



On site PCB analysis in support of a transformer rebuilding project

Ken Li^{a,*}, Michael Landriault^a, Merv Fingas^a, Albert Potvin^b

^a *Emergencies Science Division, Environment Canada, Environmental Technology Centre, River Road, Ottawa, Ont., Canada K1A 0H3*

^b *Natural Resources Canada, Ottawa, Ont., Canada K1A 0H3*

Abstract

In December 1997, Emergencies Science Division (ESD) was contracted by Natural Resources Canada (NRCAN) to perform on-site analyses in support of a transformer-rebuilding project at Sault Ste-Marie, Ont. Using a gas chromatograph with electron capture detector (GC/ECD) mounted in a mobile laboratory, PCB analyses were conducted on the original transformer oil, surface wipes, Varsol rinsing of the transformer tank interior and cooling fins. To assess the efficiency and validity of the decontamination process, PCB contamination was monitored closely on the rinse solvent. Surface wipe samples after wash down showed surface concentration of several hundred μg Aroclor 1254/100 cm^2 , well below the acceptable limit of 8000 $\mu\text{g}/100 \text{cm}^2$. Because of the relatively large percentage of the internal surface area, the fin banks had to be rinsed exhaustively to meet the decontamination criteria. Final rinses of each of the seven fin banks of transformer 1 still showed presence of PCB, ranging from 80 to 590 ppm ($\mu\text{g}/\text{ml}$) with a mean value of 280 ppm. Upon completion of rebuilding, analysis of the R-Temp retro fill fluid showed 5 ppm at the initial power-up, increasing slightly to 16 ppm after 1 year of operation, which was far below the regulatory limit 50 ppm. The second transformer, by comparison, had a lower mean concentration of 54 ppm in the final fin rinse during decontamination. However, the backfill R-Temp showed an initial concentration of 38 ppm and remained essentially unchanged at 32 ppm after approximately 10 months of operation. Extensive comparison of GC and the quick test Clor-N-Oil kit were also carried out and showed generally good agreement. The use of an on-site GC was crucial in providing rapid and accurate analysis on-site, thus, enabling quick modifications to the decontamination strategies in order to meet the target PCB level. For projects of this nature, a GC/ECD was far superior to quick test kits by providing the selectivity and sensitivity for the diverse nature of the sample media. © 2001 Published by Elsevier Science B.V.

Keywords: PCB; GC; Transformer; On-site analysis; Mobile lab

* Corresponding author. Tel.: +1-613-991-9485; fax: +1-613-990-3219.
E-mail address: li.ken@etc.ec.gc.ca (K. Li).

1. Introduction

During 1997, NRCan was seeking an acceptable method to rebuild and decontaminate two transformers at the Great Lakes Forestry Centre, Sault Ste-Marie, Ont. A novel rebuilding method was proposed by W. Robertson & Associates [1]. The rebuilding process involved several stages starting with draining the transformer and removing the core and coil assembly. The entire interior of the transformer was wiped down with Varsol and rinsed with a heated replacement hydrocarbon fluid (R-Temp). At this point decontamination was considered complete. The new core and coil assembly were installed and the rebuilt transformer was filled with R-Temp. The trial took place between December 1997 and January 1998 for two 2000 KVA transformers. The role of ESD was to operate the mobile laboratory and perform all PCB analyses during the rebuilding process.

The accessible interior surfaces were cleaned adequately by wiping with Varsol. The banks of cooling fins presented a special problem because of the narrow passageways that severely limited accessibility, and the significant percentage of surface area, estimated to be 80% of the total surface area [2]. The only recourse was by exhaustive solvent flushing, since any residual transformer oil could contaminate the retro-fill R-Temp fluid. In the original method, developed and tested with a decommissioned transformer, only one Varsol flushing of the fins was to be carried out. A specially designed tool was used to collect wipe samples from the fins. To gain a better understanding of the decontamination process, it was decided the PCB level in the Varsol be closely monitored. The number of times a particular component needed to be washed were decided by analysing all rinse solvent or surface wipe samples.

As a result of our participation, significant changes to the original methodology were made. In this paper we will present data demonstrating the advantages of having the proper analytical instrument on-site. By providing valuable data to assist in critical stages of the rebuilding process, it is far better than relying on a simple set of procedures developed from a pilot scale project. The GC analysis is also superior to quick-test kits, which might not have the sensitivity and selectivity, nor the flexibility required to handle different sample matrices. Despite of some initial difficulties, the rebuilding project was successfully carried out, and final concentration of the retro-fill fluid was well under the 50 ppm target value.

2. Instrumentation and equipment

For this project the Level 2 Mobile laboratory was deployed. The mobile laboratory is based on a custom-built cabin mounted on a Ford Cargo Van. The lab area has two rows of benches, an internally vented fume hood and two Sola signal conditioners to stabilise output from the onboard generator. Although designed for self-contained operation, for this project a landline of 60 A/220 V was used to supply power to the van. A description of the onboard equipment and functional details can be found in an earlier work [4]. The main instrumentation was a HP 5890 Series 2 GC equipped with dual flame ionisation and electron capture detectors (ECD), although only the latter was used in this work.

2.1. Analytical equipment

A capillary column (DB-5, 30 M \times 0.25 mm, film thickness 0.25 μ m) was installed in the HP 5890 Series 2 GC.

Lab GC/MS analysis was carried out on an identical GC. Additional confirmation runs were performed on a HP 5890 Series II GC/mass selective detector (MSD). It was operated in a linear scan mode (40–450 amu) and interfaced directly to the GC equipped with an identical capillary column and operated with the same temperature program.

2.2. Sampling and miscellaneous equipment

Sampling jars with Teflon lined caps were used to store the gauze wipe samples and the extracts. Disposable templates 10 cm \times 10 cm were cut from a brown paper folder. Sterilised gauze pads (10 cm \times 10 cm, 12-ply) were used to wipe down an area delineated by the template. To reach inside the cooling fins, a special tool was fabricated using a flexible 120 cm long fish wire with a 2.5 cm \times 5 cm metal plate soldered approximately 30 cm from one end. The flat surface was fitted with a gauze sack secured with drawn strings. This was designed to go through the header (connecting the bank of cooling fins to the main tank) to reach the interior surface. Miscellaneous lab supplies consisted of gloves, custody sheets, sampling vials and jars, pipettes, labels, GC supplies of auto sampler vials, etc. Clor-N-Oil 50 kits were from Dexsil, Connecticut [3]. Distilled-in-glass grade solvents (hexane, acetone, etc.) were purchased from Caledon (Belleville, Ont.). Analytical standards of Aroclor 1254 and the internal standard of decafluorobiphenyl were obtained from Ultra Scientific, RI.

3. Procedure

3.1. Sampling was done in accordance with methodology described in CCME PCB transformer decontamination standards and protocol (CCME EPC-HW-105E, 1995)

Surface wipe samples were collected by wiping down a 10 cm \times 10 cm area with a hexane-soaked 12-ply sterilised gauze pad. The pad was stored in a glass jar and sealed with a custody label. Surface samples of the cooling fins were taken by the fish wire sampler. A batch of 12-ply gauze bags was made with a drawn string-enclosure, which was tied on the sampler and inserted through the header of the fins. A surface area equivalent to 100 cm² was rubbed down, consisting of two 50 cm² patches from two opposing surfaces over a distance of 20 cm. The sampler was moved over the surface a number of times, being careful to follow the same path to ensure a representative surface sample was taken. Each wipe sample was extracted in the sampling jar container by shaking with 30 ml of hexane for approximately 1 min. The extract was decanted through a funnel into a 100 ml volumetric flask. The procedure was repeated two more times. The extracts were combined and made up to 100 ml.

Rinse samples of Varsol were diluted 1000-fold in hexane. Fluid (oil) samples of R-Temp and transformer oil was weighed out (0.1 g aliquot) and dissolved in 10 ml of hexane. In all

cases, no sample cleanup was performed. An internal standard of decafluorobiphenyl was added to all sample and standard solutions to give a final concentration of 1 ppm.

3.2. Analytical conditions

GC temperature program used was as follows: 50°C initial for 0.5 min, to 200°C at the rate of 25°C/min, to final temperature of 310°C and held for 1 min. Injector and detector temperature were 270 and 320°C, respectively. A column pressure of 12 psi was maintained giving a nominal flow rate of 1 ml/min. Detector purge flow of nitrogen was approximately 30 ml/min. A 1 µl aliquot was injected by HP 7673 auto sampler under splitless condition, with split purge off for 1 min. An initial multi-point calibration was constructed up to 10 ppm in blank R-Temp fluid in the same dilution as the samples. Daily calibration of the GC was performed using a minimum of two standards of 0.2 and 2 ppm, bracketing the sample concentration.

3.3. Quantitation

All samples exhibited an Aroclor 1254 pattern, which eluted from 10 to 20 min. Six prominent peaks from trichlorobiphenyl and tetrachlorobiphenyl isomer group were summed. These peaks correspond to PCB 31 and 32 (co elute), 38 of trichlorobiphenyl, 46, 50, 54, and 58 of tetrachlorobiphenyl using the IUPAC numbering system. Because of inevitable co elution, plus changes in column conditions, which degraded peak resolution, the peaks were visually compared to the daily calibration standards and manually integrated. In some instance the presence of chlorobenzenes in the original transformer fluid (found in the first or second Varsol rinses mostly), interfered with the internal standard peak so the external standard quantitation was used. The areal sum was converted to concentration units using the response factor of a 2 ppm Aroclor 1254 standard. Fig. 1 shows some typical GC/ECD

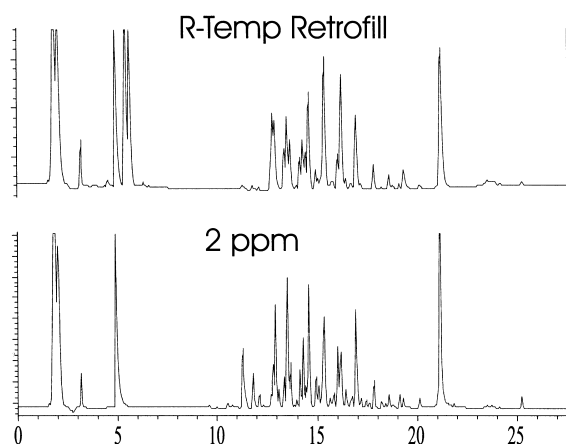


Fig. 1. Typical GC/ECD chromatogram.

chromatograms. A GC/MSD total ion chromatogram of the original transformer fluid (before rebuilding) is included in the appendix with the library search of the major peaks. It can be seen this fluid was comprised mainly of trichorobenzenes eluting from 3 to 4 min and Aroclor 1254 eluting from 9 to 13 min.

Clor-N-Oil 50 kits were also used initially to provide an independent verification of GC results. The kit was used in accordance with the procedures supplied with the kit (Dexsil Clor-N-Oil manual).

4. Results and discussions

4.1. Preliminary studies

Oil background interference: for simplicity, a 'dilute-and-shoot' GC/ECD method was adopted for on-site analysis. The quick test kits were only used as a backup. The ECD is much more tolerant to background oil compared to a mass spectrometer, which makes it ideal for this type of work. Only minimal sample workup involving simple extraction or dilution in hexane, are required. An initial study was carried out to find out the amount of dilution necessary to reduce the oil interference to an insignificant level.

A 0.1 g aliquot of the R-Temp backfill fluid was dissolved in hexane to give nominal dilutions of 1/50, 1/100, 1/500 and 1/1000. Each solution was spiked with 10 μg Aroclor 1254 and 1 μg internal standard (decafluorobiphenyl) to give concentrations of 2 and 1 ppm, respectively. Each solution was injected on the GC/ECD in triplicate to determine the response factor in various levels of oil background. Results are summarised in Table 1, from which it was concluded that the effect of oil background was insignificant at all dilutions. Repeatability varied from 4 to 11%, with a mean value of 9.5% using the uncorrected areal sum, which was generally within the variability of the analytical method. Interestingly, using the relative response data, obtained by dividing the areal sum by the response of the internal standard, the range of repeatability was 3–13%. Provided the internal standard is free from interference, either internal or external methods of quantitation were considered acceptable. Later on, to improve the detection limit of the method for the R-Temp fluids, standards were made up in 1/25 blank R-Temp fluid to match the dilution of the sample (0.2 g dissolved in 5 ml hexane).

Wipe sample extraction study: the wipe sample consisted of a 10 cm \times 10 cm 12-ply gauze used to wipe down a surface area of 100 cm². A blank gauze wipe was spiked with 5000 μg Aroclor 1260 and 1 ml of an actual transformer oil (composition unknown), which was previously analysed to be free of PCB contamination to simulate an actual wipe sample. The wipe was extracted three times in 30 ml hexane and made up to a final volume of 100 ml. This raw extract was further diluted 1/10 in hexane so the final oil background was nominally 1/1000th of the original oil. The extraction study was carried out in triplicate. Results are summarised in Table 2. Recoveries are based on a 1260 standard made up in 1/1000th in the same oil. It can be seen that while recoveries for PCB were between 84 and 113%, the variation of internal standard response was much higher. The only explanation was that this particular oil might cause interference in the region where the internal standard eluted.

Table 1
Oil interference study

	Response, internal standard	Response, area sum ^a	Mean	S.D.	R.S.D. (%)	Relative response ^b	Mean	S.D.	R.S.D. (%)	Ratio response ^c	Ratio relative response ^d
Standard 1	1440	4636				3.219					
Standard 2	1456	5036				3.459					
Standard 3	1361	5321	4998	344	7	3.910	3.529	0.350	9.9		
Spk oil 1/2000											
Trial 1	1534	6002				3.913					
Trial 2	1484	5761				3.882					
Trial 3	1499	5545	5769	229	4	3.699	3.831	0.115	3.0	1.154	1.086
Spk oil 1/1000											
Trial 1	1338	4899				3.661					
Trial 2	1334	4577				3.431					
Trial 3	1382	4631	4702	172	4	3.351	3.481	0.161	4.6	0.941	0.986
Spk oil 1/100											
Trial 1	1757	5922				3.371					
Trial 2	1636	4381				2.678					
Trial 3	1728	4607	4970	832	17	2.666	2.905	0.403	13.9	0.994	0.823
Spk oil 1/50											
Trial 1	1512	4032				2.667					
Trial 2	1410	3848				2.729					
Trial 3	1448	3744	3875	146	4	2.586	2.660	0.072	2.7	0.775	0.754
Mean, standard and sample	1488	4863									
S.D.	131	727									
R.S.D. (%)	8.8	14.9									

^a Area sum of five major peaks.

^b Relative response = PCB response/internal standard response.

^c Ratio response = mean PCB response/mean standard response.

^d Ratio relative response = mean relative PCB response/mean relative standard response.

Table 2
PCB recovery of spiked wipe samples^a

	Response, IS area counts	Response, PCB area counts	Recovery (%)	Mean recovery	S.D.	R.S.D. (%)
Pad 1	40.9	67.1	113.2			
Pad 2	21.4	56.2	94.8			
Pad 3	17.8	49.8	84.0	97.3	14.8	15.2
Pad 1 re-extract	50.1	4	6.7			
Pad 2 undiluted run (oil diluted in 1/100)	8.6	202	34.1			
PCB standard, 16.7 ppm	Response, IS	Response, PCB				
Standard in Hx-1	19.3	274				
Standard in Hx-2	18.6	260				
Standard in Hx-3	21.6	290		274.7	12.3	4.5

^a 1 ml oil spiked onto 10 cm × 10 cm gauze pad extracted in 100 ml hexane, diluted in 10 times further: total dilution in 1/1000.

To assess the completeness of extraction, wipe sample number 2 was extracted one more time (3 × 30 ml hexane each) and analysed. The second extraction showed only 5.6% of the original PCB spike remaining. In the same table a run was also made using only 1/100th dilution (representing a higher oil background of 10 mg), suppression of response was noted. In the course of this work, the wipes had oil loading well below 1 g, consequently it could be safely assumed the extraction was adequate for field extraction purpose.

4.2. Field analysis of high voltage compartment, tank and fin banks rinse samples

In the rebuilding protocol, all the non-replaced components of the transformer were cleaned simply by wiping down with sorbent pads soaked with Varsol. The effectiveness was demonstrated by analysis of the surface samples taken before and after cleaning. Samples WP-1–8 had an initial contamination in excess of 22,000 µg/100 cm², this was reduced by roughly 99% (WP-10–12) after cleaning.

The specially constructed fish wire sampler designed to take surface samples of fin banks did not perform as expected. The wire was not flexible enough to negotiate the narrow and multiple bends of the passageway leading into the fins. Rather than running a potential risk of losing a gauge pad inside the fins, this sampling procedure was not pursued further. As a result, the only means to assess the cleaning process was to analyse the Varsol rinsing. The sensitivity and the speed of analysis of an automated GC/ECD were crucial to handle such a high volume of samples.

4.2.1. Rinse (contact) time investigation

The duration of each rinse was studied by circulating 50 l Varsol in fin bank number 2. The change in PCB concentration during a 1 h interval is illustrated in Fig. 2. The leaching process was observed to be rather gradual since there was no significant increase in PCB concentration in the Varsol after 30 min of rinsing. Because of the time constraint, a rinse time of 15–20 min was considered a reasonable compromise.

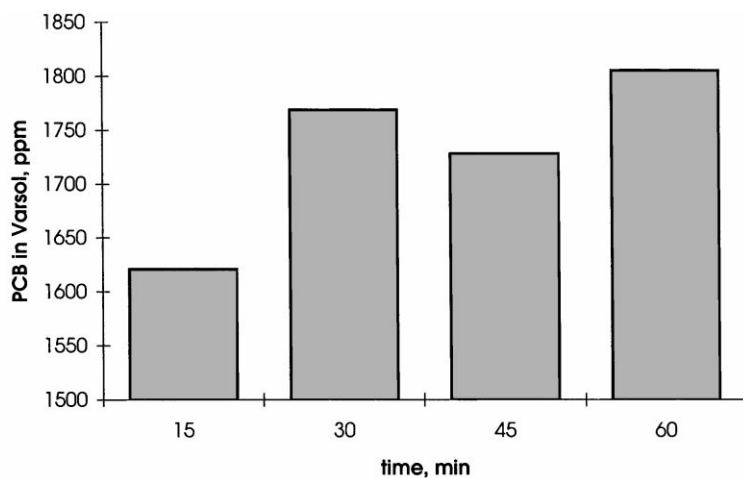


Fig. 2. Increase of PCB concentration in Varsol over rinse time.

4.2.2. Number of rinsing

Continual monitoring of the Varsol rinses showed one single rinsing was clearly inadequate. Successive Varsol rinses generally showed declining PCB concentrations, as illustrated in fins numbers 1, 2 and 4 (Fig. 3). Even after three or four rinses, PCB was still being leached from some fins.

4.2.3. Recycling of Varsol

To minimise the usage of Varsol and reduce disposal costs, a scheme to recycle the Varsol was attempted. Varsol previously used to rinse a 'clean' fin was re-used for 'dirty' fins. For example, the first rinse for fin 4 (still 'dirty') was taken from rinse 2 of fin 3, and that in turn was from rinse 3 of fin 3. Results were promising but because of the lack of suitable container to keep different batches of Varsol apart to minimise cross contamination, this was not pursued any further. Subsequently only fresh solvent was used for rinsing.

Fig. 3 also showed some abnormalities in the trend: the last rinse of fin 2 showed an unexpected jump to 414 ppm (rinse 4), from 73 ppm of rinse 3. Similarly, fin 1 showed a jump from rinse 2–3. In both cases fresh Varsol was used. This observed irregularity belied the difficulty in an uncontrolled environment typical in fieldwork, in this case sources of contamination could be from the suction pump or the container drums.

The effectiveness of rinsing procedure was dependent upon a number of factors, among them the choice of solvent as the removal agent, contact or rinse time and the degree of agitation or turbulence. Depending on the service life of the transformer, the Askarel could be adsorbed very strongly on rough surfaces or the built-up varnish layer. In both cases, simple rinsing would not be very effective. Moreover, removal of any residual solvent after each rinse required a properly designed vacuum tool that could reach into all corners of the transformer to remove all rinse solvent.

The above considerations were borne out by analysing the residual Varsol left at the bottom of the fin banks overnight (sample numbers FB1B to 7B). After 10 h, PCB in some

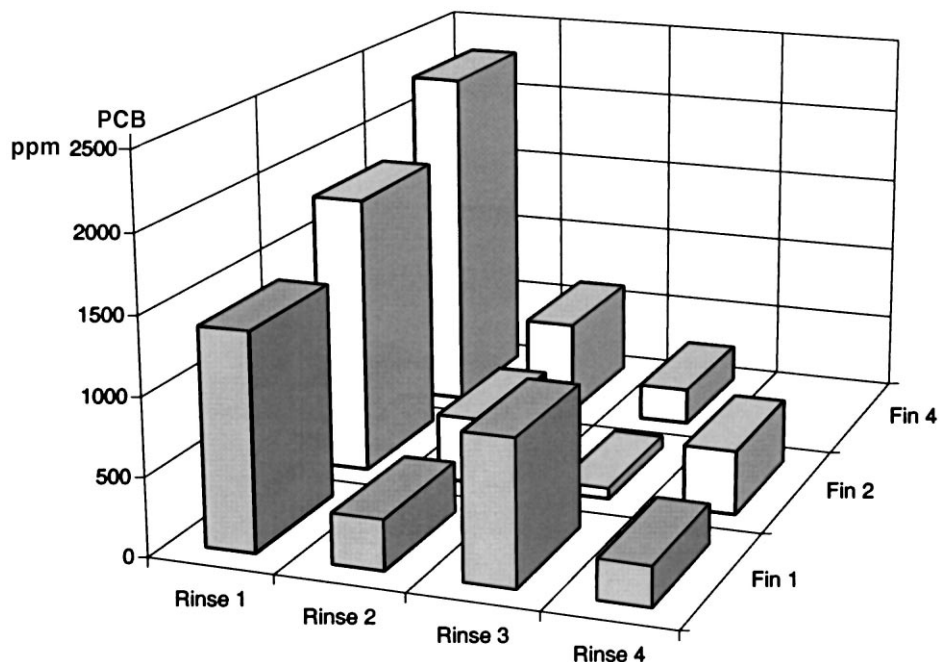


Fig. 3. PCB in successive Varsol rinsing of transformer 1 cooling fins.

cases was found to be as high as 5170 ppm: an increase of almost 20 times over the original concentration, suggesting a slow solvation process.

The last point was confirmed visually during the final R-Temp fluid spray wash, which replaced the residual Varsol before retro filling. Staff of PCB Disposable Company devised a tool using a long quarter-inch copper tubing attached to a drill pump (model No. 2202 by Wolfcraft, Ithaca, NY) to vacuum up the residual R-Temp fluid collected at the bottom of fin banks. As suction proceeded, they reported seeing droplets of what appeared to be Askarel and metallic-coloured varnish flakes through the clear Tygon tubing. The significance of this observation was that at this stage each bank had been rinsed with a minimum of three times, each with 50 l Varsol with a total contact time of more than an hour. Yet some Askarel still persisted in the fin banks. This belied the danger of relying on a simple set of cleaning protocol developed from a pilot scale project. Without considering the operational history of the transformer and the availability of reliable on-site data, a heavy built-up of varnish could be disastrous for rebuilding project.

Transformer 1 was energised during the week of 15 December 1997 and five R-Temp samples were collected on 17–18 December 1997. The samples were shipped to the ESD lab and analysed by GC/ECD. The concentration ranged from <1 ppm in the high voltage (HV) compartment to 5 ppm in the main tank (there is no exchange in the two compartments). After approximately 1 year of continuous operation the concentration was 16 ppm in the main tank.

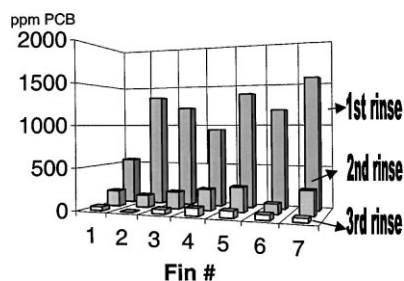


Fig. 4. Progress of PCB removal by Varsol rinses.

Work on transformer 2 began during the week of 19 January 1998 and ESD mobile lab was again mobilised. With the experience gained from the first one, work proceeded smoothly. Each fin was rinsed with three fresh batches of 50 l Varsol. Results of the on-site analysis showed PCB concentration decreased linearly with successive rinse and there were no abnormal jumps in concentration (Fig. 4). The mean concentration of the final Varsol for all seven fins was 54 ppm; significantly lower than 280 ppm of the first transformer. Fig. 5 illustrates a comparison of the final rinse results of all fins in both transformers.

Upon power up, the retro fill fluid from transformer 2 was found to be 38 ppm in the main tank and 37 ppm in the HV compartment. Concentration in the main tank since then had remained more or less stable after 11 months of operation. However, concentration in the HV compartment has increased to 117 ppm in a sample collected on 22 April 1998. A plausible explanation is the HV compartment was not completely decontaminated during rebuilding. Fortunately, this compartment can be cleaned separately without having to drain the main tank. This was rectified and in the sample collected in November 1999, PCB content dropped to 14 ppm. Fig. 6 shows final PCB concentrations in each of the transformers since

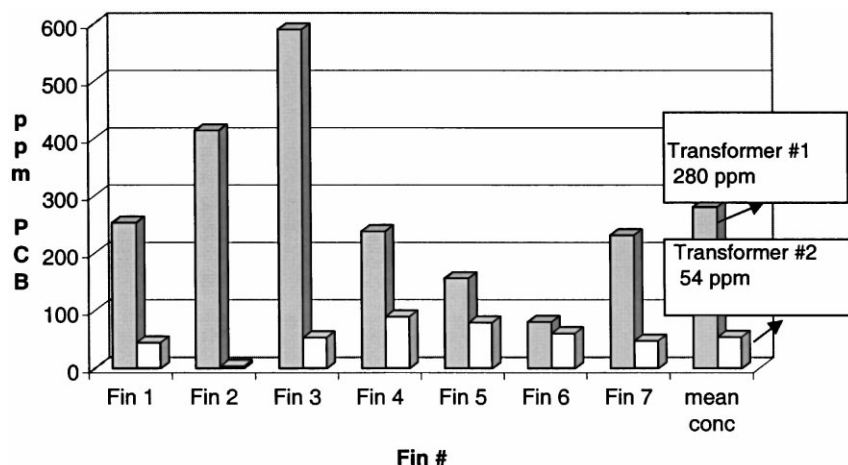


Fig. 5. Transformer 1 and 2 final rinse.

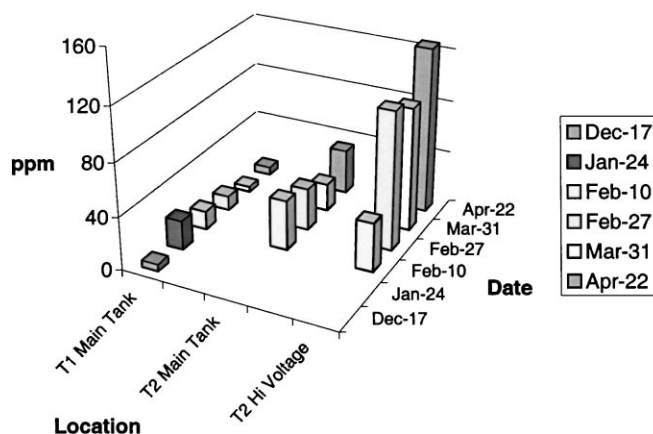


Fig. 6. Final Aroclor concentration in transformer oil.

rebuilding. In summary then, after 1 year of operation, none of the R-Temp fluid samples from the main tanks exceed the 50 ppm limit so the rebuilding can be considered successful.

4.3. Clor-N-Oil 50 quick test comparison

As an on-going evaluation of field portable equipment, these quick kits were used in selected oil and rinse samples. The 50-series kit reported 50 ppm and above as positive. Results were shown in Table 3. Although there were no false negatives (above 50 ppm

Table 3
Verification of Cloro-N-Oil 50 quick test analyses, all samples from transformer 1^a

Sample	GC results, ppm in solution	Cloro-N-Oil 50	Comment on quick tests
Original Askarel	Diluted to approximately 200	+	Correct
WP-1	543	+	Correct
WP-2	40	+	False positive
WP-3	338	+	Correct
WP-4	482	+	Correct
WP-6	562	+	Correct
WP-8	296	+	Correct
Var-1	1389	+	Correct
Var-2	320	+	Correct
WP-9	3	-	Correct
WP-10	2	+	False positive
R-Temp (trsf1; 22 January 1998)	22	-	Correct
XFR1-1 (trsf1; 17 December 1997)	4.9	-	Correct
XFR1-2 (trsf1; 17 December 1997)	0.73	-	Correct
XFR1-3 (trsf1; 18 December 1997)	4.8	-	Correct
XFR1-4 (trsf1; 18 December 1997)	5.3	-	Correct
XFR1-5 (trsf1; 18 December 1997)	5.3	-	Correct

^a Positive denotes above 50 ppm.

reported as below), there were two cases of false positive out of 12 tests. The chemistry of the kit was designed to bias towards false positive; oil at <50 ppm sometimes could be reported as above. In that aspect the kit performed as expected. However, sample WP-10 had <2 ppm yet gave a false positive. It must be pointed out the test kit was primarily designed for oil samples while some of sample extracts were in hexane, so the matrix factor could contribute to the inaccuracy. In any case, the much lower cost per analysis and the sensitivity of a GC made it the method of choice in projects of this nature. The speed of quick test was not considered a significant advantage (5 min quick test versus 20 min GC analysis, but could be shortened further with some loss of separation). With the auto sampler, the GC/ECD could be operated unattended overnight, enabling large number of samples to be analysed.

5. Conclusion

An on-site PCB analysis in support of a transformer-rebuilding project was successfully carried out. The advantages of having a laboratory grade instrument were clearly demonstrated. A simplified sample workup with proper GC/ECD instrumentation provided superior sensitivity and selectivity to enable detection of PCB in the low ppm level, together with the flexibility in handling a wide variety of sample matrices. Due to these virtues, rapid modification to the methodology in the rebuilding project was made, thus, avoiding any costly mistakes or delays during rebuilding. Both transformers were cleaned and rebuilt without any major problems and all retro fill fluid samples in the main tank had shown to be well below the regulatory 50 ppm level.

References

- [1] W. Robertson, A Proposal: Removal of PCB from Transformers Servicing the Great Lakes Forestry Centre, 1219 Queen Street, Sault Ste-Marie, Ont., 1997, submitted to NRCan.
- [2] W. Robertson, A Final Report: Removal of PCB and Rebuilding of the Transformers Servicing the Great Lakes Forestry Centre, 1219 Queen Street, Sault Ste-Marie, Ont., Contract Number NRCan-97-0040, February 1999, submitted to NRCan.
- [3] Dexsil, Instructions for Cloro-N-Oil 50 kit.
- [4] K. Li, M.F. Fingas, M.R. Bélanger, J.R.J. Paré, The vehicle-portable analytical system of the emergencies science division of environment Canada, *J. Hazardous Mater.* 43 (1995) 141–154.