VOLUME 1
July 1996

SIS Thermal Desorption Newsletter

For Users of Thermal Desorption Equipment

FEATURES

Comparison of Injection Techniques for Volatile Organics.. 4

CONTENTS

Information Available on the WEB

- **SPTD System**
- **Cryo-Trap**
- **Application Notes**
- **Adsorbent Resin break through volume data**

Scientific Instrument Services is pleased to introduce its new thermal desorption newsletter designed to meet the needs of its existing customer base as well as to attract potentially new customers. This newsletter, approximately 8 pages in size, will be published twice a year. Several sections are planned and we are open to additional new ideas based on your input. There will be at least one feature article per edition as well as a New Products section and a Thermal Desorption Tips section.

If you have any further suggestions or comments about the content or format of this newsletter we would be glad to hear from you.

SIS is also excited about its own new web site. Explore the latest techniques in Thermal Desorption in addition to numerous application notes and technical bulletins. Also find information on breakthrough volumes on adsorbent resins, the new TD-4 System and the new Micro Cryo-Trap.

Since SIS began our WEB pages in September of last year the response has been outstanding. Our pages on the Internet continue to receive expanded usage by our customer base. We have been quite pleased with the response by our customers and the new leads that this advertising medium has generated.

Visit us at the Eastern Analytical Symposium in Somerset, NJ Nov. 18-21, 1996.

SIS Presentations at EAS 1996

1. **Thermal Desorption Instrumentation for Characterization of Odors and Flavors** - Monday 11:20 am
   Oral Presentation Author: John J. Manura

2. **A New Micro Cryo-Trap for the Trapping of Volatiles at the Front of a GC Column** - Tuesday
   Poster Presenting Author: John J. Manura

3. **Selection of Thermal Desorption and Cryo-Trap Parameters in the Analysis of Teas** - Tuesday
   Poster Presenting Author: John J. Manura

4. **Evaluation of Septa Using a Direct Thermal Extraction Technique** - Tuesday - Poster Presenting Author: Santford V. Overton

5. **Identification of Volatile Organic Compounds in Office Products** - Tuesday - Poster Presenting Author: Santford V. Overton

6. **Seasonal Variation in Flower Volatiles** -
   Tuesday - Poster Presenting Author: Santford V. Overton

Scientific Instrument Services, Inc. *1027 Old York Road* *Ringoes, NJ 08551* *(908) 788-5550*

New Products

New Short Path Thermal Desorption Model TD-4

The new Model TD-4 Short Path Thermal Desorption system was specifically designed to fit the top of the redesigned Hewlett Packard Model 6890 Gas Chromatograph. In addition the electronics console will operate the new Micro Cryo-Trap (see page 7). All other features of this system are identical to the Model TD-3 Short Path Thermal Desorption system. The Model TD-4 is recommended primarily for use on the HP 6890 GC and where the user wishes to use the Micro Cryo-Trap. The Model TD-3 is recommended for other models of Gas Chromatographs and where the 4" GC Cryo-Trap is preferred.

Both models of the Short Path Thermal Desorption System are designed for mounting on top of the GC injection port to desorb volatiles from adsorbent resin traps or from solid matrix samples directly into the GC injection port. This 'short path' for sample delivery results in elimination of 'memory effects' common in other desorption systems and it also results in higher sensitivity and enables the detection of higher molecular weight analytes from your samples.

For additional details visit our WEB site or give us a call and we will send you more information.

Part No.	Description	Price
784000	SPTD-TD-4	$9500.00

Tenax TA Breakthrough Volume Chart

This new handy wall chart can help guide you through the determination of the adsorption and desorption properties of Tenax TA for use with your thermal desorption applications. This chart is the result of more than 6 months of work in which more than 200 organic compounds were analyzed at 20 degree temperature intervals from 0°C to 300°C.

The Breakthrough Volumes are listed in Liters of air per gram of Tenax TA resin. The chart is color coded with Breakthrough Volumes less the 0.010 Liters (10 milliliters) indicated in red and Breakthrough Volumes greater the 10 Liters indicated in blue. This makes it easy to determine the gas volume which can be passed through the Tenax TA resin bed and retain specified analytes at a particular temperature as well as the temperature required to elute or desorb a particular range of organics off the Tenax TA resin during the thermal desorption process.

Tenax™ TA poster available free with the purchase of 10 grams of Tenax ™TA.

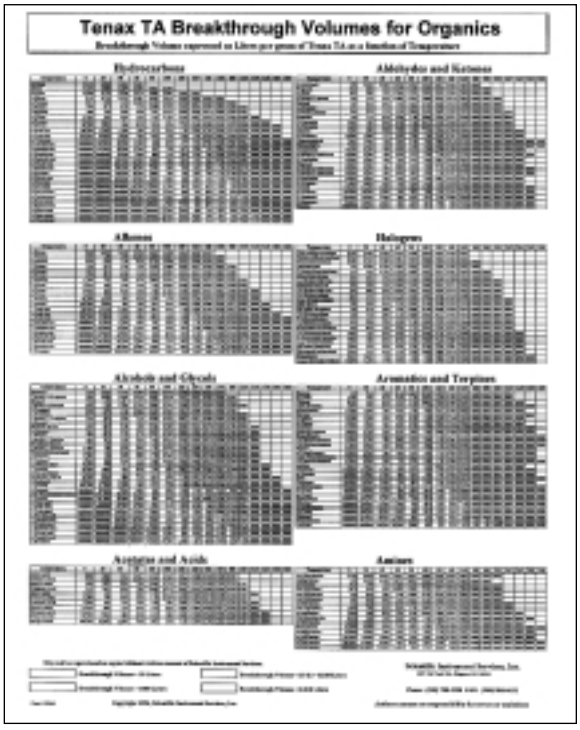
Micro Cryo-Trap

New - Programmable Micro Cryo-Trap for use with the Model TD-4 SPTD System

The new 1.0" micro cryo-trap consists of a small heating/cooling chamber which mounts beneath the injection port inside the GC oven. Either liquid CO_2 or LN_2 can be used as a coolant to be introduced into the cryotrap and exhausted through an outlet. The smallness of its size makes it very easy to install.

The micro cryo-trap shown here can be used as an accessory with the TD-4 system for use on the HP6890 GC for use in purge & trap systems, GC headspace sample analysis and multi-dimensional GC applications. *Two models are available, Model 971 for CO_2 and Model 981 for LN_2. Control is provided by the Thermal Desorption System. Other models of the Micro Cryo-Trap with an independent controller are also available - see page 7.

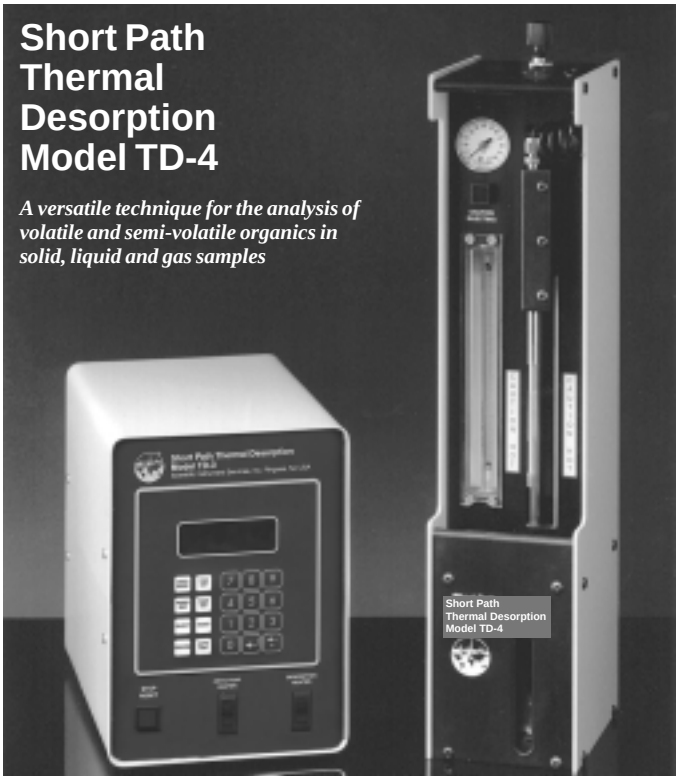
Part No.	Description	Price
972000	Model 971 for CO_2	$1495.00
982000	Model 981 for LN_2	$1495.00



Part No.	Description	Price
99560	Tenax TA Poster	$65.00
979302	10 grams of Tenax TA, with Free Poster	$90.00

Introducing

Short Path Thermal Desorption Model TD-4



The new Model TD-4 Short Path Thermal Desorption system was specifically designed to fit the top of the redesigned Hewlett Packard Model 6890 Gas Chromatograph.

Features:

- High sensitivity Thermal Desorption and Direct Thermal Extraction of samples.
- "Short Path" of sample flow provides for the maximum sample delivery to the GC.
- Eliminates solvent extraction and other tedious sample cleanup.
- Mounts over top GC injection port. Easily removable and transferable.
- Temperature programmable heating blocks permits the desorption of samples from 20°C to 350°C.
- Optional GC Micro Cryo-Trap permits the trapping of volatiles at front of GC column at temperatures down to -180°C.
- Automatic programming of desorption temperatures and times as well as GC Cryo-Trap control and remote start of GC.
- Glass lined stainless steel (GLT) sample tubes are both inert to samples and strong for sample handling and transporting.

Applications:

Thermal Desorption (Purge & Trap)

- Environmental Air Analysis
- Flavor and Fragrance Analysis
- Off odor/Off-flavor Analysis
- Forensic- Arson Analysis

Residual Gas, Solvents and Chemicals in:

- Pharmaceuticals
- Packaging Materials
- Building Products
- Food Products
- Natural Products

Direct Thermal Extraction of:

- Plastics
- Synthetic Fibers & Materials
- Spices
- Natural Products
- Pharmaceuticals
- Finished Products

Scientific Instrument Services, Inc.
1027 Old York Rd., Ringoes, NJ 08551
Phone: (908) 788-5550
FAX: (908) 806-6631
E-Mail: http://www.sisweb.com/contact
Home Page: http://www.sisweb.com

FEATURE

Comparison of Sensitivity of Headspace GC, Purge & Trap Thermal Desorption and Direct Thermal Extraction Techniques for Volatile Organics in Olive Oils

Introduction

A variety of techniques are available for the analysis of volatiles and semi-volatile organics in solid, liquid and gas samples. No one method or technique is optimum for all types of samples. The selection of a sample collection and GC introduction technique is dependent upon a large number of variables. One must select the optimum method depending on the sample matrix, boiling point range and concentration of analytes in the sample, interfering compounds and equipment available.

Table I - Variables to be Considered in the Selection of Analysis Technique

- Sample Matrix - Gas - Liquid - Solid
- Amount of Sample Available for Analysis
- Concentration of Volatiles in Sample Matrix
- Detection Limit of GC Detector
- Amount of Water in the Sample
- Solvents or Major Interfering Compounds
- Thermal Stability of the Analytes
- Boiling Point Range of Analytes in Sample
- Lowest Range of Volatiles Desired in Analysis
- Highest Range of Boilers Desired in Analysis
- Number of Samples to be Analyzed
- Sample Preparation Time
- Use and Disposal of Solvents
- Cost of Analysis

In order to analyze the volatile and semi-volatile organics in various sample matrices, a variety of GC sampling techniques can be utilized **(Figure 1)**. Each of these injection techniques has unique advantages and disadvantages for the analysis of volatile and semi-volatile organics. All of the above factors or variables **(Table I)** must be considered to determine the optimum method of analysis for a particular sample. In this study the static headspace GC technique was compared to conventional purge and trap thermal desorption and also to the direct thermal extraction (DTE) technique in order to determine the relative sensitivities of these techniques for the analysis of volatile organics in olive oil.

Comparison of GC Sampling Techniques

	Sample Matrix	Sample Size	Detection Limit	Range of Volatiles Analyzed (gases volat. semi-vol non-volat.)	Sample Automation	Sample Prep Time
Headspace	L/S	0.1-10	ppm		yes	5-10
P&T TD	G/L/S	1-1000	ppb		no	10-30
SPME	G/L	0.1-10	ppt		yes	5-15
Solvent Extract	L/S	0.1-10	ppb		no	30 +
SFE	L/S	0.1-10	ppb		yes	10-60
DTE	S	0.1-1.0	ppb		no	5-10
		grams		-100 0 100 200 300 400 boiling point		minutes

G = Gas, L = Liquid, S = Solid
ppt = parts per thousand, ppm = parts per million, ppb = parts per billion

Fig. #1

GC Headspace Analysis

Static GC Headspace sampling is a widely used injection technique. It is most suited for the analysis of the very light volatiles in samples that can be efficiently partitioned into the head space gas volume from the liquid or solid matrix sample. Higher boiling volatiles and semi-volatiles are not detectable with this technique due to their low partition in the gas headspace volume. In addition the sensitivity of the technique is limited, typically to concentrations in the ppm to ppt range. However the technique is a preferred method for the analysis of gases and very light volatiles which can not be analyzed by other techniques such as P&T Thermal Desorption. The technique is also a preferred technique when sample automation is required such as in a quality control method or in sample screening.

The LEAP Model CTC HS500 Headspace Autosampler was attached to the injection port of a HP Model 5890 Series II GC with electronic pressure control. This headspace system uses a heated syringe concept to directly inject the headspace volatiles from a heated sample into the GC injection port.

Five ml samples were placed into 10 ml headspace vials, sealed with Teflon lined septa, heated to 90°C with agitation for 15 minutes in the sample block after which 1 to 2.0 ml gas samples were injected into the GC injection port. The samples were injected very slowly (25 µl/sec or 1.5 ml/min). This slow injection assures the full delivery of the analytes to the capillary column. Faster injection would result in sample splitting due to the backpressure design of the HP injection port. After injection into the cooled GC Cryo-Trap, the trap was maintained at the cryo-cooled temperature for at least another 3.0 minutes before the volatiles were released and the GC program begun.

P&T TD

Dynamic Purge and Trap (P&T) Thermal Desorption is routinely used for the analysis of volatiles in environmental samples as well as food samples. Through the proper selection of adsorbent resins such as Tenax TA, water can be eliminated from being introduced into the GC. This is important for the analysis of high water content samples such as food products and water samples. Typical sensitivity is in the ppb range. By purging samples at higher temperatures, higher molecular weight compounds can be detected. However the purge and trap technique requires more time for sample preparation and can not normally be automated. In

addition very light volatiles and gases will not be trapped on the adsorbent resins and therefore will be missed in the analysis.

Sample sizes of 1 ml of the olive oil were pipetted into a 10 ml test tube and heated to 80°C for 30 minutes. Samples were purged with high purity helium at 20 ml/min with an additional 25 ml/min dry purge using the S.I.S. Purge and Trap System. Volatile analytes were purged from the liquid matrix and carried to a preconditioned 4.0 mm i.d. glass-lined stainless steel desorption tube packed with 100 mg of Tenax™TA.

Direct Thermal Extraction

A new technique entitled "Direct Thermal Extraction" using a thermal desorption apparatus attached to the injection port of a GC/MS system permits the direct thermal extraction of volatile and semi-volatile organics directly from small sample sizes (mg) without the need for solvent extraction or other sample preparation. The samples are ballistically heated and together with the carrier gas flow through the samples the volatiles are outgassed into the injection port and onto the front of the GC column for subsequent analysis via the GC and/or GC/MS.

Approximately 10 µl of each of the oil samples to be analyzed by "Direct Thermal Extraction" were injected into a 4.0 mm i.d. glass-lined stainless steel desorption tube containing 25 mg of Tenax™TA. The samples were then purged for 5 minutes at 80 ml/min to remove any moisture from the traps.

Once the samples were collected in the desorption tubes via P&T or DTE they were spiked with a mixture of 100 ng of d-8 toluene, 200 ng of d-14 cymene and 50 ng of d-8 naphthalene internal standard by injecting 1 µl of the stock solution in methanol by syringe injection into the Tenax matrix. An additional purging of 120 ml of purge gas was required to remove the methanol from the Tenax trap.

The desorption tubes were then attached to the Scientific Instrument Services Short Path Thermal Desorption System and thermally desorbed at 250°C, at a desorption flow rate of 4 ml per minute for 5 minutes into the GC injection port. The GC injection port was maintained at 250°C and the volatiles were cryo-focused at the front of the GC column using the Scientific Instrument Services GC Cryo-Trap at a temperature of -100°C. After the desorption process was complete, the GC Cryo-Trap was ballistically heated to 200°C to release the trapped volatiles in a narrow band for chromatography.

Samples of olive oil were studied via these three injection techniques in order to determine the range of volatiles that could be detected via each technique. The sensitivity of analysis was also compared for each of the injection techniques. The volatile organics present in the oil were quantified using matrix spiked deuterated internal standards.

Results & Discussion

In order to compare the various injection techniques a sample of olive oil was analyzed via the three injection techniques **(Figs. 2-4)**. The headspace analysis of 5.0 ml of olive oil produced only minor peaks **(Fig. 2)**. In the purge and trap technique 1.0 ml of oil was purged at 40 ml/min for 30 minutes to purge the volatiles from the oil and trap them on the adsorbent resin trap. For the direct thermal extraction technique, 10 µl of oil was injected directly onto 25 mg of Tenax and subsequently thermally desorbed into the GC for separation and identification via MS.

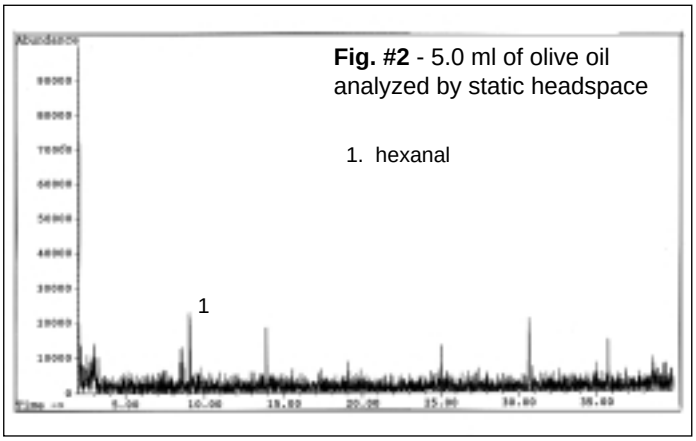


Fig. #2 - 5.0 ml of olive oil analyzed by static headspace

1. hexanal

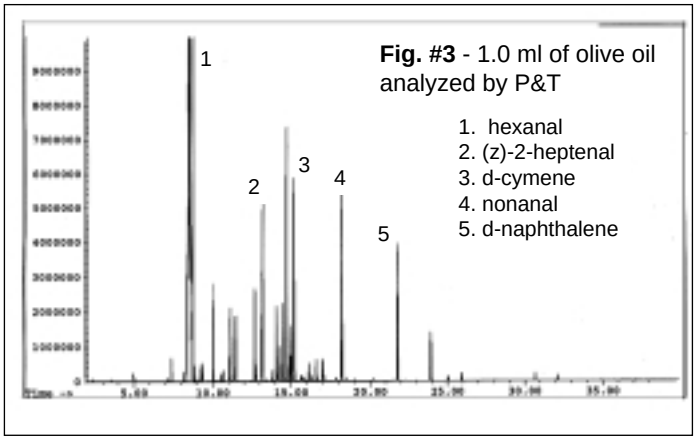


Fig. #3 - 1.0 ml of olive oil analyzed by P&T

1. hexanal
2. (z)-2-heptenal
3. d-cymene
4. nonanal
5. d-naphthalene

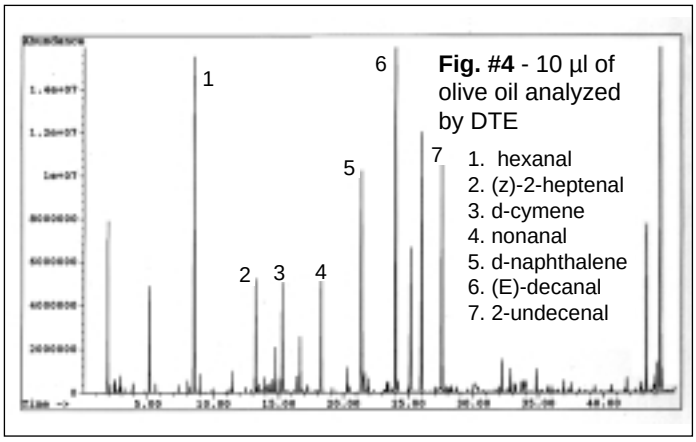


Fig. #4 - 10 µl of olive oil analyzed by DTE

1. hexanal
2. (z)-2-heptenal
3. d-cymene
4. nonanal
5. d-naphthalene
6. (E)-decanal
7. 2-undecenal

The dynamic purge and trap (P&T) technique permitted the analysis of a wider range of both volatile and semi-volatile organic compounds and was more sensitive by a factor of at least 100 as compared to the static headspace technique **(Fig. 2&3)**. The "Direct Thermal Extraction" technique offered several unique advantages over the dynamic Purge & Trap technique including greater sensitivity and the detection of a wider range of volatile organics including higher molecular weight compounds and is more sensitive by a factor of at least 1000 as compared to the Purge & Trap technique. **(Fig. 3&4)**. Although "Direct Thermal Extraction" is not suitable for every application, in this case, it can easily be incorporated into troubleshooting techniques to detect problems in a wide variety of commercial food products, to compare various competing manufacturers' products as well as the implementation of a quality control program for the food industry.

Thermal Desorption TIPS

USE OF GUARD COLUMNS IN THE GC CRYO-TRAP

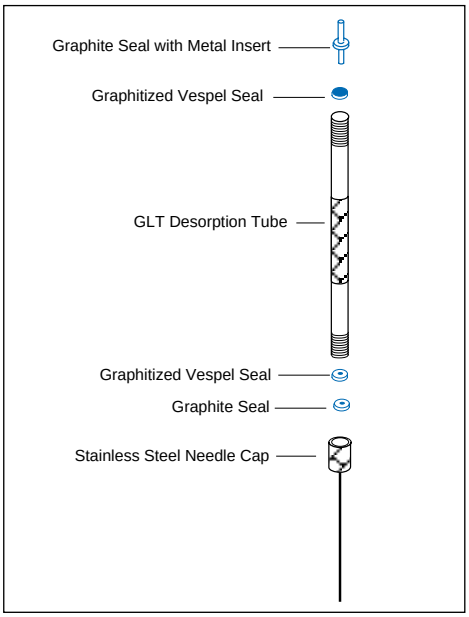
Coated capillary guard columns used in the GC Cryo-Trap increase the efficiency of trapping of lower boiling volatiles at trapping temperatures greater than -70°C. Thicker film guard columns such as a 1.5 µm film thickness DB5-MS megabore guard column are recommended for use in the CO_2 Cryo-Trap. It provides greater efficiency in trapping volatiles than the uncoated guard at temperatures of -70°C. In addition this film thickness and type provides for minimal phase bleed from the guard column. The megabore column was selected due to its larger inside diameter which increases the dynamic loading capabilities and minimizes the chance of ice plugs when samples containing significant amounts of water are analyzed. When utilizing CO_2 as the cryo-cooling gas, a trap temperature of -70°C is recommended.

When using liquid nitrogen as the cryo-cooling gas at temperatures < 100 °C, uncoated deactivated fused silica guard columns are recommended because the liquid phase of coated guard columns lose activity below -100°C resulting in peak broadening.

This methodology can readily be utilized for the analysis of thermal desorption as well as headspace GC samples for a wide range of volatile organics. For the trapping of very low boilers such as ethane, formaldehyde and ethylene oxide, the PLOT columns such as the GS-Q PLOT column from J&W is recommended for use with the GC Cryo-Trap. However this column may present problems if less volatile compounds are analyzed in that they may not be eluted off the guard column. Depending on the range of volatiles that need to be analyzed, a wide range of guard columns and cryo-trapping temperatures can be selected for the optimum results when using the GC Cryo-Trap.

ELIMINATE POTENTIAL LEAKING PROBLEMS WITH DOUBLE SEALS

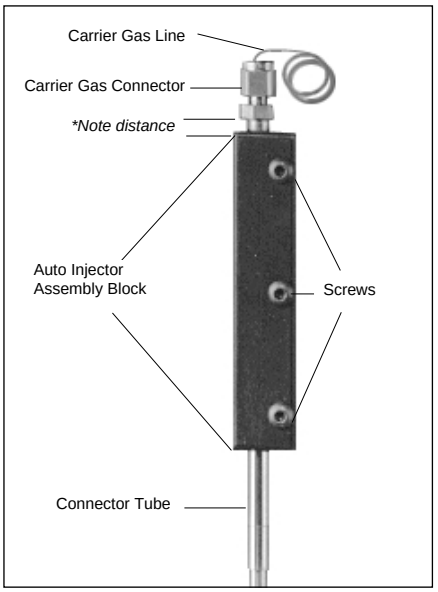
Seals are utilized in a variety of locations in the Short Path Thermal Desorption Unit. One such location is in the Desorption Tube Syringe Needle. It is imperative that these seals are leak tight even at pressures up to 30 p.s.i. for the proper operation of the Desorption System and to provide for the complete delivery of the desorbed sample into the GC injection port. If a pressure leak develops in the Desorption Unit, a prime candidate for this problem would be the seal in the syringe needle. Therefore, it is recommended that 2 seals be used in the syringe needle when a sample is being analyzed. The first seal placed in the syringe needle is a graphite seal which is physically soft but has excellent sealing properties and temperature limits. The second seal is provided by a graphitized vespel seal which contains 40% graphite and physically are harder than graphite seals. Since these seals are harder than graphite, they hold their shape better and have a longer life. With the use of these 2 seals, a leak tight system is maintained to provide for the complete delivery of the sample into the GC injection port.



SILICONE PROBLEMS?

Siloxanes are used as a basis for silicone lubricating oils which are applied to the O'rings to form seals in the rotameter of the Desorption Unit. Because of this, silicone peaks may appear during a thermal desorption sample analysis. If this is the case, this problem can be eliminated by using a conditioned connector tube filled with approximately 200mg of Carbosieve SIII (Supelco, Inc.) to trap the siloxanes that are outgassed from the rotameter. The connector tube essentially serves as a precolumn.

1. First, disconnect the carrier gas line from the carrier gas connector and note the distance of the tube from the top of the Autoinjector Assembly Block.
2. Next, loosen the screws on the Assembly Block with an allen wrench.
3. Push the assembly down and remove the connector tube.
4. Remove the seals (graphitized vespel seal & graphite seal with a metal insert) from the bottom of the connector tube and insert a glass wool plug.
5. Fill the connector tube with approximately 200mg of Carbosieve SIII.
6. Insert a glass wool plug to hold the adsorbent in place.
7. Replace the 2 seals at the bottom of the connector tube with new ones.
8. Bake out the tube with resin under helium at 25 ml/min for 3 hours at 300°C in a conditioning oven.



Once the connector tube with adsorbent has been conditioned with flow, allow it to cool and replace in the exact position as it was previously. By doing this, the Carbosieve SIII will serve as a trapping agent for the troublesome silicone peaks that appeared previously. Recondition monthly.

Tips & Ideas
If you have any ideas to share we would like to publish them in our next issue.
Call SIS: (908) 788-5550 or FAX: (908) 806-6631

Micro Cryo-Trap

New - Programmable Micro Cryo-Trap for the Cryo-focusing of Volatiles and Semi-volatiles at the Head of GC Columns

Features

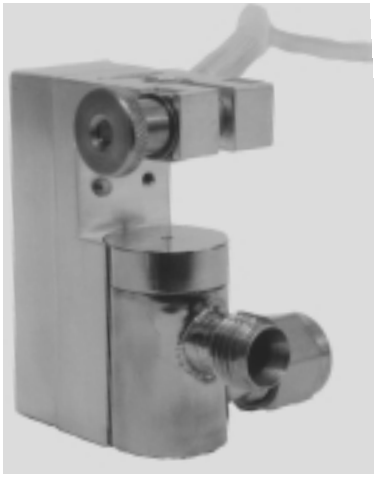
- **Only 1.0” long- uses minimum amount of cooling gas.**
- **Reduction of CO_2 or LN_2 use by 97% as compared to cooling the entire oven.**
- **Dual programmable cryo cooling and heating cycles.**
- **Remote input connector for switching between cryo-cooling and heating cycle via GC, Desorption System or manually.**
- **Rapid heating up to 400°C at >1000°C per minute.**
- **Clamp Mounts onto GC Injection Port**

Applications

- **Thermal Desorption Sample Trapping**
- **Purge and Trap Systems**
- **GC Headspace Sample Analysis**
- **Multi-dimensional GC Applications**

Controller

Cryo-Trap Only 1.0 Inch Long



Models available for use with the Model TD-4 SPTD System - see page 2.

For the cooling operation, the cooling gas is pulsed into the chamber. Liquid CO_2 (Model 971) will cool down to -70 degrees C. Liquid Nitrogen (Model 981) will cool down to -180 deg. C. The cooling temperature can be set to any temperature between room temperature and the lower limits of the cooling gas. The temperature controller will pulse the cooling gas into the chamber to accurately control the temperature to the value you set. The thermocouple provides the feedback to both regulate the temperature as well as display the GC Cryo-Trap temperature on the display of the temperature controller.

Model 971 Micro Cryo-Trap with controller for use with Liquid $C0_2$

The Model 971 Micro Cryo-Trap is designed for use with liquid CO_2 tanks with a DIP tube. The minimum cooling temperature is -70^{o} C.

Part #	Description	Price
971001	Micro Cryo-Trap for use with liquid CO_2 on HP Gas Chromatographs.	
971002	Micro Cryo-Trap for use with liquid CO_2 on Varian Gas Chromatographs.	
971003	Micro Cryo-Trap for use with liquid CO_2 on Shimadzu Gas Chromatographs	

Model 981 GC Cryo-Trap with controller for use with Liquid LN_2

The Model 981 GC Cryo-Trap is designed for use with liquid nitrogen tanks (low pressure). The minimum cooling temperature is -180^{o}C.

Part #	Description	Price
981001	Micro Cryo-Trap for use with liquid LN2 on HP Gas Chromatographs	
981002	Micro Cryo-Trap for use with liquid LN2 on Varian Gas Chromatographs.	
981003	Micro Cryo-Trap for use with liquid LN2 on Shimadzu Gas Chromatographs.	

The Cryo-Trap consists of a small heating/cooling chamber which is 3/4" in diameter and 1.0" long and mounts to the bottom of the GC injection port just inside the GC oven. In the center of the chamber is a small stainless steel capillary through which the capillary column freely passes. Capillary columns up to megabore (0.53mm I.D.) diameters can be used. Around the stainless steel capillary tube a heating coil is wound to provide for the rapid heating of the capillary tube. A thermocouple provides accurate measurement of the cryo-trap temperatures. Either Liquid $C0_2$ or Liquid Nitrogen for cooling is introduced into the Cryo-Trap (Cooling Gas In), and is exhausted through the outlet. The exhaust can either be vented into the GC Oven or a tube can be attached to vent the cooling gas external to the GC.

The control of the Cryo-Trap is provided via an independent Cryo-Trap Controller provided with the system. Both the Cryo-Cooling and heating temperatures are set via this digital temperature controller.The system can be used either manually to switch between cooling and healing or can be operated automatically via an input signal from a controlling device or from the GC.

Scientific Instrument Services is now on the Internet

- **Visit our WEB site for Thermal Desorption information in the form of application notes, technical bulletins, related articles and other reference materials that have been published over the last 18 years.**

- **Check out the GC Cryo-Trap section featuring not only application notes but operational instructions as well as complete installation instructions.**

- **Our catalog section provides information about Thermal Desorption along with an on-line fill-in form to order your free catalog as well as other valuable literature available from S.I.S.**

Scientific Instrument Services, Inc. **Phone: (908) 788-5550**
1027 Old York Rd. **FAX: (908) 806-6631**
Ringoes, NJ 08551 **E-Mail: http://www.sisweb.com/contact**
Home Page: http://www.sisweb.com

Scientific Instrument Services
1027 Old York Rd.
Ringoes, NJ 08551

Bulk Rate
US Postage
PAID
Davenport, IA
Permit No. 291