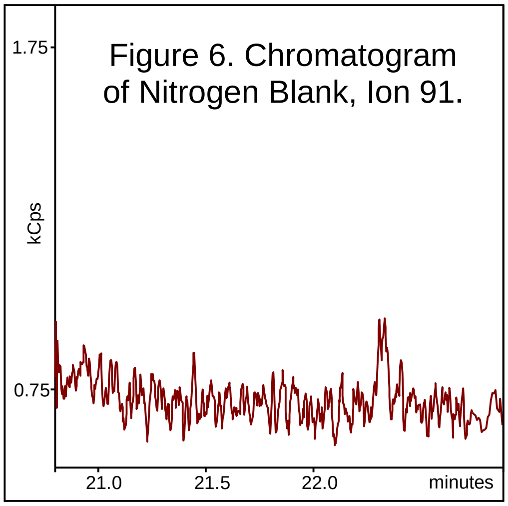
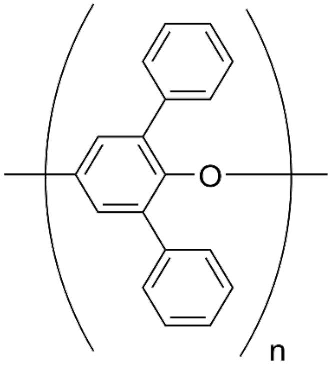


Figure 6. Chromatogram of Nitrogen Blank, Ion 91.

Tenax Adsorbent Trap Material

Tenax TA has been used as a common adsorbent for trapping organics during the concentrating steps in the sample loading process. This material (structure shown in Figure 7) is a manufactured polymer to provide effective trapping material for a wide range of target analytes. However, this material readily degrades from repetitive temperature cycling, releasing breakdown products of benzene and toluene by cleaving off phenyl groups from the polymer backbone. This effect increases in concentrations with repetitive use. Figure 8 illustrates typical results after nine repetitive temperature cycles, showing an added contamination to toluene measurements, typically near 5.8 pmol/mol. This level severely limits the ability to properly measure concentrations under 20 pmol/mol.

Figure 7. Chemical Structure of Tenax TA.[11]



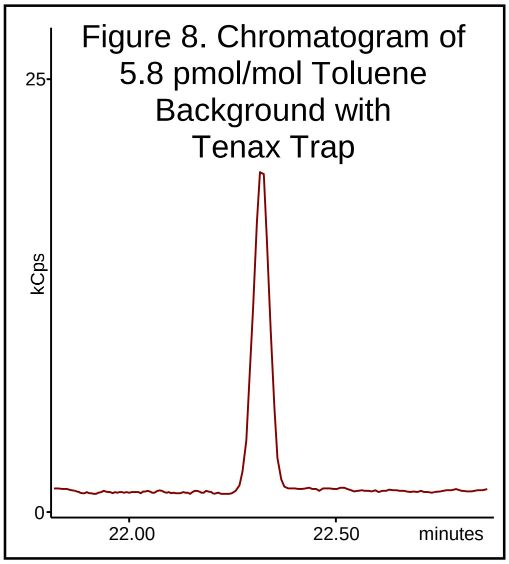


Figure 8. Chromatogram of 5.8 pmol/mol Toluene Background with Tenax Trap

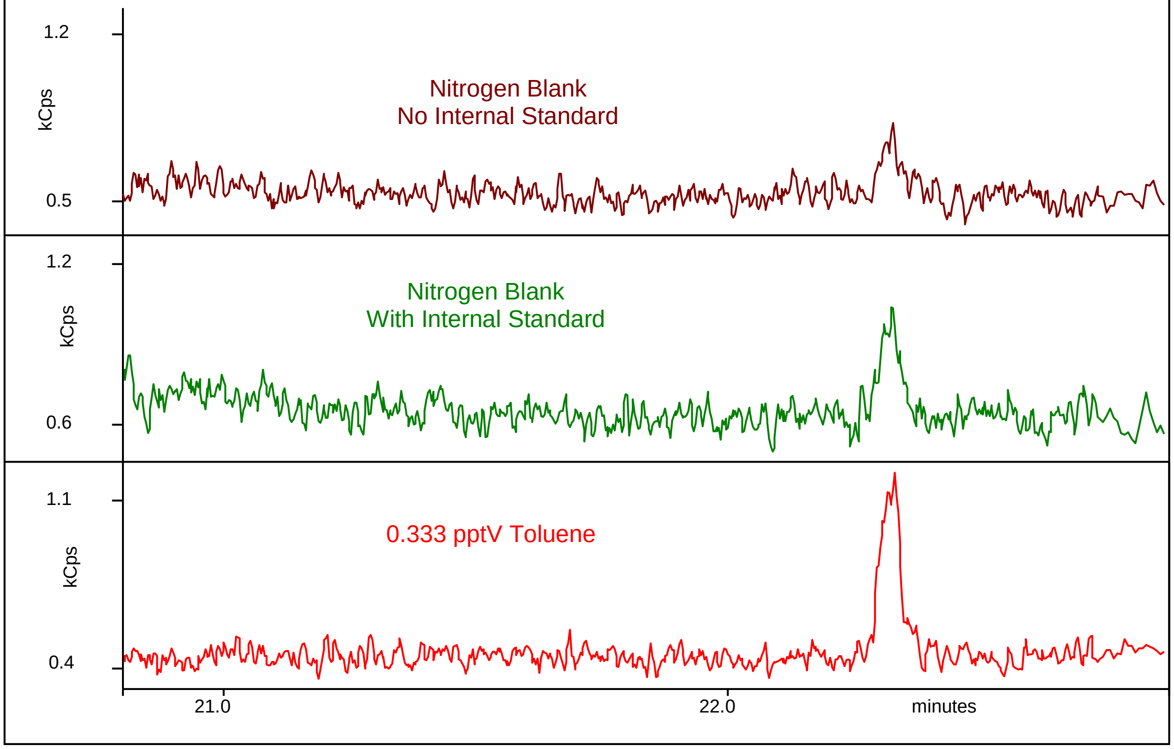
Better hydrophobic adsorbent trapping material is use of a multi-bed carbon-based adsorbents in a trap. These materials allow a wide temperature range and do not suffer from discharge of contamination byproducts. All other results reported here use these adsorbents.

Impurities in Internal Standards

The primary purpose of internal standards in this measurement is to correct for variations in responses with the mass spectrometer.[12] Internal standards must be pure, especially free of target compounds. Top performing TO-15 systems are now capable of measuring target analytes from below 1 pmol/mol V/V to well in excess 100 nmol/mol - a linear range in excess of 100,000.

To meet the purity mandate for internal standards, their starting materials must be pure to greater >99.9%, for internal standard concentrations of 0.333 nmol/mol. Since many of these standards end up being chemically related to many analytes, invariably some of these analytes show up as impurities in the internal standard mix and will then lead to elevated reported concentrations, especially at the lower levels. Toluene, as the target analyte with nitrogen blank runs with internal standard added (Figure 9), shows a level of contamination in the internal standard at 0.201 pmol/mol, while the nitrogen bank without addition of the internal standard mix is below 0.088 pmol/mol for toluene. This result can have a major impact on low level measurements below 3 pmol/mol. Modern spectrometers are now very stable,[11] and internal standards offer little assistance in correcting for the minimal drift realized in these instruments.

Figure 9. Chromatograms of
Nitrogen Blank with and without Internal Standard - SIM 91



Carryover

Another source for contamination causing difficulties in measuring very low levels is carryover of the previous sample to affect the next sample results. Samples often involved in this measurement can range in concentrations from low levels for ambient air studies to extremely high values for source testing, such as vapor intrusion. The measurement system used to measure the full range of sample types must be qualified to handle this wide range with minimal carryover of a high level sample disturbing results from low levels just from analytes tied up in the hardware matrix and then being released in subsequent runs. This carryover can be realized from active sites in the sample pathway and from unswept portions of the plumbing of the sample channel. An effective approach to minimize these effects is to provide continuous purge flow on nearly all pathways in the valve and trap plumbing, to keep all components in contact with sample progressively increasing in temperature, from the exit of the sample canister to the tubing injecting the final trap contents to the column. Possible cold spots, other than traps, need to be strictly avoided. Figure 10 is the first run of 100 nmol/mol Toluene to set up carryover test. Figure 11 is a nitrogen blank run directly following 100 nmol/mol, with toluene concentration reported as 48 pmol/mol. The ratio of these concentrations indicates the amount of analyte showing up in the next blank run. The result is <0.005% carryover.

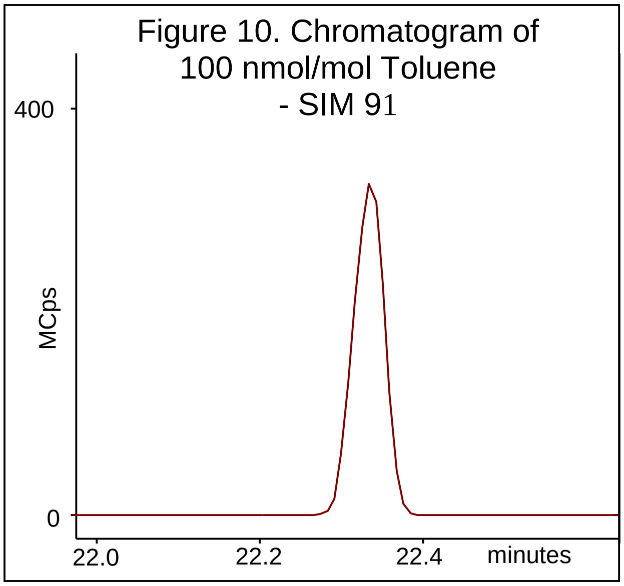


Figure 10. Chromatogram of 100 nmol/mol Toluene - SIM 91

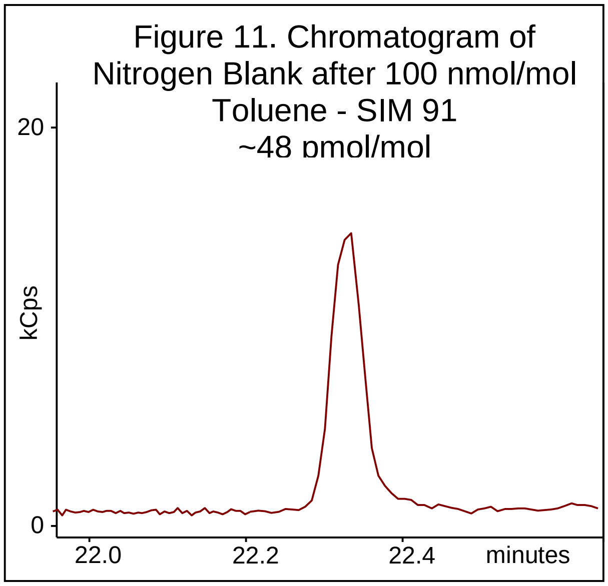


Figure 11. Chromatogram of Nitrogen Blank after 100 nmol/mol Toluene - SIM 91 ~48 pmol/mol

SUMMARY

Graphing Cartesian plots of area versus concentration puts undue visual emphasis on high concentrations, with low concentration calibration graph points bunched very tightly together near the origin. Log-log plots allow display over a very wide range, but deviations from linearity are hard to discern. Display of response factors versus log[concentration] allows an easy visual check of concentration that are within method mandates for standard protocols, even over ranges in excess of 300,000.

Intense precautions must be undertaken when setting up a system for very low level measurements of TO15 analytes, including:

- Locate all operations involved in this protocol away from all processes involving solvents, especially solvent extractions.
- Use dedicated canisters not previously utilized for higher levels.
- Perform canister cleaning of these dedicated canisters separated from others.
- Provide very high purity helium carrier gas of 99.9999%.
- Install chromatographic-grade stainless steel tubing for all supply gases.
- Hook up nitrogen supply for trap purging and blanks derived from headspace liquid nitrogen dewar.
- Install high performance filtering of supply gases, including after pneumatic components.
- Provide continual purging of all pathways, especially traps, even when flows are not in active use.
- Allow new sample to flow through sample inlet for at least one minute, bypassing the initial trap just prior to loading to flush sample line to eliminate carryover.
- Abstain from use of Tenax trapping materials.
- Verify stability of spectrometer performance and purity of Internal Standards, and then refrain from adding internal standards if target analytes appear in nitrogen blanks.

With this dramatic increase of the operating range with use of Extended Dynamic Range, vapor intrusion samples, for example, with high concentrations of 1,1,1-Trichloroethane (420 nmol/mol), can be assayed on the same analytical run as significantly lower levels of Carbon Tetrachloride (0.0095 nmol/mol) or a required concentration range in excess of 44,000. This capability dramatically reduces the requirement for sample reruns, when concentrations fall outside the limited operating concentration ranges of most conventional instrumentation.

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