



A New State of the Art in Thermal Desorption

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Thermal Desorption

• Generally accepted as," A technique by which a known volume of air or gaseous sample is drawn through a tube packed with solid sorbent to collect volatile organics. The tube is then thermally desorbed, by rapid heating and sweeping of the volatiles with an inert gas into a GC or other analyzer."

Multi-Bed Sorbent tube



Standard TD Techniques

- AIR Monitoring
 - -Chemical Agents Dynatherm's Beginning
 - -TO Methods EPA Ambient Air montioring
 - -Industrial Hygiene/Worker Safety
- Product Emissions



Advantages of Thermal Desorption

- Increased sensitivity
- Very Cost Effective
 - Elimination of solvents
 - Minimal sample preparation
 - No Cryogens or extra gases needed (with the right system)
- Flexibility!





Problems with Traditional Thermal Desorption Systems

- Collection and Analysis of High Boiling Analytes
 - Classical sampling done at ambient temperatures.
 - Systems limited to 200° C valves or ovens
- Analysis of Volatile Gases require Peltier or Liquid cryogen.
 - Peltiers are problematic
 - Liquid Cryogens can be expensive & difficult to use.

Goal: Develop a system that can answer both problems and then some!





Problem # 1

• The U.S. Army has been trying to develop air monitoring methods for VX (Boiling point 298°C) and higher boiling compounds that will not require sample derivitazation, allowing for continuous monitoring in a near-real time scenario. Although, several systems are commercially available to provide a portion of their requirement, no system was capable of meeting all of their needs





Items of Concern

- Need for elevated collection and system temperatures (up to 375° C)
- Need for Higher sampling flow rates (up to 1.5 L/min)
- Need for quicker cycle times (Heat-up/cool down)
- Flexibility and ease of use are critical





The Solution



Agilent 5975T with CDS 9350



Key elements of the solution



Fast Flow Tubes

New CDS 9350 with Heated Sampling Line





VX Analysis with System

- Calibration Curve by liquid injection approach. Process performed with injection through Sample line (TL) and CDS injection port.
- Calibration results illustrates instability of analyte (VX). Through the TL 25ng is the low point. Through injection port 12.5ng is the low point.
- Improvements are underway to improve the analyte transmittance. For non-reactive analyte VX di-sulfide 0.1 ng is detected.





VX Analysis with System









VX Composition







VX Composition with LTM Chromatographic Separation



CASARM = Chemical Agent Standard Analytical Reference Material

LTM = Low Thermal Mass chromatographic oven designed for Fast-GC



Thermal Desorption of Di-Pinacolyl Methyl Phosphonate and Ton Container VX

Abundance



Illustrates difference in VX composition coming from Ton Container versus CASARM Preparation



Thermal Desorption of Di-Pinacolyl Methyl Phosphonate and Ton Container VX



Illustrates difference in VX composition coming from Ton Container versus CASARM Preparation





VX Problem Demonstrated Fixes

- CDS-9350 with Agilent 5975T MSD provides repeatable transport of VX without carry over between sampling or silver fluoride pad conversion of VX to G analog.
- Collects and detects 25ng on column VX from vapor stream passing through 15 foot heated sampling line (flow rate of sampling 1.5L).
- CDS-9350 Injection port makes liquid calibration simple and does not require sampling tube changes,
- Operates with continuous sampling providing sampling turnover every 20 min for VX at 25ng in 24L of vapor at a 1.5L/min sampling rate.





VX Problem Demonstrated Fixes

• System reproducibility illustrated for GB and HD .



GB and HD Vapor collected at same time starting as soon as generator is connected to CDS-9350 thermal desorber. Data points for alternating properly match tubes.





Problem # 2

• A commercial environmental laboratory wants to set-up a mobile lab with the capability of doing volatile organics in air water and soil, and PAHs in soil, but lacks the funds to do solvent extraction and purchase both a Thermal Desorption System and a Purge & Trap System.



Mobile Lab Needs

- Be able to analyze Air Tubes, Canisters, Water and Soil samples.
- Limited space and funds to outfit lab.
- Can't use Peltier or Liquid cryogen
- Flexibility and ease of use are critical



Environmental Analyses

- General VOC's in ambient air or Soil gas
 - EPA methods TO-17, TO-14/15, TO-1/2; Trace Volatile Compound Collection Methods in Air.
- Water & Soil Samples for VOC SW-846 methods or EPA wastewater methods.
- Semivolatile screening for Pesticides/PCBs and PAHs.





The Solution



CDS 9350 with Purge & Trap accessory on your favorite GC



Ambient air monitoring (TO-17)





Tank Removal Project





But do we have PAHs in the soil as well?

- **0.5** grams of soil thermally extracted at 325° C
 - Empty TD tube
 - Pre-dry sample or Dry Tube

Phenanthene

Benzo (a) Pyrene

- 1 ppm standard (~ 0.5 ug)
- LOD 1 5 ng, but is that really achievable in the field?





Client has a water sample they need analyzed!!

Abundance





Pesticides in Soils and waters

- Extract at 325° C
- Glass/Tenax Focus trap
- Dry focus trap to remove moisture
- Desorb FT at 300° C
- GC/MS
- DB-5 column







PCBs



- Extract at 325° C
- Glass/Tenax Focus
 trap
- Dry focus trap

- Desorb FT at 300° C
- GC/MS
- DB-5 column



Larger Vessel Headspace

- Plastics, molded parts etc. can be too large for Direct thermal desorption.
- Large vessel Dynamic Headspace, followed by thermal desorption is a good alternative







Simplified view of sorbents

Boiling point	-50	0	50	100	150	200	250	300	350	400
Molecular Sieve	200	300	400							
Carboxen			200	300	400					
Carbotrap				100	200	300				
Tenax-TA				100		200		300		
Glass Beads								100	150	200
			100	300	Temperat	emperature required to				
			200	400	Desorb analytes off sorbent					

Many applications require the use of multi-bed tubes



Direction of Flow



Collect on to tube Tenax/Carboxen/carbosieve

→ Desorb off of tube Carbosieve/Carboxen/Tenax

Tubes always go into Autosampler Frit Down, and into 9300 Frit towards the valve oven (Back)







Sampling Techniques

• Passive badges (Typically charcoal), transferred to an empty "sorbent tube"

• Personal Sampling pump, like this SKC pump, with adjustable low flow holder.





Dual Channel Sampler



Tedlar BagFast FlowVacuumTime setNEMC: 08/2011Tubecontrol





Questions



Hernan Diaz (Agilent Technologies)