Evaluation of a Novel Dechlorination Reaction as an Analytically Useful Derivatization Reaction. Part 2. A Screening Technique for the Determination of PCBs in Waste Oils

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EVALUATION OF A NOVEL DECHLORINATION REACTION AS AN ANALYTICALLY USEFUL DERIVATIZATION REACTION
PART 2. A SCREENING TECHNIQUE FOR THE DETERMINATION OF PCBs IN WASTE OILS

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Potassium glycolate was used as the dechlorinating agent in the development of a screening technique for the determination of PCBs in waste oils. Due to the high extraction efficiency of polyethylene glycols in terms of removing PCBs from mineral oil, the analytical samples were directly applied to the dechlorination-reaction mixture. The samples were then analyzed for chloride using a flow-injection analysis system with a thin-layer amperometric detector employing a silver working electrode. This system demonstrated a low detection limit for chloride of 100 ng (at S/N = 3) and a 3% precision. The detection limit of the dechlorination reaction – chloride analysis system was limited by the detection limit of the latter. This corresponds to a detection limit of 0.9 mg/kg for Aroclor 1260. This detection limit is well below the regulatory limit of 50 mg/kg which defines whether a waste oil is contaminated with PCBs.

KEY WORDS: Dechlorination, potassium glycolate, polychlorinated biphenyls, polyethylene glycols, chloride analysis, thin-layer amperometric detector.

INTRODUCTION

As a result of government regulations relating to the disposal of PCBs in contaminated fluids, accurate and simple screening techniques applicable to large numbers of environmental samples are highly desirable for reducing the number of samples requiring further analysis

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through more sophisticated techniques. Several screening methods for PCBs have been suggested and/or developed[1]. For simplicity, most of these techniques are based on the determination of total chlorine rather than specific isomers. One such technique, for example, is neutron activation analysis (NAA)[2]; even though, however, NAA is both accurate and reliable, neutron sources (i.e. reactors) are not generally available, and analysis using this technique is too costly to be used for screening purposes. Another technique that is based on the determination of total chlorine involves the use of any one of a number of commercially available TOX analyzers. The problem with these analyzers, however, is that their pyrolysis tubes are made of quartz, which means that the analyte can not be heated to temperatures higher than 1100°C (strain point of quartz). The recommended operating range is, therefore, 800–950°C[3]. PCBs are completely combusted to CO_2, H_2O and HCl at temperatures well over 1100°C[4]. In fact, uncontrolled combustion below 700°C, produces various toxic materials including polychlorinated dibenzofurans and dibenzodioxins[5].

Less expensive and more widely available screening techniques are provided through a number of commercial colorimetric kits, which are designed for use in field tests for the purpose of establishing if the PCB concentrations in oils are within the EPA disposal limits. These kits usually establish if the PCB concentration is greater than 50 mg/kg and/or greater than 500 mg/kg depending upon the kit used. The accuracy of the results obtained with colorimetric kits has recently been questioned, however, especially for analyses near the lower regulatory limit of 50 mg/kg[6]. It is the objective here to introduce an alternative screening technique which does not involve the combustion of PCBs and which is simple, rapid, inexpensive and reliable for the purpose of significantly reducing the number of samples to be subsequently analyzed by more sophisticated and/or congener-specific techniques such as GC-ECD and GC-MS.

In order to evaluate the dechlorination reaction discussed in a previous paper in this issue in terms of limits of reliable measurement, a technique had to be found capable of detection limits for chloride lower than those provided by the common amperometric and potentio-metric techniques. The detection limit of these latter two techniques is theoretically and practically limited by the solubility product constant of AgCl in the solvent in which the chloride is present; it cannot be lower than the square root of K_{sp} of silver chloride.

An analysis system was devised that theoretically, at least, does not suffer from the problem described above. This system is a typical flow injection analysis system which employs a thin-layer amperometric detector with a silver working electrode. The rationale for having a silver electrode in a detector of this type can be illustrated through the following electrochemical equations and potentials:

$$Ag^+ + e^- \rightarrow Ag \qquad E° = +0.799 \text{ V} \qquad\qquad\qquad \text{(Rxn 1)}$$

$$AgCl + e^- \rightarrow Ag + Cl^- \quad E° = +0.222 \text{ V} \qquad\qquad\qquad \text{(Rxn 2)}$$

The reduction potentials associated with Rxns 1 and 2 suggest that, to a good approximation, if one has a silver electrode held at a potential lower than +0.799 V and higher than +0.222 V then, as chloride passes by the electrode in a flow system, the silver would be oxidized to AgCl, producing a current proportional to the Cl^- concentration. This hypothesis is based on the assumption that for reversible or nearly reversible systems the $E_{1/2}$ (half-wave

potential) for a redox couple is approximately equal to its corresponding oxidation-reduction potential. A similar approach was previously used by Pihlar and Kosta[7,8] for cyanide analysis; their method is based on the oxidation of the silver electrode in the presence of cyanide to produce the silver cyanide complex and a current proportional to the cyanide concentration.

EXPERIMENTAL

The nature of the samples

The dechlorination reaction described in the previous paper in this issue, was applied to the analysis of two samples of PCB-containing fluids obtained from Thomson Electric (5710 Notre Dame St. West, Montreal); the first sample originated from a transformer while the second from a capacitor (Thomson Electric is in the business of servicing transformers and capacitors in the Montreal area). In addition, three simulated samples of PCBs in mineral oil were analyzed.

Mixtures of chlorinated aromatic hydrocarbons commonly known as askarels have been used as insulating and/or dielectric fluids in electrical equipment. When PCBs are present, they are part of a series of complex mixtures of PCBs, chlorinated benzenes and trace contaminants. In North America, PCBs were marketed solely by Monsanto Company, St. Louis, Missouri; they were sold under the trade name Aroclor.

The primary purpose of a transformer is to convert electrical power from one operating voltage to another. Immersion of a transformer core in a tank of askarel allows for good electrical insulation between the coil windings. Most askarel transformers should last for about 30 years; however, power handling capability, operating temperature and amount of physical abuse determine its actual lifetime. Preventive maintenance to preclude operational and environmental hazards is of the utmost importance. Sparks inside the transformer occur as a result of lightning, switching surges and transient fault conditions on the power line. As a result of askarel decomposition, hydrogen chloride gas, carbon dioxide, askarel vapor and other hydrocarbon gases as well as carbon particles are produced[9]. Small changes in temperature are expected but normally the temperature should remain much less than 105°C. Excessive temperatures indicate that the transformer is overheating, possibly due to loss of askarel. Action must be taken immediately, as the rate of deterioration of insulating materials in the transformer can double for every 8°C rise over normal operating temperature.

Capacitors allow for the more efficient use of electrical power through power factor correction. Capacitors are hermetically sealed to reduce leakage risk and, therefore, cannot be tested to verify the contents. However, almost every electrical capacitor manufactured since the 1930's has been made with PCB fluids, so it must be assumed that all capacitors still in existence today contain PCBs except where alternative (non-PCB) liquids are clearly indicated on the nameplate of new equipment. An askarel capacitor usually has a lifetime of about 10 to 20 years. Most capacitors are equipped with fusing to de-energize the capacitor in the event of a breakdown. This prevents the capacitor from bursting open[9].
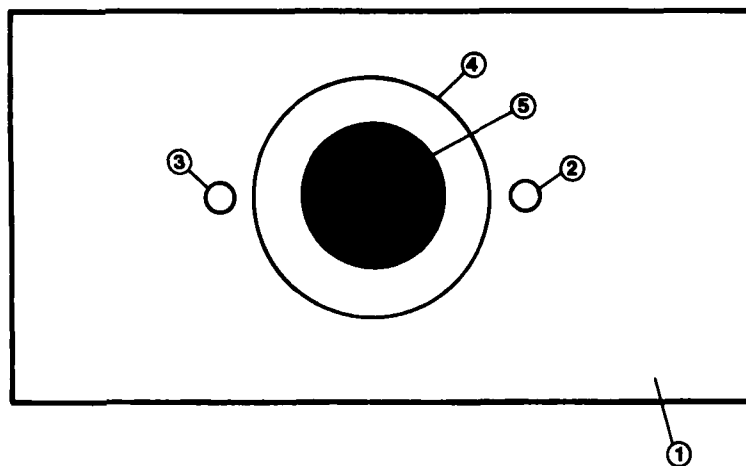
Figure 1   Cross-section of chloride amperometric detector. Legend: 1, Kel-F matrix; 2, inlet; 3, outlet; 4, silver working electrode (diameter, 1.6 cm); 5, platinum auxiliary electrode (diameter 1 cm). The total exposed area of the working electrode was 10.8 mm^2 and the cell volume 75.4ml.

Besides askarel-containing electrical equipment, a large number of mineral oil-containing transformers and other equipment contain millions of gallons of oil contaminated with PCBs at a level of 5 mg/kg and higher. This resulted from inadvertent cross-contamination caused in part by the use of common pumping and transfer equipment during the period when PCBs were not considered a problem. Because of this situation the Environmental Protection Agency of the United States has proposed regulations requiring that PCBs in transformer oil be monitored.

A flow-injection amperometric technique for the analysis of chloride

All chloride analyses were carried out using a flow-injection analysis system consisting of a mobile phase reservoir, a Waters model 6000A pump, a Rheodyne Model 7125 injector with a 100-μl loop, a 4.5-cm analytical column pre-packed with 37–75μm C$_{18}$ bonded-phase silica, a Princeton Applied Research (PAR) 174A polarographic analyzer for controlling the potential and measuring the current, a Microohm Model SE120 strip-chart recorder and a detector.

The detector used was a thin-layer amperometric detector of a design developed in our laboratory[10]. Besides using a silver working electrode, some other minor changes were introduced to this design with respect to the cell volume and the placement of the auxiliary electrode. The working electrode employed was a ring-shaped silver wire of a 1.6 cm diameter embedded in a Kel-F (Fluorocarbon, Anaheim, California) matrix. The total exposed area of the working electrode was 10.8 mm^2 while the detector cell volume was 75.4 μl. Co-centric to the silver ring was a circular platinum auxiliary electrode of a diameter of 1 cm (see Figure 1). The silver ring was polished to a shiny colour using silver polish (Brasso Eng.). A Ag/AgCl electrode was used as the reference electrode and placed

downstream from the working electrode. This electrode was prepared by a procedure similar to the one found in Sawyer and Roberts[11].

A piece of stainless steel tubing downstream from the working and reference electrodes was found to perform better than the platinum as auxiliary electrode, in terms of providing higher S/N ratios. Typical conditions for experiments and analyses carried out with this system are the following: flow rate: 1 ml/min; injection volume: 5–100µl; applied voltage: 0.7 V; temperature: ambient; chart speed = 0.5 inch/min; mobile phase: aqueous phosphate buffer, pH = 7.2, ionic strength = 0.2 M, distilled and deionized water (passed through a Barnstead water purification system) was used for the preparation of all buffers; these were deaerated by stirring under vacuum.

Analytical procedure

Various standard Aroclor mixtures as well as the analytical samples were dechlorinated using an optimized and simpler version of the experimental system and general procedure outlined in the experimental section of the previous paper in this issue. The specific system and procedure used is as follows.

The reaction system consisted of a 100-ml Erlenmeyer flask equipped with a stopper with two holes for allowing the entrance and escape of nitrogen from the reaction mixture as well as the escape of hydrogen formed during the reaction. The flask was held in an oil bath at 110°C and the contents were continuously stirred using a magnetic bar.

The reacting solution was composed of 10 ml polyethylene glycol (PEG), MW: 400, previously dried over activated molecular sieves type 3A (8–12 mesh). The molecular sieves were activated by placing them overnight in an oven, equipped with a vacuum line, and held at 300°C. The active reagent was prepared by reacting PEG and metallic potassium (0.4 g) at a temperature of 110°C for 30 minutes under nitrogen. About 10 mg of the Aroclor standard or analytical sample was then added to the reaction mixture. Small amounts of potassium and PEG were added to the reaction mixture as well at 30, 60, 90, 120 and 150 minutes after the initiation of the reaction. The reaction was allowed to take place for 180 minutes under nitrogen. After the reaction products were cooled down, 5 ml of methanol was added with caution, to dissolve any residual potassium, followed by 45 ml of water to dissolve the potassium chloride produced by the reaction. The reaction products were then analyzed for chloride using the system described above. It should be noted here that it is not necessary for the dechlorination reaction step to last as long as three hours; even if the dechlorination reaction is allowed to take place for as short a time as five minutes, the reaction yields will be sufficiently high and reproducible to provide reliable results for the determination of PCBs in waste oils. Moreover, since the reaction set-up is very simple and inexpensive, one could have numerous samples derivatized in parallel.

It was previously shown that PCBs can be efficiently extracted from mineral oils using PEGs[12]. Since PEGs constitute the reaction medium used in our analytical procedure, it was decided to add the PCB-containing fluid(s) directly into the reaction mixture thus avoiding a time-consuming extraction step. A 10-ml sample of the PCB-containing mineral oil (Texaco 55) was added to the reaction mixture and allowed to mix with the reaction constituents.
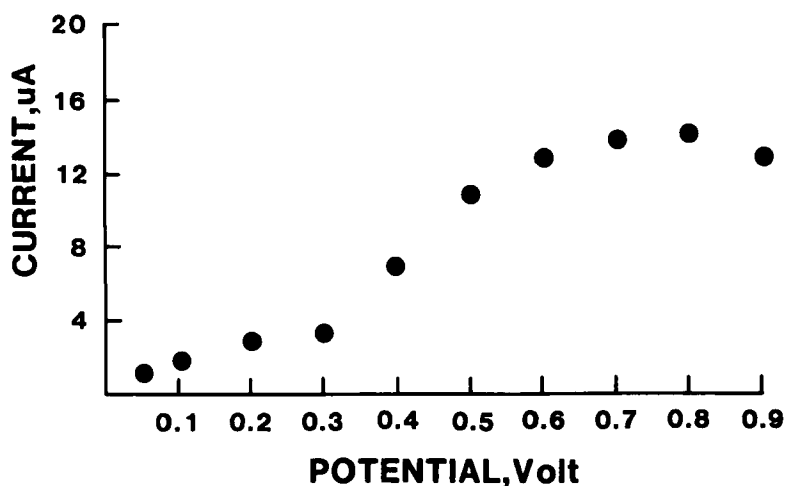
Figure 2 Hydrodynamic voltammogram obtained by the repeated injection of 10 μg (10 μl of a 1 mg/ml solution) of potassium chloride at various potentials ranging from 0–0.9 V. Conditions were: mobile phase: aqueous phosphate buffer (0.2 M, pH=7.2); flow rate: 1 ml/min; temperature: ambient.

RESULTS AND DISCUSSION

Optimization of chloride analysis system

In order to establish at which potential the working electrode of the thin-layer amperometric detector should be held, a hydrodynamic voltammogram was obtained. Figure 2 demonstrates such a voltammogram obtained by the repeated injection of 10μl of a 10 mg/ml solution (10 μg) of potassium chloride at various potentials ranging from 0–0.90 V. As seen in this figure, the current appears to level off at about 0.60 V. The decrease in current response at higher potentials is likely to be due to other competing reactions to the one of interest, probably oxidation of silver to form an oxide or hydroxide, thus poisoning the electrode surface[13]. A curve of a similar shape was obtained when 10 μl of a 10 mg/ml solution (100μg) of potassium chloride was injected and also when the flow rate was either smaller (0.5 ml/min) or larger (2 ml/min).

A small negative dip was often observed following each chloride peak for potentials lower than 0.5 V (see Figure 3); this is likely to be due to the reduction of AgCl deposited on the electrode. Since there was no longer chloride in the solution next to the electrode (as it had all eluted), and since the potential was below the diffusion-controlled plateau, AgCl reduction was favored in order to satisfy the Nernst equation. Since the reference electrode was a Ag/AgCl electrode, it appears that a biamperometric system was in operation. In such systems one electrode acts as an indicator electrode and the other assumes the role of the reference electrode[14]. These roles changed once the pulse of solution containing chloride exited the amperometric detector area and was in contact with the silver/silver chloride
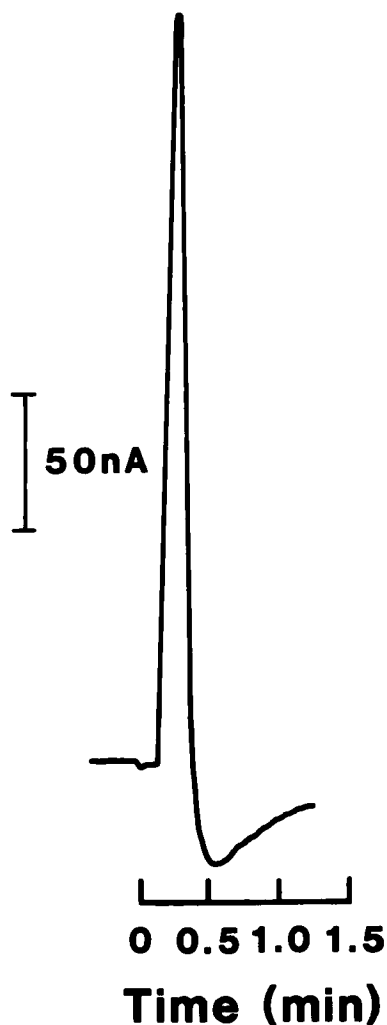
Figure 3   Signal obtained when 10 μl of a 1 mg/ml solution of KCl (10 μg) were injected into the flow-injection analysis system. The applied potential was 0.2 V which is lower than the diffusion-controlled potential; for this reason a negative dip is observed after the signal.

"reference" electrode. In contrast to the single polarizable electrode technique, in biamperometry the potential of the indicator electrode may not be on the diffusion plateau for the electroactive species. For a more detailed discussion of biamperometry the reader is referred to a monograph by Stock[15].

On the basis of the hydrodynamic voltammograms and the peak shape, it was decided to maintain a potential of 0.7 V between the working and reference electrodes in all subsequent analyses. At this potential the calibration curve shown in Figure 4 was obtained. This curve appears to be quite linear in the 1 – 3 μg range. In general, such plots were found to be linear at low concentrations whereas at higher concentrations, an increase in concentration
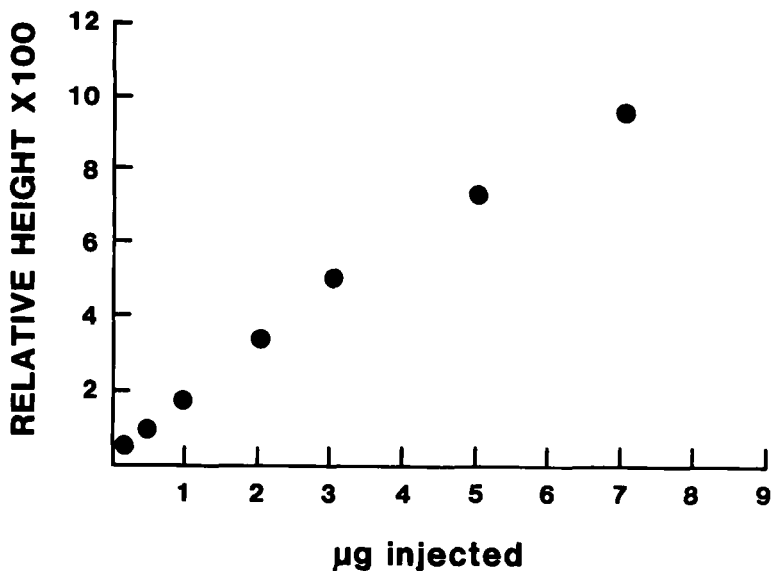
Figure 4   Typical calibration curve for the analysis of chloride. Conditions were: applied voltage: 0.7 V; mobile phase: aqueous phosphate buffer (0.2 M, pH=7.2); flow rate: 1 ml/min; injection volume 100μl; temperature: ambient.

produced a smaller increase in current as shown by a levelling-off of the calibration curve.

With a 100-μl injection loop the detection limit for chloride was found to be 100 ng (at S/N = 3). In order to find out if the electrode response changes significantly over time, it was decided to inject the same amount of chloride over an extended period of time. 100 μg (10 μl of a 10 mg/ml solution) of KCl were injected successively, every two minutes, for a period of two hours. The signal obtained decreased initially during the first ten injections and then stabilized to a steady level as shown in Figure 5. The reproducibility of peak heights for repeated injections of chloride was 3%. A steady response was observed for a period of about a month of intermittent experiments. Moreover, Figure 5 clearly demonstrates that, following dechlorination, at least thirty samples per hour can be analyzed for chloride using this approach; the speed of analysis could, in fact, be further improved following optimization of this procedure.

After the above series of injections, the electrochemical detector was opened up and a thin layer of AgCl was observed on the silver wire, especially the part that was closer to the outlet of the detector. It was interesting to observe that the deposition of a layer of AgCl on the working electrode surface did not poison the electrode. Similar behaviour was observed by Shimizu and Osteryoung[16] who have shown that the Levich equation is obeyed in the case of anions that depolarize silver even though the anion reaction at the electrode gives rise to a solid film on the electrode. According to the Levich equation the diffusion current is proportional to the concentration of analyte in the bulk of the solution.

The detection limit of the dechlorination reaction – chloride analysis technique in combination, was limited by the detection limit of the latter which was found to be 100 ng
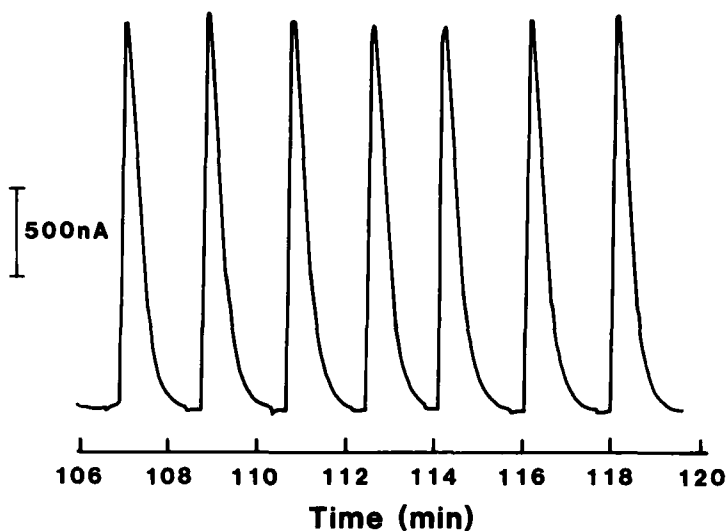
Figure 5 Response of silver electrode to repeated injections of chloride. Conditions: 100 μg of KCl (10μl of a 10 mg/ml solution) were injected every two minutes over a 2-hour time period. The reproducibility of peak heights for repeated injections was 3%. Other conditions as in Figure 4.

of injected chloride (for S/N = 3); this was the case without any further attempt at optimizing the chloride detecting system. Assuming a 100-μl injection, this corresponded to a concentration of injected material of 1 μg/ml chloride. Since the reaction contents were diluted by a factor of 6 before injection, the concentration of chloride in the reaction mixture was 6 μg/ml. Assuming that Aroclor 1260 (6.3 chlorine atoms per PCB molecule) was the reaction substrate, this implied a concentration of Aroclor of 0.9 μg/g as the detection limit of the two combined techniques.

Determination of PCBs in waste oils

PCB commercial formulations are actually made up of a mixture of congeners of a polychlorinated biphenyl ring. Aroclor is the commercial name for the formulations that were mostly sold in North America and the last two digits after the name indicate the per cent by weight of chlorine that is to be found in a given formulation. Most screening techniques use this percent weight chlorine to calculate a potential PCB value from the measured chlorine value. Erickson[1] indicates that most PCBs found in oils will be Aroclors 1242, 1254, and 1260. Assuming that Aroclor 1242 will be the least chlorinated PCB found in oils, a potential PCB value can be determined by dividing the concentration of chlorine measured in unknown samples by 0.42. This will give a conservative number for possible PCB concentration, because the actual PCB value would be lower for the more highly chlorinated PCBs. When the total chlorine content of the sample is less than 21 mg/kg, the maximum PCB content is less than the EPA control limit of 50 mg/kg and the oil may be disposed of without any further analysis.

Table 1 Dechlorination reaction yields of chlorinated compounds.

Chlorinated Compound	Concentration (μg/ml)	Dechlorination Yield %
chlorobenzene	1000	46
1,2-dichlorobenzene	905	62
1,4-dichlorobenzene	941	65
1,3,5-trichlorobenzene	1052	75
1,2,4-trichlorobenzene	986	77
1,2,3,4-tetrachlorobenzene	1105	80
1,2,4,5-tetrachlorobenzene	1063	82
hexachlorobenzene	1057	86
Aroclor 1221	1024	75
Aroclor 1242	969	83
Aroclor 1254	968	86
Aroclor 1260	947	87
Aroclor 1268	1070	90
Aroclor 1216	1008	85
pentachlorophenol	1047	84
hexachlorocyclohexane	964	92

Table 1 presents a list of chlorinated compounds and mixtures, their original concentration in the reaction mixture and the yield obtained after dechlorination using the procedure outlined above. As seen in this table, the dechlorination reaction yields for PCB mixtures are higher compared to chlorobenzenes. This may be due to the higher horizontal and vertical molecular cross-sectional area of PCBs. The latter results from the fact that the two rings are at an angle to each other. Biphenyl is reported to be non-planar in solution[17-19] and the interplanar angle (also referred to as twist or torsional angle) between the two benzene rings (see Figure 6) is affected by the nature and position of the substituents[19]. Table 2 presents the chlorine content of two different analytical samples as determined by using the procedure outlined above. Sample 1 originated from a capacitor (Thomson Electric) which was initially loaded with Aroclor 1016. Aroclor 1016 is a mixture of Aroclor 1221 and 1254 and contains
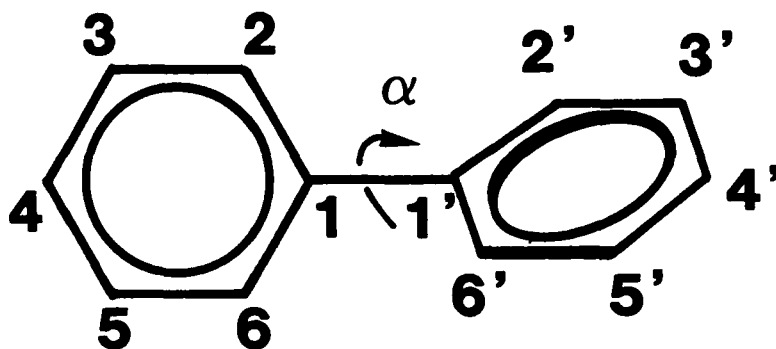

Figure 6 Biphenyl structure. The numbers indicate the positions of substituents. α indicates the relative angle between phenyl rings.

Table 2 Chlorine composition of used up capacitor and transformer oil.

Sample No.	Sample Type	Amount Reacted (mg)	Cl Detected (mg)	Cl%
1	capacitor oil	10	3.25	38.2
2	transformer oil	12	4.70	45.0

41% chlorine. Since the dechlorination yield obtained for this sample was 38% (1.17×32.5%) instead of 41%, it appears that some minor degradation of the Aroclor had taken place. This was in agreement with the fact that some free chloride was detected in the underivatized sample.

Sample 2 originated from a transformer (Thomson Electric) which was originally loaded with an Askarel containing about 70% Aroclor 1260 and 30% tri- and tetra- chlorobenzenes. Since trichlorobenzenes are 58.7% chlorine and tetrachlorobenzenes are 65.4% chlorine it can be assumed that on the average an equimolar mixture of the two would be about 62% in chlorine. This implies that the overall chlorine content of the askarel mixture would originally be about 60.6%. Since the dechlorination yield obtained from this sample was 45% (1.15×39.1%) instead of 60.6% it appears that major degradation of the Aroclor mixture had taken place.

Samples 3, 4 and 5 were simulated samples of PCBs in mineral oil. They were made by dissolving approximately 25, 250 and 1000 mg/kg, respectively, of Aroclor 1260 in mineral oil. The objective for preparing these samples was to find out whether the analytical technique developed could be used as a screening technique for establishing what treatment is required, if any, for various PCB-contaminated oils. EPA and Canadian government regulations specify different handling and disposal procedures for electrical apparatus and insulating fluids containing PCBs at <50 mg/kg, 50–500 mg/kg, and >500 mg/kg. The three simulated samples were therefore made to contain PCB levels within these three ranges. It should be mentioned here that besides mineral oil, PCBs can also be found in certain hydraulic and heat exchange fluids, rinsing solvents and containers for PCB wastes and unused fluids due to cross-contamination. As seen in Table 3, the reaction yields obtained for these three samples were very close to the theoretical ones suggesting that indeed this reaction can occur in the presence of mineral oil without any detrimental effect to the reaction yield. It should be noted, however, that a small decline in reaction yield is observed with decreasing concentration of PCB in the mineral oil, probably as a result of reduced extraction efficiency from the oil into the PEG reaction medium.

Table 3 Dechlorination reaction yields of waste oil samples.

Sample No.	Sample Type	PCB Conc. in Oil (mg/kg)	Cl (Detected) (mg/kg)	PCB (mg/kg)	Extraction Eff. (%)
3	mineral oil	27	12.0	22.8	84.4
4	mineral oil	263	123.6	239.1	90.9
5	mineral oil	985	488.5	913.8	92.8

CONCLUSIONS

This paper has described the application of the dechlorination reaction, discussed in the previous paper in this issue, to the development of a screening technique for the determination of PCBs in waste oils. As shown in this paper, the developed reaction does indeed meet most criteria for an analytically useful reaction, since, under the optimized conditions reported above, it can achieve high and reproducible yields, with analytical quantities of substrate and in short periods of time. The reaction is simple, safe and does not involve the use of any toxic and/or expensive reagents. An important advantage of this procedure over other methods is that the reaction set-up is sufficiently simple and inexpensive to allow the parallel processing of numerous analytical samples.

Due to the high extraction efficiency of PEGs in terms of removing PCBs from mineral oil, the analytical samples were directly applied to the dechlorination reaction mixture thus avoiding a time-consuming extraction step; such a step could also be the source of significant experimental error in the overall analysis scheme. Following dechlorination, the samples were analyzed for chloride using a flow-injection analysis system with a thin layer amperometric detector employing a silver working electrode. This system was shown to be able to analyze at least as many as thirty samples per hour. Without any serious attempt at optimizing this system, its low detection limit for chloride was found to be 100 ng (at S/N=3) and the reproducibility of peak heights 3%. The detection limit of the dechlorination reaction-chloride analysis system was limited by the detection limit of the latter. This corresponds to a detection limit of 0.9 mg/kg for Aroclor 1260. This detection limit is well below the regulatory limit of 50 mg/kg which defines whether a waste oil is contaminated with PCBs.

The silver working electrode is likely to enable the detection of several important anions, such as iodide, cyanide, sulfite, sulfide, bromide and thiocyanate, as well as of other oxidizable and complexing species. Since, however, the half-wave potential ($E_{1/2}$) for the oxidation of silver in the presence of chloride is quite high, all other anions mentioned above will be acting as interferences if they were present. Although the presence of these anions is highly unlikely in the PCB samples we have encountered in this work, it is possible to minimize their effects by preceeding the amperometric detector with an ion-exchange column (e.g. IC PAK column)[20].

As mentioned previously, transformers and capacitors were usually filled with Aroclors, which are PCB mixtures, or with askarels which, in addition to the Aroclor mixture, they contained small amounts of chlorinated benzenes (tri and tetra chlorobenzenes). In the case of transformers, it was sometimes necessary to add makeup chemicals in order to replenish the PCB liquids lost as a result of leakage or sample testing. Under the regulations of the Environmental Contaminants Act, topping up with PCB liquids was prohibited and, therefore, a suitable substitute such as tri/tetrachlorobenzene or refined paraffinic oil was used. Since, however, excessive amounts of makeup fluid could have altered the transformer performance or softened the insulation on the transformer windings, the added amounts were not allowed to exceed about 30% of the tank size[9]. Capacitors were always hermetically sealed to reduce leakage risk and, therefore, there was no need for makeup chemicals to be added. In either case, since, on a weight basis, tri and tetra chlorobenzenes contain, on the average, the same number of chlorines as the typical Aroclor mixtures used in transformers

and capacitors, and since, furthermore, their dechlorination reaction rates are about the same as the PCBs contained in these mixtures (see Table 1) then, in the worst of cases, the PCB concentration value obtained would be about 30% higher than the actual one. Given that the major objective of our analysis scheme is to use it as a screening technique for limiting the number of samples sent to analysis via GC-MS, errors of this magnitude can be tolerated. In any case, given these analytical considerations, if the measured concentration is within 30% of the regulatory limit, it would be advisable to send it for further testing using a more sophisticated and selective technique.

Acknowledgements

References

1. M.D. Erickson, *Analytical Chemistry of PCBs* (Butterworth Publishers, Boston, MA, 1986), Chap. 7, pp. 259–265.
2. G. Lunde, J. Gether and B. Josefsson, *Bull. Env. Contam. Toxicol.*, **13**, 656–661 (1975).
3. S.M. Odendahl, K.M. Weishar and D.W. Reeve, *Pulp Paper Can.*, **91**, 60–63 (1990).
4. R.F. Addison, *Can. Chem. News*, 15–17 (February 1986).
5. H.R. Buser and C. Rappe, *Chemosphere*, **3**, 157–174 (1979).
6. C.R. Sutcliffe, E.S. Gladney, D.M. Seitz and G.H. Brooks, *Anal. Chem.*, **61**, 2682–2686 (1989).
7. B. Pihlar and L. Kosta, *Anal. Chim. Acta*, **114**, 275–281 (1980).
8. B. Pihlar, L. Kosta and B. Hristovski, *Talanta*, **26**, 805–810 (1979).
9. J. de Gonzague and S. Lawrie, *Handbook on PCBs in Electrical Equipment* (Environment Canada, Ottawa, Ontario, 1982), Chap. 3, pp. 11–20.
10. B.R. Hepler, S.G. Weber and W.C. Purdy, *Anal. Chim. Acta*, **113**, 269–276 (1980).
11. D.T. Sawyer and J. L. Roberts Jr., *Experimental Electrochemistry for Chemists* (John Wiley & Sons, New York, 1974), Chap. 2, pp. 34–58.
12. S.W. Osborn, F.J. Iaconianni, A.J. Saggiomo, P.A. Landau and J.C. Biordi, EPRI EL-3345, Project 2028–2, May 1984.
13. N.A. Hampson, K.I. MacDonald and J.B. Lee, *J. Electroanal. Chem.*, **45**, 149–151 (1973).
14. W.C. Purdy, *Electroanalytical Methods in Biochemistry* (McGraw-Hill Book Company, New York, 1965), Chap. 7, pp. 191–222.
15. J.T. Stock, *Amperometric Titrations* (Interscience Publishers, New York, 1965), Chap. 4, pp. 45–81.
16. K. Shimizu and R.A. Osteryoung, *Anal. Chem.*, **53**, 2350–2351 (1981).
17. E.D. Schmid and B. Broza, *J. Chem. Phys.*, **56**, 6267–6268 (1972).
18. D.S. Egolf and P.C. Jurs, *Anal. Chem.*, **62**, 1746–1754 (1990).
19. K.L.E. Kaiser, *Environ. Pollut.*, **7**, 93–101 (1974).
20. P. Jandik, D. Cox and D. Wong, *Amer. Lab.*, 115–125 (March 1986).