

## IMPROVED EXTRACTION METHOD FOR PCBs FROM TRANSFORMER OIL USING SULFOXIDE MODIFIED SILICA SPE

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### Introduction

Polychlorinated biphenyls (PCBs) were once widely used as insulating fluids, dielectrics, and lubricants. This included their extensive use in electrical transformers (1). PCB use has been banned in many countries; and the Stockholm Convention currently prohibits the production and use of PCBs. Parties to the Convention are required to discontinue use of PCBs in existing equipment, including electrical transformers, by 2025 (2). There are many transformers still in service that contain PCBs, and these must be identified (if not already). This has resulted in a need to identify and quantify the PCBs present in these transformers so as to ensure that oil waste is handled properly (3).

There are several options in sample preparation of transformer oil for PCB analysis. Sulfoxide-modified silica, available commercially as Supelclean™ Sulfoxide, offers an advantage over traditional sample preparation techniques. It does not require the large columns used with normal phase SPE sorbents such as florisil and silica gel, and does not require the handling of hazardous chemicals such as in acid cleanup, or time consuming procedures such as GPC or liquid-liquid partitioning (4,5,6).

Supelclean Sulfoxide SPE consists of a sulfoxide-modified silica gel. Retention of PCBs is facilitated through interaction between the electrophilic sulfur atoms in the Sulfoxide SPE and the  $\pi$ -electrons in the aromatic rings of the PCBs. This allows preferential retention of PCBs while weakly retained hydrocarbon matrix is removed with a wash step. Sulfoxide SPE was originally developed for use in Japan, where laboratories do congener specific analysis by GC-MS, and are required to meet a detection level of 0.5 mg/Kg for PCB in transformer oil. In order to meet this detection level, high recovery must be achieved from the extraction method. Use of Sulfoxide SPE with a method using 13-25 mL of hexane for elution has been found to obtain recoveries to meet this requirement (7). Other widely used methodologies analyze PCBs in transformer oils as commercial mixtures by GC-ECD (4,5). In this work, we investigated the use of Supelclean Sulfoxide SPE for analysis of PCBs in transformer oil as Aroclors. Aroclors are commercial PCB mixtures manufactured from 1930-1979, and were commonly used in the United States (1). As an alternative to the larger hexane volumes used for the congener-specific GC-MS analysis, we evaluated a lower volume elution using a combination of hexane and acetone. Working with a smaller volume of elution solvent has the cost benefits of reduced solvent usage. In addition, the smaller volume eliminates the need for a concentration step, thus increasing the speed and ease of sample preparation.

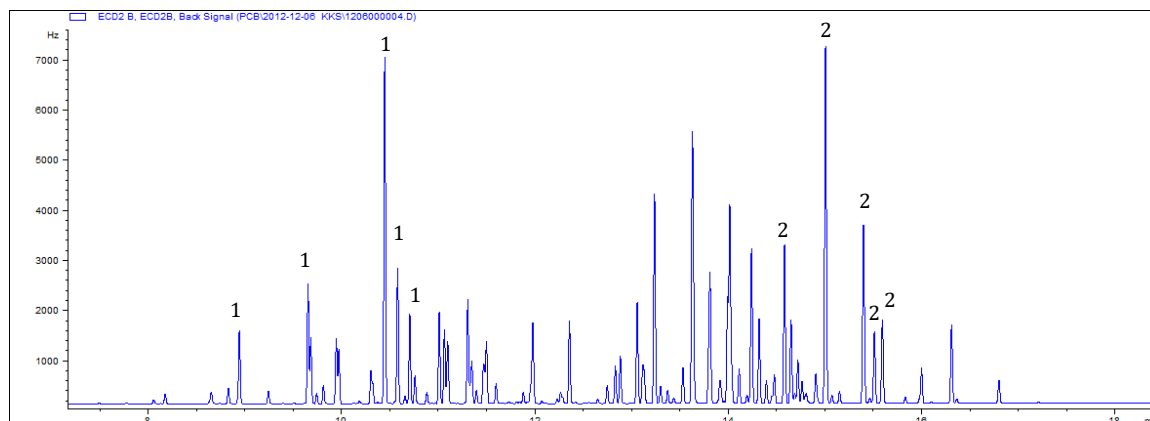
### Materials and methods

The 6 mL/3 gm Supelclean Sulfoxide SPE cartridges were from Sigma-Aldrich. As part of the SPE method, cartridges were conditioned with 10 mL of acetone and equilibrated with 20 mL of hexane. 125  $\mu$ L of transformer oil, accurately weighed, was mixed with 125  $\mu$ L of hexane and loaded onto the equilibrated cartridge. The cartridge was washed with 5 mL of hexane, and the sample eluted with either 25 mL hexane or 5 mL of 1:1 acetone: hexane. The eluent was collected and adjusted to a final volume of 10 mL. The resulting sample was then analyzed on an Agilent 7890 GC/ $\mu$ -ECD. The GC column used was a Supelco SLB-5ms, bonded and highly crosslinked; silyphenylene polymer with polarity equivalent to poly(5% diphenyl/95% dimethyl siloxane), 20 m x 0.18 mm I.D., 0.18  $\mu$ m. The GC oven conditions were 70 °C, hold for 1 minute, ramp at 12 °C/minute to 340 °C and hold for 2 minutes. The  $\mu$ -ECD temperature was 340 °C. Hydrogen was used as the carrier gas at 1.2 mL/min., constant flow. A 1  $\mu$ L splitless injection was done, with a splitless time of 0.75 min. The inlet temperature was 250 °C, and the liner style used was a 4 mm I.D. FocusLiner™, with taper, containing quartz wool.

Calibration standards containing a mix of both Ar1016 and Ar1260 were prepared in hexane from 1 mg/ml stock mixtures. A 125  $\mu$ L aliquot of each calibration standard was processed using the Supelclean Sulfoxide SPE method and adjusted to a final volume of 10 mL prior to GC analysis.

Samples extracted and quantitated consisted of standards of Ar1016 and Ar1260 in transformer oil, and a transformer oil certified reference material (CRM) containing Ar1260. Quantitation was done using a 5-point calibration curve constructed with standards at 1, 15, 50, 75, and 100 ug/mL in solvent, which were extracted with each set of samples. Responses were generated for standards and samples using area summation of 5 unique peaks in each Aroclor. The peaks chosen for summation are indicated in Figure 1.

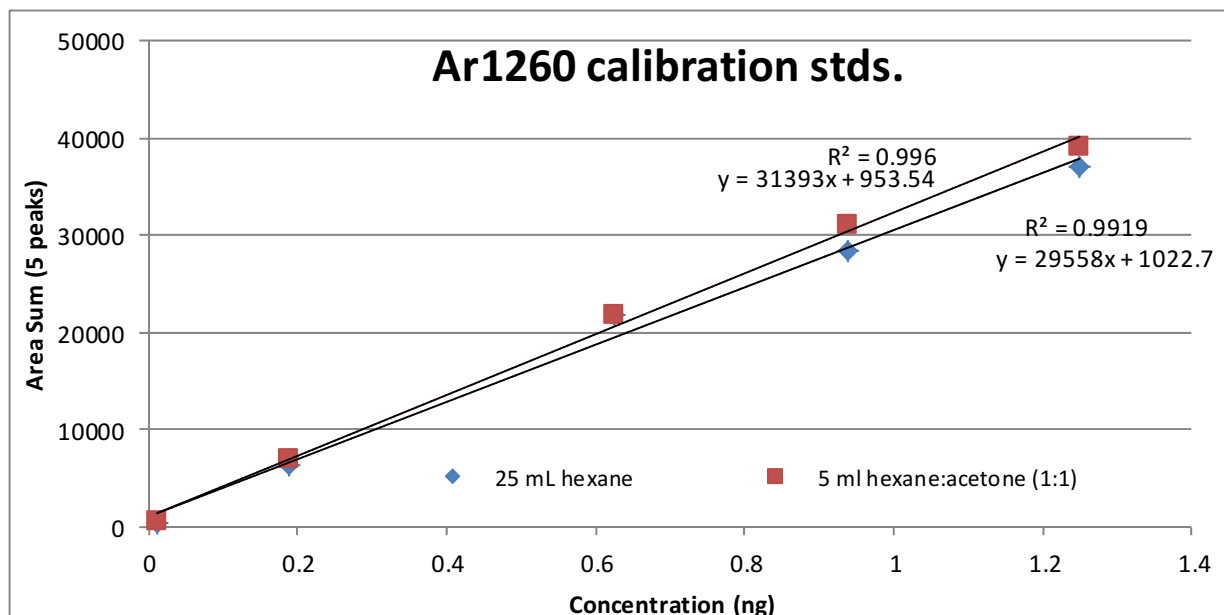
**Figure 1. 50 ug/mL extracted standard mixture of Ar1016 and Ar1260, peaks used for quantitation indicated. 1=Ar 1016 peak, 2=Ar1260 peak.**



### Results and discussion

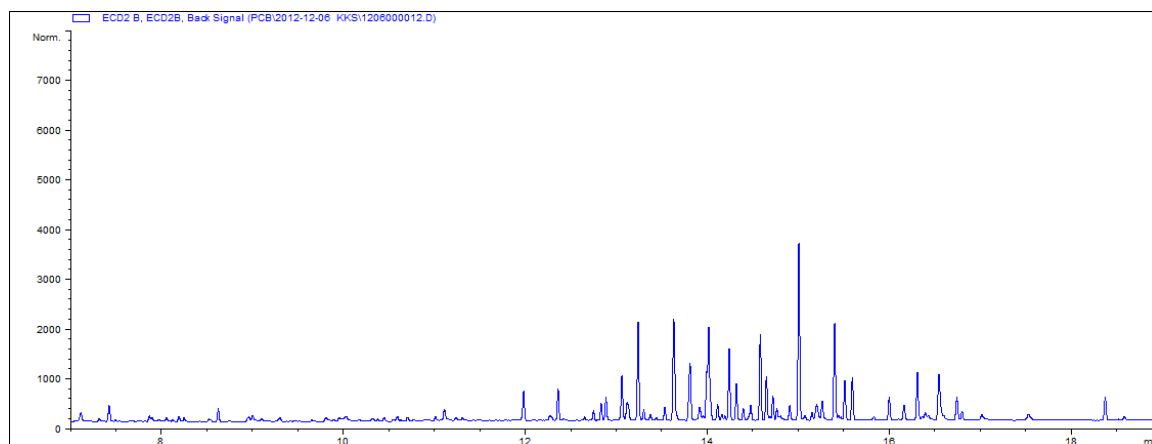
Calibration curves generated from extracted standards prepared using each of the elution methods were compared directly and indicated similar recovery for the Aroclor mixtures out of solvent (Figure 2).

**Figure 2. Ar1260 calibration curves generated using extracted standards and elution with 5 mL acetone hexane (1:1) and 25 mL hexane.**

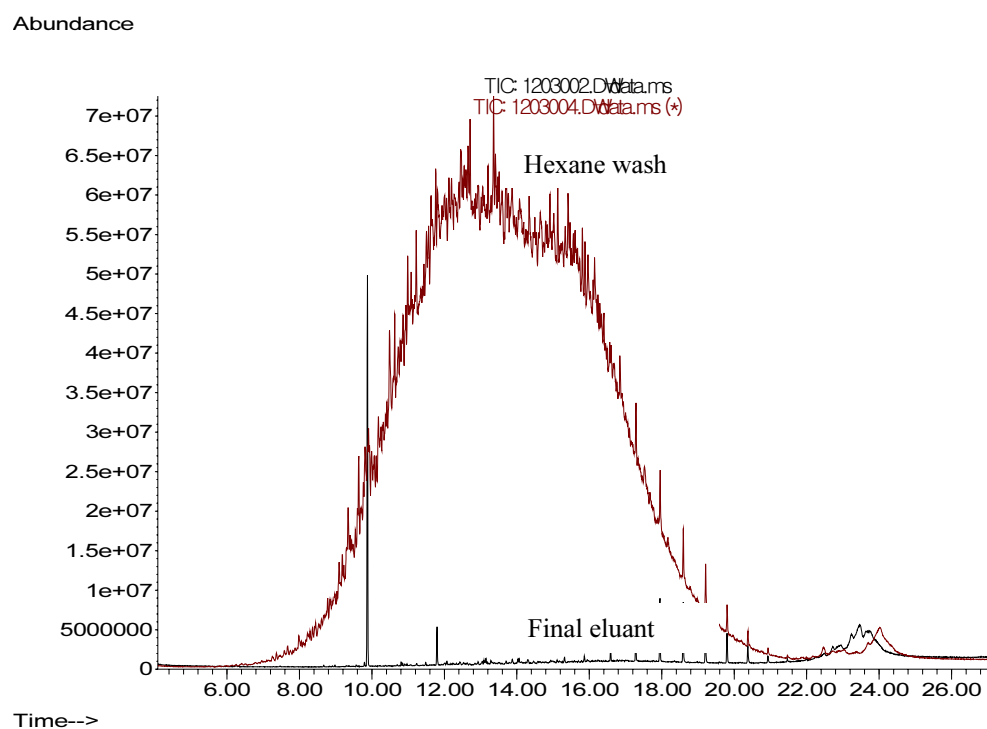


Both SPE elution solvents produced extracts with little matrix interference, as detectable by GC-ECD (Figure 3). Since hydrocarbons do not produce a response by ECD, the hexane wash was collected and analyzed by GC-MS to verify cleanup. The final extract after elution with 1:1 hexane:acetone was also analyzed by GC-MS for comparison. An overlay of the resulting TICs (Figure 4) shows the difference between the hexane wash and final acetone:hexane eluent, confirming that the hydrocarbon matrix had been removed during the wash step.

**Figure 3. GC-ECD analysis of transformer oil CRM extracted using Supelclean Sulfoxide SPE.**



**Figure 4. Overlay of GC-MS analyses of hexane wash step and final eluant of Supelclean Sulfoxide SPE method.**



A comparison of the Aroclor recoveries obtained for the oil standards and CRM are presented in Table 1. Duplicate oil standards of Ar1016 and Ar1260, and three replicates of the CRM were extracted and analyzed. In the case of the CRM, % RSD values were calculated and are indicated in parentheses to the right of the % recovery value.

The best recoveries were obtained using 25 mL hexane elution. The recovery values obtained using 5 mL of hexane:acetone were 85 - 92% of the values using 25 mL hexane. However, the 25 mL volume of solvent was difficult to work with and required a tedious concentration step prior to GC analysis. To try and increase recovery using the acetone:hexane elution, the volume was increased from 5 to 10 mL of solvent. However, this approach did not show any advantage over the smaller volume.

Compared to values reported on the certificate of analysis for the oil standards and CRM, the values obtained with the low volume acetone:hexane method were within 75-80% recovery for the oil standards and 90% recovery for the Ar1260 CRM. The reason for this difference in recovery between the oil standards and CRMs is not known for certain. However, there is ambiguity involved in the calculation of aroclor concentration due to the existence of multiple peaks and weathering of the Aroclor mixture in environmental samples. As a result, acceptance criteria for recovery is often wide. Recoveries obtained with 5 mL of acetone:hexane may be acceptable, depending on the method and QC requirements being followed by a particular laboratory. The % RSD of the CRM was < 5% for all elution schemes, indicating good reproducibility with Supelclean Sulfoxide SPE regardless of the elution scheme used.

**Table 1. Recoveries of Aroclors from transformer oil standards and certified reference material using Supelclean Sulfoxide SPE, comparison of elution methods.**

	Concentration listed on C of A: (mg/Kg)	25 mL hexane (mg/Kg)	5 ml hexane:acetone (1:1) (mg/Kg)	10 ml hexane:acetone (1:1) (mg/Kg)	
Ar1016 oil standard	50*	47.6	40.9	36.9	n=2
Ar 1260 oil standard	50*	42.0	38.7	36.6	n=2
Ar1260 transformer oil CRM	35.2**	36.8 (1)	31.6 (4)	32.0 (2)	n=3

\*conc. based on gravimetric calculations

\*\*study mean, based on laboratory round-robin testing

### Conclusions

It has been shown that Supelclean Sulfoxide SPE can be used to extract PCBs from transformer oil. The method using 25 mL of hexane for elution gave the best recovery results, however the volume of solvent was difficult to work with. An alternative elution to consider is hexane:acetone (1:1), of which a considerably smaller volume (5 mL in our study) can be used. Evaluation of recovery using this scheme will depend on the method used for quantification as well as the specific acceptance criteria under which a lab is operating. In our case, quantitation was done using 5 distinct congener peaks from each PCB mixture, and the result reported as the specific Aroclor to which the sample was quantitated.

### References

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