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Technical Report

A Tool for Selecting an Adsorbent for Thermal Desorption Applications

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There are varieties of adsorbents used in the field of thermal desorption. Often choosing the right adsorbent can be difficult. The goal in selecting the proper adsorbent is to choose one that can retain a specific or group of analytes for a specified sample volume. However, just as important the adsorbent must also be able to release the analyte(s) during the desorption process. This report sheds some light on choosing the right adsorbent by demonstrating the relative differences between those most commonly used. Some of the adsorbents investigated in this research were Tenax TA®, Carbotraps™, Carboxens™, Carbosieve™, charcoals, and glass beads. The test probe for this research was a gas mix containing forty-three different analytes whose physical properties ranged from 50 to 260 in molecular weight and -30 to 215°C in boiling point. The analytes in this mixture are a subset of the EPA Hazardous Pollutant list. EPA method TO-17 is the typical method you use to sample these analytes. We introduced this gas mixture to each of the adsorbents using the flash vaporization technique and then challenged each with various sampling volumes ranging from 0.2 to 100 liters. We thermally desorbed each of the adsorbents into a GC/MSD system.

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Introduction

Our goal in performing this research was to develop a simple and easy to use tool for thermal desorption users. This "tool" demonstrates the relative difference between the adsorbents based on their capability to efficiently retain and release an analyte when challenged with various sample volumes. Several other conditions such as sampling flow rate, storage conditions, and the relative humidity of the sampled air can all influence the ability of an adsorbent to retain an analyte during the sampling process. This research covers only the sample volume aspect.

The challenge we posed to each of the adsorbents was to spike a known quantity of a test mix onto the adsorbents. Then challenge the adsorbent by subjecting it to a constant flow of clean nitrogen until we obtained the desired volume. We then thermally desorbed the adsorbents into a GC system to determine what analytes remained (recovered) on the adsorbent after it we subjected it to the challenge volume. This was repeated for six different volumes of nitrogen.

An analogy that depicts the challenge posed by this research is that of packed column chromatography. For this, we pack the adsorbent into a coiled column; we apply a carrier gas to carry the analytes from the injection port through the column to the detector at the opposite end. Essentially the same concepts exist here when sampling with a thermal desorption tube. The adsorbent is packed into an empty thermal desorption tube (very small column). The carrier gas for this research was nitrogen, but in the real world, it would be air. The Adsorbent Tube Injector serves as the injection port to introduce the gas mix into the nitrogen gas stream. The analytes migrate through the adsorbent bed where at some point in time, some of the analytes break-through whereas, others are retained by the adsorbent. Instead of having a detector at the end of the tube to analyze what broke-through, this research looks at what analytes the adsorbent retained. Thermal desorption of the tube releases the analytes in the GC/ MS system for detection.

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Experimental Details

Adsorbents Tested

We tested twenty-four different adsorbents. Carboxen(s), Carbosieve S-III, and Carbopack(s) are exclusive to Supelco and have been used in the field of thermal desorption and purge and trap for years. We also chose adsorbents such as Tenax, silica gel, and glass beads because of their traditional use in the field of thermal desorption. Porapak®, Chromosorb® and HayeSep® are also used in some thermal desorption applications. Coconut and petroleum charcoal predominately have been used for solvent desorption applications, but some uses of these materials do exist in thermal desorption applications.

For this research, only one lot per adsorbent was tested. **Table 1** shows the list of adsorbents tested and the physical properties of the adsorbents such as the mesh size, packing density, and bed weights.

Analytes Used as the Test Probe

The analytes chosen as test probes for this research are a subset of the EPA Hazardous Pollutant list, and are also common to many industrial hygiene sampling methods. We used a gas mix containing the 43 analytes listed in **Table 2**. This mix contained a broad spectrum of volatile organic analytes with physical properties that range from (50 to 260) in molecular weight, and (-30 to 215°C) in boiling point. The gas mix is available as a Supelco stock product Catalog #500429. The concentration of each analyte in the gas mix is 1000ppb. We introduced a 20 milliliter undiluted volume of this gas mix to each adsorbent. (**Table 2** shows the calculated mass of each analyte contained in the 20mL volume).

We chose the gas mix for several reasons. First, the analytes are in the gas phase to simulate a real world sample. Second, if we had used a liquid solvent mix, such as methanol, it could alter the results because it too may occupy the pore sites of the adsorbent. This could create a competition for sorption sites with the analytes of the test mix. Third, the use of a solvent would interfere in the detection of the very volatile analytes. This is due to the chromatographic conditions that we chose to optimize the transfer of the analytes to the capillary column.

Analytical Equipment

Thermal Desorber

GERSTEL® loaned the thermal desorption unit used in this study to Supelco. The GERSTEL TDS A, shown in **Figure 1,** provided the means to automate the analysis of the adsorbents. The TDS A interfaces with the GERSTEL CIS4 Inlet that serves as the cryo-focusing trap for the desorption of the adsorbents.

Figure 1. GERSTEL TDS A Coupled to a HP6890GC/5973MSD

Cryo-Focusing Trap

The GERSTEL CIS 4 inlet was used to re-focus the analytes desorbed from the adsorbents. The injection port liner of the inlet contained two different materials to facilitate the retention of the very volatile analytes in the test mix. We used liquid nitrogen to cool the inlet liner to -150°C during the desorption of the adsorbent tubes. We desorbed the inlet at 350°C. We used a standard inlet liner (available from GERSTEL GC07540 10) and packed the inlet with the following adsorbents:

- Carbotrap C 20/40 mesh: 10mm bed length (25 milligrams)
- Glass Beads 60 mesh: 6mm bed length (25 milligrams)

This inlet configuration was determined after we performed several experiments to optimize the chromatography of the gas mix. **Figure 2** shoes an example of the chromatography achieved with this set-up. (Notice the resolution of the first five analytes).

Figure 2. The Results of the Test Gas Desorbed from a Carbotrap 300

The large CO₂ is concentrated onto the refocusing trap during the process of the TDS A loading the adsorbent tube into the desorber oven.

Gas Chromatograph

Supelco used a Hewlett Packard 6890 GC with a 5973 mass selective detector (Turbo Pump System) for the study. The capillary column was a 60 meter x 0.25mm ID, 3.0µm film SPB-1 column.

Other Equipment Used

- Supelco's prototype "Adsorbent Tube Injector System" served as the device to transfer the gas mix onto the adsorbent packed tubes.
- Dynatherm Model 60 Six-Tube Conditioner served as a means to condition the packed adsorbent tubes. A second unit served as a way to control the flow rate through multiple tubes simultaneously for the following volume challenges: 1, 2, 5, 10, 20, and 100 liters.
- Mettler Balance model AE100 served as a way to determine the actual bed-weights of each packed adsorbent tube.

Table 3 shows the operating conditions for the equipment.

Table 1. Physical Properties of Adsorbents

Packing density differs from free-fall density for it takes into account the particle to ID relationship of the specific inside diameter of the glass tube to the shape and mesh size of the adsorbent material. These values were determined from the actual lot number of the adsorbents tested in this research. The packing density can be used to calculate the approximate bed weight in a given volume of a 4-millimeter ID tube.

Sequence of Events

Preparation of the Adsorbents

We packed each of the adsorbents into a 4mm ID x 6mm OD x 178mm fritted glass tube, based on a fixed volume of 0.5cc. We constructed a 0.5cc vessel by cutting a 3.7cm length of tubing from a representative empty glass tube. We packed the adsorbent into the vessel and vibrated it to assure we obtained a consistent volume of the adsorbent. We then poured the contents of the 0.5cc vessel into the empty tube. We inserted a small plug of untreated glass wool on top of the adsorbent bed along with a small stainless steel clip to provide additional support to keep the adsorbent in place. We thermally conditioned each of the packed adsorbent tubes for eight hours with a continuous flow of clean nitrogen. **Figure 3** illustrates the packed adsorbent tube. **Table 1** lists the actual bed weights of each tube and the conditioning temperatures used for each adsorbent. Further details on our tube packing procedure can be found in the Questions & Answers section.

Table 3. Operating Conditions

GERSTEL TDS A Parameters

GERSTEL CIS-4 Inlet Parameters

Cryo-Focusing Trap CIS-4 Inlet Liner (Physical Data)

Figure 3. Drawing of the Packed Adsorbent Tube Depicting the Bed Length of Each Adsorbent

HP-6890 GC Parameters Oven Program

Capillary Column: 60 meter x 0.25mm ID, 3.0µm film SPB-1 (Available from Supelco as a custom product).

HP-5973 MSD

Adsorbent Tube Injector System

Setting Up the Challenge Volume

The study looked at six different challenge volumes: 0.2, 1, 5, 10, 20, and 100 Liters. The 0.2-Liter volume simulates the small sample volume used in most purge and trap applications. The 1, 5 and 10 Liter volumes are typical sample volumes used in thermal desorption applications (1,2). The higher volumes of 20, and 100-Liters were chosen for two reasons. First, it will provide users additional information if they need to use larger sample volumes to increase detection limits by increasing their sample size (volume). Second, you can use these larger sample volumes to differentiate one adsorbent from another. An example of this would be a user that needs to obtain a 10 liter sample of analyte X. He/she can use the performance charts to compare the adsorbents and choose the one that has good recoveries that extend into 20 or 100-Liter range. By choosing the adsorbent that has capabilities beyond the desired sample volume, the user can safely assume they have chosen the appropriate adsorbent. **Table 4** shows the challenge volume parameters used in this research. The challenge flow rate of 0.05 Liter/min was constant.

Table 4. The Challenge Volume Parameters

Challenge Volume (Liters)	Challenged Flow Rate (Liters/min)	Challenge Time (hours)
0.2L	0.05 L/min	4 min
1L	0.05 L/min	20 min
5L	0.05 L/min	100 min (1 hr 40 min)
10 _L	0.05 L/min	200 min (3 hr 20 min)
20L	0.05 L/min	400 min (6 hr 40 min)
100L	0.05 L/min	2000 min (33 hr 20 min)

The Analysis Matrix

With twenty-four different adsorbents to test, six different volumes for each adsorbent, and two desorptions of the same adsorbent, this matrix adds up to over 288 analysis excluding calibration and blank tubes. To minimize the effect of storage time on recovery, we conducted the analysis and prepping of the tubes in five series, as shown in **Figure 4**. This reduced the effect of storage time, since the analysis of the first tube to the last tube spanned less than 5 hours.

Spiking the Test Gas Mix on the Tubes

We introduced the 43 analyte gas mix onto each adsorbent packed tube by using the technique of flash vaporization. This was conducted by using a prototype device developed by Supelco that is presently named the "Adsorbent Tube Injector System" (See **Figure 5**). This device incorporates a Swagelok® union fitted with vespel/graphite ferrules that connected the inlet of the tube to a glass injection chamber fitted with a septa port. A block of aluminum surrounds the glass injection chamber. This transfers the heat of the Multi-Blok® Heater to the glassware. A continuous flow of clean nitrogen sweeps the injection chamber. We maintained the nitrogen flow rate for this research at 0.05L/ min using a constant flow controller.

A 20mL syringe volume of the undiluted 43-analyte gas mix was injected into the septum port of the glassware while nitrogen swept the test mix onto the inlet of the tube that was at ambient temperature. After 4 minutes had elapsed, we removed the tube. The 0.2 Liter volume of nitrogen was enough to completely sweep the test mix onto the adsorbent contained in the tube.

Figure 4. The Analysis Matrix

However, for the other five volumes studied, we physically removed the tubes from the Adsorbent Tube Injector and placed them into one of the six-ports of a Dynatherm tube conditioner.

We chose the Dynatherm Six-tube conditioner to provide the rest of the challenge volumes. The Six-tube conditioner has six individual ports that the flow rate can be controlled independently (See **Figure 6**). Each of the flow ports were set to deliver 0.05L/ min. (Only the pneumatic section of this device was used, at all times during the challenge volume the packed adsorbent tubes remained at ambient lab temperatures).

Figure 6. Dynatherm Six-Tube Conditioner with the Tubes In-Place During the Volume Challenge

This freed up the Adsorbent Tube Injector to spike the next tube of the series by using the Dynatherm conditioner. After the desired challenge volume had elapsed, the tubes were removed and loaded into the TDS A thermal desorber. A sequence was set to analyze the tubes overnight. We analyzed each tube independently, and the results compared to a calibration curve.

Calibration Procedures for the Analytical System

It was not feasible to make syringe injections of liquid or gas standards directly onto the column for two reasons. First, the transfer line of the GERSTEL TDS A connects directly to the inlet by a fitting that replaces the septum port. Second, the large volume of the test mix could not be injected quantitatively. It is not practical to inject a 20mL syringe volume of the test gas directly on to a capillary column without altering the flow dynamics of the GC system.

Therefore, the model we chose to determine the recovery was to spike the same 20mL syringe volume of the test mix onto a multibed Carbotrap 300 using the same technique as performed in the previous section. The gas mix was swept onto the Carbotrap 300 tube with a total volume of 0.2 Liters using with the Adsorbent Tube Injector. This was enough volume to sweep the entire gas mix onto the tube, but would not pose a challenge to the combined adsorbents of this multi-bed tube. With such a small sample transfer volume (200mL), no loss of any analyte was expected. We assumed 100% recovery from the Carbotrap 300. **Figure 7** illustrates the flow direction we used to sample and desorb the collected analytes.

Figure 7. Picture of the Carbotrap 300 Tube Used for the Calibration

Constructing the Calibration Curve

Six analytical runs made up the single-point curve for each series. For each challenge volume (set) a Carbotrap 300 tube was spiked with the same 20mL syringe volume of the test mix and analyzed along with the adsorbents of that series. We copied the actual responses from the analysis directly into Microsoft® Excel. We set up a spreadsheet template to perform all the recovery calculations. We averaged the analyte responses from these six calibration runs and divided them by 100 to calculate the average response factor for each analyte. We then considered the response factors as the model of 100% percent recovered. We created a separate calibration curve for each series of adsorbents tested. This procedure reduced the effect of detector drift over time, since the completion of the research took several months.

Calculating the Recovery of the First Desorption

We divided the analyte response from each adsorbent by the average response factor derived from the calibration curve (above) and multiplied it by 100%. The result was the percent recovered from the adsorbent.

We identified the analytes using the primary and secondary quantitation ions of each analyte. The primary ion was used to determine the area response of each analyte. (See **Table 2** for the primary and secondary ions used in this research.)

Calculating the Recovery of the Second Desorption

Each adsorbent tube was re-desorbed at the same temperature immediately following the primary desorption of each series of adsorbents. If we found any of the analytes from the test, then the recovery was determined. This information is important because if the analyte(s) can not be efficiently released from the adsorbent during the primary desorption then either the analyte is too strongly adsorbed or irreversibly adsorbed. The difference is that "too strongly adsorbed "means that adsorbent retains the analytes to the point that they are not efficiently released from the adsorbent during desorption and a portion of it can be observed in the second analysis. Where as, "irreversible adsorption" indicates the analyte can not be released from the adsorbent, and is not observed in the second analysis.

Regardless of whether the adsorbent retains the analyte too strongly or irreversibly adsorbs it; the user should choose a different adsorbent for that analyte. In an effort to help users choose the right adsorbent the performance charts include this (*) symbol next to the analyte name if we observed more than 5% of that analyte in the second analysis. This allows users to quickly observe which analytes they should not sample with certain adsorbents.

Results: How to Use the Charts

To simplify the use of the reams of data generated by this research we developed a simple scheme so users can visually see the recovery based on color rather than comparing multiple columns of numbers. We used the analogy of a traffic signal to display the results. The performance charts are color-coded, with **Green** indicating the recovery is greater than or equal to 80%. The **Yellow** indicates the recovery is between 21 and 79%. **Red** indicates the recovery is less than or equal to 20%. Using the feature of "conditional formatting" in the Excel program, we displayed the raw data by color instead of displaying the actual

values. This concept makes it easier to compare the adsorbents when you view the charts together.

Recoveries of 80% or greater are typically considered acceptable in most thermal desorption methods. Recoveries between 21 and 79% indicates a significant amount of the analyte was recovered from the adsorbent, but warns the user that breakthrough occurred or that the analyte is too strongly retained. A recovery of less than 20% is simply not suitable for any sampling application.

The performance charts allow the user to see the relative differences between the adsorbents and assists them in choosing an adsorbent that will retain the analytes of interest at a specific volume. You can also use these charts to choose a combination of adsorbents to construct a multi-bed tube, which can retain a wide range of analytes. The performance charts illustrate that no one single adsorbent can retain and release the entire list of analytes.

The best way to use the performance charts is to look for the trends of green color for the analytes of interest. As seen in the example chart below, the recoveries of most of the very volatile analytes are good. As the challenge volume increases, some of the recoveries decreased due to the analytes breaking through the adsorbent. In respect to this example (Carboxen-1000), when sampling for analytes that have higher boiling points, greater than Benzene, you should use a weaker adsorbent bed in front of this adsorbent. This is because the analytes are either too strongly adsorbed (denoted by the asterisk * symbol), or irreversibly adsorbed

General Guidelines for Interpreting the Trends

- You should use the performance charts as a quideline when choosing an adsorbent.
- We list the analytes by their retention order from an SPB-1 capillary column. They are in the order of their boiling point, with the exception of Acrylonitrile and 1,2-Dichloroethane. (**See Table 2**)
- The adsorbents were desorbed at their maximum desorption temperature. (**See Table 1**)
- You should consider the effects of water when choosing an adsorbent, since we based this research on the challenge of dry nitrogen.

Observing the Trend Left to Right - Across the Rows: (Increased volume per analyte)

Starting at the 0.2-Liter volume, looking at one analyte:

- 1. If the row is solid Green across all six volumes then this adsorbent is a good choice for this analyte.
- 2. If the row starts Green and changes to Yellow and/or Red, then the analyte is breaking through the adsorbent. Note: When sampling, maintain a sample volume within the green limits.
- 3. If the row is Yellow or Red Choose another adsorbent.

Observing the Trend Top to Bottom - Down the Columns: (Increased Boiling-point per analyte)

Starting at the 0.2-Liter volume, looking at one volume:

If the chart is green at the top and changes to Yellow, and/or Red– then the adsorbent is capable of efficiently retaining and releasing the analytes with low boiling points. As the boiling point of the analytes increase, they become too strongly adsorbed (as indicated by the * symbol or are irreversibly adsorbed). The Carboxen(s) are a good example of this trend). Always place a weaker bed of adsorbent in front of this type of adsorbent to keep these analytes from reaching this adsorbent.

If the chart is Red and/or Yellow at the top and changes to Greenthen the adsorbent is capable of efficiently retaining and releasing the analytes with higher boiling points. As the boiling point of the analytes decrease, they begin to break-through the adsorbent. The Carbopack(s) and Porous Polymers are a good example of this trend. Place a stronger adsorbent behind this type of adsorbent to retain and release the low boilers.

Using the Charts to Design a Multi-Bed Tube

You can use the data from the charts to construct a multi-bed adsorbent tube. As the data illustrates there is no one adsorbent that will both retain and release the entire list of analytes. You can construct a multi-bed tube by placing a weaker adsorbent at the inlet followed by a stronger adsorbent. You can create two, three and four bed tubes. You can tailor the adsorbent configuration for the sampling application. The Carboxen(s)/Carbosieve S-III should always be used along with a weaker adsorbent if the environment to be sampled contains higher boiling point analytes.

You can use a single or multi-bed tube packed with a Carbopack or a Porous Polymer and not include Carboxen(s)/Carbosieve, allowing the low boiling analytes to pass through the tube. For example, in many cases when using a liquid standard, it is often desirable to allow the solvent (i.e. Methanol) to pass through the adsorbent while the higher boiling point analytes are retained.

The example below illustrates the trend to look for when designing a multi-bed tube. In this example, the goal is to choose a combination of three adsorbents that can retain the entire list of 43 analytes for a sample volume up to a 1-Liter. The large gray X(s) indicate those analytes that are retained by the absorbent bed that precede it. The black arrows illustrate those analytes that break-through the first bed, and are then retained by the second bed. Note, one of the analytes (indicated by black) actually break-through the second bed and is retained by the last bed. The gray arrows illustrate those analytes that break-through the second bed and are retained by the third (last) bed. The dotted black line denotes the 1-Liter volume**.**

Discussion of Results

The following comments are valid with respect to the analytes and conditions we used in this research. The comments may not hold true for other analytes and/or testing conditions.

General Observations on Carboxen Adsorbents

As expected the recovery was poor for those analytes with boiling points higher than Benzene. This is because the Carboxen(s) have small pores designed specifically to retain and release only the analytes with low boiling points. The Carboxen(s) should always be used with a weaker adsorbent bed placed in front. A bed of one or more of the Carbopack(s) or a Porous Polymer can be used so the higher boiling point analytes are kept from getting in contact with Carboxen.

In the actual analysis, both Carbon Dioxide and Sulfur Dioxide were observed in most of the Carboxen adsorbent analyses (no Sulfur Dioxide was observed from the Carboxen-1016 or 1018). This is common to most carbon molecular sieves, and does not present a problem unless the user is trying to sample for these two analytes.

Carboxen-1016 is a newly developed adsorbent by Supelco that demonstrates excellent performance across both a wide range of analytes and sample volumes. This can be observed by reviewing its performance chart. It is a good candidate for numerous thermal desorption applications.

The recoveries of Trichloroethane were high (greater than 145%) for Carboxen-1000, 1002, 1003. This was most likely due to the dehydrohalogenation of 1,1,2,2-Tetrachloroethane. The corresponding recovery of 1,1,2,2-Tetrachloroethane from these same Carboxens was very low (less than10%). This situation would not occur if a multi-bed tube was used because a weaker adsorbent is placed in front of the Carboxen when sampling atmospheres containing 1,1,2,2-Tetrachloroethane.

General Observations on the Carbosieve S-III

It appears that the Carbosieve S-III performance was worse than other carbon molecular sieves. The pore shape of the Carbosieve is different from the Carboxens. Carbosieves have closed pores that may have been blocked by the analytes with high boiling points. This could have prevented some of the low boiling point analytes from reaching the available pore sites. Like the Carboxens, Carbosieve S-III must have a weaker bed of adsorbent, such as one of the Carbopacks or Porous Polymer, placed in front, to prevent the analytes with high boiling points from reaching the pores of this adsorbent during sampling. Carbosieve S-III also releases Carbon Dioxide during desorption, but not Sulfur Dioxide.

General Observations on the Carbopack Adsorbents

The performance charts illustrate the increasing strengths of the Carbopacks with Carbopack F being the weakest, followed by C, Y, B, and X in order of increasing strength. The range of the F, C, and Y would extend into higher boiling point analytes not investigated by this research. The recovery of the very volatile analytes from the Carbopack X extends beyond that of Carbopack B. The recovery of 1,3-Butadiene from Carbopack X extended well into 20-Liter challenge volume. This is significant because no other adsorbent in this research performed so well with this analyte. The Carbopack X closes the gap between the other Carbopack(s) and the Carboxen(s)/Carbosieve S-III in respect to its ability to

retain the analytes across the challenge volumes. However, Carbopack X should have a weaker adsorbent bed placed in front of it when sampling analytes with very high boiling points. All of the Carbopack(s) are virtually hydrophobic and are good choices when sampling in an environment where high humidity exists.

General Observations on the Porous Polymers

None of the porous polymers could retain the very volatile analytes. Both Tenax TA and Tenax GR performed well for those analytes that had boiling points higher than Benzene. The capabilities of Tenax TA and Tenax GR can be broadened if a bed of Carboxen is place after the Tenax.

The Porapak N, Chromosorb 106, and HayeSep D all showed similar patterns with the recoveries of the mid to higher boilingpoint analytes. The background generated from these adsorbents caused problems with obtaining clean blanks. The analytical system had to be baked out to reduce the contamination level between each analysis.

General Observation on the Charcoals

It is common knowledge that charcoal itself is not a good adsorbent for thermal desorption for several reasons. The adsorptive strength of charcoal can be too strong and heat alone does not always cause the release of the analytes. This was apparent in this research. First, the recoveries of almost all the analytes from the first desorption were poor with the exception of a few very volatile analytes. Second, a significant amount of the analytes was also observed from the second re-desorption of the tube. The same trend was seen on both the coconut and petroleum based charcoals. However, there are applications where charcoal is and can be used as an adsorbent bed in multitube, to retain and release the very volatile analytes such as, Halocarbon 12 and Chloromethane.

General Observations on Silica Gel

Silica gel showed fair recovery of the very volatile analytes at the 0.2-Liter challenge. Silica gel should also have a weaker adsorbent bed placed in front of it when sampling analytes with high boiling points. Silica gel may have applications where Carbon Dioxide would interfere in the analysis of the very volatile analytes, since no Carbon Dioxide was observed in the analysis.

General Observations on Glass Beads

As expected the glass beads do not have the ability to retain many analytes. They have applications if used as the first bed in a multi-bed tube to prevent very high boilers to come in contact with a stronger adsorbent.

Conclusion

The result of this research provides the users of our adsorbents and thermal desorption tubes with a new tool for choosing an adsorbent(s) for their application. By using the colored performance charts, one can compare and choose an adsorbent or construct a multi-bed tube for a specific range of analytes across various sample volumes. There is no one adsorbent available that can both retain and release all the analytes. However, there is clear evidence that some of our new adsorbents such as, Carbopack X and Carboxen-1016 will benefit the field of thermal desorption.

Questions & Answers

Why were the adsorbents packed by bed-volume versus bed-weight?

Because the density range of the adsorbents tested varied significantly, packing the adsorbents at the same bed-weight was not feasible. For example, if we would have packed the adsorbents all at the same bed-weights, some of the adsorbents would have extended past the heated zone of the thermal desorber. Other tubes would have had too little adsorbent in the tube for the tests. The actual bed-weights and mesh size of each adsorbent can be seen in **Table 1**. The advantage of packing the tube by bed-volume for this research is that the bed-length of 3.7cm occupies about half of the average heated- zone of most thermal desorbers. This allows at least two different adsorbents to be packed in most thermal desorption tubes. By using the same bed-volume of adsorbent as conducted in this research, the user can expect similar performance from the adsorbents by using the colored charts.

What mesh size were the adsorbents?

The mesh size of the adsorbent ranged from 20/40 mesh to 60/80 mesh. It is virtually impossible to acquire the adsorbents all at one mesh size.

Why was nitrogen used instead of air to challenge the tubes?

Nitrogen was used because of its purity compared to compressed air. If compressed air would have been used the adsorbents would have concentrated the slightest contaminants. Also there is a significant amount of water in most air systems, which would have required extensive efforts to reduce the moisture content.

Why was 50mL/min chosen as the sampling flow rate?

The flow rate used during the challenges remained constant at 50mL/min. The US EPA TO-1 method (3) recommends that the linear flow velocity through an adsorbent tube be 50-500cm/ minute. Using Equation 1, the calculated linear velocity through a 4mm sampling tubes used in this study was 398cm/min).

Equation 1

What does a 20mL syringe volume of the 1000ppb gas mix relate to in a real world sample?

The table below illustrates what the ppb concentration of the 20mL syringe volume would represent based on if the contents were released into the corresponding volumes. Example: If the 20mL syringe volume of the 1000ppb test gas mix were released into a 5-Liter sealed volume, the concentration of the gas mix would be diluted to 4ppb.

Were any test analytes retained on the glass frit at the inlet of each tube?

No, not any of these analytes. We tested this by spiking the gas mix on to the empty fritted glass tubes and analyzed them right away. No significant quantity of any analyte was detected

Why was an Internal Standard not used?

An internal standard could not be used, because no one or group of analytes could have been retained on all the adsorbents. For example, there were only a few analytes retained on the glass beads. So if we had used a high boiling point analyte for the glass beads, the same analyte would not have been released from the Carboxen(s)/Carbosieve S-III. A separate internal standard would have been needed for each of the adsorbents, thus making the use of this technique not very helpful.

How can we assume 100% recovery from the Carbotrap 300 used for the calibration?

For this research, all we could do was assume 100% recovery. Other models could have been researched, but the important thing to keep in mind that performance charts are meant to illustrate the relative difference between the various adsorbents. We do not attempt to say the recoveries are absolute.

Could the desorption temperature have an affect on recovery?

Yes, the desorption temperature could have both positive and negative affects on recovery. For this research, our attempt was to choose the highest temperature typically used.

What is the difference between Carbopacks and Carbotrap?

The only difference is the mesh size of the adsorbents. Carbotraps are 20/40 mesh, and Carbopacks are 40/60 mesh or smaller. The performance charts can also be used in comparing the Carbotrap adsorbents.

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- 3. Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air EPA TO-1 Determination of VOCs in Ambient Air Using Tenax Adsorption and GC/MS page TO-1 thru 9

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Patents

Carbosieve Adsorbent — German Patent No 1935500. Patent Holder — Badishe Anilin-&Soda-Fabrik Aktiengesellschaft.

Carboxen-564 Adsorbent — US pat. No. 4,839,331

Trademarks

Celite Corp. - Chromosorb Crawford Fitting Co. - Swagelok Enka Research Institute Arhem - Tenax Gerstel GmbH - GERSTEL Hayes Separations Inc. - HayeSep Lab-Line - Multi-Blok Microsoft Corporation - Excel Sigma-Aldrich - Carbopack, Carbotrap, Carboxen Waters Associates. Inc. - Porapak

Carbopack F

(Graphitized Carbon Black) Surface Area: $5 \frac{m^2}{g}$ **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

Carbopack C

(Graphitized Carbon Black) Surface Area: 10 m^2/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

Carbopack Y

(Graphitized Carbon Black) Surface Area: 24 m^2/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

Carbopack B

(Graphitized Carbon Black) Surface Area: 100 m² /g Desorption Temperature: 330 °C

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

Carbopack X

(Graphitized Carbon Black) Surface Area: 240 m² /g Desorption Temperature: 330 °C

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

(Carbon Molecular Sieve) Surface Area: 510 m² /g Desorption Temperature: 330 °C

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

SSUPELCO

(Carbon Molecular Sieve) Surface Area: 400 m² /g Desorption Temperature: 330 °C

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

(Carbon Molecular Sieve) Surface Area: 485 m²/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

SSUPELCO

Not Recommended: Recovery is less than 20% ** indicates this analyte was strongly adsorbed*

(Carbon Molecular Sieve) Surface Area: 1200 m² /g Desorption Temperature: 330 °C

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79% **Not Recommended:** Recovery is less than 20% **SSUPELCO**

(Carbon Molecular Sieve) Surface Area: 500 m²/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

SSUPELCO

Not Recommended: Recovery is less than 20% ** indicates this analyte was strongly adsorbed*

(Carbon Molecular Sieve) Surface Area: 1100 m²/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79% **Not Recommended:** Recovery is less than 20%

(Carbon Molecular Sieve) Surface Area: 1000 m²/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79% **Not Recommended:** Recovery is less than 20%

(Carbon Molecular Sieve) Surface Area: 75 m²/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

SSUPELCO

Not Recommended: Recovery is less than 20% ** indicates this analyte was strongly adsorbed*

(Carbon Molecular Sieve) Surface Area: 700 m²/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79% **Not Recommended:** Recovery is less than 20%

Carbosieve S-III

(Carbon Molecular Sieve) Surface Area: 820 m²/g **Desorption Temperature: 330 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79% **Not Recommended:** Recovery is less than 20%

TENAX TA

(Polymer) Surface Area: 35 m²/g **Desorption Temperature: 300 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

TENAX GR

(Polymer) Surface Area: 24 m²/g **Desorption Temperature: 300 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

SSUPELCO

Not Recommended: Recovery is less than 20% ** indicates this analyte was strongly adsorbed*

Chromosorb 106

(Polymer) Surface Area: 750 m²/g **Desorption Temperature: 180 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

SSUPELCO

Porapak N

(Polymer) Surface Area: 300 m²/g **Desorption Temperature: 180 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

HayeSep D

(Polymer) Surface Area: 795 m²/g **Desorption Temperature: 180 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

Glass Beads

Surface Area: <5 m² /g Desorption Temperature: 330 °C

Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79% **Not Recommended:** Recovery is less than 20% **SSUPELCO**

Silica Gel

Surface Area: 750 m²/g **Desorption Temperature: 180 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20% ** indicates this analyte was strongly adsorbed*

Coconut Charcoal

Surface Area: 1070 m²/g **Desorption Temperature: 180 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79% **Not Recommended:** Recovery is less than 20%

Petroleum Charcoal

Surface Area: 1050 m²/g **Desorption Temperature: 180 °C**

Performance Key

Safe to use: Recovery is greater than 80% **Caution:** Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

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