CDS 7000C Purge and Trap Performance with CTC PAL Automation

Application Note

Environmental, VOCs in Water, EPA method compatible, automation, off-line, on-line analysis

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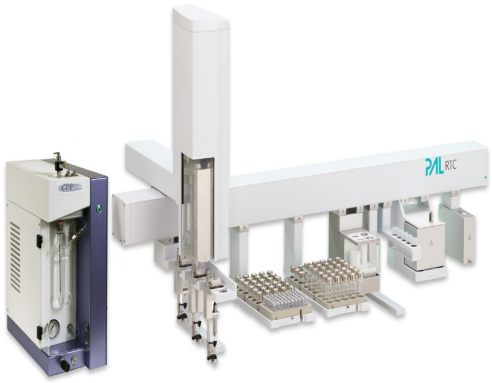
Abstract

CDS Analytical and CTC Analytics AG have joined forces to add EPA compatible Purge & Trap capabilities to the PAL RTC and RSI Autosamplers. The analytical performance of the combined CDS 7000C Purge and Trap concentrator and the PAL RTC Autosampler was evaluated in accordance of EPA method 524.2 and 8260, by testing VOC fortified water samples with a range of 1 to 200 ppb. A 64 component mix was used demonstrating linearities better than 0.999 for most analytes. The RSD of the response factors of the gaseous compounds ranged from 6.8% - 12.4%, and those of BTEX ranged from 2.8% - 8.5%. The reproducibility of the internal standards response for a 5 day period was < 4.0 %. Carryover from a 200 ppb standard to a blank was <1.0% for VOCs; and <2.5% for analytes with high boiling points above 200°C.

The combination of the CDS Purge & Trap units with the CTC PAL autosampler offers unique features for the environmental laboratory:

- Highest degree of P&T Automation.
- Automated Calibration and Internal Standard Addition.
- PAL method flexibility to Headspace, Liquid, DHS etc.
- Various Vial types (40mL VOA, 20ml HS Vials etc.)
- High throughput by scheduled sample overlapping.
- Online option for tap water analysis by flow cell.
- GC Mounted for small footprint.



7000C P&T/PAL

Introduction

Purge and Trap (P&T) is a principle way to analyze VOCs in water or soil samples by environmental laboratories. Over the past 40 years, the P&T technique has been well commercialized and developed. Coupling with an autosampler, a P&T concentrator can efficiently handle up to 48 samples a day (more if analytical method is modified) freeing analysts up to be more productive. Normally the samples are collected from target sites and stored in standard vials in compliance to regulations and standard methods, e.g., USEPA methods, so that after transport to a laboratory, an autosampler-equipped P&T concentrator can readily process them and then transfer the analytes to a GC/MS for analysis.

CDS Analytical has been a manufacturer of Purge and Trap systems for over 40 years and has a number of industry firsts, such as the first microprocessor based purge and trap system and the first to incorporate a foam sensor to avoid trap contamination. The CDS 7300 and 7400 P&T Autosamplers, introduced in 2012, have shown to be a reliable addition to many laboratories.

In recent years, the need for analytical flexibility in sample preparation and analyses has risen. To meet these analytical requirements, CTC Analytics AG, a well-known GC sample introduction technology provider in Switzerland, developed the PAL Autosampler. The PAL is a state-of-art direct sample introduction system capable of providing a wide array of sample introduction techniques for GC and GC/MS. These techniques include: direct injection, SPME, and Headspace, but when a customer needed more sensitivity, they had to turn to another technique, Purge & Trap, on another system.

In this application note, a CDS 7000C P&T Concentrator was combined with a PAL RTC Autosampler and a GC/MS to test samples according to EPA Method 524.2 and 8260. The addition of a Purge & Trap Concentrator adds an immense potential to expand the flexible use of the CTC PAL System for automated high sensitivity P&T analysis. The analytical capacities, reproducibility, precision of the response factors and linearity of the calibration of the combined system were evaluated.

Experimental

Chemicals and reagents

All standards were purchased from Supelco (Bellefonte, PA, USA).
8260 Internal Standard: Supelco CRM861183;
8260 Surrogate Standard Mix: Supelco 861135
8260 Volatiles Calibration Mix: Supelco 500607;
Volatile Organic Compounds Mix 6: Supelco 47408.
ACS grade Methanol was from Sigma-Aldrich (St Louis, MO, USA).

Instrumentation

A Shimadzu GCMS-QP 2010 system was set-up with a CDS 7000C Purge and Trap Concentrator and a PAL RTC Autosampler to perform all the tests. The transfer-line to the GC injector was connected to keep the injector free for other applications, e.g., direct liquid injections, SPME, etc.

Solutions and standards

5 mL of a 62.5 µg/mL stock Internal Standard (IS) solution was prepared from a 2500 µg/mL standard with methanol and transferred into the IS vial of the IS addition module attached to the PAL RTC Autosampler.

A mixture of 200 µg/mL volatile organic compounds in methanol was prepared as a stock solution. A series of dilutions with D. I. water were conducted to produce fortified samples in different concentrations.

2 µL of IS solution was added automatically by the IS module to each sample, to produce 25 µg/L IS compounds in the water sample.

With Chronos software and PnT Plugin, a batch of P&T samples can be scheduled easily along with a GC/MS sample sequence, which can be triggered to acquire data automatically for every sample. Overlapping in the schedule reduced the total analyzing period, so that an individual period of 55 (P&T plus 25 min GC/MS runtime, besides cooling time) could be finished in 30 min. This permits about 2 samples to be run in 1 hour.

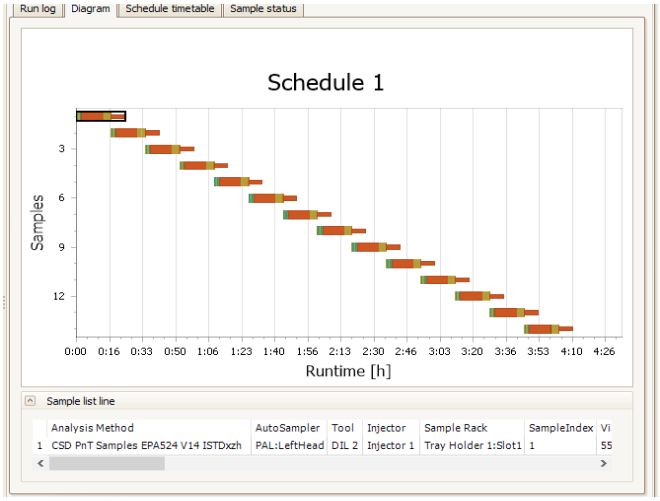


Figure 2. An overlapped CTC PAL/CDS 7000 P&T schedule

Instrumental Conditions

Purge and Trap conditions (EPA compatible)

Sample Volume: 5.0 mL
Purge Time: 11 min
Purge Temp.: 40 °C
Purge Flow: 40 mL/min
Trap Ready (Adsorption) Temp.: 35 °C
Dry Purge Time: 0.5 min
Dry Purge Temp.: 35
Dry Purge Flow: 100 mL/min
Pre-Desorb Temp.: 230 °C
Desorb Temp.: 250 °C
Desorb Time: 2 min
Desorb Flow: 300 mL/min
Desorb gas: He (carrier gas)
Trap Bake Temp.: 260 °C
Trap Bake Time: 8 min
Trap Bake Flow: 200 mL/min
Wet Trap Ready: 45 °C
Trap Bake Temp.: 260 °C
Valve Oven Temp.: 130 °C
GC Transfer Line Temp.: 130 °C
Hot Water Rinse Temp.: 70 °C

GC conditions

Column: Rtx-VMS, 30 m, 1.40 μm, 0.25 mm
Carrier: Helium
Oven Temp.: 35 °C
Injection Temp.: 135 °C
Injection Mode: Split
Split Ratio: 30:1
Flow Control Mode: Linear Velocity
Column Flow: 1.0 mL/min
Purge Flow: 3.0 mL/min

Oven Temp. Program:

Rate	Temp. (°C)	Hold Time (min)
-	35.0	4.00
5.00	90.0	0.00
12.00	150.0	0.00
30.00	220.0	2.67

Purge Flow Program:

Rate	Flow (mL/min)	Hold Time (min)
-	3.0	4.00

MS conditions

Ion Source Temp.: 200°C
Interface Temp.: 220°C
ACQ Mode: Scan
Event Time: 0.30 s

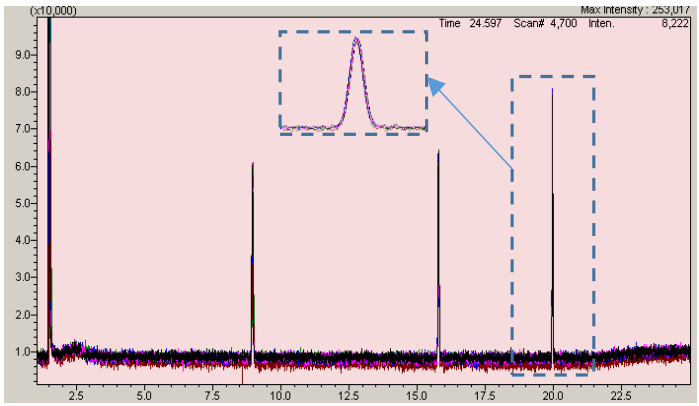


Figure 3. Five overlapped Internal Standard blank chromatographs

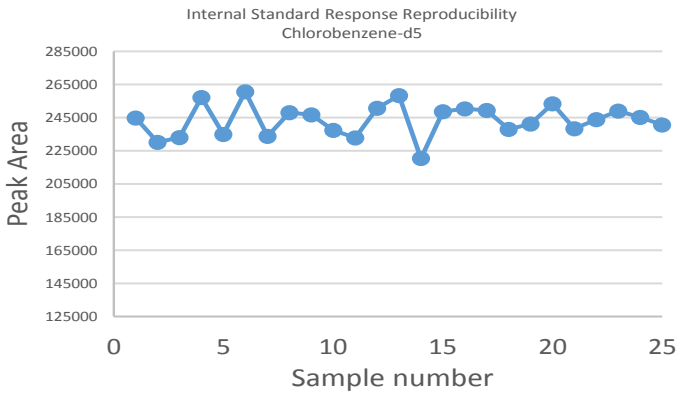


Figure 4. Long term reproducibility of Chlorobenzene-d5 peak areas

An example chromatogram of 64 compounds, including 6 gaseous compounds, 524.1 VOCs, surrogates, and IS compounds, is shown in Figure 5.

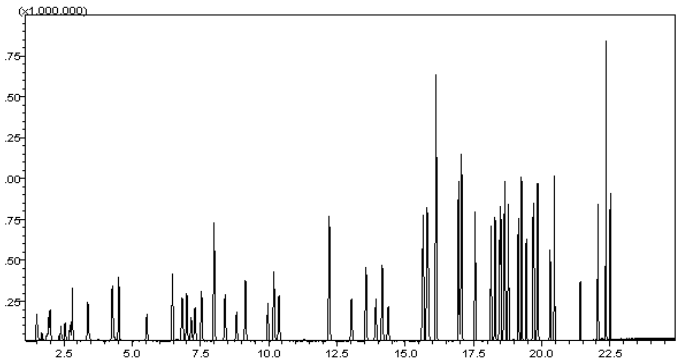


Figure 5. Chromatograph of 64 VOCs

The linearity of these compounds is partially illustrated in Figure 6 – Figure 8, representing the early, middle, and late elutes. Better than 0.999 of linear correlative coefficients were achieved for most of the compounds and all of the 64 VOCs showed linearity <0.995 in the range of 1 - 200 ppb.

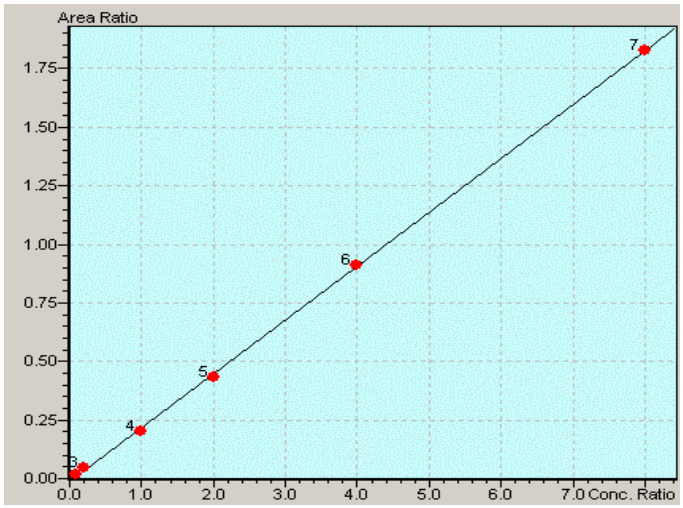


Figure 6. Dichlorodifluoromethane linearity

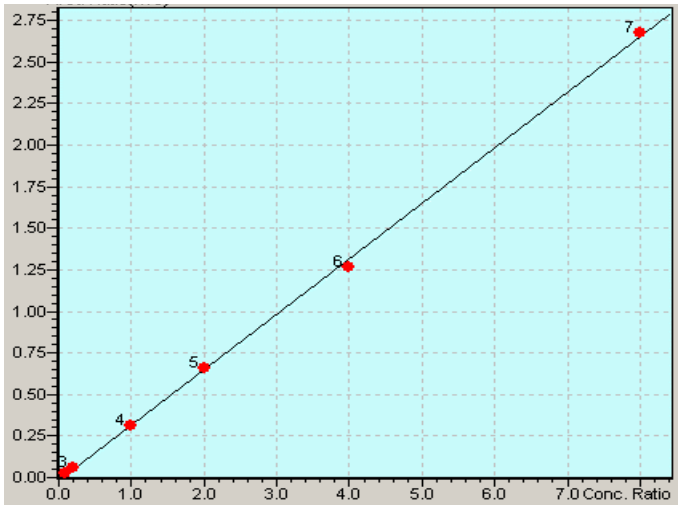


Figure 7. m,p-Xylene linearity

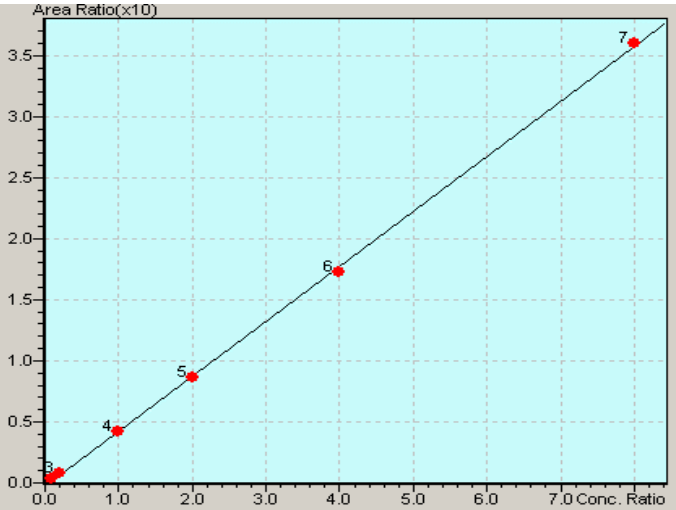


Figure 8. Naphthalene linearity

The response factors of gaseous compounds and BTEX (Benzene, Toluene, Ethylbenzene, and Xylene) at the concentrations of 1, 2, 5, 25, 100, and 200 µg/L in the water samples are illustrated in Figure 9 and 10, respectively. While the RSD of the gaseous compounds ranged from 6.79% to 12.4%, the range of the less volatile BTEX compounds was from 2.78% to 8.45%.

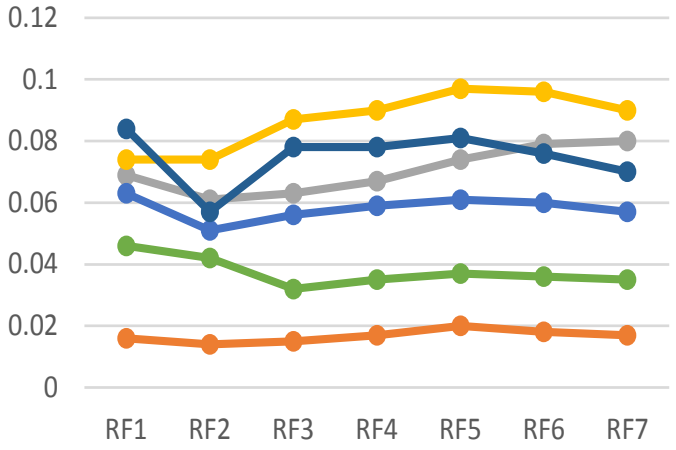


Figure 9. VOCs mix 6 response factors

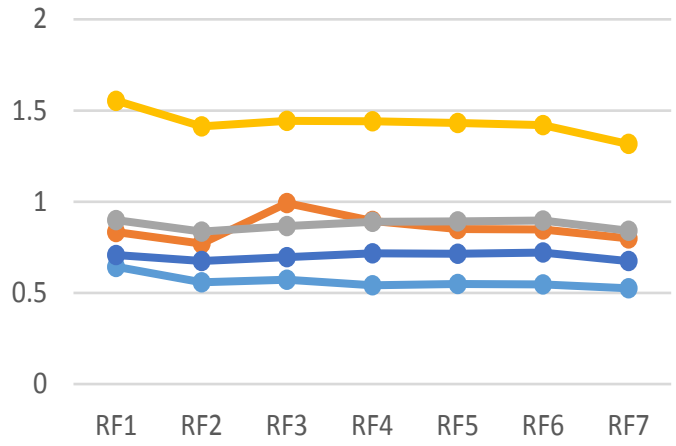


Figure 10. BTEX response factors

In these experiments, response factors at low level, e.g., below 2 µg/L can be significantly impacted by any trace contamination, e.g., from air or residue of the containers. A solvent-free environment for volatile analysis must be provided.

Conclusions

With the first-time combination of CDS 7000C P&T concentrator with PAL RTC Autosampler, analytical performances were evaluated. The reproducibility of the internal standards response was 3.97% for a 5-day period. A wide range of 64 VOCs were tested producing excellent chromatography. All the linearities of 1-200 µg/L 64 VOCs compounds were better than 0.995 and most of them were better than 0.999. The RSD of the response factors of the gaseous species were 6.79%-12.4%, and those of BTEX were 2.78%-8.45%. The system demonstrated excellent analytical performances for VOCs determination in water.

Water sample for analysis can be supplied with the standard 40 mL P&T vials. Using a flow cell with the CTC PAL autosampler extends the P&T application to on-line analysis of separate tap water streams in automated unattended operation.

References

[1] EPA Method 8260C (SW-846): Volatile Organic Compounds by Gas Chromatography-Mass Spectrometry (GC/MS).
[2] EPA Method 5030C: Purge-and-Trap for Aqueous Samples.

For More Information

For More Information on our products and services, please visit our web site at www.cdsanalytical.com.

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