

Analysis of Ethylene Oxide at Low Part-Per-Trillion Levels by GCMS Utilizing a Next Generation, Non-Cryogenic Preconcentrator with Multi-Capillary Column Traps to Reduce Background Interferences for Improved Method Detection Limits

Application Note: A-3747-01

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Abstract

The analysis of Ethylene Oxide at low part per trillion levels is demonstrated in air samples using a cryogen-free preconcentrator with improved elimination of water vapor and fixed gases relative to preconcentrators using packed trap technology. Standards were prepared in Silonite canisters at Sub-PPB levels, with an appropriate amount of CO₂ added to mimic indoor air levels (1000 PPMv). Multiple Capillary Columns of increasing strength are used in series to trap Ethylene Oxide and all other TO-15 compounds while completely removing the fixed gas background to levels not possible using packed traps to reduce mass spectral interferences at the major ions in the Ethylene Oxide mass spectrum. This creates a lower and consistently "smooth" baseline to allow the poorly responding EtO peak to be more easily resolved from instrument background levels. A calibration curve from 10 – 200 ppt is shown with %RSDs below 5%, with calculated MDLs of 3 part per trillion when running 7 replicate injections of a 20 ppt standard, demonstrating a detection limit well below most ambient air background levels of 30-80 ppt.

Introduction

Ethylene Oxide is a highly toxic chemical that increases carcinogenic, reproductive, and developmental risks even at part per trillion levels. The EPA recently increased its toxicity levels by 60x, reducing the 10⁻⁴ lifetime exposure limit to just 11 ppt, which is the new MDL levels that emerging methods should meet to allow its detection in even rural areas.



Ethylene Oxide sampling and analysis down to these low part per trillion levels has been a challenge. EtO is too light to be collected on diffusive sampling tubes, so canisters are required for sampling and laboratory analysis. Relatively short sampling times for canisters vs diffusive tubes (1 day vs 14 days) and the growth of Ethylene Oxide in many canisters over a holding period after sampling have raised concerns, although these issues are being addressed using newer canister coatings and more sophisticated canister sampling solutions.

The analysis of EtO by GCMS at low part per trillion levels reveals two primary challenges. First, the overall response of EtO is very low, and even lower than most other light, oxygenated PVOCs (Polar VOCs), requiring optimized MS sensitivity. Newer GCMS technology operating in SIM mode is typically needed to achieve a 10 ppt MDL. Secondly, the primary EtO fragment ions are also major ions for CO₂ and N₂, which are impossible to completely eliminate in the MS background. Elevated CO₂ and N₂ is a result of either incomplete removal during sample preconcentration, elevated levels in the carrier gas, or diffusion into the flow path or MS from room air through fittings, ferrules, or the Viton O-ring seal on most mass spectrometers. Although N₂ and CO₂ have little or no affinity to the sorbents used to preconcentrate samples in most preconcentrators, adsorbent particles with a mesh size of 15-100 have enough internal volume to make more than a 99.99% removal virtually impossible, simply due to statistical outgassing rates. At an outdoor concentration of 500 PPM, or 500,000 PPB, a 99.99% removal would still leave a 50 PPB injection of CO₂ into the preconcentrator. When using a packed micro trap focuser, the residual CO₂ will bleed out of the focuser during the entire 1-4 minutes injection period to create elevated CO₂ levels well past the normal CO₂ elution time, potentially overlapping with the Ethylene Oxide peak.

A different kind of sample preconcentrator is presented here that uses multiple capillary columns of increasing strength to first trap and then focus the entire range of TO-15 compounds from lightest to heaviest, with dramatically improved elimination of moisture and fixed gases relative to packed trap technology. Particles on the walls of capillary PLOT columns have up to 1000x less internal volume, allowing non-retained compounds to outgas almost instantly due to a much shorter path/distance to the surface of each particle. Dramatically improved fixed gas and moisture removal using Multi-Capillary Column Trapping was evaluated in this application note as a way to reduce interferences and improve detection limits for EtO in ambient air.

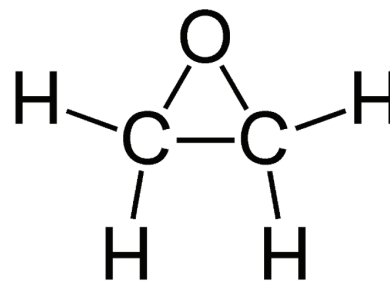


Figure 2 - Ethylene Oxide, and highly strained and reactive epoxide.

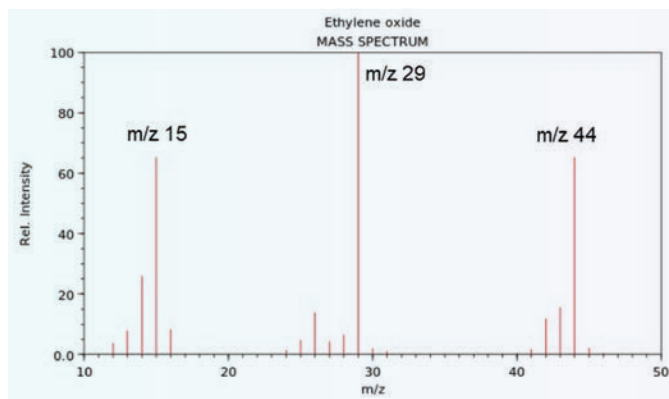


Figure 3 - The largest EtO fragment ions by EI-MS have significant interferences due to CO₂ and N₂ background and their incomplete removal from samples.

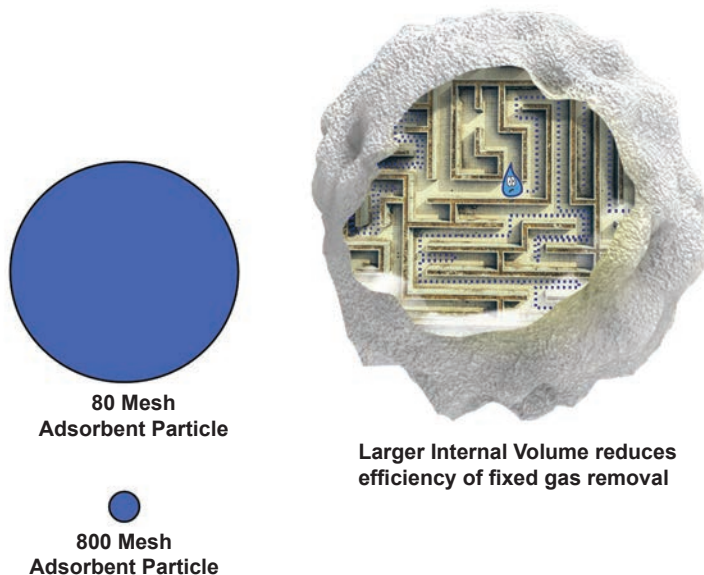


Figure 4 - Typical Packed Trap particle at 80 mesh compared to an approximate 800 mesh particle found on the walls of PLOT columns. Water, Nitrogen, and CO₂ can outgas much faster from PLOT column sized particles, improving their elimination from the sample more completely than when using packed traps.

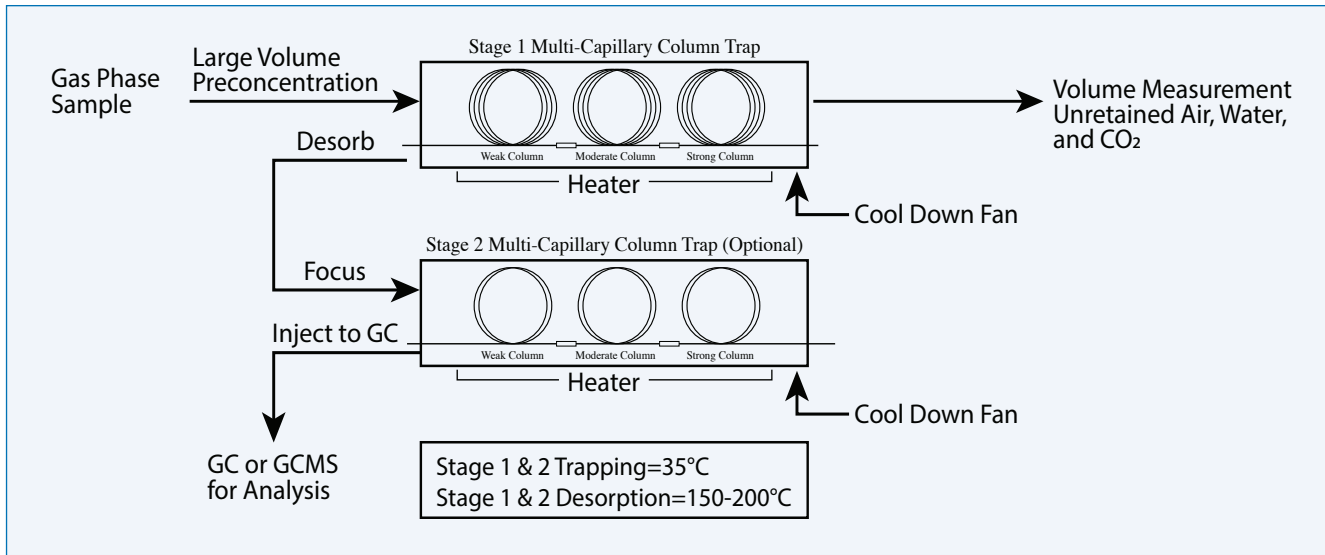


Figure 5 - 7200CTS - Multiple Capillary Traps of increasing strength are first used to trap up to 400cc of sample, followed by focusing onto a focusing version of the same trap, for fast injection into a GCMS.

Figure 5 illustrates the 7200CTS “Multi-Capillary Column Trapping System Preconcentrator” collecting a sample and subsequently focusing it for rapid injection into a GCMS. Connecting 3 GC columns of increasing strength is analogous to having a 3 sorbent bed trap with sorbents arranged weak to strong. By selecting the column strengths and lengths appropriately, a much more consistent trapping system is achieved compared to other packed trap based preconcentrators. **Figure 6** shows how the smaller particle size used in capillary traps can release Vinyl Chloride much faster to provide more narrow peaks with better S/N ratios than packed focusing traps.

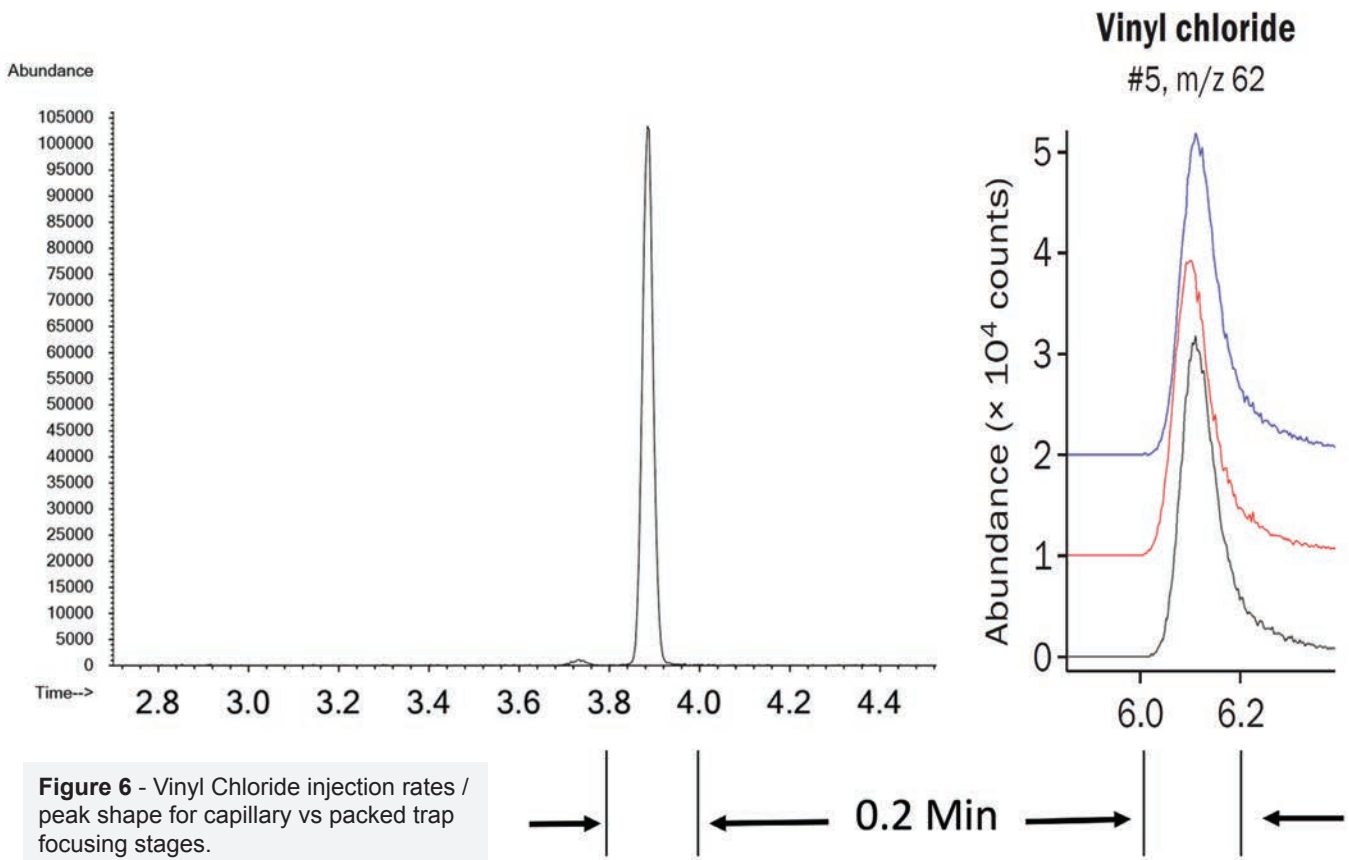


Figure 6 - Vinyl Chloride injection rates / peak shape for capillary vs packed trap focusing stages.

300cc 10ppb TO15 with 50% CO2

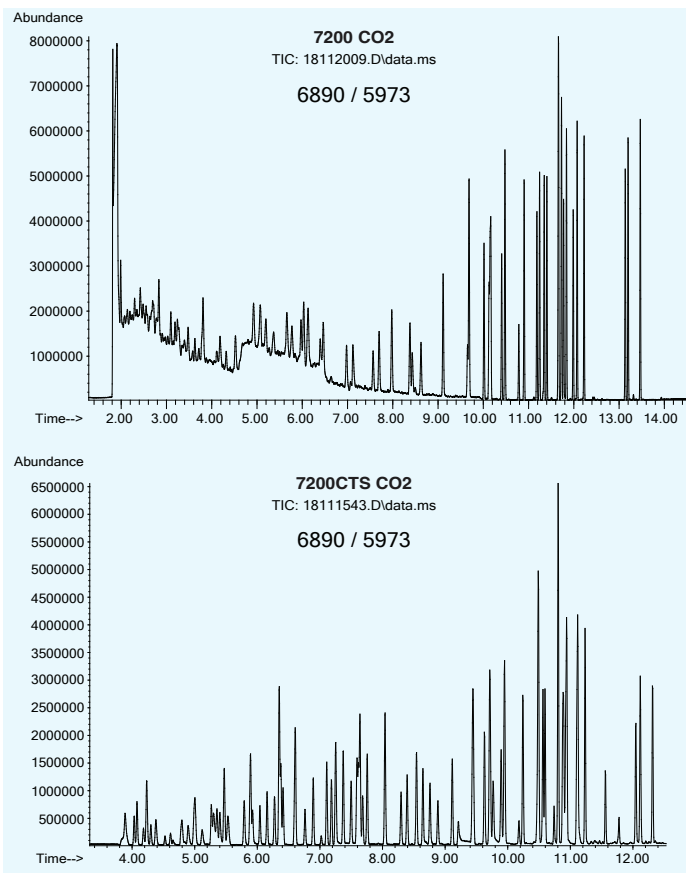


Figure 7 - 10 PPB TO-15 Standard in a 50% CO₂ Matrix analyzed using a cryogenic packed trap system (top) and the 7200CTS Capillary Trapping System (below).

A TO15 standard was prepared at 10 PPB using a 1:1 ratio of Nitrogen and Carbon Dioxide as the diluent gas. Although at ambient levels, Cold Trap Dehydration can generally remove enough CO₂ to prevent attenuation of the response of the TO-15 analytes, at a concentration of 1000x higher (50% vs 0.05%), simply too much CO₂ remains in the packed preconcentration trap. However, the substantially faster elimination of CO₂ using a Multi-Capillary Column Trapping system provides a chromatogram that looks substantially like those obtained with 100% Zero Air or Nitrogen used as the balance gas (**Figure 7**).

Figure 8 shows a TO-15 standard analyzed by GCMS in full scan mode starting at m/z 17 to include the water response. Water in air is at 10-30 million PPB (1-3%, at 30-100% RH at 25° C), and although 95% of the water was removed by CTD, a relatively large peak still exists which can reduce the GCMS response when injected sample after sample. The 7200CTS reduces water to the point where it appears like a 10 PPB level compound, resulting in zero impact on the MS response, even after repeated injections.

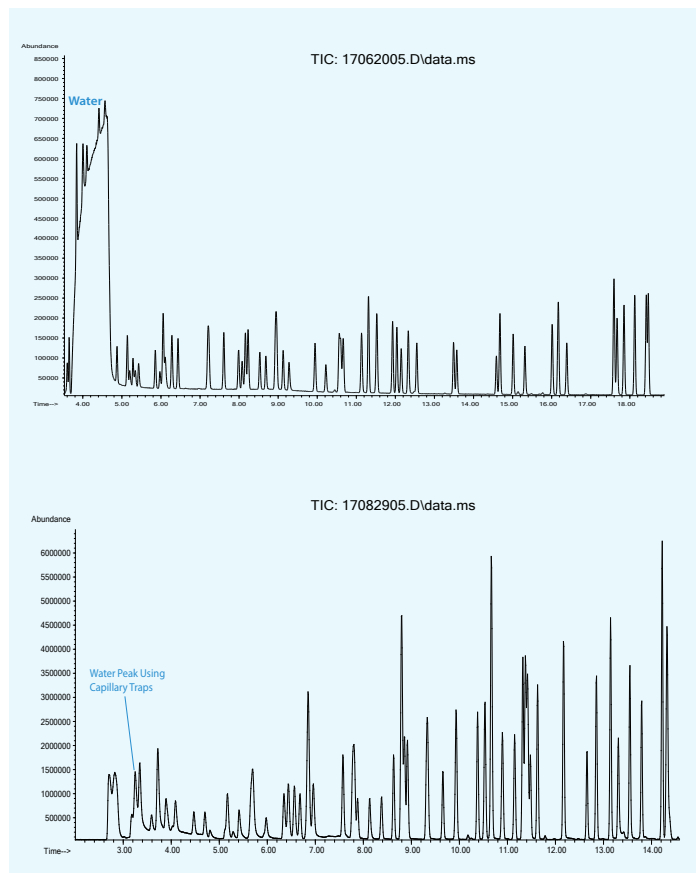


Figure 8 - Moisture Removal comparison using Cold Trap Dehydration (Top), and the 7200CTS Capillary Trapping Systems (below).

Experimental

A TO-15 standard that included Ethylene Oxide was prepared at 200 ppt using a 4700 Precision Static Diluter (Entech Instruments, Simi Valley CA). The balance gas was Zero Air, with 14.3 cc of CO₂ added to the final 35 psia standard to create a concentration of 1000 PPM in the canister, to verify how well the CO₂ could be eliminated by the 7200CTS Capillary traps to avoid interference with the Ethylene Oxide m/z 44 peak. CO₂ is nearly unretained on standard WCOT columns, but Ethylene Oxide is only retained for an extra 1-1.5 minutes typically when starting at 35° C, so nearly complete CO₂ removal is needed to achieve a flat baseline around the Ethylene Oxide peak.

The 7200CTS Preconcentrator and Silonite canisters (Entech) were used in this study. An 8890/5977B GCMS with HES source (Agilent Technologies) was used to maximize the response of Ethylene Oxide.

7200CTS Method Parameters

	Trap Temp	Preheat Temp	Desorb (°C)/Time (min)	Bake (°C)/Time (min)	Cool To Trap Temp (min)
Primary CTS Trap	35	90	140	160/5	3-4
Focusing CTS Trap	35	100	160	180	3-4
Lines/Rotary Valve	150	150	150	150	
Sample Line In	80				
GC Transfer Line	140	140	140	140	

Volume (cc)	
Internal Std	50
Calibration Std	10-500
Sample	10-500
To Focuser	30
Focuser Bakeout	60

Table 1

GCMS Method Parameters

Parameter	Specifications
Column	HP-1 60m x 0.25mm ID x 1um
Source/Quad	HES, 230° C/150° C
Tune	HES-Atune
Acquisition	SIM Low Resolution
Gain	4
Column Flow	Pressure Ramp, 0.3ml/min to 1.2ml/min

Table 2

8890 GC Oven Program

	Rate (°C/min)	Value (°C)	Hold (min)
Initial	-	35	2
Ramp 1	20	80	0
Ramp 2	10	220	0
Ramp 3	40	40	0
Post Run	40		

Table 3

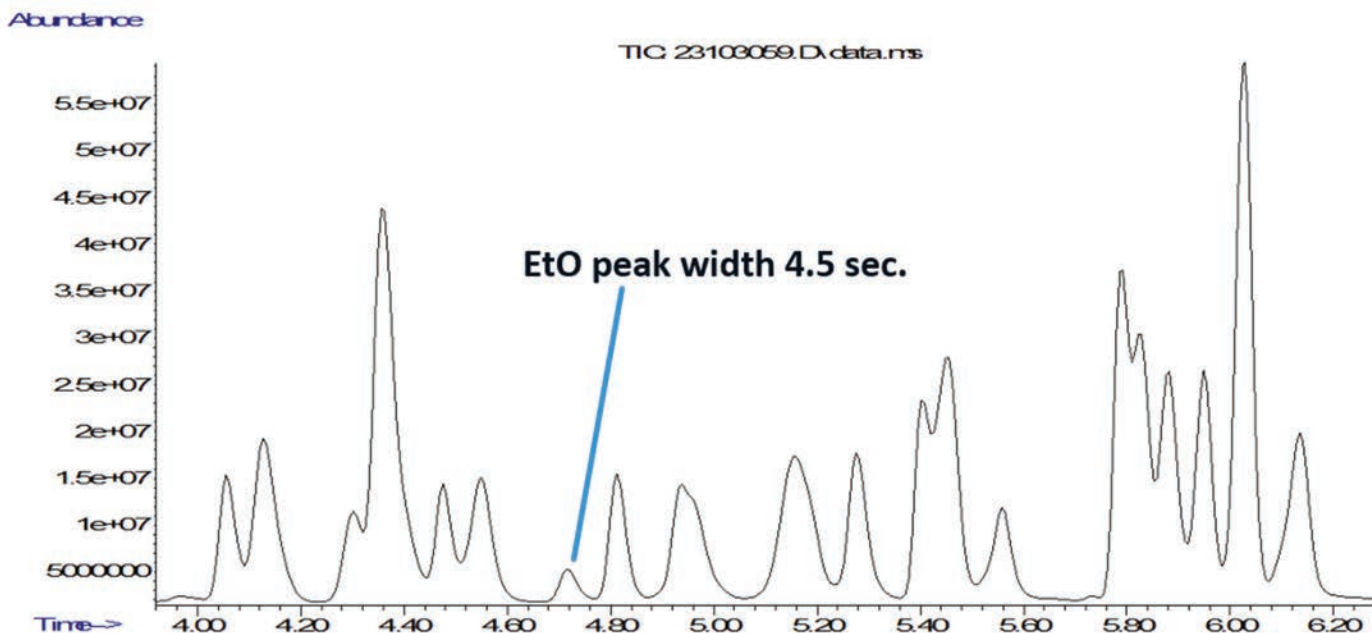


Figure 9 - Full Scan Chromatogram of a TO-15 standard containing Ethylene Oxide. The response of EtO is low relative to other VOCs, even when starting the scan at m/z 29 to include the base ion in the EtO spectrum.

Hi Performance Trapping and GC Injection Rates

When capillary GC columns were introduced, they were often referred to as “High Performance GC Columns”, because they were so superior to pack GC columns in the number of theoretical plates, and their amazing resolving power. This was the result of both a narrow ID, and a very fast equilibration rate between the gas phase and stationary phase, resulting in far less band broadening compared to packed GC columns.

The 7200CTS Capillary Trapping System brings this same level of advanced performance to VOC preconcentration systems. Narrow light end peaks, resulting from fast injection rates as shown in **Figure 9**, rival those of liquid Nitrogen focusing trap injection rates, while virtually eliminating moisture which can be problematic with systems employing cold trapping. Due to the complete elimination of CO₂ that was in the sample, there is no need to cryo-cool the GC oven to obtain greater separation of EtO from the residual CO₂ peak left by packed traps that cannot be completely purged out due to the high initial levels of CO₂ (500 PPM = 500,000 PPB). This saves on the cost of LN₂ during each analysis, and the loss of productivity when LN₂ tanks run out during unattended operation.

Fast Trap Cool Down and Lower Desorption Temps

Both the primary CTS trap and the secondary focusing trap are operated at temperatures between 35° C and 180° C, with occasional conditioning at 200° C. The low thermal mass of the traps and the large trap mandrel surface area allows trap cool down to 35° C in just 3-4 minutes, dramatically boosting throughput over electronically cooled traps that can take 20 minutes or longer in some cases to cool down.

Due to the efficiency of small particle traps, the full release of TO-15 compounds can occur at temperatures as low as 150° C, which not only places less thermal stress on the sample allowing better recovery of thermally labile compounds, but also reduces the stress on the traps themselves. These capillary columns are rated to at least 260° C, but by keeping them at lower temperatures, the lifetimes of these traps becomes substantially longer than typical packed traps. Systems operating continuously in the field are nearing 20,000 runs without needing a trap change. Actual lifetimes would depend on the sample matrix, although extreme performance for dirty soil gas samples has also been demonstrated using capillary traps.

Capillary Trap Water Management Secrets Revealed

Dry purging of multi-bed traps has been suggested as an ideal way to remove water while retaining VOCs of interest. So why hasn't this worked for the analysis of whole air samples? Preconcentration system suppliers that used to promote dry purge water management have moved to Cold Trap Dehydration systems that add extra complexity to the overall preconcentration process. So why doesn't dry purging to remove water vapor work very well when using packed traps? It has already been stated that due to the larger adsorbent particle size used in packed traps, the removal of all of the water becomes a statistical impossibility. That is, perhaps 95-97% of the water can be removed, but typically nowhere near 99% or 99.99+% as when using particles with 1000x less internal volume as found in Capillary Traps. When removing 97% of the moisture, the total water injected into the GCMS now becomes dependent on the relative humidity of the sample itself, as 97% removal of water at 9% RH yields an on-column injection of 10 times less water than when removing 97% of the water in a 90% RH sample. A water peak that is 10 times larger tends to be much broader on the GC column, thereby co-eluting with more VOCs. Water can impact the response of VOCs by as much as 30-60%, so when water levels are high, the response of some compounds may be 60% lower than when water levels in the sample are low. For Purge & Trap, humidity levels are always at 100% coming out of the sparge vessel, allowing dry purging to be a viable approach to remove at least a consistent amount of water prior to GCMS desorption, although dry purging will not eliminate the water altogether, especially when using water retaining sorbents such as Carboxens and Silica Gels.

Capillary traps are uniquely capable of using the simple dry purge water removal technique, as the water is removed so completely that even a 100% RH in a canister sample results in a low PPB size water peak on-column, which simply cannot cause any attenuation of any VOCs eluting before, with, or after the water peak. Therefore, whether the sample relative humidity is low or high, no impact on VOC response in the MS occurs.

Extra Benefits of Enhanced Moisture Elimination

In addition to eliminating any VOC response attenuation due to co-elution with water, the near elimination of water introduction into the GC and mass spectrometer has other important benefits. Injection of water run after run typically results in a decreased response in the MS throughout the day. Most EPA methods allow up to a 50% decrease in overall Internal Standard response throughout an analytical sequence, or over a certain number of samples analyzed, and if the response drops more than 50%, analyses are no longer valid, and time must be given for the mass spectrometer to pump the excess water out to restore more normal sensitivity levels. However, even if the response drops by 10-20%, method MDLs will also decrease a proportionate amount, so any drop in sensitivity will have an effect on method performance. The EPA limiting this to 50% was just their way of trying to be practical, knowing that perfect water removal wasn't possible. That is no longer the case. With capillary traps that remove virtually all of the water, no drop in MS sensitivity throughout the day is experienced. Therefore, quoted MDLs are truly those that a lab can offer for all samples analyzed, whether at the start, middle, or end of an analytical sequence.

Yet another problem with water injection into a GCMS is the creation of column bleed that in turn will dirty the source faster, requiring more source cleanings. Impact of water on most WCOT capillary columns is minimal at lower temperatures, but can cause major damage and resulting Siloxane bleed at higher temperatures. Although most of the water included in a sample injection is introduced to the GC when the GC oven is relatively cool, the zone between the GC oven and the mass spectrometer source is usually maintained at temperatures of 230° - 250° C for volatiles analysis, and this can cause major hydrolysis of the column when the water peak passes through this hot region. To make matters worse, this part of the column is under a strong vacuum, so even very heavy Siloxanes of 1000 amu or larger can bleed into the MS source, effectively sticking to lenses and other surfaces in the source, requiring more source cleanings. It's typically not VOCs that are building up as residue in the source, but rather the Siloxane bleed. Reduce the bleed, and the frequency of source cleanings can drop dramatically.

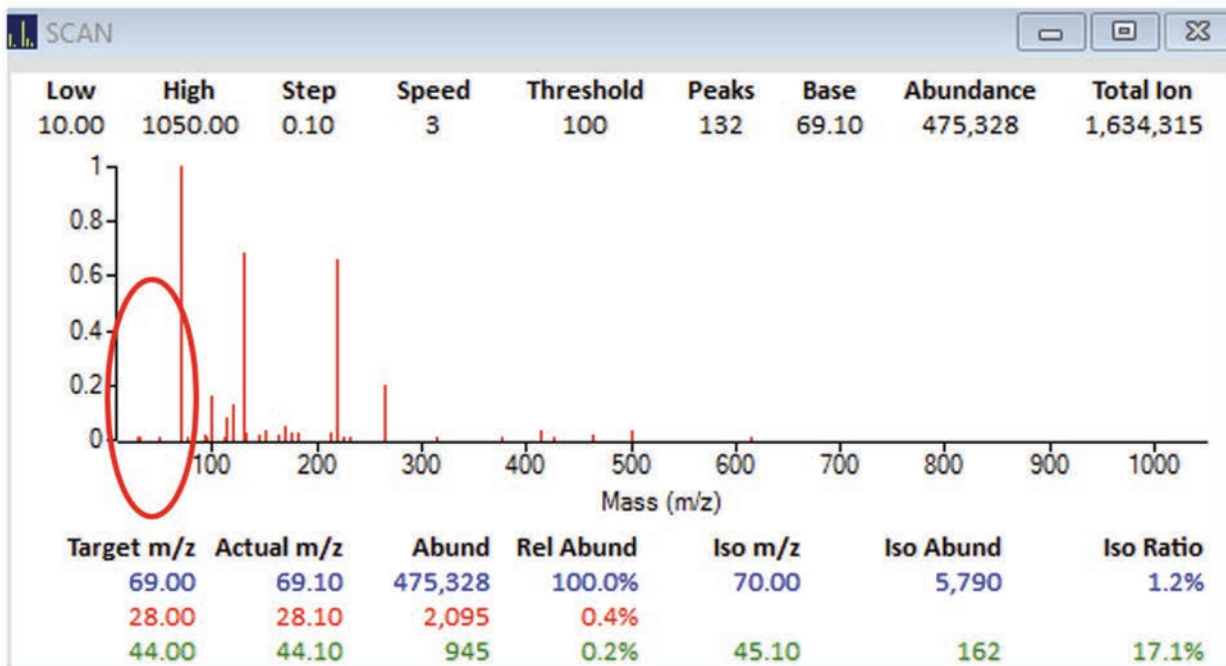


Figure 10 - Air/Water Check Performed after running 10 standard injections at 50% Relative Humidity shows no increase in water in the source.

Data For Ethylene Oxide in Air

Figure 11 shows the S/N ratio obtained for Ethylene Oxide at 20 ppt using Single Ion Monitoring to enhance the sensitivity. Although m/z 29 has the higher response, it has more interferences from light hydrocarbons, so the m/z 44 peak was selected as the quantitation ion, and 29 was used for confirmation. The retention times using the 7200CTS were virtually perfect, typically within +/-0.3 seconds or the equivalent of 1 scan duration. Combined with the narrow 4.5 second wide peaks that result from fast injection off of the capillary focusing trap, this yields a very reliable ID confirmation, making false positives less likely than with most packed trap systems. The remaining CO₂/N₂ background was not found to be coming from the air or CO₂ in the sample or standard made with Zero Air plus 0.1% CO₂ added to it, but rather due to background levels both in the carrier gas, and the trace amounts diffusing into the system. Even the large O-ring used to seal the MS source was found to contribute at least some background when capping off the GC column entrance to the source, but these background levels are relatively constant, and still allow a peak and a baseline below the peak to be determined consistently when challenging the system to a 20 ppt EtO standard.

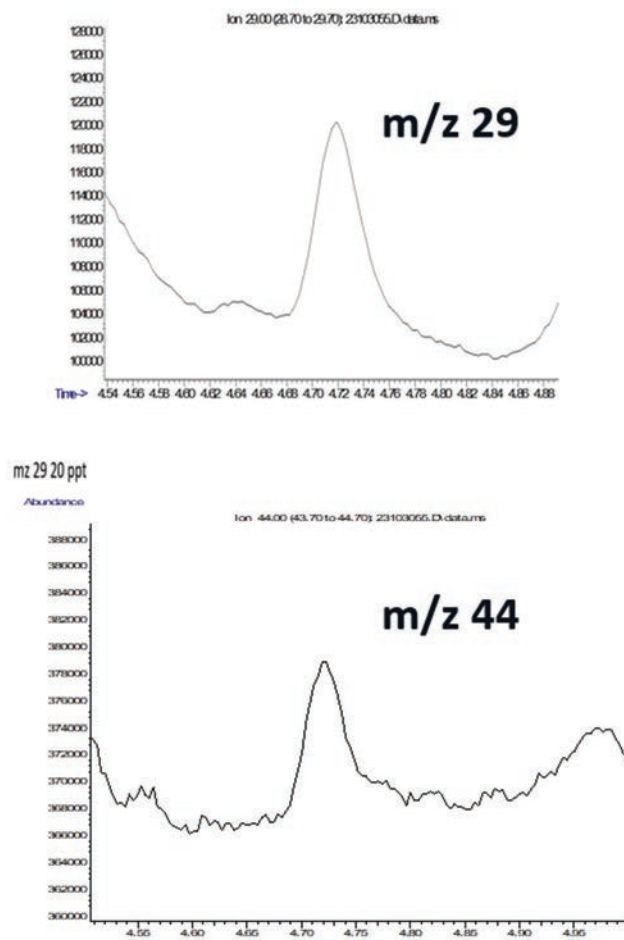


Figure 11 - 20 ppt Ethylene Oxide Standard as Concentrated from Zero Air at 50% RH, spiked with 0.1% CO₂ to create a CO₂ concentration higher than ambient air.

Calibration Files

10 =23081005.D 20 =23081007.D 50 =23081009.D 125 =23081010.D 200 =23081011.D

Compound	10	20	50	125	200	Avg	%RSD
I Bromochloromethane	-----ISTD-----						
Ethylene Oxide	1.187	1.231	1.217	1.156	1.096	1.177	4.59

Figure 12 - Calibration for Ethylene Oxide at 10-200 ppt with %RSDs less than 5%.

Calibration Linearity and EtO Detection Limits

Figure 12 shows the calibration curve results for Ethylene Oxide from 10-200 ppt. The linearity of the response is almost perfect, with a %RSD value below 5%. The maximum volume taken in this curve was 300cc, although the 7200CTS can sample up to 500cc without loss of EtO.

Method detection limits were determined by using 7 replicate runs at 20 ppt, with the results shown in Figure 13. These results were obtained from a single canister, and therefore are specifically looking at the consistency in the analysis, not in the consistency from one canister to the next. Entech is creating good progress in optimizing the Silonite coating to arrest the growth of Ethylene Oxide which has been problematic in earlier canisters from all manufacturers. Canisters that meet the TO-15A and Method 327 allowable growth rates for Ethylene Oxide and other target compounds should soon be available, thereby taking full advantage of the demonstrated performance of the 7200CTS in its ability to accurately measure even the most difficult TO-15A compounds down to low ppt levels.

Ethylene Oxide MDL (pptv)

Date Analyzed: 2308010

Analyte	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	SD	MDL
Ethylene Oxide	21.6	23.3	21.8	22.4	20.6	22.4	21	0.917813	2.882

Figure 13 - 7 Replicates at 20 ppt show a calculated MDL of less than 3 ppt, due to the very low variability of the high performance 7200CTS Capillary Trapping System. The low thermal desorption temperatures create little to no temperature induced decomposition of the relatively reactive Ethylene Oxide molecule.

Conclusion

The 7200CTS as produced since 2018 was demonstrated for its ability to measure Ethylene Oxide down to low ppt levels, meeting or exceeding the performance requirements of TO-15A and Method 327. The Capillary Trapping System (CTS) was shown to virtually eliminate the CO₂ and water vapor that would otherwise interfere with the low level detection of Ethylene Oxide and other TO-15A compounds, far better than packed trap technology. The reduction of water vapor was shown to keep water levels in the mass spectrometer below 1% relative to the m/z 69 peak from PFTBA, as demonstrated by performing an air/water check right after preconcentrating and injecting 10 standards at 50% relative humidity. The complete removal of water is expected to substantially reduce the frequency of source cleanings by reducing the column bleed resulting from the injection of water through the GC column and hot interface into the MS.

The 7200CTS supports multiple autosamplers to increase productivity, including the long standing 7016D tower autosampler, and two robotic autosamplers including the 7650A-M and the latest SkyCan Autosampler that lives above the GCMS to support the analysis of 2.5L and smaller canisters. With the ability to achieve low detection limits using only a 300cc sample size, the Next Generation TO-15A and 327 compatible canisters offer a more space-efficient and cost-effective solution compared to the conventional 6L canisters, although the canister size selected is ultimately the decision of each air analysis laboratory.



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