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Abstract:

This PETcore protocol has been established in September 2007 on the request of the PETcore organization, its objective is a technical description of all processing steps and analytical testing

The protocol has been based on the last released update from Petcore (June 2006). This proposal includes the latest information received from Petcore concerning the modifications to the existing protocol.

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Background

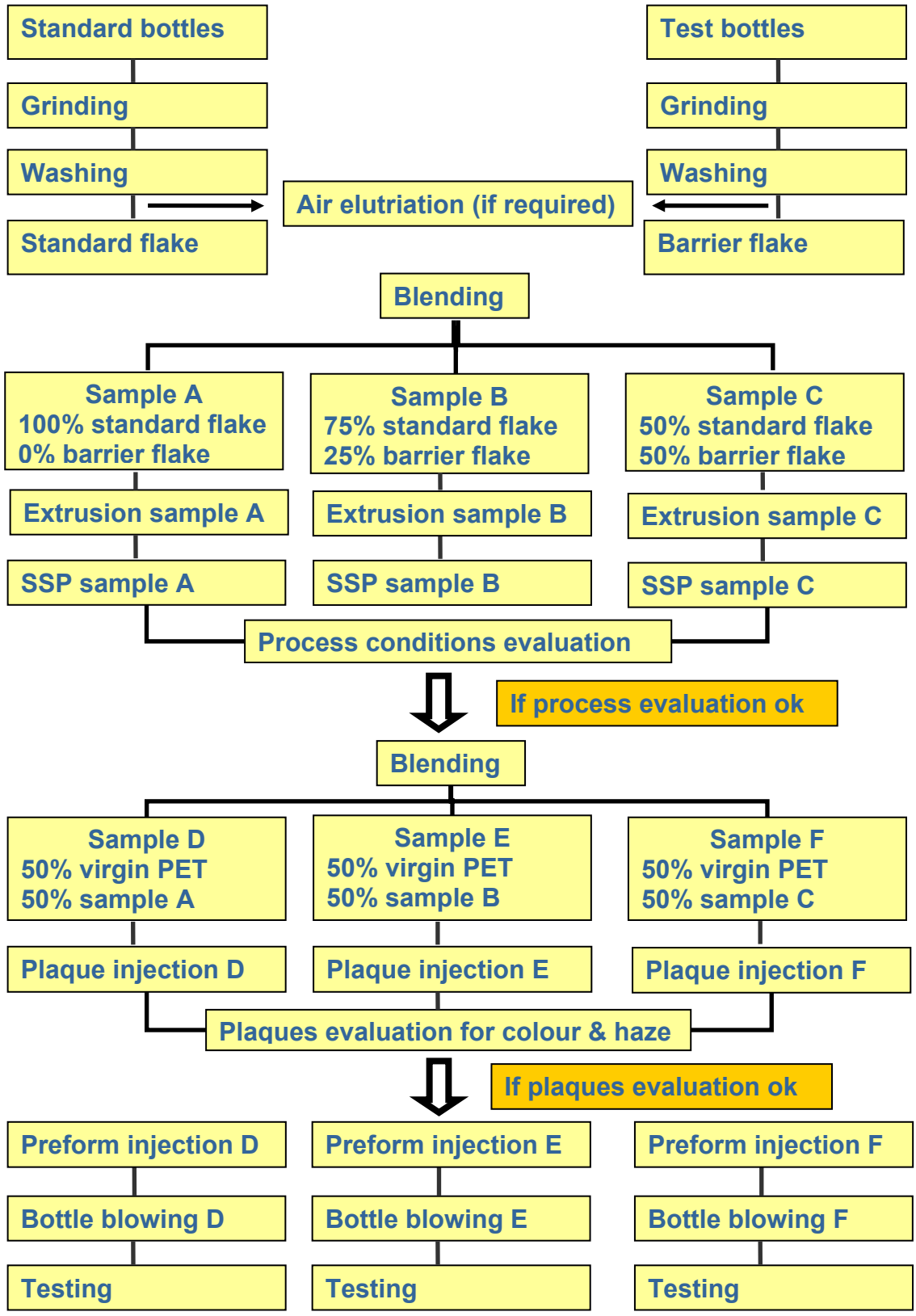
PETCORE has formulated guidelines to evaluate the influence of barrier materials or additives on the R-PET recycling processes. Commercially, the barrier materials are applied as a coating, introduced in a co-injected multilayer configuration or blended in with the matrix material. Additives are generally incorporated into the base material during polymerisation or added to the preform during injection moulding in the form of liquid or solid masterbatches. In order to judge the influence of these materials contained in bottles in main European bottle-to-bottle recycling processes, PETCORE recommends production of bottles containing recyclate from the above mentioned packaging. The following protocol can be followed to determine acceptability.

A positive test result will indicate the acceptance of the material for this recycling application (bottle to bottle) at the level conducted in the test. In combination with other test protocols (e.g. Diolen for bottle to fibre) the acceptability of the bottle containing barriers or additives for R-PET recycling can be judged.

Acceptability of a particular material is determined by comparing bottles made with clean washed flake from the test material and similarly cleaned, washed flake from identical bottles which do not contain the barrier material, coating or additive. In order to avoid the influence of extraneous variables like adhesives, labels or of the recycling process, the standard flakes and the flakes containing the material under test should be wet-washed with friction and, if necessary, once elutriated from unlabeled pre-consumer bottles. If (partial) removal of the barrier material during a reclaim step is required, both the standard flake and the barrier containing flakes should follow the same procedure in line with the appendix R1 of the guidelines describing the study of delamination and removal of barrier material during the reclaim process. If this reclaim process cannot be carried out for practical reasons, as a second alternative a mixture of barrier material and regular bottles might be composed representing the composition. Proof has to be delivered that the chosen composition is realistic.

What follows is a complete description of the required materials, processing steps and evaluation of the bottle to bottle Petcore protocol for 1 test variable. Upon request we can adapt our proposal for multiple variables.

Petcore protocol lay-out proposal as of Sept 14th 2007



Start samples

Option a) Production of the bottles by PTI-Europe

The standard clear bottles (from virgin bottles which are identical bottles to the test bottles and do not contain the barrier material, coating or additive) and clear test bottles (bottles including barrier, coating or additive) will be produced by PTI-E. The PET resin used for the production of the standard and test bottles should be a clear PET resin such as Voridian 9921W, Equipolymer Lighter C93, M&G Cleartuf P82, etc.

PTI-E will select its generic 43g preform and 1500ml generic CSD container to produce containers with both variables. They will be coded as follows:

Variable 1 = Standard bottles = reference
Variable 2 = Test bottles

A minimum of 35kg of the standard bottles and 15kg of the test bottles will be required to run the Petcore protocol as described below. To achieve this sampling quantity, PTI Europe will inject and blow the following quantities:

	Preforms	Bottles
Standard bottles	700	600
Test bottles	300	250

Option b) Delivery of the bottles by the client

The client will deliver the standard bottles and the test bottles in the required quantities to PTI-Europe. The client will make sure that both standard and test bottles are produced from the same clear PET resin. Further, the client will deliver a minimum of 60kg of this virgin PET resin to PTI-Europe for blending (see preform injection).

	Minimum weight
Standard bottles	35 kg
Test bottles	15 kg

Testing and sampling

Color (L*, a* and b*) and haze values will be measured on the standard and test start bottles. 5 bottles of the standard and test bottles will be retained for PETCORE and the client respectively.

Grinding

Standard bottles and test bottles will be ground separately to flakes with a 12 mm side size using a standard mechanical grinder.

Testing and sampling

The unwashed flakes will be evaluated for Melt IV and color values. This will allow us to measure the impact of the washing process on the color and IV of the barrier/additive flakes. 50g of the standard and test ground, unwashed flakes will be kept for PETCORE and the client respectively.

Washing

The two bottle flake materials will be washed according to a standard European wash protocol with flakes friction. This includes pre-washing the material with caustic and detergents followed by the washing process with detergents. Both processes are carried out at elevated temperatures (min. 85°C). The material will be thoroughly rinsed and dried. After washing, both flake samples will be tested for colour, bulk density and IV and a small sample (50g) will be retained for the client.

Pre-washing
Washing
Hot rinsing
Cold rinsing
Drying

Air elutriation (Optional: if required only)

The clean and dried flakes will be air separated through a laboratory scale air elutriator to separate light and thin particles such as barrier multilayer layers. The air elutriation flow will be regulated to obtain a removal rate of 0.1% on the reference flakes according to the guidelines of Petcore. The same settings will be used for the barrier flakes. The removal rate will be estimated by an oven test.

Flake evaluation

Intrinsic viscosity

Measurement of the IV of the standard and barrier/additive flakes. The IV will be measured with a Davenport Melt IV meter.

Bulk density

Bulk density of the flakes should be above 0.28 g/cm3.

Color (L*, a*, b* and ΔE_{cmc})

The color of both flake variables will be measured with a Minolta CM-3600d spectrophotometer.

Extrusion

The following blends will be prepared and extruded:

Sample A = Standard flake – 100% + Barrier/additive flake – 0%
Sample B = Standard flake – 75% + Barrier/additive flake – 25%
Sample C = Standard flake – 50% + Barrier/additive flake – 50%

The 12mm washed flakes will be grinded into 4mm flakes before extrusion to allow a good feeding of the material into the extruder. The washed bottle flake will be dried below 100 ppm moisture with a Piovan drying unit and extruded into strands using a small tonnage Arburg press converted into a continuous extrusion mode. The extruded strands will be cooled in a water bath and pelletized by chopping the strand. The extruder conditions will be set to duplicate as closely as possible the conditions used in full-scale PET extrusion/pelletization operations. The extrudate will be melt filtered with a 40/150/40 mesh melt filter pack (about 100 microns filtration). The extrudate will be rapidly cooled using a water bath and fed into a pelletizer to produce amorphous pellets. Before entering the pelletizer the strands are air dried. The extrusion process will be monitored for heat stability and the 40/150/40 mesh melt filter pack will be changed between samples for examination. The pressure differences will be noted between each material variable during processing. The extruded pellets will be tested for visual quality and IV. A small retain of each sample will be saved for the client.

Extrusion evaluation

Dried samples

A small amount of the dried samples will be extracted from the Piovan drier before entering the extruder. This will allow us to evaluate the impact of the drying process on the flake samples. A small sample will also be retained for the client.

Heat stability

No sticking, fumes or odours should be noticed when compared to control sample A. In addition, no additional thermal degradation, in the form of black specks or other inclusions should be noticed.

Filterability

The filterability of samples B and C must be compared with sample A under identical conditions representative of the actual production situation. The pressure increase in a filtration pack during an extrusion test should be identical for all the samples.
Standard conditions for control and test samples will be defined and designed to mimic actual production situations. All process parameters for each sample will be monitored and reported. Screens from control sample and study sample(s) will be analysed for any variations.

Intrinsic viscosity

After extrusion, the IV of samples B and C should be within 0.02 units of the control sample A.

Solid stating

The amorphous pellets will be first crystallized and then solid stated in our solid state reactor. The crystallization step, which will be done in a vacuum oven, is necessary to avoid sticking of the pellets in the solid state reactor during heating up. Solid stating will be performed under a heated nitrogen flow at temperatures around 200°C. About 10kg of samples A, B and C will be solid state polymerized under identical conditions in our solid state reactor up to a MIV of 0.80 ± 0.02 dL/g. Same conditions mean same vacuum level, same nitrogen flow and same temperature. The final solid-stated pellets from the material variables will be measured for color, IV and AA and a small sample will be retained for the client. Sample A will be processed first and compared to each consecutive run.

Solid stating processing evaluation

Solid stating evaluation

Time of processing

Sample B and C should reach this viscosity in a total SSP time equal to the time needed for sample A or to a maximum of 10% difference of total time for IV increase.

Intrinsic viscosity

All samples need to be solid stated to the same IV.

Acetaldehyde content

The AA content should not increase more than 0.5 ppm for samples B and C versus sample A.

Results within specifications => Proceed to next steps

Blending

A virgin resin, identical to the virgin resin used for making the starting samples, will be used for blending with the solid-state polymerized materials. A minimum of 60kg of the virgin material need to be sent to PTI Europe. The following blends will be prepared:

Sample D: 50% virgin bottle resin + 50% sample A (after solid stating)
Sample E: 50% virgin bottle resin + 50% sample B (after solid stating)
Sample F: 50% virgin bottle resin + 50% sample C (after solid stating)

Plaque injection

Test plaques with a thickness of 3.0 mm should be produced of samples D, E and F to evaluate color and haze. Those test plaques are injection molded with our Arburg machine in a special mould.

Injected plaques evaluation for colour & haze

Plaque evaluation

Haze evaluation

The percentage of haze should be measured at 550 nm. A maximum of 8% haze is allowed.

Color (L*, a*, b* and ΔE_{cmc})

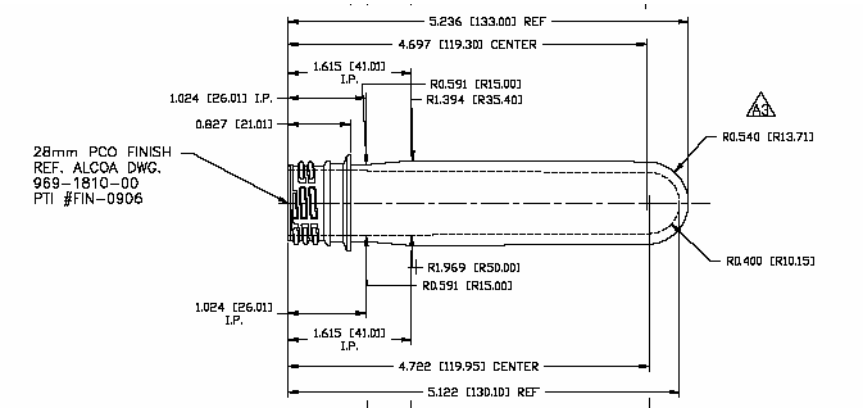
The color of the plaques will be measured with a Minolta CM-3600d spectrophotometer. The following requirements need to be met:

- ⇨ *L* = 87 minimum*
- ⇨ *a* = -3 minimum*
- ⇨ *Δb* = 1.5 maximum (compared to sample D)*
- ⇨ *ΔE_{cmc} = 3 maximum (compared to sample D)*

Results within specifications => Proceed to next steps

Preform injection molding

Samples D, E and F will be injection molded in a 43g preform with a PCO 28mm neck finish (see drawing below). The preforms will be molded on our monocavity Arburg press. Before molding the pellets will be dried a minimum of 4 hours at 160°C to obtain a moisture level below 50 ppm. The prices indicated below are only valid for this set-up, i.e. with a known preform design and known molding conditions.



Sample D will be used to set the injection molding conditions. The moulding conditions will be optimized for this sample to produce preforms free of haze and with minimal stress. All the remaining samples will then be moulded under the same conditions as sample D, if possible. If not, each sample will be compared to sample D. Approximately 200 preforms will be moulded from each sample at each of their optimum conditions. Five (5) preforms will be retained for PTI and the client from each sample. The preforms from samples D, E and F will be measured for IV and AA.

Preform injection molding evaluation

Injection processing

No significant differences in processing between samples D, E and F under optimized conditions.

Preforms

The preforms of samples E and F should be compared to the preforms of sample D and meet the following requirements:

Visual inspection

No increase in black spots, particulates or gels.

Intrinsic Viscosity

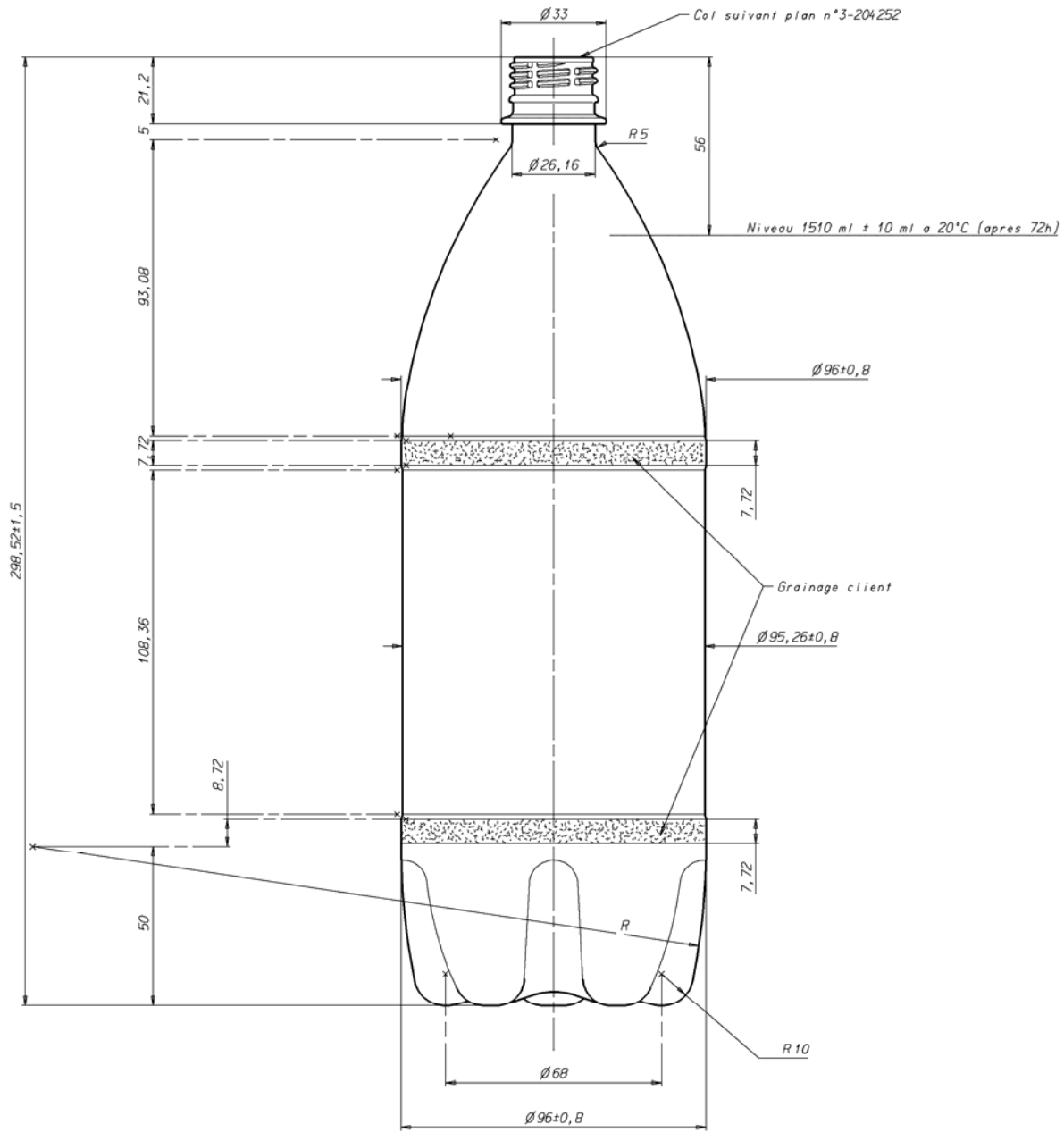
IV of the preforms of samples E and F should be within ± 0.02 units of the IV of preform D.

Acetaldehyde concentration

The preforms from sample E and F should not exhibit an acetaldehyde increase of more than 35 % compared to the preforms from sample D.

Bottle blowing

Preforms of samples D, E and F will be blown into a 1.5L straightwall container (see drawing below) on our SBO1 blow molder. Sample D preforms will be blown first. The blow moulding conditions will be optimized for sample D. Preforms of samples E and F will then be blown under the same conditions if possible. The blow moulding conditions for each sample will be compared to the corresponding control sample D. The conditions needed to blow each of the 3 samples will be recorded. A minimum of 150 bottles will be blown of each sample. Five bottles from each sample will be retained for the client. The prices indicated below are only valid for this set-up, i.e. with a known bottle design and known blowing conditions.



Bottle blowing evaluation

Processing

No significant differences in the resulting containers between samples D and E and F under optimized processing conditions. It is understood that small differences in process settings are generally necessary between different batches of preforms.

Bottles

The performance of bottles from samples E and F should not be reduced more than 5% when compared to the performance of bottles from sample D for the tests described below.

Physical performance testing

The following tests will be done on the bottles:

- Dimensions (external container dimensions)
- Weight & Capacity
- Material distribution
- Section weights
- Thermal stability test
- Vertical load (empty)
- Burst test
- Drop test

All the tests will be performed on 10 bottles (+ control bottles for the thermal stability test). We will perform the tests according to the ISBT test methods unless the client specifies differently.

CO2 retention testing (FTIR test)

This test will reveal any impact of the RPET on the shelflife of the bottle, i.e. on the capability of the bottle to retain CO2. The FTIR method for carbonation retention testing is designed to accurately assess the carbonation loss-rate of a plastic beverage bottle and to extrapolate shelf-life to a predefined loss according to the specifications of the client (standard 17.5%). The amount of CO2 is evaluated in a sample size of 10 test bottles over a 49 day period for non-refillable PET bottles, using an infrared light beam. Based on the calculated loss rate determined for this test, a shelf life can then be accurately calculated.

Standard conditions:
Filling level: 4 vol of CO2 (dry ice)
Storage and measurement conditions: 22°C / 50%RH
CO2 loss at shelf life: 17.5%

Color measurement (L*, a*, b*)
This procedure is used to determine the degree of color exhibited by resin, flake or a container sidewall. Resin and flake are measured with a colorimeter or a spectrophotometer in reflectance mode. The material is well packed in a quartz cell and the surface reflectance is measured. Duplicate measurements are necessary; therefore granules are removed from the quartz cell and re-packed each time. The container sidewall is measured in the transmittance mode.

- L*: (0) darker – lighter (100)
- a*: (-) green – red (+)
- b*: (-) blue – yellow (+)

We use a Minolta CM3600d which is able to measure from 360 to 740 nm (wavelength measurement step is 10 nm). This equipment has been approved by Petcore for color measurement of recycling studies in Europe.

Haze measurement
This procedure is used to determine the amount of haze in a container sidewall. This is an indication of how effectively the material was processed and/or the material's ability to be processed.
The haze measurement is also carried out with the Minolta CM3600d in transmittance mode.

Stress Crack Test (caustic)
Stress cracking is the crazing or cracking that may occur when a plastic is under tensile stress and subjected to negative conditions. PET (polyethylene terephthalate) material is strongest in a highly oriented state, such as the sidewall of the container. It is most susceptible to stress cracking when it is in an amorphous state and under tensile stress and internal pressure, such as the area surrounding the center of the base (gate area). The hydroxide ion is the main catalyst of stress cracking in PET bottles. A bottle that has more resistance to Sodium Hydroxide attack should be more resistant to stress crack initiators that a bottle may be exposed to during its lifetime.

Principle
Bottles are filled with still water and pressurized to 5.31 bar with pressurized air. The fill line is marked on the bottles 5 minutes after pressurization. Each bottle is placed in an individual pot containing a 0.2% caustic solution (NaOH) for 1 hour or until they burst or leak.

Summary of tests to be performed and samples to be retained as outlined in this protocol:

Start bottles	Flakes before washing	Flakes after washing	Dried flakes	Extruded pellets	Solid stated pellets	Plaques	Preforms	Bottles
Tests								
Color	Visual inspection	Visual inspection	Visual inspection	Visual inspection	Visual inspection	Color	Visual inspection	Visual inspection
Haze	IV	IV		IV	IV	Haze	IV	Physical testing
	Color	Color			Color		AA content	CO2 retention
		Bulk density			AA content			Stress cracking
								Color
								Haze
Retained samples (Petcore and client)								
5 bottles	50g	50g	50g	50g	50g	5 plaques	5 preforms	5 bottles