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Rubber — Determination of mass concentration of tire and road wear particles (TRWP) in soil and sediments — Pyrolysis-GC/MS method

Caoutchouc — Détermination de la concentration massique en particules de pneus et d'usure de la route (TWRP) dans le sol et les sédiments — Méthode par pyrolyse-GC/MS

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

Introduction

Tyre and road wear particles (TRWP) are formed as a result of tread abrasion from the road surface, and subsequent particle release to the environment. TRWP consist of tyre tread particles which include incorporated material from the road surface (Kreider et al. 2010[1]). The elastomeric fraction in TRWP contained in soil or sediment materials is quantified in this document by direct pyrolysis-GC/MS analysis. Mass concentration can be expressed on the basis of the rubber polymer, tyre tread, or TRWP. This method has been used to measure the TRWP concentration in soil and sediment samples from three geographically separated regions (Unice et al. 2012[2]; Unice et al. 2013[3]). The airborne concentration of TRWP in the PM_{10} fraction has also been characterized by a similar method (Panko et al. 2013[4]).

Specific chemical markers are generated from intact TRWP by pyrolysis of sample specimens. The chemical markers consist of characteristic and specific pyrolysis dimeric fragments of passenger and truck tyre tread polymers including butadiene rubber, styrene-butadiene rubber, and isoprene rubber. The polymer fragments generated by sample pyrolysis are subsequently separated by gas chromatography, and identified by mass spectroscopy. The TRWP mass concentration is calculated based on market average polymer use rates in tread, and prior characterization of the mineral content of TRWP. Rubber polymer specificity is achieved by quantification of dimeric polymer fragments consisting of two monomer units (Kitamura et al. 2007[5]; Harada et al. 2009[6]). Repeatability is achieved by the use of a deuterated internal standard of similar polymeric structure to the tyre tread polymers. The internal standard corrects for variable analyte recovery caused by sample size, matrix effects, and temporal variation in instrument response. The method is suitable for monitoring changes in soil or sediment TRWP concentrations over time.

Rubber — Determination of mass concentration of tire and road wear particles (TRWP) in soil and sediments — Pyrolysis-GC/MS method

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

WARNING 2 — Certain procedures specified in this document may involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document specifies a method for the determination of the soil or sediment mass concentration (µg/g) of tyre and road wear particles (TRWP) in environmental samples.

This document establishes principles for soil or sediment sample collection, the generation of pyrolysis fragments from the sample, and the quantification of the generated polymer fragments. The quantified polymer mass is used to calculate the concentration of TRWP in soil or sediment. These quantities are expressed on a TRWP basis, which includes the mass of tyre tread and mass of road wear encrustations, and can also be expressed on a tyre rubber polymer or tyre tread basis.

NOTE Tyre and road wear particles are a discrete mass of elongated particles generated at the frictional interface between the tyre and roadway surface during the service life of a tyre. The particles consist of tyre tread enriched with mineral encrustations from the roadway surface.

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 7270-1, *Rubber — Analysis by pyrolytic gas-chromatographic methods — Part 1: Identification of polymers (single polymers and polymer blends)*

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:

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

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

3.1
deuterated internal standard
compound containing at least one deuterium molecule added to a sample in a fixed amount that is nearly identical to the target analyte used to correct for instrument drift and matrix interference

3.2
dry mass
mass of solid dried in an oven for a specified time and at a specified temperature

3.3
monitoring
repeated measurement to follow changes over a period of time

3.4
percent moisture
mass of water in soil expressed as a percentage of oven dried mass

3.5
pyrolysis analysis
decomposition of organic polymeric molecules into characteristic fragments separated by gas chromatography and quantified by mass spectroscopy

4 Principle

Tyre tread polymer is quantified using internal standard calibration and the peak area of characteristic fragment ions corresponding to dimers of the raw polymer by pyrolysis-GC/MS. The thermal decomposition products of cross-linked natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR) polymers depend on the abundance of polymers in the sample. SBR pyrolysis generates butadiene, vinylcyclohexene (butadiene dimer) and styrene, whereas BR generates only butadiene monomer and vinylcyclohexene. NR is associated with isoprene monomer and dipentene (isoprene dimer). The dimer fragments have good specificity for rubber polymers, whereas both anthropogenic and natural organic substances are sources of the monomer markers (Kitamura 2007[5]). Therefore, the monomeric pyrolysis marker compounds are subject to interference from non-TRWP environmental sources, and are not suitable for quantification of TRWP mass concentration in soil or sediment. One well-known example is styrene, which is generated from pyrolysis of both SBR and diesel exhaust particles (Pierson and Brachaczek 1974[7]). The tyre polymers, and pyrolysis fragment dimers used for quantification of TRWP are shown in Figure 1.

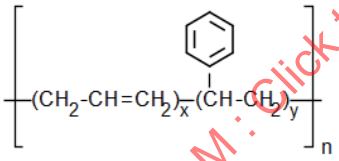
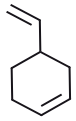
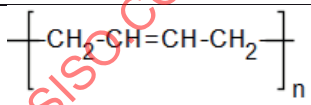
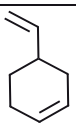
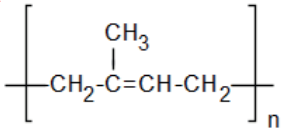
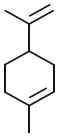
Polymer Formula	Dimer
 SBR	 vinylcyclohexene
 BR	 vinylcyclohexene
 NR	 dipentene

Figure 1 — Dimeric pyrolysis products of tyre rubber polymers

5 Reagents

Use only reagents of recognized analytical grade.

5.1 Chloroform, analytical grade.

5.2 Helium, purity 99,999 5 % by volume.

6 Apparatus

6.1 Soil or sediment sampling — Equipment and consumable supplies.

6.1.1 Sampling device.

The sampling device shall be suitable for the collection of soil or sediment samples. Suitable devices include pre-cleaned stainless steel hand trowels, coring tools or clamshell dredge devices. The collection of a sediment sample with a clamshell dredge device is illustrated in Figure 2.

NOTE Photo courtesy of Cardno ChemRisk.

Figure 2 — Collection of sample with clamshell dredge device

6.1.2 Sample containers.

Samples should be collected in clean sample containers supplied by the laboratory, or clean sample container handled in a manner consistent with laboratory standard operating procedures. The placement of a soil sample into a sample container with a trowel is illustrated in Figure 3.

NOTE Photo courtesy of Cardno ChemRisk.

Figure 3 — Placement of sample in container with trowel

6.2 Equipment for analysis.

6.2.1 Laboratory oven, for drying field collected sample(s) at a temperature of 105 °C for 24 h in a suitably clean laboratory-supplied container.

6.2.2 Sieve, for removing large aggregates unsuitable for the pyrolyser unit. The nominal opening for dry sieving can be 1 mm.

6.2.3 Precision analytical balance, for determination of sample mass as collected, after oven drying, and after dry sieving. Measurements shall be conducted in an environment of controlled temperature and humidity. The balance shall be accurate to 0,01 mg and be maintained, calibrated and certified in accordance with the manufacturer's recommendations.

6.2.4 Pyrolyser, operating at a temperature of 670 °C for 5 s in a helium atmosphere with an induction time of less than 0,2 s. A single-use or reusable sample holder shall be selected in accordance with the manufacturer's recommendation. Examples of pyrolyser systems are provided in ISO 7270-1, and include micro-furnace with quartz tube, Curie-point with holder, and platinum filament with holder. An example of one type of pyrolyser that can be used is described in Annex B.

6.2.5 Gas chromatograph/mass spectrometer, operated and maintained in accordance with the manufacturer's instructions.

6.2.5.1 Gas chromatograph, as specified below:

— carrier gas flow rate: 1,0 ml/min to 2,0 ml/min;

— injector temperature: 300 °C;

— oven temperature programme: initial temperature 50 °C for 5 min, heating at 25 °C /min up to 300 °C, maintained at 300 °C for 10 min.

6.2.5.2 Column, as specified below:

— length: 25 m to 60 m;

— diameter: 0,25 mm to 0,35 mm;

— liquid phase: 5 % diphenyl-, 95 % polydimethylsiloxane;

— film thickness: 0,20 µm to 1,0 µm.

6.2.5.3 Mass spectrometer, quadrupole mass spectrometer, magnetic-sector-type mass spectrometer or any other suitable type, having the characteristics specified below:

— interface temperature: 300 °C to 350 °C;

— ionization method: electron ionization;

— ion source temperature: 230 °C;

— ionizing voltage: 70 eV;

— scan range: mass/charge ratio: 35 m/z to 500 m/z.

7 Specimen preparation laboratory

The specimen preparation laboratories and sample containers selected for analysis shall be sufficiently free of contamination that blank analyses demonstrate an absence of polymer as established by the method detection limit (MDL). At least one laboratory blank analysis shall be performed for each type of sample container used for sample collection, and following modifications to laboratory standard operating procedures or equipment.

8 Measuring range

The range of SBR/BR polymer that can be determined in a soil or sediment sample is approximately 0,09 µg to 90 µg, and the range of NR polymer that can be determined is approximately 0,03 µg to 50 µg. Assuming a total sample mass of 0,020 g, this mass range corresponds to a TRWP concentration range in soil or sediment of approximately 24 µg/g to 28 000 µg/g.

NOTE The TRWP concentration range is based on Formula (E.2). For example, the low end of the TRWP concentration range is (0,09 µg + 0,03 µg) / 0,5 / 0,5 / 0,020 g = 24 µg/g. The first factor of 0,5 accounts for the polymer fraction in tyre tread. TRWP consists of tyre tread enriched with mineral encrustations from the roadway surface. The second factor of 0,5 accounts for the fraction of tyre tread in TRWP.

9 Limit of detection

The TRWP limit of detection depends on mass of sample pyrolysed. In practice, sampling constraints and the capacity of the pyrolysis unit determine the lowest achievable limit of detection. For a nominal sample mass of 0,020 g, the limit of detection is approximately 24 µg/g TRWP in soil or sediment.

An alternative limit of detection can be achieved by changing the calibration curve range and mass of internal standard used in the analysis. Alternative limits of detection based on adjustment of the calibration curve range and internal standard masses shall be verified by a method detection limit study.

The target TRWP detection limit shall be determined as part of the sampling plan prior to sample collection. The sample plan shall specify field and laboratory conditions sufficient to ensure that the target detection limit satisfies the sample campaign goals and objectives. A sample-specific detection limit shall be calculated based on the conditions of the analysis. The detection limit calculations are specified in 11.1.

10 Procedure

10.1 General

The method is defined for a sample mass of oven-dried soil or sediment suitable for the pyrolyser unit. Thermal energy is applied to a sample encapsulated in a pyrolyser in the absence of oxygen to decompose the sample. Secondary reactions are minimized by rapid heating of the pyrolyser to the target temperature. The nominal sample mass for the example pyrolysis unit described in Annex B is 0,020 g. The sample collection and laboratory pyrolysis-GC/MS procedure consists of the following six steps and is described in 10.2 to 10.6 respectively:

a) sample collection;

b) deuterated internal standard preparation;

c) calibration curve preparation;

d) sample preparation;

e) sample pyrolysis with polymer decomposition under defined thermal conditions;

f) dimer measurement using gas-chromatographic (GC) separation and mass spectroscopy (MS).

The procedure relies on deuterated homopolymer internal standards to increase the precision and accuracy of the measured TRWP concentration. The internal standard is used to correct for matrix effects that affect polymer pyrolysis and fragment recovery. The internal standard also corrects for changes in the mass spectrometer ion source condition and fluctuations in carrier gas flow rates. The internal standards are deuterated polyisoprene (d-PI) and deuterated polybutadiene (d-PB), which are polymers labelled with the minor stable hydrogen isotope deuterium. The pyrolysis-GC/MS thermal decomposition products of d-PI and d-PB are discriminated based on retention time and mass to charge ratio from the dipentene and vinylcyclohexene markers associated with NR and SBR/BR, respectively.

10.2 Sample collection

A soil or sediment sample is collected in clean laboratory supplied or approved sample containers. The sample shall be collected using a clean device suitable for the collection of soil or sediment samples, such as stainless steel hand trowels, coring tools or clamshell dredge devices. The standard operating procedure for sample collection shall be approved by the laboratory. A chain-of-custody form documenting sample collection and relinquishment shall be maintained. A soil or sediment mass of at least 10 g to 50 g should be collected to ensure adequate homogenization.

10.3 Deuterated internal standard preparation

Deuterated standards d-PI (1,4-d8) and d-PB (1,4-d6) of known purity shall be obtained prior to analysis (see Table 1). The purity of the standards shall be sufficiently high to prevent interference for TRWP sample concentrations at or above the detection limit or reporting limit of the analysis.

A recipe for stock internal standard solution preparation that should be used is specified in Annex A. Alternative recipes may be used to meet the objectives of the analysis. To prepare the stock solutions, raw d-PI or d-PB polymer is weighed and placed in a graduated flask. Chloroform shall be poured to two-thirds of the total volume specified in the recipe, and allowed to settle overnight to achieve complete dissolution. Immediately prior to analysis, chloroform shall be added to achieve the total volume specified in the recipe. The raw polymers should be dissolved in chloroform prior to the day of analysis to ensure sufficient time for dissolution. The stability of the internal standard solutions shall be determined by comparing the instrument response after expected storage times to that of a freshly prepared solution. The peak area should decrease by no more than 25 % to that of the freshly prepared solution at expected storage times.

Table 1 — Pyrolysis-GC/MS polymers, markers and internal standards

Attribute	Tyre polymer	
	NR	SBR, BR
Pyrolysis marker	Dipentene	Vinylcyclohexene
Pyrolysis marker retention time[a] (min)	9,7	7,7
Target m/z of marker	68	54
Diagnostic m/z of marker	136	108
Internal standard	d-PI (1,4-d8)	d-PB (1,4-d6)
Target m/z of internal standard	76	60
Calibration polymer	IR	SBR1500
Calibration points[b] (µg)	1; 5; 10; 25; 50	1; 10; 25; 50; 100

[a] Retention times are approximate, and can vary from the values presented.

[b] Alternative calibration points can be used to meet the objectives of the analysis.

10.4 Calibration curve preparation

10.4.1 Stock solutions

Stock chloroform solutions of raw polymers, including synthetic IR and SBR, shall be prepared for the calibration curves. A recipe for stock internal standard solution preparation that should be used is specified in Annex A. Alternative recipes can be used to meet the objectives of the analysis. To prepare the stock solutions, raw IR or SBR polymer is weighed and placed in a graduated flask. Chloroform is poured to two-thirds of the total volume specified in the recipe, and allowed to settle overnight to achieve complete dissolution. Immediately prior to analysis, chloroform is added to achieve the total volume specified in the recipe. The chloroform solution is added to the sample holder by micropipette and evaporated to dryness at room temperature for 30 min. The stability of the internal standard solutions shall be determined by comparing the instrument response after expected storage times to that of a freshly prepared solution. The peak area should decrease by no more than 25 % to that of the freshly prepared solution at expected storage times.

10.4.2 Calibration curves

An internal standard calibration shall be prepared by least squares regression with quadratic fit according to the instrument conditions described in 6.2. Synthetic isoprene rubber (IR) and SBR1500 rubber are used as a surrogate in the calibration curve preparation for NR and SBR/BR tread rubber, respectively. The mass of polymer analysed for the calibration samples should be 1 µg to 50 µg for IR and 1 µg to 100 µg for SBR1500 (see Table 1). Alternative calibration points may be used to meet the objectives of the analysis. The lower limit of calibration shall be equal to the limit of quantification (LOQ) for the method. The instrument signal to noise ratio (S/N) shall be equal to three at the limit of detection (LOD) and greater than or equal to five at the LOQ.

The internal standard calibration curves are generated by plotting the peak area response ratio as a function of the amount ratio using a quadratic regression. The response ratio is the ratio of the integrated peak area of the molecular marker to the integrated peak area of the internal standard. The amount ratio is the ratio of the mass of the calibration standard to the added mass of the internal standard.

The acceptance criteria for the calibration curves is a coefficient of determination (R^2) greater than or equal to 0,99. Instrument software should be used to quantify peak areas of the deuterated internal standards and molecular marker compounds. Peak areas shall be individually inspected for quality control. Stock solutions shall be replaced no more than six months after initial preparation. Calibration curve standards shall be monitored by comparison to the initial calibration. The acceptance criteria for

calibration curves shall be a percent drift of less than 20 % before and after each analysis series, using Formula (1):

$$d = (M_c - M_t) / M_t \times 100 \quad (1)$$

where

d is drift (%);

M_c is the measured mass of continuing calibration verification standard based on the calibration solution recipe;

M_t is the theoretical mass of continuing calibration verification standard as measured by the instrument.

Fresh calibration curve standards shall be prepared prior to each new analysis sequence or if drift exceeds 20 %.

Sample calibration curves and pyrograms are provided in Annex C.

10.5 Sample preparation

Samples shall be prepared for pyrolysis analysis in an environment free of polymer contamination. Samples shall not be prepared for analysis until acceptable blank analyses have been completed.

10.5.1 Oven drying

The soil or sediment sample shall be placed in a suitable container and dried in a laboratory oven for 24 h at 105 °C. The sample wet mass, dry mass and percent moisture of the sample shall be recorded, and the percent mass determined as shown in Formula (2).

$$m = \frac{M_{ww} - M_{dw}}{M_{dw}} \times 100 \quad (2)$$

where

m is percent moisture (%);

M_{ww} is wet mass (wet mass) of sample (g);

M_{dw} is dry mass (dry mass) of sample (g).

10.5.2 Sieving and homogenization

After drying, the sample should be sieved to remove large aggregates unsuitable for the pyrolyser. The nominal opening for dry sieving can be 1 mm. The sample passing the sieve should be homogenized by a suitable method such as mortar and pestle.

10.6 Sample measurement

10.6.1 Sample mass

Approximately 0,020 g or a suitable mass of the dry-sieved sample shall be selected for pyrolysis analysis, and placed in a sample holder for analysis in the pyrolysis unit. The analysed mass shall be appropriate for the pyrolyser and GC column split ratio.

10.6.2 Internal standard addition

The internal standards d-PB and d-PI shall be added to the sample in the same mass amounts as used in the calibration curve preparation. The mass addition is 76 µg of d-PB and 10 µg d-PI in chloroform solution for the typical calibration points shown in Annex A. The chloroform solution is added to the sample by micropipette and evaporated to dryness at room temperature for 30 min.

10.6.3 Pyrolysis-gas chromatograph/mass spectrometer measurement

The sample holder shall be placed in the pyrolyser for thermal decomposition analysis. The pyrolysis equipment and instrument conditions are described in 6.2.4. Equipment maintenance shall be performed in accordance with the manufacturer's instructions. A record of analysis and equipment maintenance shall be maintained in a permanent log.

The following tyre polymer and internal standard deuterated polymer thermal decomposition fragments generated by the pyrolyser shall be quantified by GC/MS:

a) dipentene (IpD) from NR;

b) vinylcyclohexene (BdD) from SBR and BR;

c) deuterated isoprene dimer (d-IpD) from d-PI;

d) deuterated butadiene dimer (d-BdD) from d-PB.

The GC/MS equipment and instrument conditions are described in 6.2.5. Equipment maintenance and equipment tuning shall be performed in accordance with the manufacturer's instructions. A record of analysis and equipment maintenance shall be maintained in a permanent log. The GC/MS equipment shall be well maintained to ensure reliable results and the calibration curve shall be verified before and after each analysis series. The mass to charge ratio for the thermal decomposition products is specified in Table 1.

11 Analysis

The mass and concentration of TRWP in soil or sediment is determined by using the GC/MS pyrograms of the dimer fragments, dipentene and vinylcyclohexene. The sample analysis consists of the following three calculations described in 11.1 to 11.3, Annex D and Annex E:

a) TRWP detection limit;

b) quantity of tyre polymer in the sample;

c) mass concentration of TRWP in the sample.

11.1 TRWP detection limit

The polymer detection limit (µg/sample) shall be estimated based on the instrument S/N ratio and method detection limit studies as specified in 10.4.2 and 12.3. The polymer detection limit shall be used to calculate the minimum detectable TRWP mass concentration in soil or sediment in units of µg/g. The formula for the calculation of target and sample TRWP detection limits is specified in Annex D.

11.2 Quantity of tyre polymer in the sample

The mass of polymer in the sample referenced to the SBR1500 or IR polymer standards should be calculated by instrument software using the calibration curve and the ratio of instrument response for the target compound to that of internal standards spiked into the sample. Peak areas shall be individually inspected for quality control.

The mass of tyre polymer in the sample is initially expressed as SBR1500 and IR based on the use of these polymers in the preparation of the calibration curve. The mass expressed as SBR1500 is converted

to a tyre polymer basis as SBR/BR using the market share average styrene content in tread SBR/BR, as compared to the styrene content in SBR1500. The mass expressed as IR polymer mass is taken to represent NR mass from tyre polymer. The formula and parameter values for calculating the amount of SBR/BR tyre polymer in the sample (µg) from the instrument determined polymer mass expressed as IR and SBR1500 is provided in E.2.

11.3 Mass concentration of TRWP

To express the result on the basis of TRWP, the polymer mass quantified by GC/MS is adjusted to account for the

a) market share ratio of SBR to BR,

b) mineral encrustation composition of TRWP, and

c) dry mass of the sample analysed.

The TRWP concentration in soil or sediment shall be expressed in units of mass concentration (µg/g) calculated using the formula and parameter values shown in E.3.

12 Performance characteristics

12.1 General

The instruments used in this procedure shall be operated in accordance with the manufacturer's instructions. The analytical method shall be performed under a continuous quality control programme. The quality control programme should employ the use of standard samples and blank samples.

12.2 Specific performance characteristics

A midpoint calibration curve check shall be analysed before and after each analysis series to verify recovery within 80 % to 120 % of the known polymer spike amount.

The target spike recovery range for matrix spike analyses is 80 % to 120 %.

Corrective action when recovery is outside the specified range includes instrument maintenance, and preparation of fresh calibration curves shall be implemented if the percent drift exceeds 20 %.

12.3 Method detection limit

An MDL for SBR1500 and IR of 0,1 µg and 0,03 µg, respectively has been established for conditions described in this protocol. As described in Clause 9, the detection limit for TRWP concentration depends on the sample mass.

An alternate MDL for the rubber polymers may be established by performing a method detection limit study. The instrument S/N ratio shall be equal to three at the LOD and greater than or equal to five at the LOQ.

13 Test report

The test report shall include at least the following information:

a) reference to this document;

b) identification of the client;

c) identification of the sample;

d) date and time of sampling, and necessary sampling data;

e) identity of the analyst;

f) any procedure not specified in this document, or regarded as optional;

g) equipment and experimental conditions including GC/MS and pyrolyser conditions;

h) description of stock calibration solutions;

i) description of stock internal standard solutions;

j) description of the IR calibration points;

k) description of the SBR calibration points;

l) description of the TRWP concentration calculation protocol;

m) summary of the oven drying procedure including pre- and post-mass, drying time, and drying temperature;

n) summary of the sieving procedure including sample mass before and after sieving, and nominal sieve opening;

o) test results for the concentration of TRWP in soil or sediment in units of mass concentration (µg/g);

p) mass of polymers detected in blanks and other quality control data;

q) supporting data including calibration curves and sample analysis GC/MS chromatograms.

Annex A
(informative)

Recipe for calibration curves and stock solutions

The following recipes should be used for preparation of stock calibration solutions and calibration curves.

A.1 Stock calibration solutions

The recipe given in Table A.1 should be used for the stock calibration solutions prepared in 100 ml of chloroform.

Table A.1 — Stock calibration solutions

Stock calibration solution	Mass of polymer per 100 ml of chloroform mg	
	IR	SBR
A-1	10	—
A-2	100	—
B-1	—	10
B-2	—	1 000

A.2 Stock internal standard solutions

The recipe given in Table A.2 should be used for the stock internal standard solutions prepared in 10 ml of chloroform.

Table A.2 — Stock internal standard solutions

Stock internal standard solution	Volume of chloroform (ml)	Mass of polymer (mg)
d-PI	10	10
d-PB	10	76

A.3 Calibration points for IR and SBR

The recipe given in Table A.3 and Table A.4 should be used for the stock internal standard solutions prepared in 10 ml or 100 ml of chloroform.

Table A.3 — Calibration points for IR

Calibration point	IR stock solutions	IR volume added to sample holder µL	d-PI volume added to sample holder µL	Mass of IR µg	Mass of d-PI µg
IR-1	A-1	10	10	1	10
IR-2	A-1	50	10	5	10
IR-3	A-2	10	10	10	10
IR-4	A-2	25	10	25	10
IR-5	A-2	50	10	50	10

Table A.4 — Calibration points for SBR

Calibration point	SBR stock solutions	SBR volume added to sample holder µL	d-PB volume added to sample holder µL	Mass of SBR µg	Mass of d-PB µg
SBR-1	B-1	10	10	1	76
SBR-2	B-2	1	10	10	76
SBR-3	B-2	2,5	10	25	76
SBR-4	B-2	5	10	50	76
SBR-5	B-2	10	10	100	76

Annex B
(informative)

Curie-point pyrolyser

B.1 General

The following conditions are representative of conditions for a Curie-point pyrolyser. Other types of pyrolysers meeting the pyrolysis conditions specified in 6.2.4 are also suitable for the analysis.

A Curie-point ferromagnetic pyrofoil is a metal alloy foil used to encapsulate the solid sample. The pyrofoil consists of an alloy that rapidly reaches a repeatable target temperature by loss of magnetic properties upon induction heating.

B.2 Sample preparation

Pyrofoils 9 mm in width with an induction heating temperature of 670 °C shall be prepared for sample addition with a foil crimper. Approximately 0,020 g of dry-sieved (< 1 mm) and homogenized sediment or soil shall be added to each pyrofoil. The internal standards d-PB and d-PI in chloroform shall be added to the sample in the same mass amounts as used in the calibration curve. The chloroform solution is added to the pyro foil by micropipette and evaporated to dryness at room temperature for 30 min. The foil shall be closed using a hand press.

B.3 Instrument conditions

B.3.1 Curie-point pyrolyser, operating at pyrolysis conditions as specified in 6.2.4. The consumable pyrofoil shall be selected in accordance with the manufacturer's recommendation. Pyrofoils 9 mm in width shall be folded with an appropriately sized foil crimper.

B.3.2 Gas chromatograph/mass spectrometer, as specified in 6.2.5.

B.4 Procedure

The specimens are placed in a Curie-point ferromagnetic pyrofoil. After placement, the pyrofoil is folded closed by a crimper and placed in the pyrolysis unit for analysis. Rubber polymer in the soil or sediment samples is thermally decomposed at 670 °C with an induction heating time of less than 0,2 s as specified in 6.2.4.

B.5 Precision

A method detection limit study for the Curie-point pyrolyser with BR or IR polymer spiked into a reference matrix of clean silica sand indicated acceptable recoveries of 106 % for the butadiene dimer marker and 83 % for the isoprene dimer marker with relative standard deviations of 7 % and 13 % for BR and IR, respectively (Unice et al. 2012[2]). Triplicate analysis of reference sediments used in ecotoxicity testing in the United States and United Kingdom indicated relative standard deviations of 10 % or less when TRWP was detected (Unice et al. 2013[3]). An analysis of field duplicate grab samples of surface sediment collected from two different locations in the United States collected within a distance of 1 m indicated relative standard deviations of less than 20 % (Unice et al. 2012[2]).

Annex C
(informative)

Representative calibration curves and pyrograms

Representative calibration curves and pyrograms for soil or sediment analyses are given below for the IR and SBR1500 calibration standards.

C.1 General

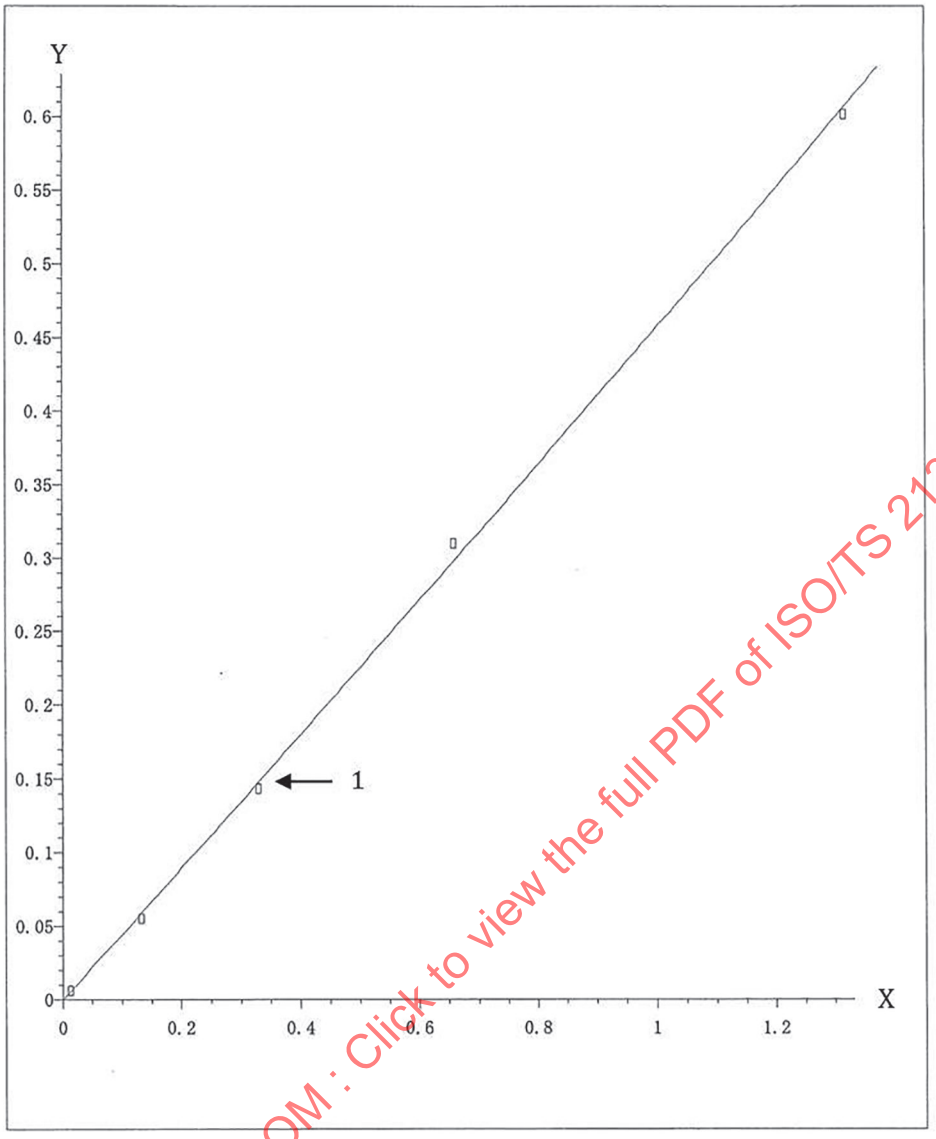
This annex presents representative pyrograms and calibration curves for the SBR1500 and IR calibration standards with d-PI and d-PB as the internal standard. The pyrograms are presented for the midpoint of the calibration curve prepared as specified in Table A.3 (IR-3) and Table A.4 (SBR-3). The mass of calibration standard was 10 µg for IR and 25 µg for SBR1500. The mass of deuterated internal standard added to the calibration standard was 10 µg p-PI and 76 µg p-PB.

C.2 Isoprene rubber

A typical calibration curve for IR (Table A.3) is given in Figure C.1. The pyrogram for the midpoint calibration standard marker (IR-3; IpD) is given in Figure C.2 a), and the pyrogram for the associated internal standard marker (IR-3; d-IpD) is given in Figure C.2 b). The amount ratio for IR-3 is (10 µg IR) / (10 µg p-PI) = 1,0. The response ratio for IR-3 is (13 518 598 IpD peak area) / (12 853 840 d-IpD peak area) = 1,05.

C.3 Styrene-butadiene rubber

A typical calibration curve for SBR1500 (Table A.4) is given in Figure C.3. The pyrogram for the midpoint calibration standard marker (SBR-3; BdD) is given in Figure C.4 a), and the pyrogram for the associated internal standard marker (SBR-3; d-BdD) given in Figure C.4 b). The amount ratio for SBR-3 is (25 µg SBR1500) / (76 µg d-PB) = 0,33. The response ratio for SBR-3 is (4 370 322 BdD peak area) / (30 460 498 d-BdD peak area) = 0,14.



Key

X amount ratio (A)

Y response ratio

1 calibration curve midpoint (IR-3)

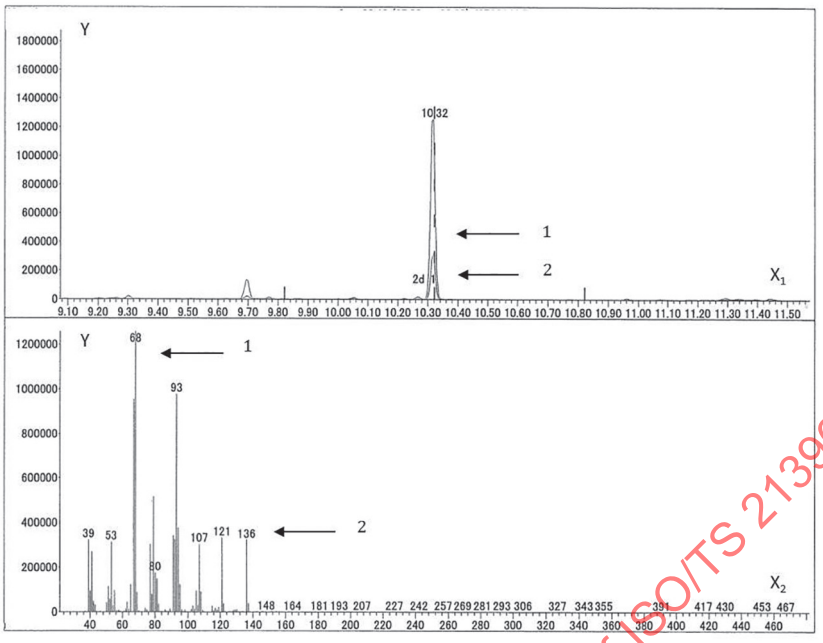
Regression formula response ratio, R, and coefficient of determination, r^2, are given as:

$$R = -0{,}015\,8\,A^2 + 1{,}14\,A - 0{,}024\,6$$

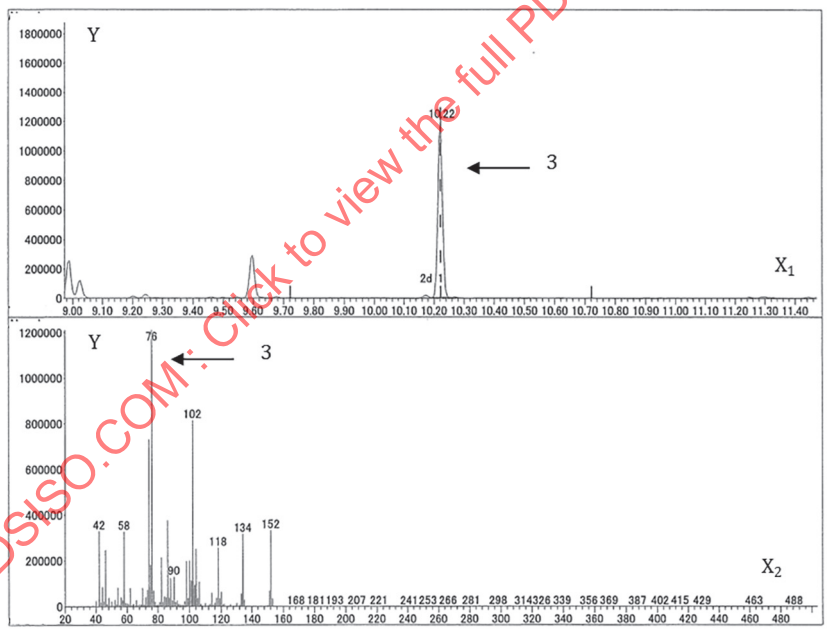
$$r^2 = -0{,}998$$

Curve fit: Quadratic w(1/a)

Figure C.1 — Example calibration curve for IR



a) IpD peak from IR calibration standard



b) d-IpD peak from d-PI internal standard

Key

X_1 time (minutes)

X_2 mass to charge ratio (m/z)

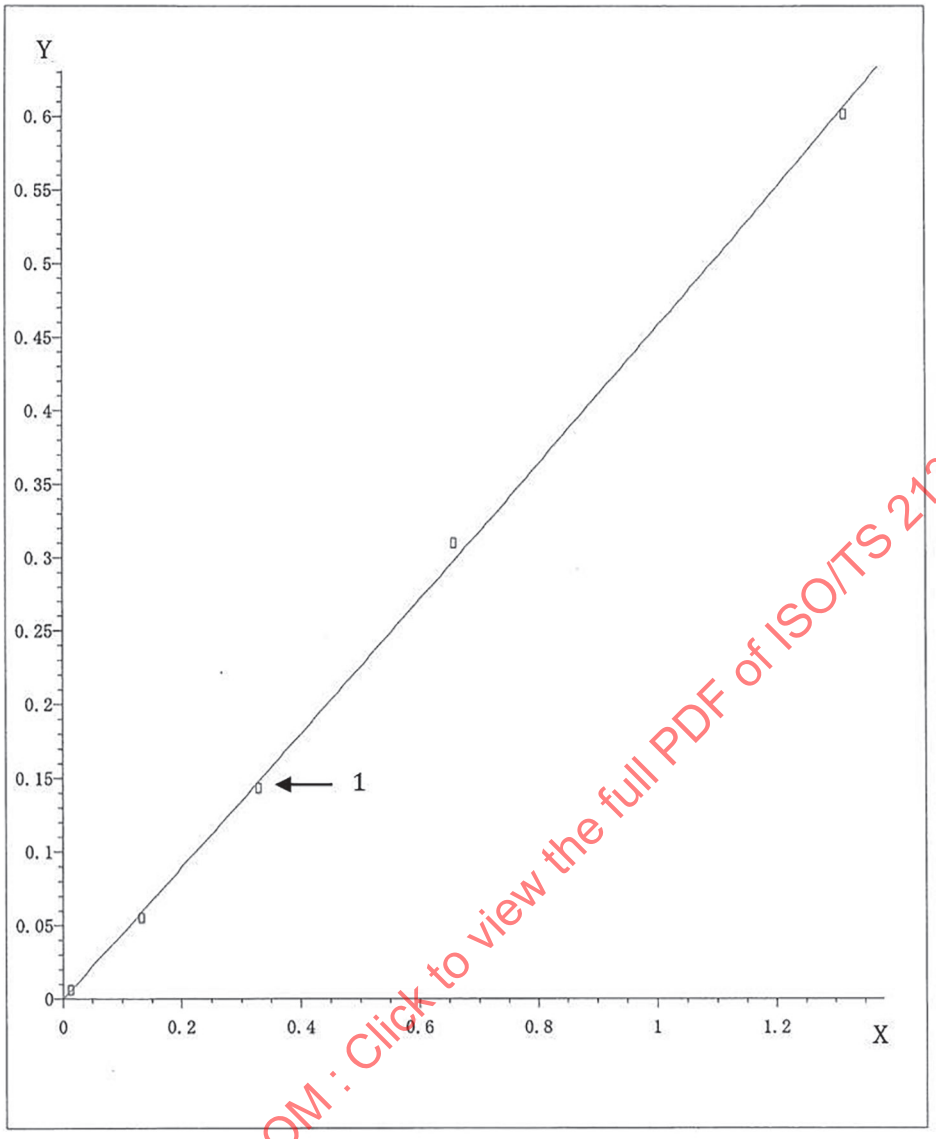
Y abundance (intensity)

1 primary IpD fragment (peak area response = 13 518 598; nominal m/z 68,1)

2 secondary IpD fragment (nominal m/z 136)

3 primary d-IpD fragment (peak area response = 12 853 840; nominal m/z 76,1)

Figure C.2 — Pyrograms and mass spectra for IR calibration curve midpoint (IR-3)



Key

X amount ratio (A)

Y response ratio

1 calibration curve midpoint (SBR-3)

Regression formula response ratio, R, and coefficient of determination, r^2, are given as:

$$R = -0,0123\,A^2 + 0,444\,A + 0,000\,019\,5$$

$$r^2 = 0,999$$

Curve fit: Quadratic w(1/a)

Figure C.3 — Example calibration curve for SBR1500