ANNEX A

# PROCEDURES FOR SAMPLING AND TESTING OF PCB IN TRANSFORMER OIL

## Contents

1.	Sampling of dielectric oil from transformers
	Structure of an electric transformer
	Special cases2
	Step by step sampling procedure
	Special cases
	Phased out and offline transformers
	Online, base mounted transformers7
	Online, pole mounted transformers10
	Sampling equipment:
	Sampling coding and chain of custody10
	Proper planning, hindrances and hidden costs
	Use of PPE12
	Sampling12
	PPE for working at height13
	Emergency preparedness response
	Fire14
	Oil spillage and Soil Contamination14
	Dermal contact with PCB contaminated oil15
	Fall from elevated working areas
	Electrocution15
	Analysis of PCB through screening test16
	Commercially available technologies
	Sources of error when testing PCB with chlorine electrodes and how to minimise them17
	Key steps in undertaking analysis with quantitative screening tests
	Management of waste generated by sampling or analysis

## 1. Sampling of Dielectric oil from Transformers

## Structure of an Electric Transformer

## **Special Cases**

An electric transformer is a highly energized device, which externally is composed by an external carcass, which is grounded; bushings and insulators, hosting the electrical cables connected to the grid; an oil conservator tank to ensure that the internal windings are always completely immersed in oil; temperature and pressure gauge; an oil draining valve, which may be also used as sampling port. Internally, the transformer contains the coils (usually tri-phase transformers contain 3 coils containing internal and external windings), cardboard and wood insulators, and the dielectric oil. The internal view of a transformer may be seen in photos



Photo 1:A demonstrative transformers showing the structure of the internal part.

## **Step by Step Sampling Procedure**

Although intrinsically simple, the procedure of sampling transformer need to be carried out in the proper manner to ensure the quality of the sample, prevent damage to the equipment, and reduce the risks for the operators and the environment. The detailed procedure for sampling dielectric oil from a transformer implies the following steps:

- 1. Identify the transformer to be sampled and ensure sample chain of custody;
- 2. Manage to put off-line and de-energize the transformer if necessary;
- 3. Prepare in advance all the sampling materials, including sampling vials, tubing, labels, waste oil containers, PPEs;
- 4. Wear proper PPE;
- 5. Establishing proper countermeasures for preventing the contamination of soil

underneath the transformer;

- 6. Identify and assess the sampling port;
- 7. Connect the sampling port with the proper tubing or mount a sampling flange if necessary;
- 8. Take and manage the sample;
- 9. Manage the waste generated during the sampling;
- 10. Manage to put the transformer back online and repowered.

These steps are described with more details in the following paragraphs:

- 1. Identify the transformer to be sampled and ensure sample chain of custody. The identification of the transformer to be sampled usually starts with a database of transformers provided by the owner. However, these databases often do not contain enough information to precisely identify the transformer. In transformer substations, or in temporary storage of phased out transformers, there may be tenths or even hundreds of transformers which can be univocally identified only through their serial number punched on the nameplate. In several cases however the nameplate may be missing, deteriorated or not easy accessible (Photo 2 and Photo 3). In these cases, as it is not possible to rely on the serial number placed on the nameplate of the transformer, is required, during sampling, to place on the transformer an additional label for the univocal identification of the transformer in association with the sampling code. This in turn requires the development of an additional database (the database of sampled transformer). The only secure way to label the sampled transformer is to use aluminum punched labels (photo) secured to the transformer by steel wires. All the other methods (plastic or paper labels, painting, permanent marker pen, etc.) proved to be not enough persistent to allow the tracing back of the transformer once the analysis of the oil sample has been completed.
- 2. *Manage to put off-grid and de-energize the transformer if necessary.* For some large transformers installed on the ground (Photo 4), or for phased out transformers, sampling of the dielectric oil can be done with the transformer online. However, in all the other cases the transformer need to be put offline and deenergized. This usually need to be planned in advance and conducted with the support of the electricity providers as the downstream users need to be informed on the timing and duration of the service interruption. Disconnecting and deenergizing a transformer has to be carried out only by the authorized staff of the company owning or managing the transformer.



Photo 2: Storage of phased out transformers. Many transformers are without nameplate.



Photo 3: Storage of maintained transformers.

The original nameplate of these transformers has been removed after maintenance.



*Photo 4: The electric distribution companies may establish procedures to sample powered transformers to prevent the interruption of the electric service.* 

- 3. *Preparing in advance all the sampling materials, including sampling vials, tubing, labels, waste oil containers, wrenches, PPE (gloves, goggles, mask, overall suits, safety shoes).* The sampling materials shall be prepared in advance before starting each day of sampling operations. A set of tubing and flanges will be ready to ensure that sampling from different kind of drains can be done easily. The list of equipment to be prepared before starting the sample is detailed in section "Sampling equipment"
- 4. *Establishing proper countermeasures for preventing the contamination of soil underneath the transformer.* During the sampling, oil can be accidentally released on soil if, for instance, the sampling port is damaged or blocked, the sampling valve is missing and only a drain opening closed by bolt is available for sampling, the sampling vial get broken, the waste oil container spills on the ground, etc. Recommended measures for preventing oil spilling on the soil during sampling are: place a plastic or metal tray under the sampling valve; place all the dielectric oil containers (sampling vials, waste oil container) over a plastic liner; ensure that the proper amount of adsorbent material is at hand during sampling. A list of recommended spillage prevention equipment is reported in section 1.1.8
- 5. *Wear proper PPE*. The personnel should always wear proper PPE when handling waste dielectric oil contaminated or containing PCBs. Recommended PPE are detailed in section 1.6. PPE shall be wear before starting the sampling operation.

- 6. *Identify and assess the sampling port.* Usually, transformer oil need to be sampled from the drain placed at the bottom of the transformer. The drain may or may not be equipped with a valve (Photo). In addition, the draining valve may be provided with safety bolts to prevent accidental opening. It is always a good practice to assess the condition of the draining valve before initiate the sampling. If the valve is blocked, rusted or damaged is preferably to drain from the top of the transformer rather than from the bottom, however this need special care and is not always possible when the transformer is online. Sampling from the oil conservator tank may be another option. If the drain is not equipped with a safety valve, and there are no other sampling options, it is recommended to try to open it partially (no more than half a turn) and wait for the oil to slowly flowing out. In case the oil does not flow, the bolt should be retightened and the sampling given up.
- 7. *Connect the sampling port with the proper tubing or mount a sampling flange if necessary.* Usually, it is sufficient to place the sampling vial under the sampling port and open slowly the valve or the drain bolt to letting the oil to flow directly in the vial. Otherwise there may be cases where this is not technical possibly, either because of the size of the sampling port, or because there is not enough room to place sampling vials and spillage tray under the sampling port. In these cases, it may be necessary to connect the threaded part of the drain to a tubing with a threaded connection of the same size. A set of threaded sampling tubing need to be therefore made available before the start of sampling operations.
- 8. *Take and manage the sample.* Before actually taking the sample, it is recommended to purge the sampling port and the sampling line, to avoid any water and sludge to be collected in the sampling vial. This is a key step to avoid future unreliability of the screening analysis. The first 100 ml of oil should be initially collected into a waste oil container. For wide sampling plans, for instance during the carrying out of large inventories, this will generate a significant amount of waste oil that will need to be properly disposed of. After that, the sampling vial will be placed under the drain and the sample collected. Sampling vials with a volume of 50 ml are large enough to allow for repeated screening analyses, as each test requires typically only 5 ml of oil. Around 10% of the volume of the vial will be left empty to allow volume expansion. The sample and the transformer should have been marked before undertaking the sample, as explained in section 1.4. If for any reason it was not possible to take the sample, that has to be recorded in the sampling register.
- 9. *Manage the waste generated during the sampling*. during each sample operation a number of different wastes may be generated. These will be: waste oil from purging operations; paper and rags contaminated by oil; used disposable
- 10. *Manage to put the transformer back online and repowered.* If sampling entailed the disconnection of the transformer from the line, after sampling completion the transformer has to be placed back on line and repowered. All the downstream electricity customers have to be alerted well in advance of the date and time of energy disconnection and re-connection, to prevent any accident (electrocution) or damage to equipment. Reconnecting and powering on a transformer has to be carried out only by the authorised staff of the company owning or managing the transformer.

## **Special Cases**

## **Phased out and Offline Transformers**

Although the sampling of phased out and offline transformer is usually the simplest case, as these transformers are offline (no electrocution risk) and usually stored on the ground, there are a number of aspects that need to be considered properly:

- storages of old phased out transformers are very likely PCB contaminated places (photos).
- other hazards like the presence of wild animals (insects, snakes, dogs) are common.
- the transformers may be stored too close each other, or even piled, making the sampling activity very difficult or even impossible
- the nameplates may have been removed
- the sampling valve may be damaged or blocked
- the transformers may have been partially dismantled, so that they rain water can have entered into the transformer body

All these aspects need to be considered and properly addressed to ensure the quality and traceability of the sample, and to prevent any risk for the operators and the environment during sampling operations.



*Photo 5: A storage area were phased out transformers are stored. The soil is completely impregnated by dielectric oil and oily sludge.* 

## **Online, Base Mounted Transformers**

Generally, base mounted transformers are either large distribution or step-up transformers (Photo 9 and Photo 10), or distribution transformer located inside buildings or factories (Photo 8).

The sampling of these transformers requires coordination with the owner of the transformer to ensure access to the site and the adoption of specific procedures to disconnect or re-connect the transformer.





Photo 6 A pole-mounted transformer located on a platform



Photo 7: Examples of pole-mounted transformers.



Photo 8: Examples of indoor, base mounted distribution transformers



Photo 9: A large step-up transformer mounted at an electric power plant



Photo 10: A large distribution transformer mounted in a distribution substation.

#### **Online, Pole Mounted Transformers**

Small distribution transformers may be mounted on poles, requiring therefore special procedures for access and sampling operations. In general, the risk associated to working at height should be considered as the prevailing risk when sampling pole-mounted transformers. There are two types of pole-mounted transformers: in the easiest case, the transformer is mounted on a platform which is accessible by a ladder (Photo 6). In this case, there is no need to use a crane or a mobile platform to access the transformer. In other cases, the transformers are just mounted on poles without platform and to access them is necessary to climb a ladder or make use of a mobile platform. In all these cases, a safety harnesses equipped with safety ropes and triple safety carabiner should be used. In case the pole is not equipped a safe ladder, it is recommended to use as a first choice a mobile platform, and as second choice a certified safety ladder. The safety procedure for working at height are summarized in chapter 1.1.6. The second significant source of risk when working on polemounted transformers, relates to the possibility of electrocution. In addition to the electric cable powering the transformer, there may be many other cables hanged to the same pole (Photo 7). Therefore, even if the transformer is disconnected, the risk of electrocution through contact with other powered cables may persist. This has to be thoroughly checked when accessing a transformer mounted on a pole.

## Sampling Equipment:

The following equipment is necessary for sampling operations:

- Sampling vials. 50 or 100 ml sampling vials are necessary for sampling (Photo 11). A good choice is borosilicate glass vials with an internal volume of 50 ml and a mouth diameter of around 20mm. Larger sampling bottles may be used, provided that a good management of the waste oil after the analysis is complete is ensured
- Sampling labelling system: adhesive sampling labels and permanent marker pen for sampling vials. Steel wire and aluminium plates to be bound to the transformers. A set of number punchers for marking aluminium label. Pliers. (Photo 12)
- A set of wrenches for opening the sampling ports and drain bolts.
- A sampling syringe to be used in case is necessary to sample from the top (internal volume at least 25 ml)
- Threaded ring connection and adapters with threaded rings of different sizes to be attached to the sampling ports. Usually there is no need to use these accessories, except when placing a vial directly under the sampling port is not possible.

## **Sampling Coding and Chain of Custody**

The attribution of a common sampling code to both the transformer and the sample is a fundamental – and too often neglected – step in any PCB inventory. Unfortunately, it is not possible to rely on the serial number reported on the nameplate of the transformers, for two simple reasons: these serial number may be not univocal (different transformer brands may have the same serial numbers) and in many cases, the transformer nameplate has been damaged or removed.

It is therefore necessary to select a method as simple and reliable as possible, limiting the amount of information to be reported on the sample and on the transformer and using permanent marking systems.

To this end, a good solution is the following:

- 1) use punchers for marking the transformers with the sampling codes. (Photo 12). Transformers may be either directly punched, or an aluminium plate may be punched and permanently attached to the transformer, for instance by mean of a steel wire.
- 2) use good permanent marker pens to label the labels on the sampling vials. Stick the label to the sampling vial before sampling and cover them with a layer of transparent tape.
- 3) adopt a coding which is at the same time univocal and as simple as possible. For instance, the numbering system may be based on a 2 + 4 number code, out of which the first 2 numbers identify the sampling operator (or the sampling team) and the other 4 numbers identify the progressive code of the transformer sampled by the team. In this way it is ensured that duplicated numbers would never exist and the sampling code is simple and univocal, even if more teams are undertaking sampling at the same time.



Photo 11: Example of sampling vials suitable for sampling. Recommended volume is 25 to 50 ml.



Photo 12: Punching letters and punched plate as a possible example to mark sampled transformers.

The sampling code shall be associated with a database (basically an excel worksheet) where the following information for each transformer are recorded

- Section 1: Identification of the equipment. Name and address of the owner (Electric cooperative or others); GPS coordinates; Serial code as from nameplate when available; Transformer brand; Country of origin; Equipment Type
- Section 2: Equipment description. Power rating (KVAr for capacitors); High Voltage (V); Low Voltage (V); Manufacturing date; Toral Equipment weight, including oil (Kg); Oil Weight (Kg); PCB content in the liquid (ppm); PCB analysis performed
- Section 3: Equipment conditions. Operational status; Condition of the equipment; Location or storage conditions; Retrofilled (Y/N); Retrofilling date; Retrofilling liquid; Maintenance company; Nameplate photo; Equipment photo

With "chain of custody" it is conventionally intended a set of procedure which ensures that:

- Samples are tracked from the source to the laboratory of destination until the analysis is performed and the analytical certificate is issued.
- The purpose of the chain of custody is to secure the univocal relationship between the

material sampled and the analytical result.

• The chain of custody (see sample form in Annex B) works by recording each time a sample is passed from a person to another (for instance, from the sampling operators to the carrier, from the carrier to the laboratory administration, from the laboratory administration to the analysis operator)

## **Proper Planning, Hindrances and Hidden Costs**

Sampling activities are the true bottleneck of any PCB inventory. Whenever a large PCB inventory has to be carried out, there is the need to thoroughly plan the sampling activity. The most common hindrances faced by large inventories, which need to be taken into account in a successful sampling plan, are the following:

- unreliability of the databases of transformers provided by the owners;
- underestimation of the logistic aspect, especially when a large number of small distribution transformers to be sampled are scattered along a wide territory and need to be identified and reached;
- neglecting the hidden cost for the transformer owner associated to the mobilization of their personnel or the disconnection of transformers from the grid;
- lacking of a trustable chain of custody to prevent fraudulent practices in sampling and to ensure that any sample is associated to a transformer which can be traced back;
- underestimation of the time and staff needed for sampling a transformer. To be on the safe side, at least two staff working for one hour are required on the average for sampling one transformer. Less time may be required for sampling phased out transformers stored in storage areas, whilst more time may be needed to sample pole transformers with difficult access;
- misunderstanding of the true risk associated with sampling. The accident of getting in contact with PCB contaminated oil may be easily mitigated by immediate washing of the exposed skin with the proper procedure (1.1.9). Other severe accidents (like electrocution, falling from height, bites by wild animals) could be fatal and need to be carefully prevented.
- lack of performing a proper purging before taking the sample. This is a common mistake made to reduce the sampling time and the amount of waste oil. This will unavoidably result in a significant number of unusable samples which can only by addressed by resampling.

## **Use of Personal Protective Equipment (PPE)**

#### **Sampling**

The personnel should always wear proper PPE when handling waste dielectric oil contaminated or containing PCBs.

The following PPE are recommended during handling of waste transformer oil in normal condition (i.e. operation like transferring oil by pumping devices, handling of drums containing waste transformer oil, feeding waste transformer oil to incineration plant through automated devices):

1) Disposable coverall. A liquid resistant coverall will be worn at the beginning of each

shift, and replaced if it has been hit by a splash of transformer oil:

- 2) Gloves. Heavy duty disposable thick rubber gloves.
- 3) Safety goggles
- 4) Hard Hat

Always observe good personal hygiene measures, such as washing hands after handling of the material and before eating, drinking and smoking. Routinely wash work clothing and protective equipment to remove contaminant.

Wearing respiratory mask is usually not necessary during normal waste handling operations as the risk of inhalation exposure is limited. However, if a preliminary survey identifies possible PCBs contamination of the site where the waste is stored, operator should also wear protective shoes, respiratory mask and a protective suit.

When performing operation in sites contaminated by PCBs, like transformer storage areas or transformers warehouses, the following additional PPE shall be used.

- Chemical protective suits providing protection to the full body against airborne solid particulates (Level C protective clothing compliant with EN ISO 13982-1 Dry particle suit) and antidust masks (i.e. EN 149 or EN 143 FFp2 or FFp3) when the main PCB contamination is expected from dust or soil;
- Chemical protective disposable suits (Level B protective clothing i.e. compliant with EN14605 Liquid tight suit, EN14605 Spray tight suit, EN ISO 13982-1 Dry particle suit) providing additional protection to the full body against liquid chemicals / aerosols and mask equipped with antidust filters and filters against gas / vapours (i.e. EN 149 with FFp2 and A-1 class filter) in sites where there is a high probability to get in contact with liquid PCB.

#### **PPE for Working at Height**

The selection of proper PPE for working at height is in this case based on the assumption of sampling transformers mounted on poles transformers. The main challenge in this case is therefore to carry and use the necessary sampling equipment up to the site of sampling.

Working at height requires a dedicated training of the staff and of the team manager. Working at height is not a job for everybody, and in particular is not suitable for people suffering of panic attack when exposed to height (acrophobia).

In general, a proper risk assessment of the situation is needed before selecting the suitable PPE. The highest priority should be given to PPE preventing workers to fall: these PPE include a restraint system (waist belt / harness), a connecting element (work position ropes electrically insulated), a connector (a multiple-safety carabiner) and a secure anchorage. In the case of working on poles requiring the use of safety ladders, fall prevention PPE coincides with the positioning PPE, i.e. PPE aimed at supporting the worker while carrying out the sampling task. Consideration should also be given to fall arrest PPE used to arrest the worker in the event that a fall should occur. A PPE fall arrest system comprises a body support element (fall arrest full body harness), a connecting element (fall arrest lanyard with built-in energy absorber), a connector (karabiner/hook) and an anchorage (lifeline/anchor).

#### **Emergency Preparedness Response**

For the management of the emergency situation associated to PCB, the following practical consideration should be kept in mind.

- 1) PCBs are not flammable. However, if exposed to fire or high temperature, they can generate dioxins. Therefore, preventing contact of PCBs with fire represents a high priority.
- 2) Although PCBs are not flammable, PCBs contaminated oil is flammable. The burning of highly contaminated PCBs oil represents a worst case in term of immediate danger for life coupled with long term effect danger caused by the release of Dioxins that would be generated.
- 3) PCBs do not have a high vapor pressure, and for this reason the direct exposure to PCBs vapours is unlikely. However, due to their long term toxicity, in case of massive PCBs leakage proper respiratory mask should be wore.
- 4) PCBs may easily enter the body through contact with the skin. Dermal exposure to PCBs represents the most probable cause of human exposure during sampling. The effects of dermal exposure can be however easily minimised by promptly wiping the oil from the body and washing with adsorbent liquids (like edible oil) and soap.
- 5) PCBs cannot be easily removed by water due to their very low water solubility. However, PCBs can be easily removed by using adsorbent materials with high organic content, like sawdust, soil with high organic matter content, organic solvents, greases.

#### Fire

PCBs exposed to fire may generate smoke and fumes highly contaminated by PCDD/F and PCBs. In addition, whilst pure PCBs are usually not flammable, PCBs contaminated oil is flammable and dangerous for its content in PCBs.

When operating in places where the risk of fire exists, sampling operators must always be informed by the site managers on the procedure to be followed in case of fire accident, including the availability and mode of use of fire extinguisher, safe evacuation rules and paths.

## **Oil Spillage and Soil Contamination**

Prior to sample any transformer is mandatory to check of the drain valve is in good condition or if any sign of rust or damage could cause the breaking or malfunction of the valve during sampling operation. NEVER SAMPLE OIL FROM BOTTOM DRAINAGE VALVE IF THESE ARE RUSTY OR IN BAD OPERATING CONDITIONS.

Prior to sample any transformer is also mandatory to check whether there are pre-existing sign of soil contamination. The owners of transformers must be informed of any pre-existing sign of soil contamination as he will be liable for the environmental damage associated to it.

In case of pre-existing soil contamination, the following rules should be strictly followed during sampling operations:

- Try to the extent possible not to walk on the stained ground
- Identify if leaking is still on-going or if the stains are the result of historical leaks
- Record the conditions of this transformers on his daily report form
- Note if the ground is paved or not

- If leaking is on-going, refer to mitigation measure listed under oil-leakage or spills
- It is the responsibility of the owner of the transformer to put online a transformer that seem to have lost a significant quantity of oil

If a transformer is leaking due to sampling operations, or if spills or leaks occur during sampling, the surveyor will try to stop the source of the spill by trying to better close the drain tap, without forcing it.

If leakage persist, the operator shall inform both the owner of the transformer and the authority in charge. reporting the location of the transformer, the information related to the identity of the transformer. and whether the leak or spill is the result sampling or not.

## **Dermal Contact with PCB Contaminated Oil**

In case of skin exposure to oil possibly contaminated by PCB, the following actions will be immediately undertaken:

- Remove contaminated clothes
- Remove excess oil from the skin with paper napkins or a clean rag.
- Use edible vegetable oil or grease to further deterge the skin
- Wash thoroughly and repeatedly the skin with water and a detergent
- Draft an accident report containing:
  - Place, date and time of the event;
  - Name of the person injured
  - $\circ\,$  Description of the event, including the part of the body entered in contact with contaminated oil.
  - Univocal sampling code of the transformers being sampled, so that it will be possible to understand whether the oil contained PCB.

All the materials (napkins, rag) used for cleaning the skin should be treated as hazardous waste after use.

## Fall from Elevated Working Areas

In order to avoid falls during sampling:

- Always wear safety harness equipped with safety rope and carabiner when working on elevated working areas;
- Do not climb on transformers

In case of major fall especially from elevated working areas, if the person is unconscious:

- Secure the area where the victim is lying (especially if the accident occurred along a roadway)
- Contact immediately the nearest hospital or the Red Cross to arrange a medical team to take the victim to the hospital
- Talk to the injured person and tap on his face and hand to try to wake him up.
- With minimum movement, try to liberate the nose and mouth of the victim to allow him to breathe more easily

If the victim is conscious, before moving him, ask him if he can feel his fingers and toes. If not, do not move the victim, secure the scene and call for help as outlined earlier.

If the person is conscious and can feel his toes and fingers:

- Move the person to a secure location very slowly asking him to help you with minimal sudden moves
- Assess the seriousness of the injury (open fracture, fracture, wounds, concussions, etc.)
- In case of bleeding, put clean napkins on the injury and press or have the victim press the wound.
- In case of apparent fracture, try to immobilize the fractured member temporarily or avoid moving it
- Take the person to the nearest hospital

## **Electrocution**

Only the owners of the transformers should be authorized to sample energized transformers. To prevent electrocution, do not sample transformer before the owner of the transformer confirms that the power has been disconnected centrally and locally. Never rely only on centrally disconnected power, instead make sure that power is cut at the level of transformer being sampled. In case of electrocution, before approaching the victim, make sure the owner of the transformer disconnects the power that caused the electrocution.

If the victim is unconscious, move her to a secure location, remove obstruction to her respiratory tracks. If the person is not breathing, induce CPR like movement on the victim. Contact the nearest hospital, or the Red Cross to arrange a medical team to take the victim to the hospital.

If the victim is conscious, move her to a secure location, and take her to the nearest hospital.

#### Analysis of PCB through Screening Test

#### **Commercially Available Technologies**

Currently, only two brands manufacture quantitative screening equipment and reagents: Dexil and Sea Marconi. These equipment are composed by 3 components: a) a signal reader; b) an electrode; c) a kit of reagents to extract the chlorine from the PCB and solubilize the chlorine in water. Both brands rely on the same Orion chlorine ion detector. Sea Marconi makes use of a commercial Orion signal reader for processing the signal of the chlorine ion detector.

In Table 1, a comparison among the two screening kits is proposed.

*Table 1:* Comparison between the Sea Marconi and the Dexil screening kits for quantitative analysis of PCB

	Sea Marconi <sup>1</sup>	Dexil <sup>2</sup>
Measurement principle	Dehalogenation of PCB through a sodium based reaction. Potentiometric measurement of chlorine by means of a chlorine-specific electrode, and conversion to PCB based on the assumption of a specific Aroclor mixture	Dehalogenation of PCB through a sodium based reaction. Potentiometric measurement of chlorine by means of a chlorine-specific electrode, and conversion to PCB based on the assumption of a specific Aroclor mixture
Type of chlorine specific electrode	Orion chloride Ion Selective Electrode 9617BNWP	Orion chloride Ion Selective Electrode 9617BNWP
Type of signal reader	Orion STAR A324 meter provided with separate software (Excel worksheet) for conversion from chlorine concentration to Aroclor mixture. Connection to a PC through USB. Up to 5 point calibration. Storage of up to 5000 data. Can be used to read the signals coming from many different electrodes and probes.	Dexil L2000 analyser with built in software for conversion from chlorine to Arochlor mixture. Automatic calibration. Built -in printer. Cannot be used with other electrodes.
Reagent used for the extraction step:	Sodium byphenil P.E.S. extraction reagent Acetic acid	Sulphuric acid Nickel Nitrate Potassium Nitrate Metallic sodium Naphtalene

<sup>&</sup>lt;sup>1</sup> Source: Sea Marconi Safety Data Sheet for the reagents; Sea Marconi technical booklet for the info concerning the PCB testing kit

<sup>&</sup>lt;sup>2</sup> Source: Dexil MSDS data sheet for the reagents; Dexil L2000 handbook for the info concerning the PCB testing kit

Chlorine	The sample is inserted through a	A plastic vial containing 2 breakable		
extraction	disposable syringe in the vial	ampules is used for the testing.		
steps	containing the reagent. After shaking,	Three steps are requested for the		
	the second reagent is added. There is	reaction involving the breaking of the		
	no need of venting. After reaction, the	ampules, venting, separation and		
	sample has to	filtering.		
	separate, then it is filtered.			
Linearity	2-2000 ppm	2-2000 ppm		
range				

#### Sources of error when testing PCB with chlorine electrodes and how to minimise them

The use of quantitative screening test for PCB based on the detection of chlorine brings a clear advantage against GC methods in term of ease of use, speed, analytical cost and portability. However, this methodology is affected by sources of potential errors and uncertainties that need to be fully understood in order to be reduced as much as possible and to ensure that the use of this method bring reliable results.

The basic assumption underlying the analysis of PCB using chlorine electrodes is that PCB concentration in the oil may be correlated with the concentration of PCB. The methodology rely on stoichiometric calculation or correlation formulas for calculating the PCB concentration starting from the concentration of chlorine in the oil. This means that if other chlorinated molecules (like for instance chlorobenzene) are contained in the dielectric oil, these will be counted as PCBs by the chlorine electrode methods. This will in general result in an overestimation of the PCB content by the chlorine method.

The user is only given the option to select among a limited number of PCB commercial mixtures characterized by a different level of chlorination (usually Aroclor 1242, 1254 and 1264). However, as in most of the cases the PCB contamination of the dielectric oil is a result of cross contamination, the actual composition of the PCB mixture in the oil is unknown. This could be the source of both over or underestimation of the actual PCB content of the oil.

Another important source of error is the quality of the sample. Samples containing water or sludge as the result of an incomplete or lacking purging before sampling are quite common. Very likely, this is the largest source of error as it affects significantly, and in an unpredictable way, the extraction step of the methodology.

The extraction step is also another potential source of error. The extraction step entails several sub-steps like shaking by hand, measuring, mixing and filtering, that need to be carried out with a high level of consistency. The vendors of the two testing equipment provide quite detailed instructions for the conduction of the extraction steps, however in case of large number of samples to be processed, there is still the need to optimize the process with special regard to shaking and filtering.

A potential source of error lies in the reading step. Poor maintenance of electrodes, inaccuracy of the calibration (for instance by using exhausted calibration chlorine solutions), inconsistent rate of shaking the electrode when reading the testing solution are all sources of errors which may lead to instability of readings.

## Key Steps in undertaking Analysis with Quantitative Screening Tests

The procedures for the analysis of PCB in dielectric oil are detailed in the manuals provided by the vendor along with their equipment<sup>1</sup>. It is mandatory to comply with the procedures reported in the manuals. Any deviation from these procedures (for instance, the use of automatic mixers, instead of shaking by hand) needs to be discussed with the manufacturer to understand the impact on the reliability of the method. Therefore, these procedures are not replicated here and, when performing a test with a chlorine based method, reference should be made to the most updated manual. However, as a number of steps are common to all commercially available, below are some of the critical and common analytical steps discussed concerning:

1. **Calibration with a chlorine solution.** Calibration against one or two standard chlorine solutions must be performed each hour or each 20 measurements. The calibration of the electrode + signal reader system again a standard chlorine solution is a basic step to verify the linearity of the readings at different chlorine concentrations. For this purpose, the signal readers are equipped with specific procedures and built in software that allow to realign the signal with the chlorine reading upon reading of one or more standard chlorine solution (calibration). It is recommendable to have at hand a number of different chlorine standard solutions to quickly check whether there is any misalignment between the signal and the expected chlorine reading. To this end, a number of standard chlorine solution may be easily prepared as follows:

Concentration of chlorine in the standard	Weight (mg) of NaCl in one litre of water
solution, in ppm weight basis	
5	8.24
10	16.48
25	41.21
50	82.42
100	164.84
250	412.11
500	824.22
1000	1648.4
2000	3296.9

The calibration against a chlorine solution ensure the accuracy of chlorine detection, and is therefore useful to identify issues related to the functionality of the electrode + signal reader system. This calibration however does not provide any information about the accuracy and repeatability of the extraction steps. For this reason, once the calibration of the electrode against a chlorine solution is successfully completed, it is recommended to perform a full calibration of the extraction method against one or more Aroclor solutions.

2. Calibration against standard Aroclor solution. The extraction and reading of an Aroclor standard should be performed periodically any time a new set of reagents is used. The calibration of the system again one or more Aroclor standard solutions need to be performed

<sup>&</sup>lt;sup>1</sup> L2000DX User's Manual – Dexil Corporation, March 2010 Sea Marconi

only after the calibration of the electrode against standard chlorine solutions has been thoroughly and successfully completed. In this way, having reduced at the minimum possible extent the source of error associated to system electrode + signal reader, the calibration against Aroclor solution provide a measure of the reliability of the extraction method upstream the reading step. To this end, it is recommended to use an Aroclor 1254 standard diluted at the desired concentration in certified PCB free dielectric oil. Two or standards at different concentration level (in the order of 20ppm and 100ppm) will be prepared by a certified laboratory starting for a certified Aroclor 1254 standard (for instance, an Aroclor 200 $\mu$ g/mL solution in methanol). To measure the reliability and stability of the extraction method, from 3 to 5 repeated extraction and reading of the same standard should be performed for each standard solution (total of 6 to 10 extractions).

- 3. Volume measurement with precision pipettors. Although the testing kits include usually standard pipettors for the measurement of oil samples or reagents, it is recommended to use precision micro pipette adjustable in the range of 1000 to 5000  $\mu$ L, equipped with disposable tips. These pipettes can also be used to dilute the samples in clean dielectric oil in case the concentration of the sample exceeds the linearity range of the method.
- 4. **Mixing / shaking.** The extraction steps of the method always entail performing a certain number of mixing / shaking reagent solution for a certain period of time. To ensure the repeatability of the measurement, it is recommended to perform the shaking / mixing operation in a consistent manner. The use of automated mixers can be considered as a good approach to ensure that mixing and shaking are always performed with the same speed. However, automated mixer should be set at a speed which ensure a good mixing without creating emulsion or foam.
- 5. **Separation.** The result of the extraction process is an oil/water emulsion where chlorine is dissolved in the aqueous component of the emulsion. Before the final step of the analysis can be carried out, the emulsion need to be separated in the two components and filtered. The settling time is usually the bottleneck of the entire process, and in case a large number of samples need to be processed, the processing time may be optimized by performing all the preceding reaction steps for a batch of samples (for instance, 10 samples) and then leaving all the samples to settle together before filtering and reading.
- 6. **Filtering:** after the separation step is successfully completed, the filtering step will allow to obtain a clear aqueous solution free of oil and suspended particles. When performing filtering it is necessary to understand that the final reading with the electrode will be not affected by the volume of the aqueous solution, as it measure a concentration, not a mass. Instead, if the aqueous solution gets contaminated with some oil drops, these drops will adhere to the surface of the electrode and may affect the subsequent readings. Therefore, is recommended better to stop the filtering process well in advance the oily supernatant enters the filter, even if this imply a smaller volume of the aqueous solution.
- 7. **Reading:** The signal readers are equipped with a built-in algorithm which ensure that that a final reading is given only when the fluctuation of the signal generated by the electrode is reduced down to a certain level (stable reading). Therefore, the duration of the reading process may vary as a function of the concentration of the chlorine in the aqueous solution, and the quality of the solution in term of contamination by oil drops or by suspended material.

Usually, lower concentration and low-quality solutions result in longer stabilisation times. Before undertaking the reading of a new sample, it's always necessary to clean the electrode by rinsing it in a proper rinsing solution and gently wiping with paper. The electrode should be placed in the aqueous solution, stirred gently for a couple of second, and then left untouched until the reading is stabilised. If the stabilisation of reading is not achieved within a reasonable time, it may be necessary to clean again the electrode and restart the reading.

#### Management of Waste Generated by Sampling or Analysis

The following classification of waste will be adopted to ensure the proper management of waste generated during sampling and analysis operation (*Please note that all PCB Wastes as defined in RA6969 under DAO 2013-22 and DAO 2004-01 are categorized/ classified as L404*):

- Remaining of oil dielectric oil samples, with a PCB content below 50 ppm: classified as Y8 under the Basel Convention (Waste mineral oils unfit for their originally intended use).
- Remaining of oil dielectric oil samples, with a PCB content higher than 50 ppm: classified as Y10 under the Basel Convention (Waste substances and articles containing or contaminated with polychlorinated biphenyls (PCBs) and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs)).
- Used PPE not contaminated by dielectric oil (normal use, not being in massive contact with dielectric oil ): not classified as hazardous waste.
- Used PPE contaminated by oil (after being in contact with accidental splashes of dielectric oil): classified under the Basel Convention as Y10).
- Oil / water emulsion, deriving from laboratory analysis of PCB: classified as Y9 under the Basel Convention (Waste oils/water, hydrocarbons/water mixtures, emulsions).

For the management of the above waste, the following procedure will be adopted:

- 1) Remaining of oil samples. These will be classified respectively as Y8 or Y10 after the analysis is completed, and stored separately in appropriate containers.
- 2) Used PPE, not contaminated by oil or by PCB: will be considered as household waste and managed accordingly.
- 3) Used PPE, contaminated by oil: will be classified as Y10 and stored separately using in appropriate containers.
- 4) Oil / water emulsion, deriving from laboratory analysis of PCB: will be stored separately in appropriate containers.

As far as disposal activities are concerned, the following should be considered:

- Y10 waste can only disposed through plants compliant with Basel Convention Technical Guidance for the disposal of POP- contaminated waste;
- Y9 and Y8 waste can be disposed through land filling in engineered landfills or physicalchemical treatment;
- Household -like waste (for instance, used PPE not contaminated by PCB oil) will be collected to be managed following the local rules.

## ANNEX B



#### Chain of Custody (COC)

**Dielectric Fluid sample** 

COC No:			 Date:	
Company:			 Address:	
Contact Person:	:			
	a.	Contact Number:	 	
	b.	Email Address:		

Reference	Sample ID	Analysis	Source	Remarks

#### PROCEDURE FOR SCREENING AND ANALYSIS

The following are the equipment and materials used in this method:

(Note that the equipment and chemicals listed is specific to the comparative evaluation performed for this method (CISE) to determine the acceptable range at which the PCB screening results are linear and accurate. Other equivalent equipment may be used subject to evaluation)

## **Equipment and Tools for Analysis**

For the purpose of demonstration, specific equipment were identified in the procedure. However, other equivalent equipment may be used subject to evaluation with a recognized standard.

- a. Equipment
  - Chloride Analyzer (e.g. ORION STAR A3240)
  - Chloride Ion Selective Electrode (e.g. Orion 9617BNWP)
- b. Chemicals
  - Sodium biphenyl solution in inert atmosphere
  - Extracting solution (PES)
  - Clorine standard solution
- c. Tools
  - 5 mL syringes with needle
  - 20mL syringes
  - 0.45 µm filters
  - Pliers
  - Mixer
  - Adsorbent paper and napkins
  - Waste bin (HW and normal waste)
  - Liquid waste container
  - Pen and notebook to recording the data
  - Multifuncion timer
  - Distilled water
- d. Personal Protective Equipment
  - Gloves
  - Goggles
  - Disposable suit

I. Preparation and calibration of the Equipment (ORION STAR A3240 Analyzer and Orion chloride Ion Selective Electrode 9617BNWP)



Figure B.1 ORION STAR A3240 Analyzer meter layout

- Switch on the ORION STAR A3240 pressing the button ON/OFF.
- Arrows to scroll the setup mode. F3 to select
- Measure Mode: ISE
- Read Type: Auto read
- Resolution: 3
- Measure Unit: ppm
- Blank Correct: Yes
- Stability: Smart
- Push the button MEASURE or "back" (F1) to go back to the main screen.

#### a. Perform Meter Self-test

#### Meter Self Test

- 1. In the measurement mode, press setup (\*\*\*).
- 2. Press (, ), (,
- 3. Press or to highlight *Self Test* and press *f2 (accept)*.
- 4. Disconnect all of the electrodes and probes from the meter, attach the BNC shorting cap to the BNC input and press *f2 (yes)*.
- 5. Press f2 (yes) to start the self test.
- 6. The meter will perform an accuracy test. When the meter displays Accuracy Test Passed, press f2 (next).
- 7. The meter will perform an EPROM test. When the meter displays E2Prom Test Passed, press f2 (next).
- 8. The meter will perform a keypad test. Press each of the keys on the keypad (including 🏵) one at a time in any order. When the meter displays *Keypad Test Passed*, press *f2 (next)*.
- 9. The meter will display *Self Test Passed*. Press 😇 to return to the measurement mode.

#### b. Activating and Restoring the Orion Chloride Ion Selective Electrode 9617BNWP

• Remove protective cap

Figure B.2 Orion Chloride Ion Selective Electrode 9617BNWP



• Fill the electrode with the electrode solution (just below the hole)



Figure B.3 Filling of electrode solution on the Orion Chloride Ion Selective Electrode 9617BNWP

• Drain the electrode in a beaker by pressing the top of the electrode



Figure B.4 Draining the electrode solution

- Refill the electrode. The level of the solution must not exceed the level of the hole
- Connect the electrode
- Turn analyser on

### c. Calibration

• Select calibration (F1)



Figure B.5 Connecting the electrode

• Rinse the electrod and place into the standard solution 1 (100 ppm)



Figure B.6 Electrode in the 100 ppm solution

۲

● Once stabilized, press F3 (edit) and enter the standard value (100) then F2→ F3



Figure B.7 Stabilized (meter stops measuring) Orion reading

- F2 for the next point
- Repeat 2 to 3 with the 1000 ppm standard
- Press F3 (cal done) to save and edit the calibration curve.
- d. Perform Electrode Stability Test



Figure B.8 Meter will indicate passed or failed during stability test

#### **Electrode Stability Test**

- 1. In the measurement mode, press 🏝.
- 3. Press or to highlight *Stability Test* and press *f2 (accept)*.
- 4. Press or which to highlight *pH/ISE Channel* and press *f2 (next)*.
- 5. Make sure the electrode or probe to be tested is connected to the channel selected in the previous step and press *f2 (yes)*.
- 6. Place the electrode or probe in an appropriate solution with a stable temperature and press *f2 (yes)*.
  - a. Orion pH 7 buffer (Cat. No. 910107, 910760 or 910710) is recommended for testing a pH electrode.
  - b. A calibration standard with a moderate concentration of the ion of interest is recommended for testing an ion selective electrode (ISE).
  - c. Orion ORP standard (Cat. No. 967901 or 967961) is recommended for testing an ORP electrode.
- 7. The meter will perform the stability test and show the mV per minute drift and noise on the display.
- 8. The meter will display *Stability Test Passed* or *Stability Test Failed*. Press *f1 (esc)* or 🐨 to return to the measurement mode.

## f. Main Test Procedure

- Have all the sample coded and recorded in a database
- With a permanent marker pen, number all the required testing vials (the sodium byphenils and the PES) with the same code of the samples

#### Test Procedure Step 1

- Withdraw 5 ml of oil with the syringe and transfer it using the needle in the vial of sodium byphenil (use lower meniscus in measurement).
- Shake for 1 minute (hints: if using a shaker, it should be at low speed to avoid bubbling or emulsion formation)

#### Test Procedure Step 2

- Open the vial and transfer all the content of the PES bottle in it. Close it and
- Shake it again for 2 minutes.





*Figure B.8 Removing the Sodium biphenyl cover using a pliers or a crimping tool* 

#### Test Procedure Step 3

- Wait at least 10 minutes to allow phase separation.
- Filtration can start after the last sample underwent phase separation for at least 10 minutes.
- After that, all the samples can be filtrated in starting from the first to the last

## Test Procedure Step 4

- Attach two 0.45 µm filters serial assembly to the tip of the 20mL syringe.
- Remove the plunger from the syringe and pour contents of the reaction bottle into the syringe.
- Insert again the plunger
- Apply a constant pressure to the plunger and filter the aqueous phase into the empty bottle of PES.
- Stop filtering as soon as the oil phase reaches the second filter.
- Oil phase must not contaminate the aqueous solution



Figure B.9 Filtering of oil from the solution

#### Test Procedure Step 5

- Rinse the electrode with deionised water and dry it properly.
- Put the electrode into the sample solution:
- Press the button MEASURE to start the measurement. When the icon AR stops spotting, log the value.
- A Chlorine reading is provided. Record it for calculation of the equivalent Aroclor (using the excel file provided).
- Remove the electrode from the sample, wash it wipe it. Drain and dispose the contents of the bottles according to current regulations under RA6969.

#### **EXPLANATORY NOTE**

In order to evaluate the results of PCB analysis using the CISE method, a comparative study was undertaken. The objective of the study was to assess the reliability and accuracy of the screening analysis using the CISE method in relation to a recognized and standard method of PCB analysis which is the USEPA 8082.

The result of the comparative study showed that the acceptable working range for this method in relation to the equipment (Orion Star A3240) and reagent (sodium biphenyl) used is from 10 ppm- 500 ppm. Above 500 ppm, dilution has to be performed to achieve accurate and reliable results. This range value does not contradict the minimum or maximum detection limit of the equipment but rather sets a workable range recognized by the Bureau for PCB screening.

Note that the screening process is not confirmatory; it is just a way of screening the material, equipment or waste for the purpose of initial identification and classification. Laboratory analysis in accordance with EMB Memorandum Circular No. 2014-007 or other methods that may be recognized by EMB is / are the only acceptable way to determine the PCB concentration for the purpose of declaring a PCB-free status.

The draft EMB MC will provide a guideline on the CISE Method in addition to Chlorine Tests under the subject "Conduct of Screening" of EMB MC 2015-007. The relevant original contents of EMB MC 2015-007 are given below:

3.2.5 Conduct of screening. Various methods are available in screening materials, equipment or wastes potentially containing PCBs. The methods, include, but are not limited to, the following:

- Density Test
- Chlorine Test

3.2.5.1 Density Test (Density Test Procedure) 3.2.5.2 Chlorine Test

Chlorine Test	Matrix	Detection	Method of Chlorine
		Limit	Detection
Clor-N-Oil 50 ppm	Oil	50 ppm	Colorimetric
			reaction
L2000 DX	Oil, soil, water,	2 ppm	Ion specific
Chloride Analyzer	wipes		electrode

#### Table 5. Chlorine Tests for PCB Identification

The screening process is not confirmatory; it is just a way of screening the material, equipment or waste for the purpose of initial identification and classification. Laboratory analysis in accordance with EMB Memorandum Circular No. 2014-007or any policy issued thereafter is the only acceptable way to determine the PCB concentration for the purpose of declaring a PCB-free status.

The presence of polychlorinated biphenyls in transformer oil can be detected through specific and non-specific methods. Specific methods such as gas chromatography-electron

capture detector (GC-ECD), in general, produce accurate and reliable results at high concentration range. However, the cost of analysis is considerably high. Moreover, the method employs more complicated equipment and facilities, qualified staff, and usually cannot be used for on-site tests. Sample turnaround time for GC-ECD method is approximately 4 hours.

Non-specific methods, such as test kits, on the other hand, employ relatively simpler analytical methods and cost less. These methods can produce results comparable to those generated by specific methods at given concentration ranges, and can be used for initial field screening tests. The sample turnaround time for PCB test kits is approximately 10 minutes; thus, non-specific methods can test relatively large numbers of samples.

In the Philippines, the large gap in the cost of analysis (e.g., PhP 8,000 per sample analyzed with GC-ECD and PhP 600 (US \$ 10) per sample analyzed with the test kit is a major issue in the screening and PCB identification prior to treatment and disposal of material, equipment, and waste oil. With this EMB Memorandum Circular, the use of PCB screening tests/kits is being encouraged on the condition that certification of a PCB-free status (i.e., less than 2 mg/kg) shall be based on the analysis using the specific and EMB recognized method (e.g., GC-ECD).

With this EMB Memorandum Circular, the use of the CISE Method using the Chloride Analyzer is being recognized for use of the regulated community covered by legislation, rules and regulations on PCB management in the Philippines, in line with the country's commitment to the multilateral environment agreements such as the Stockholm Convention on Persistent Organic Pollutants (POPs) and the Basel Convention on the Transboundary Movement of Hazardous Wastes.

The detection limit value of 2 ppm is based on the comparison of the characteristics of Sea Marconi Orion PCB/Chloride Analyzer and 3 ppm detection limit value for the Dexil L2000 PCB Testing Kitbased on their specification sheets.