Fast Analysis of Low Level BTEX using a CP-4900 Micro-GC with Sample Concentrator

Advantage: Sample detection limits can be markedly improved if analytes are concentrated before they are injected into the Varian CP-4900 Micro GC. Using the Enrichment and Desorption Unit (EDU) Sample Concentrator, the sample is adsorbed onto a porous medium. These trapped analytes are then desorbed and transferred to the Micro-GC for separation and analysis. Using this approach, enrichment can be increased by more than 230 times.

Introduction

In general, the typical detection limit of the Varian CP-4900 Micro-GC is ~ 1-10 ppm and is compound dependent. Detection limits can be improved by concentrating the sample prior to introduction to the Micro-GC by the method outlined above.

Instrumentation

Figure 1. EDU-Varian Sample Concentrator and CP-4900 Micro-GC.

Equipment:

- CP-4900, single channel (CP-Sil 5CB, 4 m)
- EDU-Varian Sample concentrator
- Adsorption Material: Tenax™
- Software: Galaxie™ Software from Varian for GC control and data handling. EDU software for control of the sample concentrator.

Principle of Operation

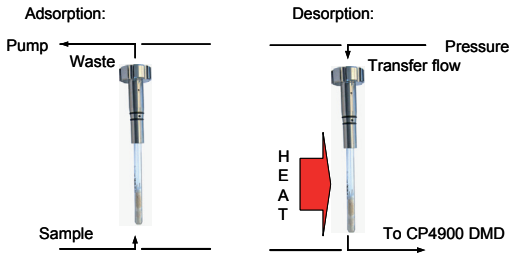


Figure 2. Principle of Operation.

Sampling Phase
The sample is pumped from its container (Tedlar bag) through a heated sample line onto the adsorption tube.
Desorption Phase
The adsorption tube is heated in "stop" flow.
Injection Phase
The adsorption tube is set in "backflush" mode and the "desorbed" sample components flow through a heated transfer line to the Micro-GC.

Materials and Reagents

BTEX Gas Sample Containing (balance nitrogen):

- Benzene 1.42 ppm
- Toluene 1.46 ppm
- Ethylbenzene 1.59 ppm
- o-Xylene 1.63 ppm
- m-Xylene 1.53 ppm
- p-Xylene 1.72 ppm
- Propylbenzene 1.38 ppm
- i-Butylbenzene 2.35 ppm
- Butylbenzene 2.79 ppm

Conditions

CP-4900 Micro-GC Settings:

- Carrier gas: Helium, 150 kPa
- Column temperature: 100 °C
- Injector time: 255 ms
- Flow mode: Continuous
- GC sampling time: Optimized

EDU-Varian Sample Concentrator Settings:

• Transfer gas:	Helium	85 kPa
• Sampling:	60 sec	30 °C
• Desorption phase:	120 sec	180 °C
• Injection phase:	30 sec	180 °C
• Clean phase:	90 sec	220 °C
• Cool phase:	100 sec	

Discussion

Utilizing the conditions listed on the previous page, the following chromatogram was obtained.

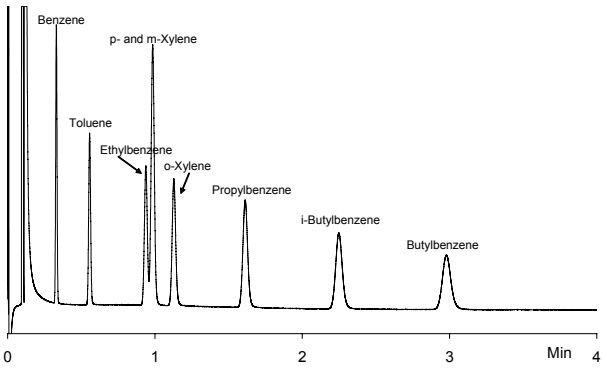


Figure 3. Example Chromatogram - BTEX Analysis.

For each application the system requires some method optimization. In particular:

- Transport delay of sample from EDU-Varian to the CP-4900 Micro-GC
- The adsorption trap material and capacity

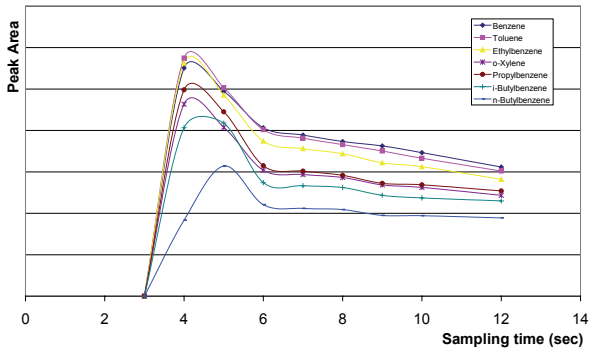


Figure 4. Sample Transport Through Transfer Line.

Figure 4 shows the measured peak area for selected components as a function of the GC sampling time. Note that prior to a sampling time of 4 seconds, no component peak areas were measurable by the Micro-GC. After a sampling time of 4 to 5 seconds an increase could be seen in the amount of component peak area measured. However at ~ 7 seconds and beyond, the individual peak area values "flatten" out considerably which adds to the robustness of the method. The desorption of the components from the adsorption tube is in backflush mode. The concentration of the components in the desorption profile is dependant on the volatility/boiling point of the component and its affinity to the adsorption material.

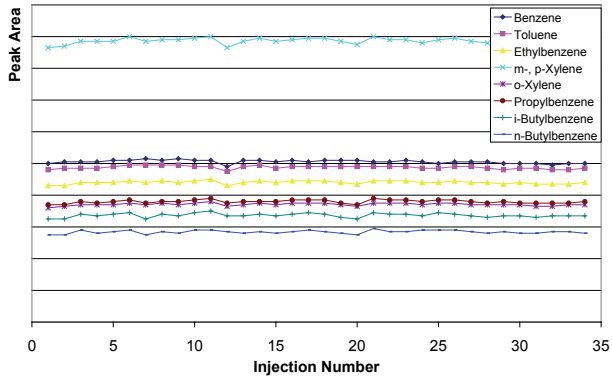


Figure 5. Repeatability Results – 34 Successive Injections.

Figure 5 shows that the repeatability for 34 successive analyses ranges from 1.0 and 1.9% with a sampling time of 7 seconds. It was also noted that the use of a shorter sampling time (5 seconds) resulted in RSD values (1.2 – 3.6%) that were slightly lower but with slightly higher sample enrichment. As with most methods, the analyst must strike a balance between the desired detection levels and required performance level.

Another important factor in application / method optimization is to determine the capacity of the adsorption material. To assess this, the 1 ppm sample was drawn through the adsorption tube for varying times at a fixed pumping rate (450 mL / min), desorbed at a fixed heating value / time onto the Micro-GC and peak areas measured. (See Figure 6).

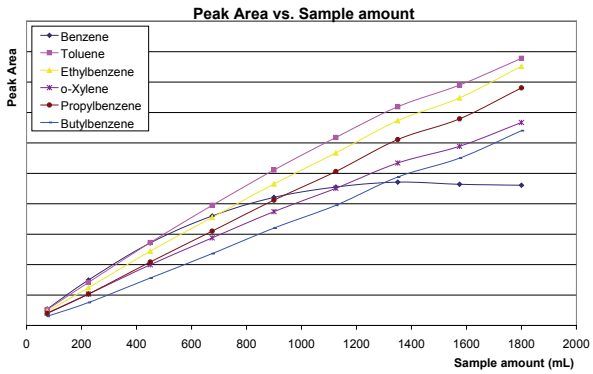
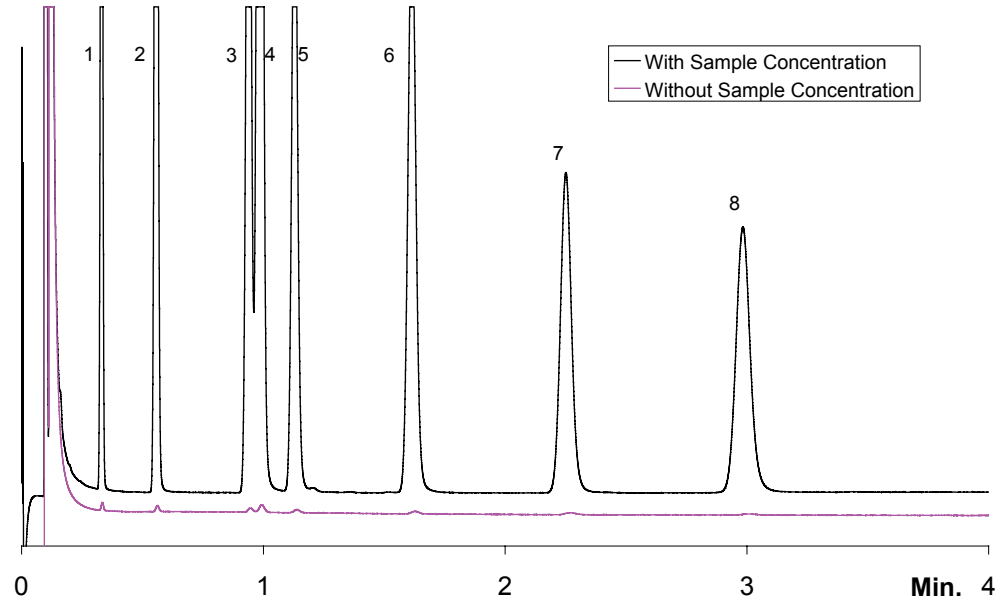


Figure 6. Linearity and Breakthrough of the Sampling.

As can be seen from the graph, the breakthrough volume varies considerably and ranges from Benzene 700 mL to 1400 mL or greater for Toluene.

To determine the enrichment factors, the chromatogram results produced from the 1 ppm sample, after direct injection, are compared with the results generated using analysis with sample concentration (1800 mL total flow).



Peak Identification
1. Benzene
2. Tolene
3. Ethylbenzene
4. p-, and m-Xylene
5. o-Xylene
6. Propylbenzene
7. i-Butylbenzene
8. n-Butylbenzene

Figure 7. Enrichment Details.

The results have been overlayed in Figure 7.
The actual sample enrichment factor varies component to component as illustrated in Figures 8 and 9.

	Benzene	Toluene	Ethylbenzene	Propylbenzene	Butylbenzene
With EDU	23.05	43.90	42.60	39.05	32.00
Without EDU	0.16	0.19	0.18	0.17	0.14
Enrichment Factor	146	237	234	230	226

Figure 8. Enrichment Factors.

	Benzene	Toluene	Ethylbenzene	Propylbenzene	n-Butylbenzene
Original Conc. (ppm)	1.42	1.46	1.59	1.38	2.79
RSD (%)	1.08	1.01	1.12	1.41	1.83
RSD (ppm)	0.015	0.015	0.018	0.019	0.051
Enrichment Factor	146	237	234	230	226
Approx Det. Lim. (ppb)	7	4	4	4	4

Figure 9. Summary Results.

Conclusion

The experimental data depicted in this note clearly shows that routine detection levels can be significantly improved with the Varian CP-4900 Micro-GC if a sample concentrator is used prior to analysis.

Enrichment factors as much as 230 x or more can be obtained depending on the sample component and chromatographic conditions. In this case the detection limit was improved from 1 ppm (without sample concentration) to 5 ppb with sample concentration for several aromatic compounds.

Relative Standard Deviations of peak area are <2%, indicating that the system stability and repeatability is quite good.

Obviously for Benzene the enrichment factor, approximately 150, is the lowest as this component is sampled beyond the breakthrough volume of the trap.
With these settings enrichment factors from 150 to 230 were reached.

The EDU-Varian Sample Concentrator in combination with the CP-4900 Micro-GC provides a new tool in achieving much lower detection limits when conducting fast GC analysis.

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