TECHNICAL SPECIFICATION

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Rubber — Framework for assessing the environmental fate of tyre and road wear particles (TRWP)

Caoutchouc — Lignes directrices pour évaluer le devenir environnemental des particules émises par l'usure des pneumatiques et de la route

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Foreword

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This document was prepared by Technical Committee ISO/TC 45, *Rubber and Rubber Products.*

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Tyres are complex consumer goods comprised of several reactive chemical additives that assist in the manufacture and function of the product. These formulated chemical additives are transformed by rubber curing processes during the manufacturing lifecycle stage. Subsequently, the remaining additives and transformation products are released from tyre tread during the service life (tyre use) stage as a component of tyre and road wear particles (TRWP), which are formed from the friction between a tyre and roadway surface (Kreider et al. 2010). TRWP contain tyre tread and pavement encrustations, and when released from tyre tread to soil and sediment ecosystems, are exposed to abiotic weathering and other environmental transformation processes. During the end-of-life stage, the additives and their transformation products in TRWP in soil or sediment have the potential to leach or become environmentally available (bioaccessible), and subsequently release into the surrounding ecosystem. As such, there is interest in studying the fate and transformations of tyre chemical additives from manufacture to the end-of-life in aquatic and sediment ecosystems (Unice et al. 2015).

Reliable analytical methods including polymer extraction methods accelerated weathering protocols, and leaching and incubator test specifications, are available to quantitatively assess the environmental processes affecting tyre additive fate in the manufacturing, service life, and end-of-life lifecycle stages. The key processes affecting the fate of additive chemicals during the lifecycle of a tyre include chemical transformations during rubber curing, physical and chemical changes during TRWP generation, abiotic and biotic transformations during TRWP weathering, leaching and sediment deposition. These processes cumulate during the lifecycle to determine the leachable or environmentally available fraction of tyre additive. The leachable fraction is the fraction of the formulated tyre chemical additive in the tread that is leached to surface water from TRWP released to soil or sediment, inclusive of pore and overlying water. The environmentally available fraction is the fraction of the formulated tyre chemical additive in the tread that is bioaccessible from TRWP in aqueous media, inclusive of overlying water, pore water and isopropanol extracted sediment.

These guidelines describe a general framework and considerations for the assessment of the leachable and environmentally available (or bioaccessibility) fraction of formulated functional tyre additives. Knowledge of the environmental fate and transport of tyre chemicals can assist in future analysis regarding the toxicity of TRWP to aquatic organisms. This framework may be useful for other complex, matrix-bound consumer products.

Rubber — Framework for assessing the environmental fate of tyre and road wear particles (TRWP)

1 Scope

This document establishes a general framework and considerations for assessing the environmental fate of tyre tread chemical additives in cured polymer and tyre and road wear particles (TRWP) throughout a tyre lifecycle. This document is applicable to laboratory-generated TRWP from cured tread polymer of known composition.

Testing strategies are described for assessing the environmental fate and transport of tyre chemicals in the following processes that can occur during the tyre lifecycle:

a) transformation of chemical additives in tread during tyre curing;

b) transformation of chemical additives during TRWP generation (tyre use);

c) transformation of chemical additives during TRWP aging and weathering;

d) leaching of chemical additives and transformation products from TRWP to water;

e) availability of chemical additives and transformation products from TRWP in sediment ecosystems.

Mass concentrations and fractions of chemicals released or available from TRWP for the five lifecycle steps are used to estimate

a) cumulative fraction of tread chemical(s) and transformation product(s) released to water, and

b) cumulative fraction tread chemical(s) and transformation products(s) environmentally available.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 22638, *Rubber — Generation and collection of tyre and road wear particles (TRWP) — Road simulator laboratory method*

ISO/TS 22640, *Rubber — Framework for physical and chemical characterization of tyre and road wear particles (TRWP)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
aging acceleration factor
factor applied to the duration of TRWP aging in a laboratory setting to determine the equivalent natural age of TRWP

3.2
end-of-life
lifecycle stage of tyre comprising lifecycle steps following tyre use and TRWP generation, including deposition of TRWP to sediment and soil, aging and weathering of TRWP, and release of chemicals from TRWP to the environment

3.3
environmentally available fraction
fraction of formulated tyre chemical additive in tread recoverable from TRWP in aqueous media, inclusive of chemical partitioned to pore water, overlying water and isopropanol extracted sediment

3.4
leachable fraction
fraction of formulated tyre chemical additive in tread leached from TRWP to surface water, inclusive of chemical partitioned to pore water and overlying water

3.5
lifecycle stages
three stages representing the typical lifecycle of a tyre, each comprised of lifecycle steps

Note 1 to entry: The three lifecycle stages relevant to this specification are tyre manufacturing, tyre use, and end-of-life.

3.6
lifecycle steps
steps within a lifecycle stage during which the chemical composition of tyre tread or TRWP may change

3.7
liquid to solid ratio
L/S
ratio of volume of leachant used in column test to mass of TRWP in column

3.8
manufacturing
lifecycle stage comprising of tyre chemical selection, formulation, curing, and finishing

3.9
service life
lifecycle stage comprising of tyre use and subsequent TRWP generation

3.10
tensile property
mechanical property of materials such as 100 % modulus and elongation at break

3.11
transformation product
chemical formed from the tyre chemical additive through processes such as hydrolysis, oxidation, and decomposition throughout the tyre tread and TRWP lifecycle

3.12
tyre and road wear particles
TRWP
discrete mass of elongated particles generated at the frictional interface between the road and the pavement surface during the service life of a tyre

Note 1 to entry: The particles consist of tyre tread enriched with mineral encrustations from the roadway surface.

4 Framework for environmental fate analysis

4.1 General

This framework provides general guidance for the assessment of the leachability and environmental availability of chemical additives selected for analysis and formulated into a test tyre tread. The chemical composition of tyre tread is altered during the manufacturing, service life and end-of-life lifecycle stages (Figure 1). As such, the leachability and environmental availability of chemicals from TRWP in aqueous media is likely to be determined by chemical transformations and mechanical alterations that occur in each lifecycle stage. This framework suggests a general testing strategy and methods to measure the fate of chemical additive(s) and transformation product(s) that reflects changes that occur in the following lifecycle steps:

a) tyre curing in the manufacturing lifecycle stage;

b) TRWP generation in the service life (tyre use) lifecycle stage;

c) TRWP aging and weathering in the end-of-life lifecycle stage;

d) leaching of TRWP in the end-of-life lifecycle stage;

e) release from TRWP to sediment ecosystems in the end-of-life lifecycle stage.

After characterization of the changes that occur in these critical lifecycle steps, the data are used to estimate release fractions to water or the environmental availability in water and sediment.

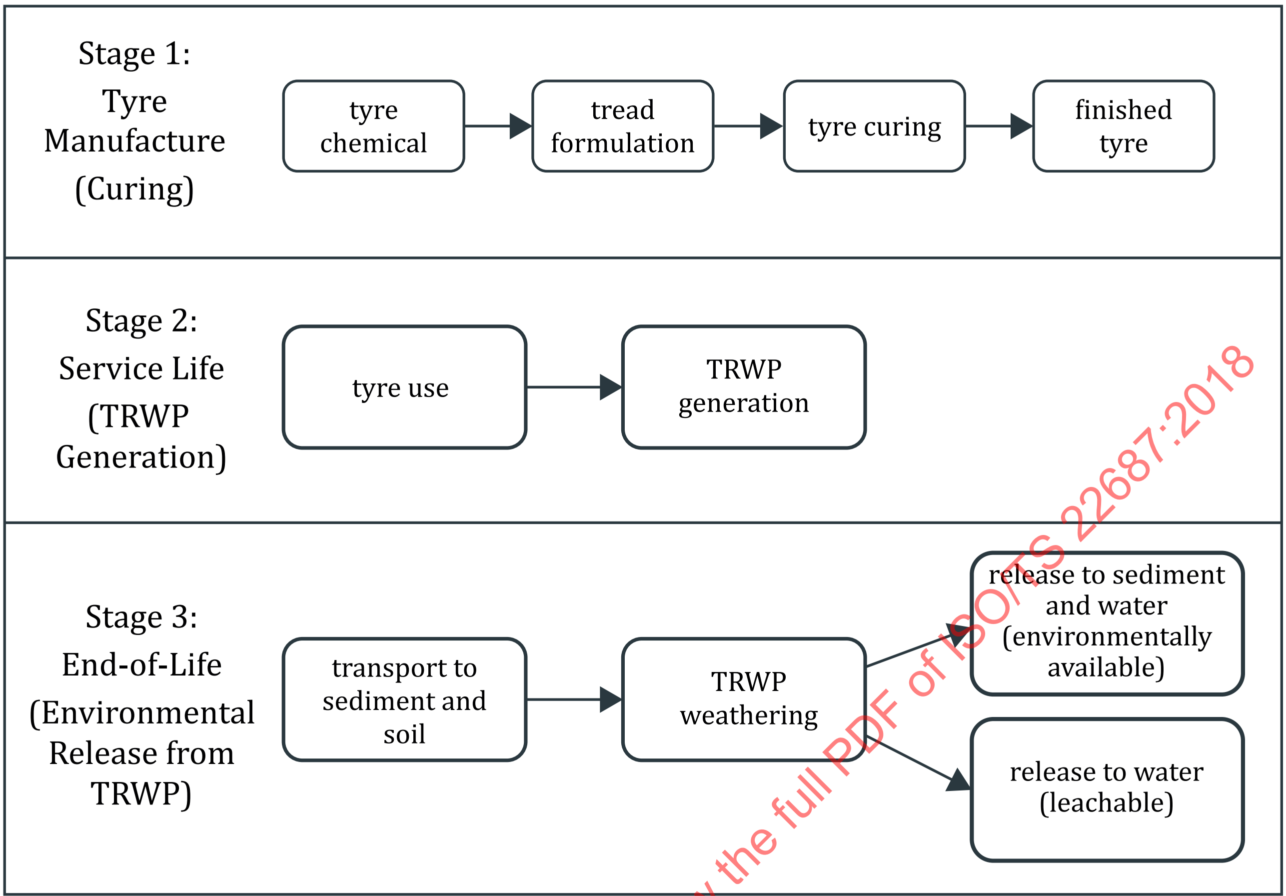


Figure 1 — Conceptual model of lifecycle of tyre tread chemicals

4.2 Tyre tread manufacture

4.2.1 General

The tyre manufacturing lifecycle stage consists of formulation of tyre polymer and chemical additives, tyre building, tyre curing, and final inspection of the finished tyre. Tyre curing is the process in which the rubber compound is moulded under elevated temperature and pressure. During curing, chemicals can be lost from the tyre tread through volatilization or they can undergo chemical transformations.

4.2.2 Chemical selection

Chemical additives of interest shall be selected for formulation into test tyre tread. The mass fraction of the selected chemicals shall be representative of marketed tyre tread formulations. The potential curing, TRWP generation, and environmental transformation products of the chemical(s) shall be determined based on chemical principles, literature, and screening mass-spectroscopy analysis. Curing transformation processes can include volatilization, chemical vulcanization reactions, as well as decomposition under elevated temperature and pressure. TRWP generation transformation processes can include mechanical stress and heat, oxidation, and volatilization. Environmental transformation processes can include hydrolysis, oxidation, and other mechanisms of decomposition. The extraction and quantification methods used for subsequent analyses shall be appropriate for the target parent chemical additive(s) and expected transformation products.

4.2.3 Tyre tread selection

The test tyre tread formulation shall be representative of those typically used in the market to provide a representative source of TRWP in accordance with ISO/TS 22638. The mass fraction of each chemical additive (M_F), and mass fraction of polymer ($W_{P,F}$) shall be recorded. The complete test tyre formulation shall be documented.

4.2.4 Tyre tread extraction

Cured tread shall be prepared for quantitative analysis using a suitable extraction method such as ISO 1407, or an equivalent method. The extraction solvent and conditions shall be appropriate for the specific chemical(s) of interest. Tyre chemicals have varying chemical and reactive properties, and may require additional analysis regarding the proper extraction conditions and/or solvents necessary for the analytical procedures to ensure adequate recovery and reliability.

A pre-determined mass of TRWP should be sieved at 150 µm and placed into a Soxhlet apparatus for extraction. The extraction can take place for 16 hours, or until extraction has been deemed complete. The extraction rate shall be calculated as the percent difference between the mass in the original sample and the mass in the dry sample following extraction.

4.2.5 Tread chemical quantification

The mass of chemical additive(s) and transformation products in cured tread (M_C) shall be determined by analysis of the sample extract prepared in accordance with 4.2.4. The mass of chemicals in the extract can be quantified using liquid chromatography coupled with high resolution tandem mass spectrometry (LC-MS/MS), or an analytical method suitable for the target chemical(s). The appropriate solvent for the standard preparation should be determined before testing. Repeatability of quantified chemical mass shall be measured as the percent relative standard deviation (RSD). Matrix, spike, and laboratory controls shall be assessed in addition to the limit of detection (LOD) and limit of quantification (LOQ). The mass fraction of polymer in cured tread ($W_{P,T}$) shall be determined using ISO/TS 22640.

4.3 Tyre tread service life

4.3.1 General

The service lifecycle stage consists of tyre use on roadways. TRWP are formed as a result of tyre wearing at the interface of the tyre and pavement. Mechanical and chemical transformations can occur during this lifecycle stage.

4.3.2 TRWP generation

TRWP shall be generated and collected using the road simulator laboratory method in accordance with ISO/TS 22638.

4.3.3 TRWP extraction and chemical quantification

The determination of the mass of target chemical(s) in TRWP (M_{TRWP}) shall be performed using the same extraction and quantification method as used for cured tread described in 4.2. The mass fraction of polymer in fresh TRWP ($W_{P,TRWP}$) shall be determined using ISO/TS 22640.

4.4 Tyre tread end-of- life

4.4.1 General

The end-of-life lifecycle stage consists of deposition of TRWP onto roadside soil and sediment ecosystems, followed by exposure to biotic and abiotic weathering processes over time. A portion of the chemical additive(s) and transformation products remaining in TRWP can leach to water. A larger fraction inclusive of the water leachable fraction is considered environmentally available based on an additional fraction representing the contribution of isopropanol extracted sediment. The isopropanol extraction represents a sediment-bound fraction that is expected to be bioaccessible to aquatic organisms.

4.4.2 TRWP weathering

The effect of abiotic weathering processes on the chemical composition of TRWP shall be determined based on an accelerated weathering protocol under laboratory controlled conditions, followed by quantification of the target chemical(s) in TRWP at the completion of the aging protocol.

4.4.3 Artificial aging test system

Accelerated aging and weathering of TRWP shall be performed in a laboratory setting. For example, ASTM D750, ASTM G151, and ASTM G154 (or equivalent methods) may be used to simulate aging and weathering of TRWP. Artificial aging and weathering of TRWP can take place in a chamber exposed to UV light with an irradiance of 0,77 W/m^2nm^{-1} at 340 nm. TRWP should be maintained at 60 °C and 45 % relative humidity. It is possible to have one or more dark periods each day during the testing, such as one eight-minute period in the morning and one seven-minute period in the afternoon.

Artificial aging shall be determined by comparing reference materials to known standards. Reference materials should also be placed in the chamber during weathering to determine the aging acceleration factor of TRWP. For example, measurements of the tensile properties of a rubber coupon in the chamber throughout the simulation can be used as a reference standard. It is also possible to measure the yellow colour change and total colour change in a high impact polystyrene reference material placed in the chamber throughout the simulation. ASTM E313, or an equivalent method, may be used to determine the yellow colour change.

4.4.3.1 Aged TRWP chemical extraction and quantification

Determination of the mass of chemical(s) in TRWP at age t ($M_{\text{TRWP,t}}$) shall be performed using the same extraction and quantification method as used for cured tread described in 4.2.

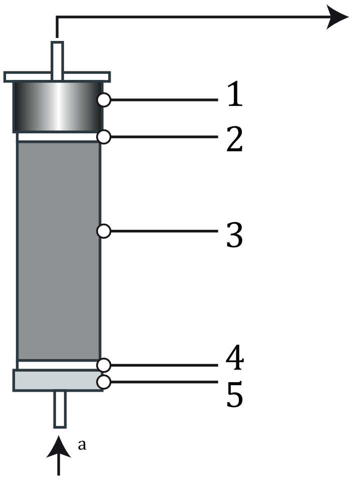
4.4.4 Release to water

4.4.4.1 General

The potential release of chemical(s) from TRWP to water shall be determined using a laboratory leaching protocol under laboratory controlled conditions, followed by quantification of the target chemical(s) in the leachant.

4.4.4.2 Column leaching test system

Up-flow column percolation tests shall be used to collect the soluble chemical(s) from fresh or aged TRWP. For example, ISO/TS 21268-3, or an equivalent method, should be used for an up-flow percolation study design. It is possible to modify the column diameter and length to accommodate the available sample size of TRWP. Glass wool and filter paper may be placed at the inlet to distribute the leachant evenly across the width of the column. Filter paper and glass beads, or an equivalent weight, shall be placed above the sample to retain the TRWP in the column during testing.



Key

1 weight
2 filter paper
3 tyre and road wear particle
4 filter paper
5 leachant dispersant
a Leachant inlet.

Figure 2 — Leaching test apparatus

A pilot study may be necessary to determine the appropriate solution to use for the column test. For example, 0,001 M calcium chloride, artificial rain at pH 4,1, or reverse osmosis water may be used as leachants. An alternative leachant(s) may be used to assess mobilization of hydrophobic substances that can be bioaccessible, but relatively insoluble in water. It is recommended that leachate samples be collected at liquid to solid ratios (L/S) of 1, 3, 5, and 10 l/kg. For example, at a flowrate of 1 ml/day, samples shall be collected following 3, 10, 15, and 30 days of testing.

4.4.4.3 Leachant chemical quantification

Determination of the mass of chemical(s) leached from TRWP at age t ($M_{L,t}$) shall be performed using an analytical method consistent with that described in 4.2. Leachate samples may be diluted with an organic solvent prior to analysis.

4.4.5 Release to sediment and water

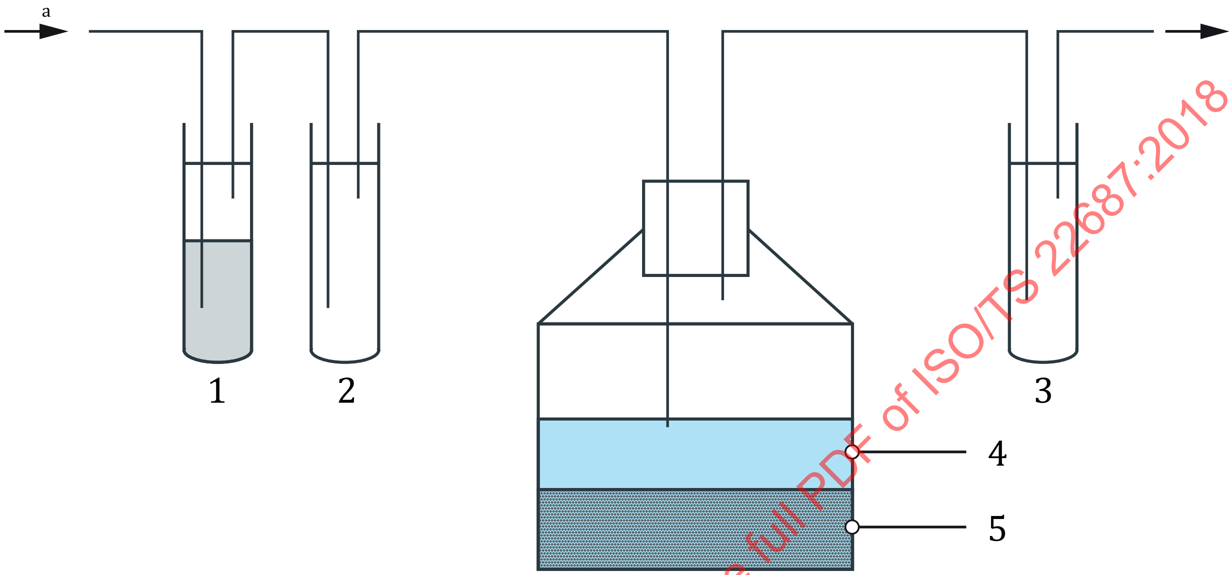
4.4.5.1 General

Tyre tread chemicals can be released from TRWP to water and sediment located in roadside ecosystems. Aerobic water-sediment incubators, such as those described in test method OECD 308, may be used to measure the chemical release from fresh or aged TRWP, as well as to characterize biotic transformations.

4.4.5.2 Sediment test system

Test sediments (with overlying and pore water) should be collected from a surface sediment location and characterized prior to TRWP addition. Sediment characteristics include organic matter content, particle size, organic carbon content, pH, cation exchange capacity, total nitrogen, total phosphorus, biomass content, and moisture content. Overlying water characteristics include temperature, pH, biochemical oxygen demand, dissolved organic carbon, total organic carbon, and total calcium, magnesium and manganese. The background TRWP concentration in the test sediment can be assessed using the method specified in ISO/TS 21396. Control (blank) incubators without added TRWP shall be used to assess background chemical composition, as well as laboratory performance.

Weighed, filtered sediment samples shall be loaded at a depth of 2,5 ± 0,5 cm in test vessels. Sterilised overlying water shall then be placed into the test vessel at a prescribed ratio to sediment and acclimate prior to the addition of TRWP (see Figure 3). Following an acclimation period, it is recommended that the overlying water temporarily be removed while a nominal mass of fresh or aged TRWP is mixed into the sediment.



Key

1 humidifier

2 empty trap 1

3 empty trap 2

4 overlying water

5 sediment and pore water

a Air inlet.

Figure 3 — Sediment test apparatus

4.4.5.3 Sample collection

Sediment and water samples for testing should be collected on multiple days throughout the test duration to assess the degradation of chemicals in TRWP. It is recommended that the test duration not exceed 100 days. Overlying water shall be transferred first to a pre-weighed container for sample collection. Pore water shall be collected from the sediment by adding 100 ml of reverse osmosis water, shaken, and then centrifuged. Sediments samples shall be extracted from the sediment in the test vessel with HPLC grade isopropanol at a known ratio of weight of sediment to volume of isopropanol, agitated, and then centrifuged.

4.4.5.4 Water and sediment chemical quantification

Determination of the mass of chemical(s) released from TRWP on day n in sediment test vessels (water, $M_{W,n}$; total sediment test vessel, $M_{A,n}$) shall be performed using an analytical method consistent with that described in 4.2. The overlying and pore water samples may be diluted with an organic solvent prior to chemical analysis. The supernatant from the sediment sample may be diluted with HPLC grade water.

4.5 Release fraction and environmental availability estimation

The fraction of tyre tread chemical additive released to water ($F_{R,t}$) or available from sediment ($F_{T,t}$) shall be estimated in accordance with the equations presented in Annex A. These fractions indicate the fraction of the chemical additive mass formulated in tread compound that will potentially be released to water, or be bioaccessible to aquatic organisms. Fractions shall be estimated for the parent chemical additive compound and transformation products.

The calculation protocol consists of several steps. First, mass concentrations shall be calculated for each lifecycle step described in 4.1, and expressed on a TRWP mass basis (μg of chemical per g of TRWP dry weight). Next, the mass concentrations shall be used to calculate dimensionless lifecycle step factors that represent the contribution of individual steps to parent chemical loss or transformation product generation. The lifecycle step factors can range from a minimum of zero to a maximum of 1. For example, the curing factor, f_C, represents the fraction of parent chemical lost or transformation product generated during the curing process in the manufacturing lifecycle stage. Finally, the cumulative contribution of the curing, TWRP generation, terrestrial weathering, leaching and environmental availability lifecycle steps shall be estimated by calculation of $F_{R,t}$ and $F_{T,t}$.

5 Test report

The test report shall include at least the following information:

a) reference to this document, i.e. ISO TS 22687:2018, and any other applicable method;

b) target chemical(s) identity and test tyre recipe/formulation;

c) methods used to identify transformation products;

d) all information necessary for characterizing the TRWP sample;

e) date and time of testing;

f) identity of analyst(s);

g) equipment and test conditions;

h) description of chemicals, standards, and reagents;

i) test results obtained and any anomalies that occurred during the tests;

j) any additional information mandated by the documents referenced in this framework.

Annex A
(informative)

Calculation of results

A.1 Mass concentrations

The cumulative release fraction calculations require the mass concentrations of chemicals for each lifecycle step expressed on a TRWP mass basis (µg of chemical per g of TRWP dry weight). Calculate the mass concentrations of chemical(s) formulated in the tyre tread compound (M_F), measured in cured tread (M_C); measured in fresh or aged TRWP at age t ($M_{TRWP,t}$), measured in column leachate of TRWP at age t ($M_{L,t}$), measured in the overlying and pore water of the sediment test vessels assayed at day n ($M_{W,n}$), and total mass measured in the water and sediment of the test vessels assayed at day n ($M_{A,n}$) using the formulas below. These equations shall be applied to detected parent compounds and transformation products.

A.1.1 Tyre formulation

$$M_F = C_F \times (W_{P,TRWP}/W_{P,F})$$

where

C_F is the chemical concentration in tyre tread recipe (µg/g);

$W_{P,TRWP}$ is the mass fraction of polymer in TRWP (g/g);

$W_{P,F}$ is the mass fraction of polymer in uncured tread (g/g).

A.1.2 Tyre curing

$$M_C = C_T \times (W_{P,TRWP}/W_{P,T})$$

where

C_T is the chemical concentration in cured tread (µg/g);

$W_{P,T}$ is the mass fraction of polymer in cured tread (g/g).

A.1.3 TRWP formation (tyre use), aging, and weathering

$$M_{TRWP,t} = C_{TRWP,t}$$

where $C_{TRWP,t,}$ is the chemical concentration in TRWP at age t (g/g).

