Automated Clean-up of PCB extracts from Waste Oil using the Agilent 7696A Sample Prep WorkBench

Application Note

Automated Sample Preparation

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Abstract

Solid waste, including petroleum based waste oils, transformer oil or mineral oil are screened for the presence of polychlorinated biphenyls (PCBs). The analysis is typically performed by GC-ECD or GC-MS after clean-up using column chromatography, solid phase extraction (SPE), or dispersive solid phase extraction (d-SPE). Clean-up on silica or acidified silica removes polar constituents that can interfere with the PCB analytes and/or contaminate the analytical system.

A miniaturized dispersive SPE method using SiOH/H_2SO_4 adsorbent was automated on the Agilent 7696A Sample Prep WorkBench system. The extracts could be purified efficiently and reproducible. In combination with GC-ECD, GC-MS or GC-MS/MS, also applying back-flushing, an automated, accurate and robust determination of PCBs in waste oils is possible.

Introduction

The determination of polychlorinated biphenyls (PCBs) in mineral oils, including transformer oil, waste oil, or solid waste in general is a routine application in environmental laboratories. After dilution/dissolvation of the oil, sample clean-up is applied to remove most of the matrix. Clean-up methods are typically based on classical column chromatography or solid phase extraction (SPE). Several SPE methods are applied and dedicated cartridges for PCB in waste (mineral) oil determination are available. According to EN 12766, for instance, a combination of an acidified silica/anion exchange (SiOH-H_2SO_4/SAX) and a silica (SiOH) is used. The oil samples are applied to the cartridge in hexane solution and the PCB fraction is immediately eluted with hexane. The polar matrix compounds remain on the SPE cartridges [1].

The solid phase extraction method can also be miniaturized and simplified using dispersive solid phase extraction [2]. In comparison to SPE, the adsorbent is added to the extract and the sample is mixed. The polar interferences bind to the active adsorbent, while the apolar solutes remain in solution. A similar approach is used in the well-know QuEChERS method used for pesticide analysis [3].

In this application note, it is demonstrated that the dispersive-SPE method can be miniaturized and automated on an Agilent 7696 Sample Prep WorkBench. From an extract/solution containing oil and (possibly) PCBs, an aliquot is transferred to a vial containing a pre-weighed amount of adsorbent. The vial is vortexed, an aliquot of the supernatant is transferred to another vial containing silica for additional clean-up, and finally, an aliquot of the PCB-fraction is transferred to an empty vial ready to be analysed by GC-ECD, GC-MS or GC-MS/MS.

As this clean-up procedure removes polar interferences, the PCB extract still contains apolar matrix compounds. These compounds will interfere less with the PCB determination, but especially high molecular weight material can build up in the analytical system and contaminate column and ion source. For this reason, it is still recommended to apply back-flushing as described in Application Note 5989-7601 EN [4].

Experimental

Chemicals

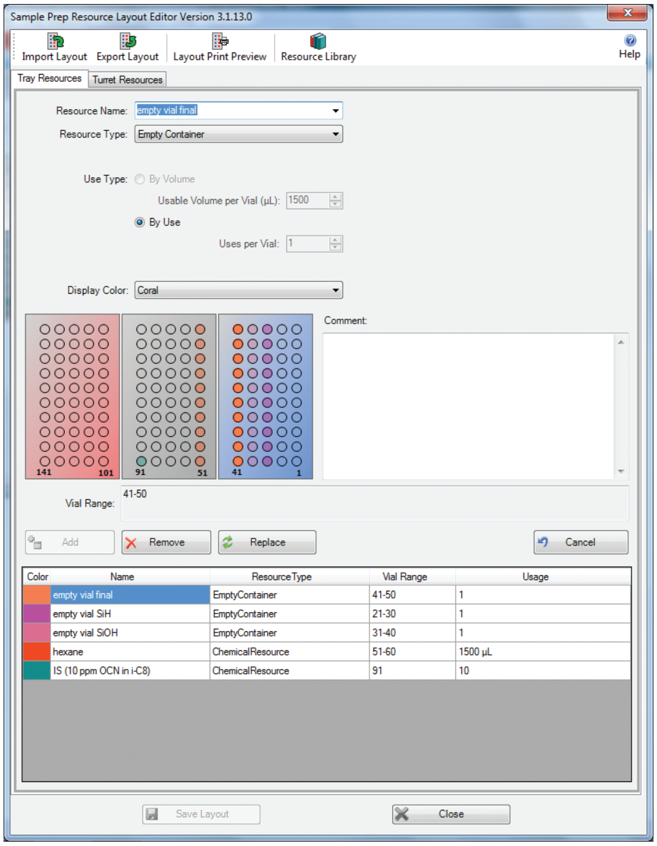
A BCR reference sample was used to demonstrated the performance of the clean-up method. BCR-449 (IRMM, Geel, Belgium) is a waste mineral oil sample, containing a high (mg/kg) level of PCBs. From the oil, a 100 mg/mL solution in hexane was prepared.

Octachloronaphthalene (Sigma-Aldrich, Beerse, Belgium) was used as internal standard. A stock solution of 10 ppm in iso-octane was used.

Three adsorbents were used: 44% H_2SO_4 coated silica gel (BONDESIL-SAX, 40UM, p/n 12213041, Agilent Technologies) and washed silica gel (BONDESIL-SI, 40UM, p/n 12213001, Agilent Technologies). To a first series of 2-mL vials, 100 mg H_2SO_4 coated silica and 100 mg SAX materials was added. These vials are labeled SiH. To a second series of 2-mL vials, 100 mg washed silica was added. These vials are labeled SiOH. All vial were closed with screw caps to protect them from humidity. All weighed amounts were with a precision: 100 mg ± 5 mg.

Sample Preparation

Aliquots of the waste oil solution are pipetted in 2-mL vials (samples). Eventually, a vial with a 100-µL insert can be used. A series of 2-mL vials containing the acidified silica/SAX material (SiH) and 2-mL vials containing silica (SiOH) are also positioned in the racks, together with empty vials with a 100-µL insert (for final extract), vials with hexane solvent (chemical resource) and vials containing the internal standard solution (chemical resource). An example of the resource lay-out of the 7696 WorkBench is shown in Figure 1.



Resource Name: empty vial final

Resource Type: Empty Container

Use Type: ○ By Volume

Usable Volume per Vial (µL): 1500

● By Use

Uses per Vial: 1

Display Color: Coral

Comment:

Vial Range: 41-50

Color	Name	ResourceType	Vial Range	Usage
🟧	empty vial final	EmptyContainer	41-50	1
🟪	empty vial SiH	EmptyContainer	21-30	1
🟥	empty vial SiOH	EmptyContainer	31-40	1
🟥	hexane	ChemicalResource	51-60	1500 µL
🟩	IS (10 ppm OCN in i-C8)	ChemicalResource	91	10

figure 1. Resource lay-out for an Agilent 7696 Sample Prep WorkBench

The WorkBench method can be summarized as follows:

1 **Add 50 uL of Sample (10% waste oil in hexane) to SiH at Front Tower.**
(A fraction of the sample is added to the vial containing the acidified silica and SAX material.)

2 **Add 1,350 uL of hexane to SiH at Front Tower.**
(Additional hexane solvent is added.)

3 **Add 150 uL of IS to SiH at Front Tower.**
(Internal standard is added, final volume is 1.5 mL, corresponds to 5 mg oil and 1,500 ng IS.)

4 **Mix SiH at 4,000 RPM for 5 min 0 sec.**
(The vortex allows good mixing of the adsorbents with the sample.)

5 **Wait for 2 min 0 sec.**
(This allows the polar fraction to bind with the adsorbents.)

6 **Add 1,000 uL of SiH to SiOH at Front Tower.**
(Transfers supernatant to a second clean-up vial.)

7 **Mix SiOH at 4,000 RPM for 5 min 0 sec.**
(The vortex allows good mixing of the adsorbents with the sample.)

8 **Wait for 2 min 0 sec.**
(This allows the polar fraction to bind with the adsorbent.)

9 **Add 200 uL of SiOH to Vial final at Front Tower.**
(Transfer of cleaned extract to a vial with an insert.)

10 **Flag Vial final as Result.**

Instrumental Configuration

The analyses were performed on an Agilent 7000 Triple Quad GC/MS system. The GC was equipped with a MMI inlet. Separation was done on a 0.25 mm × 30 m, 0.25 µm DB-5MS column (p/n 122-5532). The outlet of the column was connected to a Quick-Swap connector at 28 kPa constant pressure. The fused silica restrictor in the MS transfer line was 0.17 m × 110 µm.

The analytical conditions are summarized in Table 1.

Table 1. Analytical Conditions

Injection	1 µL, pulsed splitless
Inlet temp	85 °C (0 min) – 720 °C/min – 325 °C (5 min)
Carrier	Helium, 1 mL/min constant flow
	During backflush: –2 mL/min
Oven temp	80 °C (1 min) – 10 °C/min – 305 °C – 7.5 min hold
MS	MRM mode
	CE 25 V, dwell time 100 ms per transition
	Trichloro-biphenyls: 256.0 > 186.0; 258.0 > 186.0
	Tetrachloro-biphenyls: 293.8 > 222.0; 291.8 > 222.0
	Pentachloro-biphenyls: 325.8 > 256.0; 327.8 > 256.0
	Hexachloro-biphenyls: 359.9 > 289.9; 361.9 > 289.9
	Heptachloro-biphenyls: 393.8 > 323.8; 395.8 > 323.8
	Octachloronaphthalene (IS): 404.0 > 404.0 (CE 0V)
Backflush	Start at 23.5 min

Results and Discussion

The sample preparation procedure performed on the Agilent 7696 Sample Prep WorkBench is illustrated in Figure 2. The solution of the waste mineral oil is dark-brown, due to the presence of oil components. After transfer of an aliquot of this sample, corresponding to 5 mg oil, to a vial containing 100 mg SiOH/H_2SO_4 + 100 mg SAX adsorbent, the solution becomes much clearer, while the adsorbent turns black. This step is the most important, removing the bulk of the matrix. In a second clean-up step, some remaining contaminants are removed on silica material. Finally, the fraction is transferred in an insert vial. This solution is clear, indicating that purification was efficient.

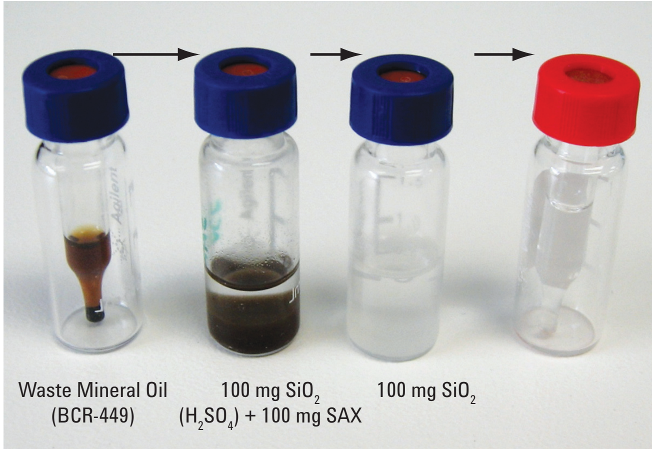


Figure 2. Picture of 2-mL vials during different clean-up steps on an Agilent 7696 Sampe Prep WorkBench.

In Figure 2, from left to right:

1. Original solution of waste oil in hexane
2. After transfer of waste oil to SiH (binding of contaminants to acidified silica/SAX material)
3. After transfer of extract to SiOH vial
4. Final extract

The obtained extracts were analyzed by GC-MS/MS. The obtained chromatograms (TIC from MRM acquisition) of 5 aliquots from the reference sample BCR-449, prepared according to the above described sample preparation method, are shown in Figure 3. The internal standard elutes at 22.8 min. The PCBs can easily be detected. From these chromatograms, it is clear that reproducibility is quite good.

In Table 2, the repeatabilities of the relative peak areas for six target compounds are given. Typically, the RSD % are around 5%.

Table 2. Repeatabilities of the Relative Peak Areas

Solute	**RT (min)**	**Rel Area (solute/IS)**	**RSD (%)**
PCB52	15,463	0,027	4,51
PCB101	17,151	0,037	6,10
PCB118	18,326	0,105	9,76
PCB153	18,731	0,086	4,54
PCB138	19,246	0,095	5,58
PCB180	20,448	0,026	4,03
OCN (IS)	22,849		

The same results are expected using GC-ECD or GC-MSD analysis.

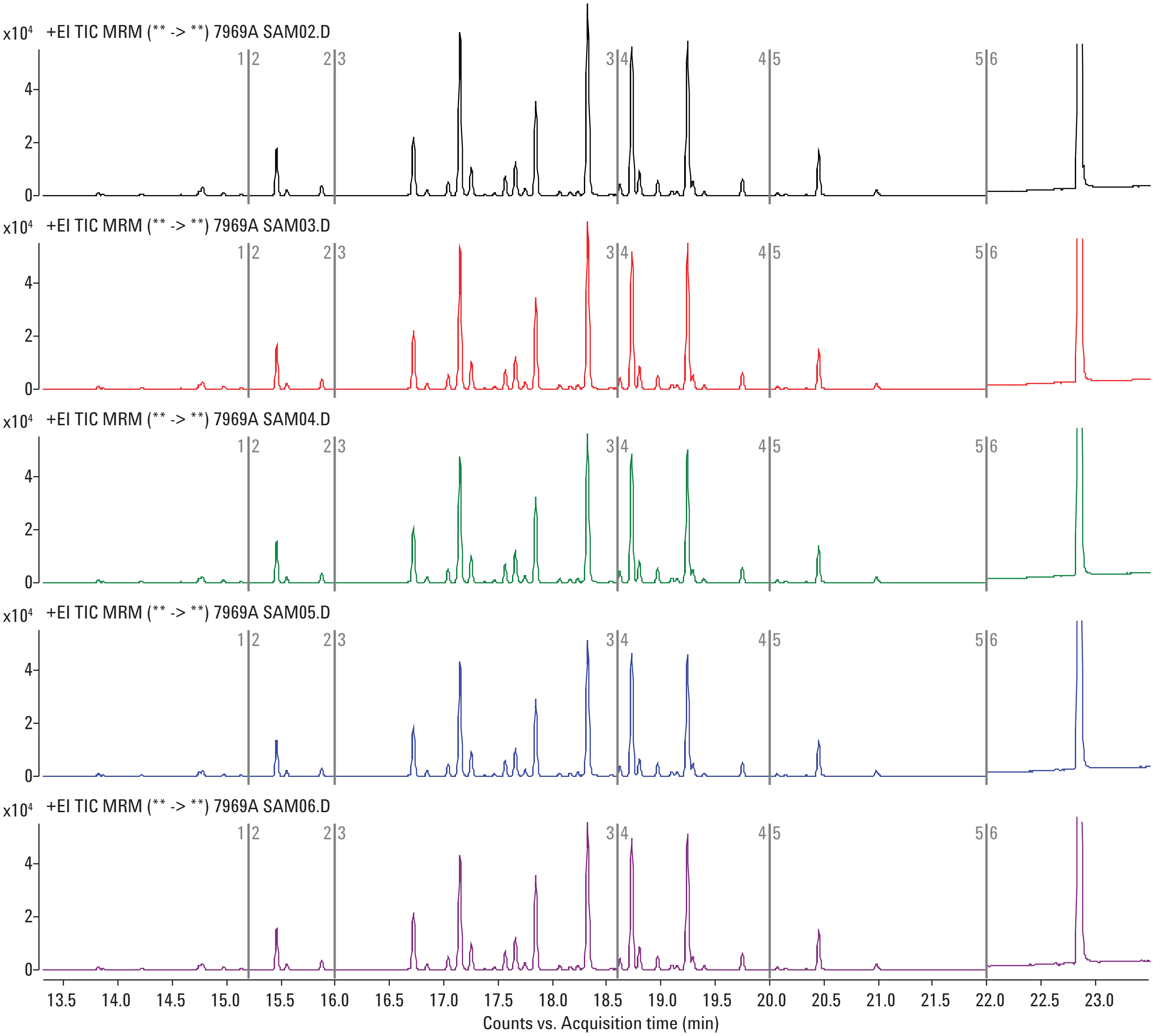


Figure 3. *TIC Chromatograms from GC-MS/MS analysis in MRM mode obtained for the extract of PCBs from waste oil.*

It should however be kept in mind that in the PCB fraction, apolar matrix compounds are still present. These compounds are not removed on the different adsorbents. In the analysis by GC-ECD, GC-MS operated in SIM mode, or GC-MS/MS in MRM mode, the co-extracted solutes are not detected. Their presence can however contaminate the inlet, column and finally also the detector. For this reason, the use of back-flushing, as described in reference [4], is still recommended.

Conclusion

A miniaturized dispersive SPE method for the determination of PCBS in waste mineral oils was automated on the Agilent 7696A Sample Prep WorkBench system. A two-step d-SPE using SiOH/H_2SO_4 + SAX adsorbent, followed by silica adsorbent was used. The extracts were efficiently and reproducibly purified. In combination with GC-MS or GC-MS/MS, also applying backflushing, an automated, accurate and robust determination of PCBs in waste oils is possible.

References

1. Information on sample preparation and analysis of PCBs in waste oils can be found in reference methods DIN EN 12766 and DIN EN 61619.
2. P. Sandra and F. David, The 1999 Belgian Dioxin Crisis: the Need to Apply State-of-the-Art Analytical Methods. Chapter 40 (pages 643–652) in A Century of Separation Science,Ed. H.J. Issaq, Publisher: Marcel Dekker, New York, 2002, ISBN 0-8247-0576-9
3. For more information on QuEChERs: http://quechers.cvua-stuttgart.de/
4. F. David and M.S. Klee, GC/MS Analysis of PCBs in waste Oil Using the Backflush Capability of the Agilent QuickSwap Accessory, 11/2007, Agilent application note 5989-7601 EN

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