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Ambient air — Determination of the mass concentration of tire and road wear particles (TRWP) — Pyrolysis-GC-MS method

Air ambiant — Détermination de la concentration en masse de particules provenant de l'usure des pneumatiques et des chaussées (TRWP) — Méthode par pyrolyse-CG/SM

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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 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

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.[3] The elastomeric fraction in TRWP contained in $PM_{2,5}$ or PM_{10} is quantified in this document by direct pyrolysis-GC-MS analysis of a sample filter. Mass can be expressed on the basis of the rubber polymer, tyre tread, or TRWP. This method has been used to measure the airborne concentration of TRWP in the PM_{10} fraction for three geographically separated regions.[4] The TRWP concentration in soil and sediment has also been characterized by a similar method.[5]

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.[6][7] 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 ambient air TRWP concentrations over a specified averaging time.

Ambient air — Determination of the mass concentration of tire and road wear particles (TRWP) — 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 and to ensure compliance with any national regulatory conditions.

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 airborne concentration (µg/m^3), mass concentration (µg/g) and mass fraction (%) of tyre and road wear particles (TRWP) in ambient particulate matter (PM) samples.

This document establishes principles for air 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 fraction of tyre tread in PM and concentration of tyre tread in air. 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.

Air sample collection is on quartz fibre filters with size-selective input in a range of $PM_{2,5}$ or PM_{10}. The method is suitable for the determination of TRWP in indoor or outdoor atmospheres.

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 4225, *Air quality — General aspects — Vocabulary*

ISO 7708:1995, *Air quality — Particle size fraction definitions for health-related sampling*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4225 and the following 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 http://www.iso.org/obp

3.1
ambient air
outdoor air to which people, plants, animals, or material may be exposed

3.2
averaging time
interval of time over which the air quality has been expressed as an average

3.3
continuous sampling
sampling, without interruptions, throughout an operation or for a predetermined time

3.4
deuterated compound
compound containing at least one *deuterium* (3.5) molecule

3.5
deuterium
minor and stable isotope of hydrogen with one proton and one neutron

3.6
internal standard
compound 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

3.7
measurement period
interval of time between first and last measurement

3.8
monitoring
repeated measurement to follow changes over a period of time

3.9
natural background concentration
concentration of a given species in a pristine air mass in which anthropogenic emissions are negligible

3.10
particle aerodynamic diameter
diameter of a sphere of density 1 g/cm^3 with the same terminal velocity due to gravitational force in calm air as the particle, under the prevailing conditions of temperature, pressure, and relative humidity

3.11
particle
small discrete mass of solid or liquid matter

3.12
particulate matter — 2,5 µm
$PM_{2,5}$
airborne *particles* (3.11) passing a size selective inlet with 50 % efficiency cut-off at a *particle aerodynamic diameter* (3.10) of 2,5 µm

Note 1 to entry: See Thoracic Convention in ISO 7708:1995, Clause 6.

3.13
particulate matter — 10 µm
PM_{10}
airborne *particles* (3.11) passing a size selective inlet with 50 % efficiency cut-off at an aerodynamic diameter of 10 µm

Note 1 to entry: See High-Risk Respirable Convention in ISO 7708:1995, Clause 7.

3.14
pyrolysis analysis
decomposition of organic polymeric molecules into characteristic fragments separated by gas chromatography and quantified by mass spectroscopy

Note 1 to entry: The principle of sample decomposition is the application of thermal energy to a sample encapsulated in a pyrolyser in the absence of oxygen. Secondary reactions are minimized by rapid heating of the pyrolyser to the target temperature.

3.15
sampling time
interval of time over which a single sample is taken

3.16
tyre and road wear particles
TRWP
discrete mass of elongated *particles* (3.11) generated at the frictional interface between the tread of the tyre and the roadway 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.

3.17
thoracic convention
mass fraction of inhaled *particles* (3.11) which penetrate beyond the larynx

3.18
respirable convention
target specification for sampling instruments when the respirable fraction is of interest

4 Symbols and abbreviated terms

4.1 Symbols of units (see also ISO 4226)

µg	microgram (10^{-6} gram)
cm	centimeter (10^{-2} meter)
m^3	cubic meter
cm^2	square centimeter
$µg/m^3$	microgram per cubic meter

4.2 Abbreviated terms

BdD	vinylcyclohexene (butadiene dimer)
d-BdD	deuterated butadiene dimer
d-IpD	deuterated isoprene dimer
d-PI	deuterated polyisoprene
d-PB	deuterated polybutadiene
BR	butadiene rubber
GC-MS	gas chromatograph/mass spectrometer

IpD	dipentene (isoprene dimer)
IR	isoprene rubber
LOD	limit of detection
LOQ	limit of quantification
PM	particulate matter
$PM_{2,5}$	airborne particles with an aerodynamic diameter less than 2,5 µm
PM_{10}	airborne particles with an aerodynamic diameter less than 10 µm
NR	natural rubber
SBR	styrene-butadiene rubber
TRWP	tyre and road wear particles

5 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. 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.[6] Therefore, the monomeric pyrolysis marker compounds are subject to interference from non-TRWP environmental sources and are not suitable for quantification of TRWP mass or fraction in air. One well-known example is styrene, which is generated from pyrolysis of both SBR and diesel exhaust particles.[8] The tyre polymers and pyrolysis fragment dimers used for quantification of TRWP are shown in Figure 1.

The procedure relies on deuterated homopolymer internal standards to increase the precision and accuracy of the measured TRWP concentration. An internal standard is a chemical compound that is nearly identical to the target analyte, but with sufficient differences in mass or functional groups to be discriminated from the target analyte by the analytical method. The internal standard is used to correct for matrix effects that affect polymer pyrolysis and fragment recovery. This correction is made by comparing the instrument response for the internal standard of known amount to the instrument response for the target analytes. 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 (m/z) from the dipentene and vinylcyclohexene markers associated with NR and SBR/BR, respectively.

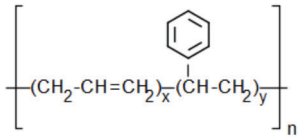
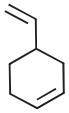
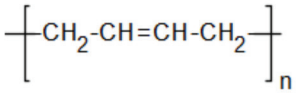
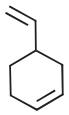
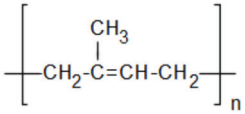
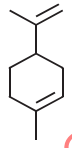
Polymer Formula	Dimer
 SBR	 Vinylcyclohexene
 BR	 Vinylcyclohexene
 NR	 dipentene

Figure 1 — Dimeric pyrolysis products of tyre rubber polymers

6 Reagents

During the analysis, use only reagents of recognized analytical grade.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

6.1 Chloroform, analytical grade.

6.2 Helium, purity 99,999 5 %.

7 Apparatus

7.1 Air sampling — Equipment and consumable supplies

7.1.1 Quartz fibre filter.

A 47-mm quartz fibre filter consisting of woven filaments is required for compatibility with the pyrolysis-GC-MS method. The filter should be suitable for $PM_{2,5}$ or PM_{10} measurement by forming an appropriate seal with the sampling device. The filters shall lie flat in the sampling device remaining intact during handling. The filter selected shall be compatible with the ambient air particulate sampling device. Quartz fibre filters are brittle and shall be handled with care for accurate mass measurement. Preparation of the filter is not required, but the absence of contamination should be verified by at least one blank filter analysis in accordance with 7.2.

7.1.2 Ambient air particulate sampling device.

The ambient air particulate sampling device shall be designed in a manner consistent with an identified national or international guideline or reference method for the collection of PM samples.

7.2 Specimen preparation laboratories

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

7.2.1 Gravimetric PM determination laboratory.

Samples shall be prepared for gravimetric PM determination in an environment free of polymer and particulate contamination. Samples shall not be prepared for analysis until acceptable blank filter analyses have been completed. The laboratory shall condition the quartz fibre filters in accordance with the national or international reference method identified in the collection of the $PM_{2,5}$ or PM_{10} sample.

7.2.2 Pyrolysis analysis laboratory.

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

7.3 Equipment for analysis

7.3.1 General

Prior to pyrolysis analysis, the total mass of PM collected on the filter is determined gravimetrically. After determination of PM mass, the destructive pyrolysis analysis is completed using an integrated system consisting of a pyrolyser interfaced to a gas chromatograph/mass spectrometer (GC-MS).

7.3.2 Precision analytical balance, for determination of total mass collected on the quartz filter and operated in accordance with the national or international reference method identified in the collection of the $PM_{2,5}$ or PM_{10} sample. Measurements shall be conducted in an environment of controlled temperature and humidity. The balance shall be maintained, calibrated and certified in accordance with the manufacturer's recommendations.

7.3.3 Pyrolyser, operated 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.

7.3.4 Gas chromatograph/mass spectrometer, operated and maintained in accordance with the manufacturer's instructions, with a split ratio suitable for the sample density, and pyrolysis-GC interface and transfer line temperature maintained at 300 °C. A DB-5MS equivalent ultra inert column (30 m × 0,25 mm i.d., 1 µm film thickness) shall be used to separate the pyrolysis products. The initial GC temperature shall be 50 °C for 5 min followed by heating to 300 °C at a rate of 25 °C min^{-1}. The MS shall be operated in scan mode with m/z range of 35 to 500 and tuned using perfluorotributylamine at m/z = 69, 212, and 502 prior to each analysis sequence in accordance with the manufacturer's instructions.

7.4 Consumables

7.4.1 Pyrolyser sample holders, selected in accordance with the pyrolyser manufacturer's instructions and operated at a target temperature of 670 °C with a tolerance of ±0,1 °C. An example of one type of sample holder that can be used is described in Annex B.

8 Measuring range

The nominal surface area of the 47-mm quartz filter is 11,94 cm^2, of which a fraction of approximately 3,98 cm^2 is analysed to allow for multiple destructive pyrolysis measurements from the sample. The range of SBR/BR polymer that can be determined for a filter specimen area of 3,98 cm^2 is approximately 0,1 µg to 25 µg, and the range of NR polymer that can be determined on the filter is approximately 0,03 µg to 12 µg. Assuming a total volume of air of 24 m^3, this mass range corresponds to a TRWP concentration range in ambient air of approximately 0,06 µg/m^3 to 13 µg/m^3. Assuming a total $PM_{2,5}$ or PM_{10} concentration of 20 µg/m^3, the measurement range of mass fraction of TRWP to PM ranges from 0,3 % to 50 %.

9 Limit of detection

The TRWP limit of detection (LOD) depends on the volume of air drawn through the filter, as well as the fraction of the total filter pyrolysed. In practice, sampling constraints and the capacity of the pyrolysis unit determine the lowest achievable LOD. For nominal conditions of 24 m^3 air, area of filter analysis of 3,98 cm^3, and a total $PM_{2,5}$ or PM_{10} concentration of 20 µg/m^3, the LOD is approximately 0,06 µg/m^3 TRWP in air. For the same nominal conditions, the minimum detectable mass fraction of TRWP to $PM_{2,5}$ or PM_{10} is 0,3 %.

The LOD can be lowered by analysing an increasing fraction of the total sample filter, or by drawing a greater volume of air through the filter. The analysis of an increased filter surface area may require the use of sequential pyrolysis with cryogenic cold trapping prior to GC-MS analysis. A LOD of 0,02 µg/m^3 or lower, and minimum mass fraction of TRWP to $PM_{2,5}$ or PM_{10} of 0,1 % or lower may be achievable by analysis of the total filter. The lower LOD, however, requires destruction of the entire filter in pyrolysis, eliminating the possibility of repeat or future analysis of the sample.

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 11.3.

10 Procedure

10.1 General

The method is defined for 47-mm or similar quartz fibre filters suitable for $PM_{2,5}$ or PM_{10} determination through which a known volume of air is drawn. The sample collection and laboratory pyrolysis-GC-MS procedure consists of the following six steps described in 10.2 to 10.7:

a) sample collection with quartz filter;

b) deuterated compound internal standard preparation;

c) calibration curve preparation;

d) sample preparation;

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

f) dimer measurement using GC separation and MS.

10.2 Sample collection

The ambient air particulate sampling shall be performed in a manner consistent with an identified national or international guideline or reference method for the collection of $PM_{2,5}$ or PM_{10} samples. The selected sample collection reference method or guideline shall be valid for determination of $PM_{2,5}$

or PM_{10} in accordance with the definition of thoracic convention and high-risk respirable convention, respectively, as defined in ISO 7708. Examples of suitable methods for $PM_{2,5}$ and PM_{10} measurement include United States Environmental Protection Agency 40 CFR Part 50, Appendices J[9] and L,[10] as well as the European Committee for Standardization (CEN) European Standard EN 12341.[11]

An airborne particulate sample is collected from ambient air on a 47-mm quartz fibre filter. The selected guideline or reference procedure shall consist of the collection of a measured air volume by continuous sampling over a specified time and measurement period. A quartz filter is specified because it is thermally stable and does not interfere with the detection of rubber pyrolysis fragments generated by pyrolysis. The quartz filter is selected and conditioned in accordance with the identified reference method for at least 48 h at known temperature and humidity for reliable determination of total PM_{10} and $PM_{2,5}$.

The quartz fibre filters shall be handled with care to prevent disruption of the sample media prior to pyrolysis analysis.

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-third 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 solution shall be determined.

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; 2; 4; 8; 12	1; 2; 5; 10; 25

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

[b] Alternative calibration points may 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 isoprene rubber (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 may 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 solution shall be determined.

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 7.3. Synthetic IR is used as a surrogate in the calibration curve preparation. SBR1500 rubber is used as a surrogate for SBR/BR tread rubber. The mass of polymer analysed for the calibration samples should be 1 µg to 12 µg for IR and 1 µg to 25 µg for SBR1500 (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 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 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 theoretical mass of continuing calibration verification standard;

m_t is the measured mass of continuing calibration verification standard.

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

10.5.1 Filter conditioning

The quartz filter shall be conditioned in accordance with the identified reference method for total $PM_{2,5}$ and PM_{10} prior to post-measurement of weight by precision analytical balance. No additional pre-treatment of the sample filters is required.

10.5.2 Total $PM_{2,5}$ and PM_{10}

Total $PM_{2,5}$ or PM_{10} mass quantities shall be determined according to the identified reference method. The following quantities shall be recorded:

a) identity of $PM_{2,5}$ or PM_{10} reference method;

b) reference method conditions;

c) sample air volume from field report (m^3);

d) filter pre-weight (g);

e) filter post-weight (g);

f) PM mass (mg).

10.5.3 Filter preparation

After determination of total particulate matter at the selected cut point, the quartz air filter sub-sample is prepared by cutting out specimens from the filter. The fraction of the filter prepared for analysis shall be appropriate for the pyrolyser and GC column split ratio. The specimens are placed in a sample holder for analysis in the pyrolysis unit.

10.5.4 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 7,6 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 Sample pyrolysis

The sample holder shall be placed in the pyrolyser for thermal decomposition analysis. The pyrolysis equipment and instrument conditions are described in 7.3.3. 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.

10.7 Sample measurement

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 7.3.4. 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

11.1 General

The mass and concentration of TRWP in PM is determined by using the GC-MS pyrograms of the dimer fragments, IpD and BdD. The sample analysis consists of the following five calculations described in 11.2 to 11.6, Annex D, and Annex E:

a) total $PM_{2,5}$ or PM_{10} concentration;

b) TRWP detection limit;

c) quantity of tyre polymer in the sample;

d) air concentration of TRWP;

e) mass fraction of TRWP in the sample.

11.2 Total $PM_{2,5}$ or PM_{10} concentration

The total $PM_{2,5}$ or PM_{10} concentration in air in units of $\mu g/m^3$ shall be calculated using the sample air volume (m^3) and PM mass (mg) according to the selected reference method.

11.3 TRWP detection limit

The polymer detection limit (µg/filter) 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 concentration in units of $\mu g/m^3$, and the minimum detectable mass fraction of TRWP in PM (%) or mass concentration of TRWP in PM (µg/g). Calculation of the mass fraction or mass concentration of TRWP in PM requires the calculated average $PM_{2,5}$ or PM_{10} concentration specified in 11.2. The formulae for the calculation of target and sample TRWP detection limits are specified in Annex D.

11.4 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 collected on the sample filter 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.

11.5 Air 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) fraction of the filter analysed.

The TRWP concentration in the ambient air $PM_{2,5}$ or PM_{10} fraction shall be calculated in units of $\mu g/m^3$ using the formula and parameter values shown in E.3.

11.6 Mass concentration of TRWP

The mass of TRWP in $PM_{2,5}$ and PM_{10} shall be expressed as mass fraction (%) and mass concentration (µg/g) using Formula (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 of 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

A method detection limit 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 volume of air drawn through the filter, and the detection limit for the mass fraction of TRWP to $PM_{2,5}$ also depends on the airborne concentration of PM.

An alternate method detection limit 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) a reference to this document, i.e. ISO/TS 20593;

b) identification of client;

c) identification of the sample;

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

e) identity of 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 TRWP concentration calculation protocol;

m) summary of gravimetric test results for $PM_{2,5}$ or PM_{10} analysis including sample ID, pre- and post-filter weight, total mass of $PM_{2,5}$ or PM_{10} on the filter, sample air volume, and $PM_{2,5}$ or PM_{10} concentration;

n) test results for concentration of TRWP in $PM_{2,5}$ or PM_{10} in units of air concentration (μg/m^3), mass concentration (μg/g), and/or mass fraction (%);

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

p) supporting data including calibration curves and sample analysis GC-MS chromatograms. The test report may contain the following optional supplemental information:

   1) test results for concentration of elastomer in $PM_{2,5}$ or PM_{10} in units of air concentration (μg/m^3), mass concentration (μg/g), and/or mass fraction (%);

   2) test results for concentration of tyre tread in $PM_{2,5}$ or PM_{10} in units of air concentration (μg/m^3), mass concentration (μg/g), and/or mass fraction (%).

Annex A
(informative)

Recipe for calibration curves and stock solutions

A.1 General

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

A.2 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	—	100

A.3 Stock internal standard solutions

The recipe given in Table A.2 should be used for the stock internal standard solutions prepared in 10 or 100 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	100	76

A.4 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 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	20	10	2	10
IR-3	A-2	4	10	4	10
IR-4	A-2	8	10	8	10
IR-5	A-2	12	10	12	10

Table A.4 — Calibration points for SBR

Calibration point	SBR stock solutions	SBR volume added to sample holder µg	d-PB volume added to sample holder µg	Mass of SBR µg	Mass of d-PB µg
SBR-1	B-1	10	10	1	7,6
SBR-2	B-2	2	10	2	7,6
SBR-3	B-2	5	10	5	7,6
SBR-4	B-2	10	10	10	7,6
SBR-5	B-2	25	10	25	7,6

Annex B
(informative)

Curie-point pyrolyser

B.1 General

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

The following conditions are representative of conditions for a Curie-point pyrolyser. Other types of pyrolysers meeting the pyrolysis conditions specified in 7.3.3 are also suitable for the analysis.

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. Three approximately 1,327 cm^2 quartz air filter specimens 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 pyrofoil 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 7.3.3. 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 7.3.4.

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 particulate samples is thermally decomposed at 670 °C with an induction heating time of less than 0,2 s as specified in 7.3.3.

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.[5]

Annex C
(informative)

Representative calibration curves and pyrograms

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 4 µg for IR and 5 µg for SBR1500. The mass of deuterated internal standard added to the calibration standard was 10 µg p-PI and 7,6 µg p-PB.

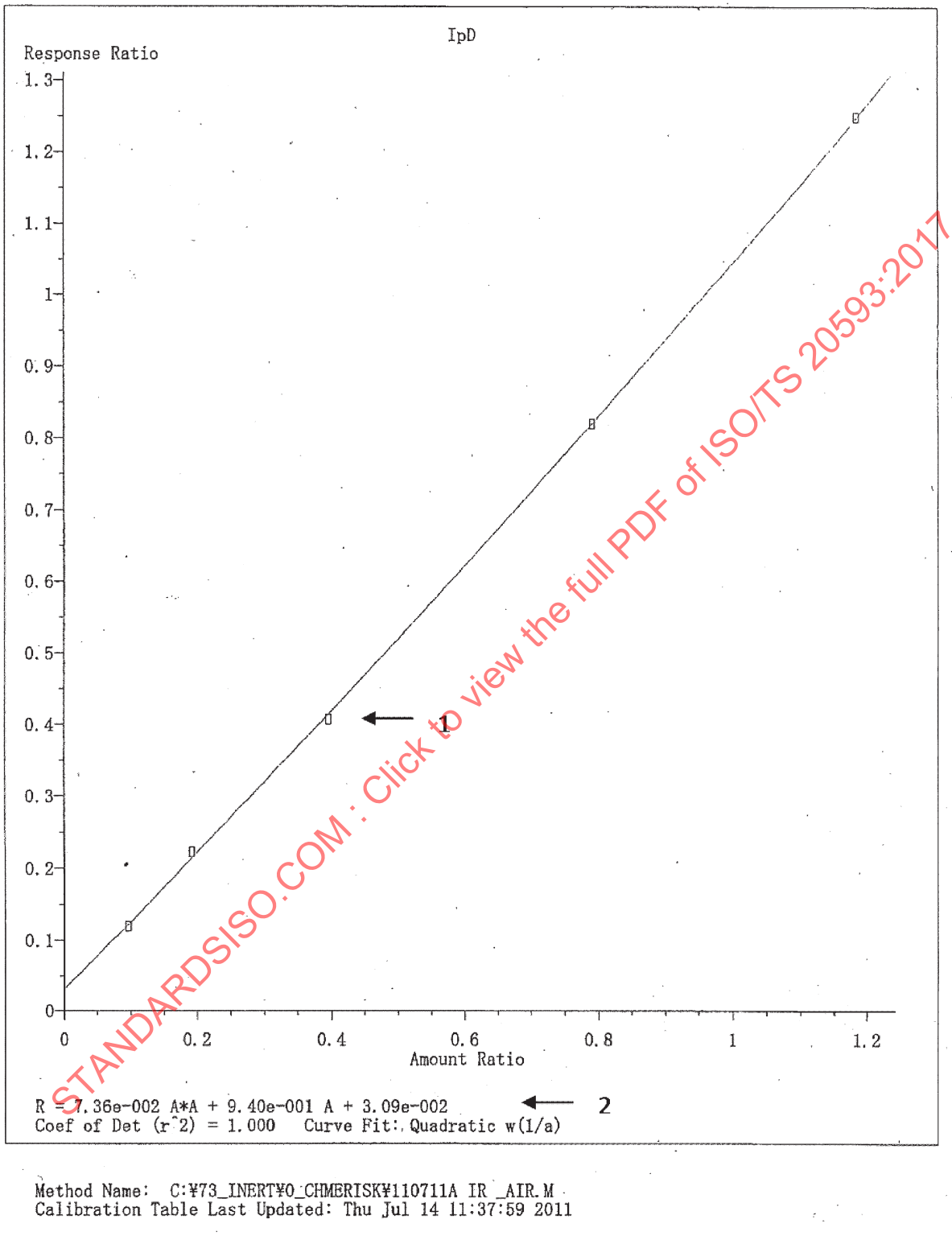
Representative calibration curves and pyrograms for air analyses are given below for the IR and SBR1500 calibration standards.

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 (4,0 µg IR)/(10 µg p-PI) = 0,40. The response ratio for IR-3 is (3 982 904 IpD peak area)/(9 768 503 d-IpD peak area) = 0,41.

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 (5 µg SBR1500)/(7,6 µg d-PB) = 0,66. The response ratio for SBR-3 is (662 500 BdD peak area) / (2 592 297 d-BdD peak area) = 0,26.



Key

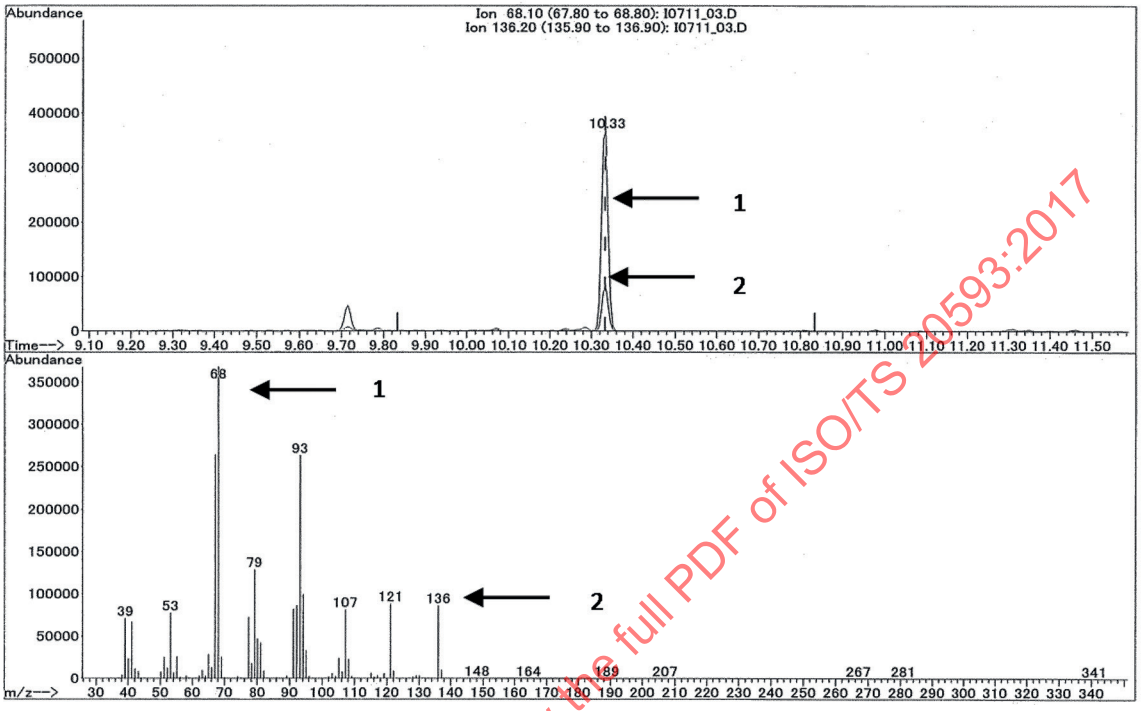
1 calibration curve midpoint (IR-3)

2 regression formula and coefficient of determination

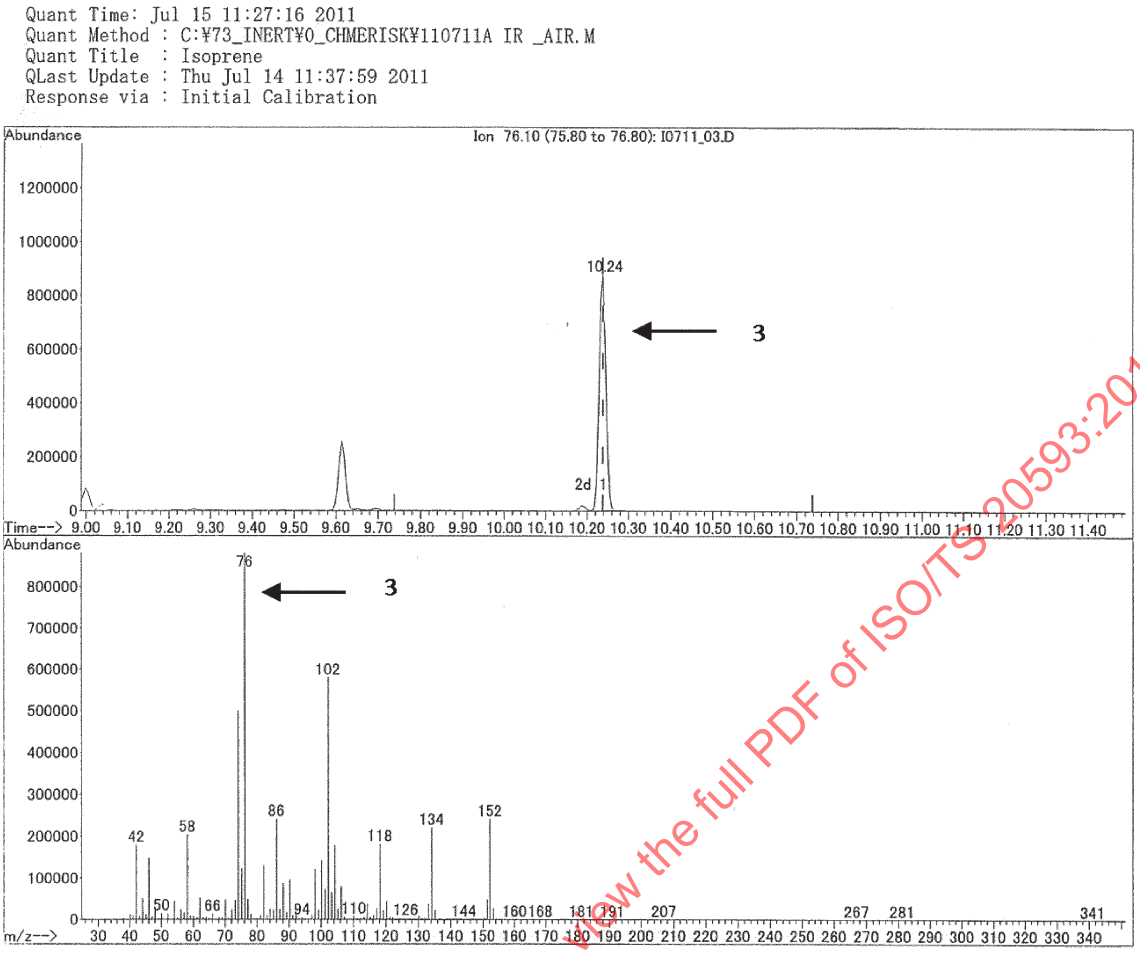
Figure C.1 — Example calibration curve for IR

Sample : STD-3
Misc :
ALS Vial : 1 Sample Multiplier: 1

Quant Time: Jul 15 11:27:16 2011
Quant Method : C:¥73_INERT¥0_CHMERISK¥110711A IR _AIR.M
Quant Title : Isoprene
QLast Update : Thu Jul 14 11:37:59 2011
Response via : Initial Calibration



a) IpD peak from IR calibration standard



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

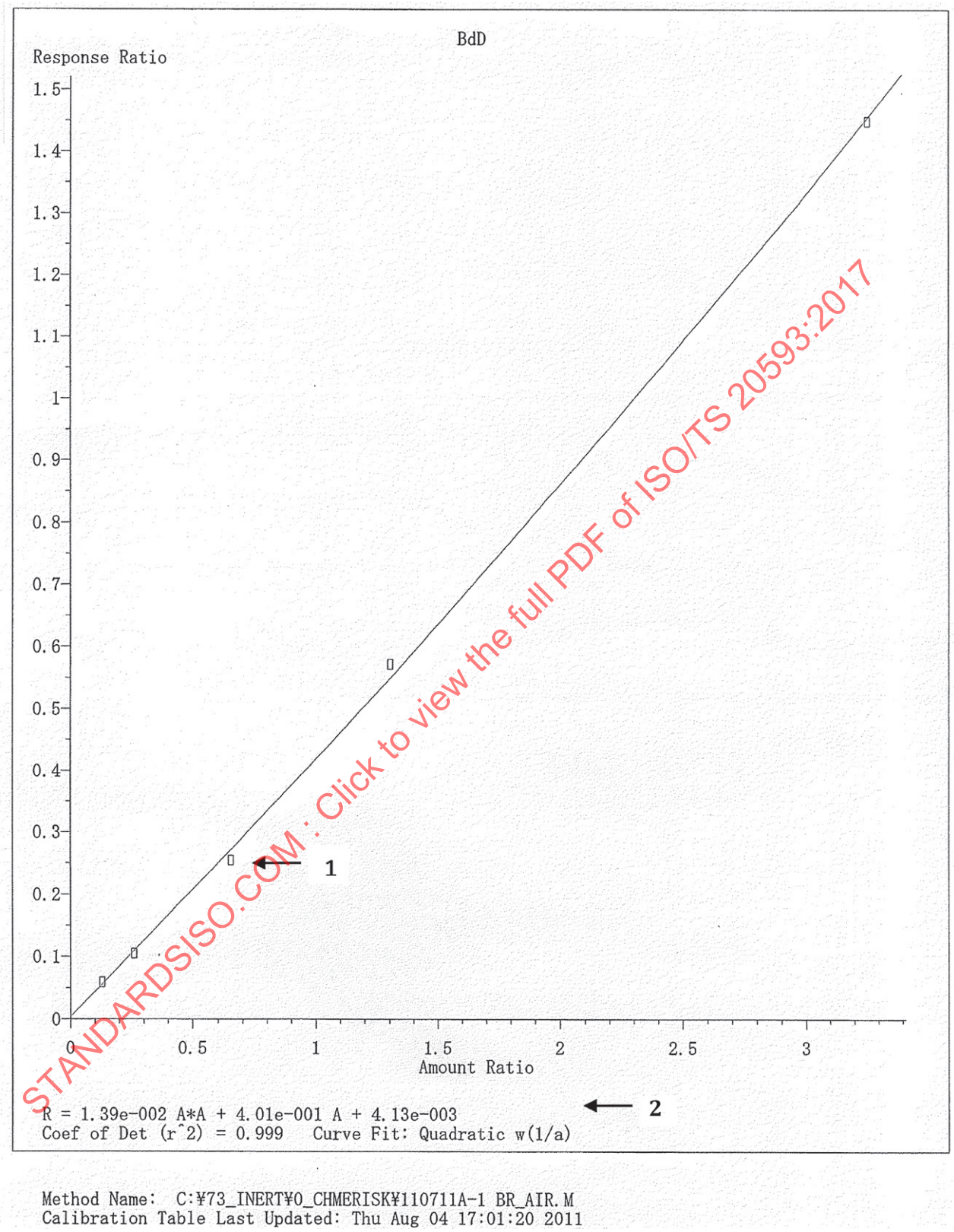
Key

1 primary IpD fragment (peak area response = 3 982 904; nominal m/z = 68,1)

2 secondary IpD fragment (nominal m/z = 136)

3 primary d-IpD fragment (peak area response = 9 768 503; nominal m/z = 76,1)

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

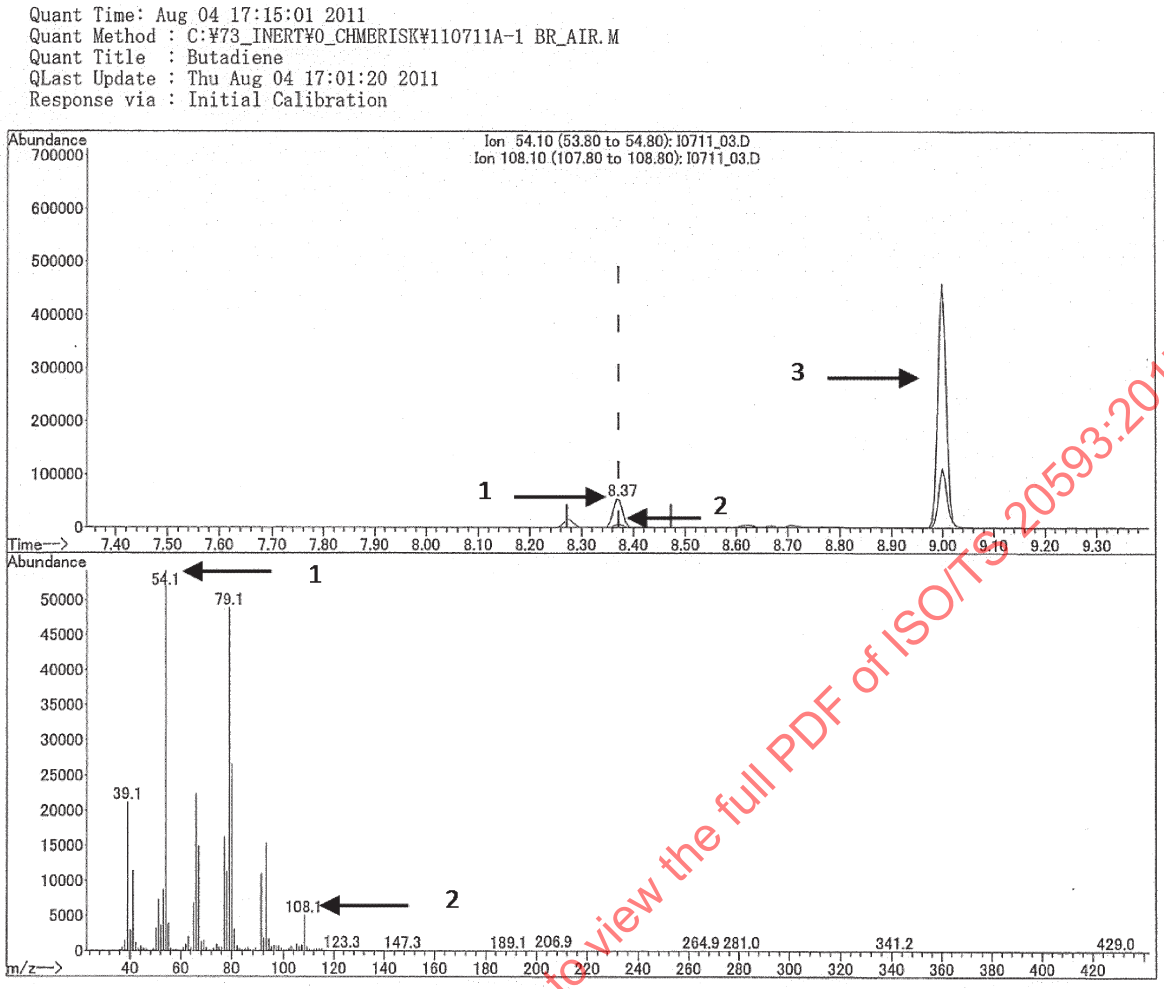


Key

1 calibration curve midpoint (SBR-3)

2 regression formula and coefficient of determination

Figure C.3 — Example calibration curve for SBR1500



a) BdD peak from SBR1500 calibration standard