

An Assessment of Various Aprotic Solvents to Separate PCB from Oils

Poole G., Thibert, B., Lemaire, H. Sheridan, B., and Chiu, C. Analysis and Methods Division, Environment Canada, Environmental Technology Center, Ottawa, Ontario, K1A- 0H3

1) Introduction

Regulations in Canada limit the concentration of PCBs in recycled oil and in new products to less than 2 ug/g. An unequivocal method of analysis using mass spectroscopy was recently developed to support these regulations. The main hurdle to overcome was the inherent sensitivity of mass spectrometers to oils such that as little as 0.2 % (w/v) of oil inhibits accurate quantification. A cleanup procedure therefore, was developed to remove at least 99.8 % of the oil matrix to accurately quantify PCB at the regulated limit.

The use of aprotic solvents to separate aromatic compounds from an oil matrix has been practiced for quite some time. An examination of the literature(1-4) reveals that several different aprotic solvents have been used for various applications.

This paper will illustrate the amount of oil removed and the recovery of PCB from motor oil and transformer oil using dimethyl sulfoxide, dimethylformamide, acetonitrile and n-methyl pyrrolidone. The results indicate that dimethyl sulfoxide is the most effective solvent for this application.

2) Materials:

The oils used during the experiment were neat oils from the SRM 1581 kit available from NIST. The PCB mixture containing 1 ug/ul of Aroclor 1242 in isooctane was purchased from Supelco. The solvents used were of the highest available grades purchased through Caledon. An inhouse supply of deionized water was used during the study.

3) Instrumentation:

The weight of the oils remaining in the extract were determined on a Mettler Model H-54 analytical balance with a readability to 0.01 mg.

The analysis of PCB concentration was accomplished using a 1 uL splitless injection into a Hewlett Packard Model 5890 Series II gas chromatograph equipped with a 30 m, DB-5 column, 0.25 mm I.D., and a film thickness of 0.25 um. An electron capture detector (ECD) was used to detect PCB.

The confirmational analysis was achieved with an HP 5890 GC coupled to a mass selective detector (MSD) HP 5970A. A 2 uL, on column, injection was made onto a DB-5 column as

noted above. The MSD was operated in the electron impact and selective ion monitoring modes.

4) Methodology:

Each sample, consisting of 500 mg of oil spiked to a concentration of 1.0 ug/g with Aroclor 1242, was dissolved in 15 mL of hexane. The samples were transferred into a separatory funnel and extracted with 3 x 10 mL aliquots of aprotic solvent. The solvents tested included acetonitrile (ACN), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP). Each solvent was pre-extracted with hexane prior to use to eliminate interferences. Triplicate analyses were performed with each solvent. A schematic of the extraction process is presented in Figure 1.

The combined extracts were washed with 10 mL of hexane. The hexane was then extracted with an additional 10 mL of aprotic solvent which was added to the original extract.

Two hundred milliliters of deionized water was added to the aprotic solvent before the PCB was back extracted sequentially with 100, 50 and 50 mL of hexane.

The hexane was concentrated, passed through a modified silica column to remove interferences, then reduced to 0.5 mL for GC/ECD analysis to determine the recovery of PCB from the oil.

Each sample was then blown down to dryness in a preweighed 1.5 mL vial. The difference in weight represented the mass of oil remaining in the extract.

5) Results/Discussion:

The results assessing the oil removal efficiency of the various aprotic solvents indicated that each had a very low affinity for the oil matrix (Fig.2). No significant differences for the solubility of oil in DMSO, DMF or ACN could be detected. The solubility of oil in NMP however appeared to be greater than the other aprotic solvents tested. It was apparent that the transformer oil was slightly more soluble in the solvents than was motor oil.

Figure 2

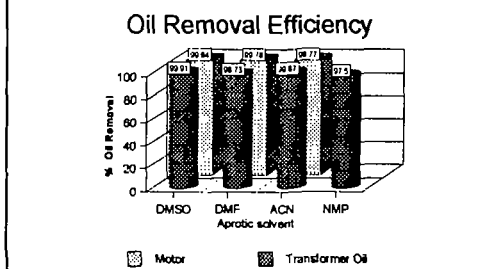
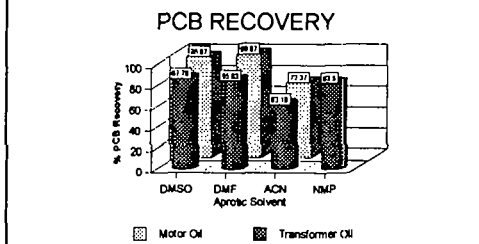


Figure 3



Analysis of the cleaned-up extracts for PCBs using GC/ECD revealed that the solvents tested had a different affinity for PCB (Fig.3). The recovery of PCB from each of the oils extracted with ACN was significantly lower using any of the other solvents tested. A slightly lower recovery of PCB using NMP was also noted. The recovery of PCB from motor oil was greater than the recovery from transformer oil.

Subsequent studies to optimize the recovery of PCBs from oil focussed on the use of DMSO and DMF as a result of the lower recoveries obtained using ACN and NMP to extract the oil.

Further research indicated that DMSO was able to extract more PCBs from oil, with less oil in the extract, when compared to the same extractions using DMF. Mass selective detection of the DMF extracts was severely impaired in the tri and tetra-chlorinated biphenyl regions due to interferences from the oil matrix.

Eventually the oil matrix was virtually eliminated from the sample extracts using DMSO diluted with 2.5% water (v/v).

An estimation of the method detection limit was made by using the method to extract 10 replicate samples of blank transformer oil spiked with 0.075 ug/g each of 19 PCB congeners ranging from tri to deca-chlorinated biphenyls. The sample extracts were analysed using a benchtop mass spectrometer. The standard deviation of these analyses was multiplied by the factor supplied from the Student's t-value tables using (n-1) degrees of freedom with a 99 % confidence interval. Method detection limits were determined to be 0.01 to 0.04 ug/g per congener.

References:

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Figure 1

Extraction Schematic for PCB in Oil