KBBPPS
Knowledge Based Bio-based Products Pre-Standardization

Work package 3
Bio-based carbon content

Deliverable N^o 3.1:
Overview of current relevant sampling and biogenic carbon standards on global level

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List with abbreviations

AFS	American Foundry Society
AMS	Accelerated Mass Spectrometry
API MPMS	American Petroleum Industry – Manual of Petroleum Measurement Standards
AS	Australian Standard
ASTM	American Society for Testing and Materials
BI	Beta Ionization measurement
CEN	European committee for standardization (Comité Européen de Normalisation)
CRM	Common-Source Reference Materials
EPA	Environmental Protection Agency
GB	Guobiao, Chinese for national standard
GM	Geiger-Müller
IRM	Industry Reference Materials
IRMS	Isotope Ratio Mass Spectrometry
IS	Indian Standard
ISO	International Organization for Standardization
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
LSC	Liquid Scintillation Counting
MIL-HDBK	Military Handbook
MS	Manual Sorting method
NIST	National Institute of Standards and Technology
pMC	percentage Modern Carbon
RVP	Reid Vapour Pressure
SDM	Selective Dissolution Method
SRF	Solid Recovered Fuel
SRM	Standard Reference Materials
TAPPI	Technical Association of the Pulp and Paper Industry
TC	Total Carbon
TGA	Thermo Gravimetric Analysis
TR	Technical Report
TS	Technical Specification
VOC	Volatile Organic Compounds

1 Publishable summary

In this report all relevant standards on a global level are reviewed with respect to the biogenic carbon content determination. In general it is an overview of all standards that can be used when determining the biogenic carbon content and will give directions when no relevant standards are available.

This review is focussed in all standards concerning the sampling, pre-treatment and ^{14}C determination of all product types, which includes solids, liquids, gasses and mixtures of these. Due to the fact that all three steps in the process of biogenic carbon determination are equally important, all the three steps are covered in separate chapters.

Sampling with respect to biogenic carbon determination

The main purpose of sample preparation is that a sample is reduced to one or more test portions that are in general smaller than the original sample. The main principle for sample reduction is that the composition of the sample as taken on site shall not be changed during each stage of the sample preparation. Each sub sample shall be representative of the original sample. To reach this goal every particle in the sample before sample division shall have an equal probability of being included in the sub-sample following sample division.
Both ISO 13833 and ASTM D7459 give some sampling guides and cover determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide using radiocarbon sampling and analysis.

Solid:	In most cases solids introduce no practical difficulties in obtaining a representative sample. However, practical difficulties can occur when sampling materials containing volatile components.
Liquid:	When sampling, all liquids should be either single phase or relatively homogeneous. The homogeneity in many cases can be achieved by stirring or centrifuging of a sample. In case of viscous liquids or materials with volatile components the transfer problems exaggerate weighing problems.
Solid / liquid:	When a liquid containing a sediment fraction is sampled, homogenization by stirring can be done. Another approach is to separate the clear liquid and the sediment by centrifuging and then to examine them separately.
Gas:	Only stirring of the gas should be used when a mixture of gasses with different mass is sampled. When stirring is not possible, special care should be taken in obtaining a representative sample.

Generally, independently of solid, liquid or gaseous state of a material or product to sample, attention should be paid to representativeness of a sample, its required minimal size, its homogeneity and pre-treatment procedure.

Pre-treatment with respect to biogenic carbon determination

Generally, to release all carbon, material needs to be completely combusted, irrespectively of solid, liquid, or gaseous state of material. After the combustion procedure, all available carbon is collected as CO_2 in a suitable absorber: the CO_2 present in a representative stack gas sample is absorbed in an alkaline medium or transferred to a gas bag or lecture bottle. After sampling, the collected CO_2 is prepared for ^{14}C analysis.

In this report a list of the standards that can be used for sample preparation procedures for different samples depending of their state is presented. Due to the large amount of different pre-treatments, care should be taken with regard to the procedure.

For solid sample preparation procedures especially the complete combustion of the material, so that all (also non-organic carbon) is transformed to CO_2 is essential.
For liquid sample preparation procedures especially the presence of volatile liquid components is cause for concern.
For gaseous sample preparation procedures care should be taken by the combustion of some gasses, due to the large amount of energy produced. Also care should be taken by combusting mixtures to be sure that a good homogeneous sample is combusted.

Irrespectively of solid, liquid, or gaseous state of materials or products, the American ASTM D6866 standard can be applied if there is no other standardized pre-treatment procedure for a specific material or product.

^{14}C determination with respect to biogenic carbon determination

For the biogenic carbon determination of Solid Recovered Fuels (or other waste), there are three methods known for the determination of the bio-based content:
a) selective dissolution method (SDM)
b) manual sorting method (MS).
c) biogenic carbon (^{14}C) determination method.

Within the ^{14}C determination method, three techniques are distinguished:
1) AMS - accelerator mass spectrometry
2) LSC - liquid scintillation counting
3) BI - beta-ionization technique

These three techniques are considered to be equivalent. Each of these techniques requires different amount of the CO_2: for AMS measurements the minimum amount of CO_2 is 4 ml, for BI measurements 2 – 10 litre CO_2 is required, and for LSC measurements the required amount of CO_2 depends on the way the sample is prepared for measurement, but at least a few gram will be required.

While the selective dissolution and the manual sorting methods allow us only the distinguishing between organic and inorganic content of materials or products, the ^{14}C methods allow discrimination between ^{14}C and ^{12}C isotopes and therefor more accurate determination of the biogenic content.

To summarize, the ^{14}C isotope method is applied in a variety of samples to determine the ratio of biogenic and fossil carbon. Biogenic and fossil carbon can be distinguished based on the measured amount of the ^{14}C isotope in the sample.

Complete combustion is carried out in a way to comply with the requirements of the subsequent measurement of the ^{14}C content and shall provide the quantitative recovery of all carbon present in the sample as CO_2 in order to yield valid results. The calculation of the bio-based carbon content includes the following steps:

- determination of the total carbon content of the sample expressed as a percentage of the total mass or the determination of the total organic carbon content of the sample expressed as a percentage of the total mass;
- calculation of the bio-based carbon content by mass using the ^{14}C content value, determined by calculation from one of the test methods mentioned in ASTM D6866.
- calculation of the bio-based carbon content as a fraction of the total carbon content or as a fraction of the total organic carbon content.

2 Introduction

In this report all relevant standards on a global level are reviewed with respect to the biogenic carbon content determination. In general it is an overview of all standards that can be used when determining the biogenic carbon content and will give directions when no relevant standards are available.

The biogenic carbon determination of all materials is scrutinized. This include not only solid, liquid and gaseous materials, but also mixtures of these. For a reliable biogenic carbon determination it is necessary that all three steps in the process are performed soundly. These steps are:

- sampling of the material,
- treatment of the material and
- ^{14}C determination.

The sampling of the material is essential to obtain a sample that is representative for the batch it has been taken from. The sampling from homogeneous material is relative simple, whereas the sampling from heterogeneous material sometimes can cause large difficulties. Especially volatile liquids, gaseous material incorporated in solid material or the combination of liquid and solid can give sampling problems. For each product the right sampling technique should be used and in Chapter 3 all available standards are presented.

The treatment of material with regard to the biogenic carbon determination is only aiming at getting all the carbon out of the sample and into a desired, most often CO_2, form. In general the complete combustion of the sample should be done, but care should be taken to the presence of non-organic carbon, which is often much more difficult to combust. For this non-organic carbon, like minerals, pure carbon and ceramics, special additions of catalysts are necessary and/or higher temperatures and pressures.

Finally the determination of the ^{14}C content is much more standardized. When a sample contains CO_2 or pure carbon, the ^{14}C determination is a completely standardized process. With the use of the data of the ^{14}C present to date in the atmosphere and the percentage ^{14}C in the sample, the biogenic carbon content is known.

It should be realized that the biogenic carbon content is related to the amount of biogenic carbon and fossil carbon in the product. It is not related to the biogenic content, because only the carbon is taken into account and no other biogenic elements like hydrogen and oxygen. Also the biogenic carbon content is not related to the total mass of the product. The biogenic carbon content of a painted metal structure is only related to the biogenic carbon content of the paint and has no connection with the total mass of the metal structure, which contains no carbon.

In order to ensure transparent communication, specifications and labelling systems need to be developed. Standardized test methods form the cornerstone for specifications, which encompass well-defined pass criteria with regard to different characteristics (e.g. biodegradation, environmental safety, bio-based (carbon) content, performance, etc.). These criteria are chosen in function of the objective of the specification. The specifications are designed to form the basic principle for labelling systems (Figure 1). Currently, specifications, acceptance criteria and labelling systems are already clearly defined.

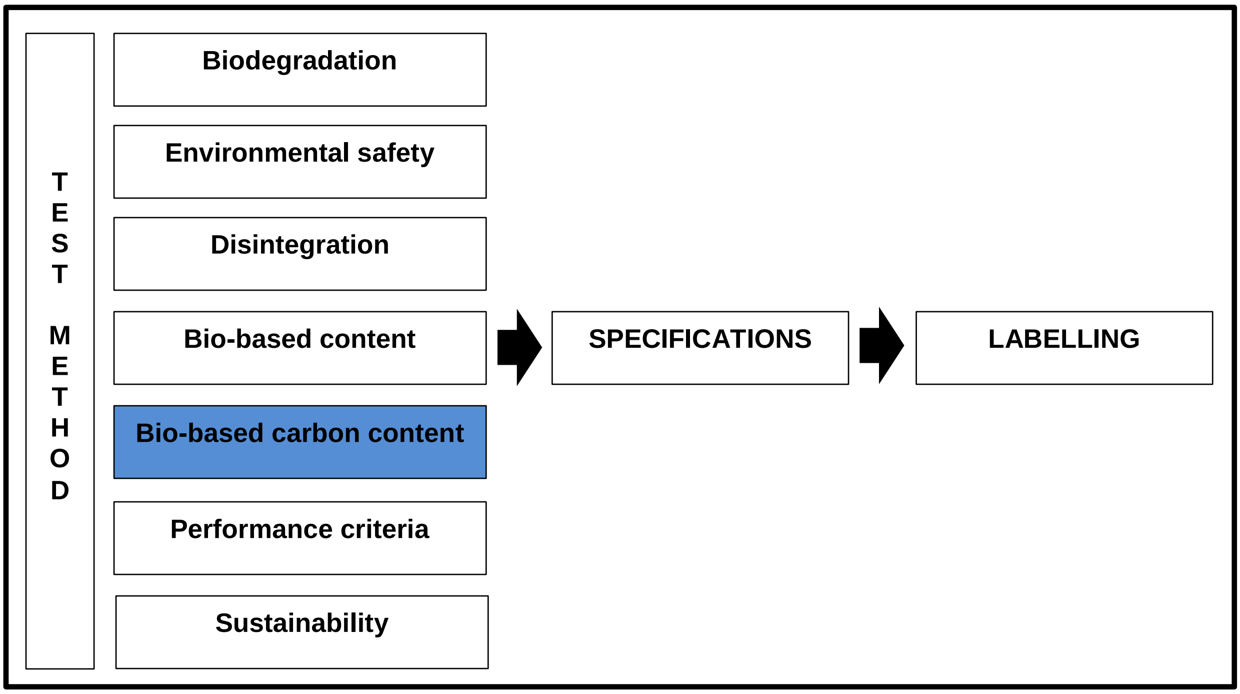


Figure 1 Relation between test methods, specifications and labelling systems

3 Sampling

A unified approach to sampling and sample preparation is important in obtaining a representative sample and thus in achieving reliable results of quantitative chemical analysis of a product of interest. This paragraph describes the sampling standards that can be used for sampling of some specific classes of materials mentioned below. For the sake of simplicity, this paragraph is divided into three groups namely “Solid materials and products”, “Liquid materials and products” and “Gaseous materials”. Within each group, a subdivision into narrower product classes is made and description of applicable standards is given.

3.1 Solid materials and products

Sampling procedures will depend on the nature of the raw material, in process or finished product, lots, conveying and sampling equipment. Sample preparation of solid samples mostly introduces no practical difficulties, though sometimes can be demanding. This because in some cases the sample matrix is not completely combustible (like in case of ceramics). In such situation a specific approach is required and often a development of a laboratory sampling method is needed.

The prior knowledge of the product data and sampling resources is necessary before a choice of an appropriate sampling procedure has to be made. Therefore, when defining the sampling procedures one should consider the purpose of sampling, the laboratory analysis the samples will undergo and the characteristic of the ingredients and finished products. Sampling protocols should meet scientifically recognized principles and procedures.
The use of recognized international standards for sampling is recommended. To ensure that a unified approach for sampling is accomplished and samples preparation brings to a representative sample of a material of interest. This is important for achieving reliable results of quantitative chemical analysis of a product of interest.

3.1.1 Plastics / Polymers / Ceramics / Glass / Concrete / Construction materials

For sampling of plastics, polymers, ceramics, glass, concrete and construction materials the standards mentioned below can be used.

3.1.1.1 International / European standards

Definitions and specific techniques for the preparation of samples for the chemical analysis of silicon-carbide (ceramic) containing raw materials and refractory products are given in ISO 21068-1.

ISO 21068: Chemical analysis of silicon carbide containing raw materials and refractory products. Part 1: general information and sample preparation
The standard is applicable to graphite brick containing silicon carbide, silicon carbide brick (including the bricks containing silicon nitride), refractories containing carbon and/or silicon carbide mixed with clay, refractories containing carbon and/or silicon carbide mixed with silica (and fused silica), refractories containing carbon and/or silicon carbide mixed with high alumina material, refractories containing carbon and/or silicon carbide mixed with magnesia (and dolomite), refractories containing carbon and/or silicon carbide mixed with chrome

mineral or magnesia chrome materials and to other forms of refractories containing carbon and/or silicon carbide.

Sampling shall be carried out in accordance with ISO 5022 for shaped refractory products and accordingly to ISO 8656-1 for unshaped refractory products unless otherwise is agreed by the user and the producer.
With the exception of raw materials, samples are generally in large pieces that require jaw crushing prior to the fine grinding stage. Because of contamination, particularly by iron, it is essential that size reduction by jaw crushing is done as minimal as possible, commensurate with obtaining a representative sample and achieving the maximum size that can be tolerated at the subsequent fine grinding stage. If free iron or total iron is required, a separate sample should be crushed in an iron-free device. Grinding, sieving, drying and weighing and combustion procedures are described in the standard too.

3.1.1.2 American standards

ASTM C322: Standard practice for sampling ceramic white-ware clays
This practice covers procedures for sampling bulk and bagged ceramic white-ware clays. It is summarized as: for bulk shipment consisting lumps, samples shall be taken from different parts of the rail car or truck during unloading. Sampling of hopper car or hopper truck shipments is to be done during unloading of the car or truck. For bulk shipment consisting shredded or coarsely ground clay, samples may be taken with a shovel, or with a grain sampler. For bagged lots of ground or air-floated clay, samples may be taken by a grain-sampler or similar sampling instrument. For a clay shipped in slurry form, a sample may be obtained by taking a single grab sample from any portion of the shipment except by skimming the top surface.

ASTM C224: Standard practice for sampling glass containers
This practice covers the standard for sampling of glass bottles, jars, and other containers intended for use in testing mechanical strength, dimensions, and other measurable characteristics. Sampling from a continuous manufacturing process shall be in accordance with a time schedule. When testing for annealing affected characteristics, samples shall be taken from the exit of the lehr (pattern) (or from packed cases whose continuity in point of time is known). For characteristics not affected by the degree of annealing, quickly cooled samples may be taken ahead of the lehr. Sample may come from the lot as a whole or it may be necessary to sort the lot before sampling. Sorting may be based on style, colour, size, manufacturer, or mould designation. Containers packed in cases shall be removed from the lot at random. The minimum number of cases to be selected shall be in accordance with the military standard prescribed herein.

ASTM C172: Standard practice for sampling freshly mixed concrete
This practice covers procedures for obtaining representative samples of fresh concrete as delivered to the project site on which tests are to be performed to determine compliance with quality requirements of the specifications under which the concrete is furnished. The practice includes sampling from stationary, paving and truck mixers, and from agitating and non-agitating equipment used to transport central-mixed concrete. Composite samples are required by this practice, unless specifically excepted by procedures governing the tests to

be performed such as tests to determine uniformity of consistency and mixer efficiency. Procedures used to select the specific test batches are not described in this practice, but it is recommended that random sampling is used to determine overall specification compliance.
This practice also covers the procedures to be used for preparing a sample of concrete for further testing where it is desirable or necessary to remove the aggregate larger than a designated size. This removal of larger aggregate particles is preferably accomplished by wet-sieving.

ASTM C1704: Standard test method for sampling and testing structural cementitious panels
These test methods cover sampling and testing of structural cementitious panels. Structural cementitious panels are non-combustible, water durable, fibre reinforced inorganic composite panels intended for use as structural panels when fastened to supports spaced in accordance with the span rating in inches.

ASTM D3665: Standard practice for random sampling of construction materials
This practice covers the determination of random locations (or timing) at which samples of construction materials can be taken.
The selection procedures and examples in this standard provide a practical approach for ensuring that construction material samples are obtained in a random manner. Additional details concerning the number of sample increments, the number of samples, the quantities of material in each, and the procedures for extracting sample increments or samples from the construction lot or process are covered by Practices C172, C183, D75, D140, D979, D5361, and Test Method D345. Additional sampling guidance is provided in Practice E105 concerning probability sampling, Practice E122 concerning choosing sample sizes to estimate the average quality of a lot or process, and in Practice E141 for acceptance of evidence based on results of probability sampling.

The best and most practical method for ensuring that samples of construction materials include the full range of a construction process is by incorporating a stratified-random sampling procedure into the sampling process. To implement a stratified-random sampling procedure, it is suggested to divide the lot to be sampled into the desired number of equal sub-lots and randomly sample each sub-lot in accordance with this standard. If the sub-lots are of unequal size, it will likely be necessary to weight the samples in order to maintain a fair and defensible sampling process.

3.1.1.3 Other standards

Not found.

3.1.1.4 Comparison

Subsection 3.1.1 covers standard practices for sampling solid materials and products in particular ceramics, glass, concrete, cementitious panels and construction materials. The common factor for these separate classes of materials is preparation of a representative and a homogenised sample.
However, there is only one international standard and no European standards available, but there are a number of American standard about this topic. Due to the fact that there are no

overlapping standards available no comparison can be made and only the described sampling practice will be presented.

For sampling freshly mixed concrete and construction materials, a procedure of random sampling is recommended (ASTM C172 and ASTM D3665 respectively).
For plastic, ceramics, polymers and glass materials and products (possibly also for freshly mixed concrete and construction materials after random sampling is done), in order to obtain a homogenised and representative sample, usually crushing of a sample material is done prior to its combustion and CO_2 trapping. A practical challenge which is common for all classes often lays in size reduction of initial sample to a final sample which can still be representative for the initial sample. To fulfil this requirement, powdered or granular materials must be well mixed to prevent segregation of particles by size and density.

3.1.2 Fuels: Solid Biofuels / Solid Recovered Fuels / Coal / Coke

For sampling solid biofuels, solid recovered fuels, coal and coke, the standards mentioned below can be used.

3.1.3 International / European standards

EN 14778: Solid biofuels -- Sampling
This European standard describes methods for preparing sampling plans and certificates and taking samples of solid biofuels, for example, from the place where the raw materials grow, from production plant, from deliveries e.g. lorry loads, or from stock.
The choice of sampling tools and equipment for both automated and manual sampling is also describes within the standard. It may be possible to use this standard on other solid biofuels. The methods described in this standard may be used, for example, when the samples are to be tested for moisture content, ash content, calorific value, bulk density, durability, particle size distribution, ash melting behaviour and chemical composition. The methods are not intended for obtaining the very large samples required for the testing of bridging properties.

Usually it is difficult to take samples in a way that satisfies the principle of correct sampling, stating that all individual parts of the lot shall have an equal probability of becoming part of the final sample. The chance that this can be achieved when the material is stationary (for example, in a silo or stockpile, or in a lorry or ship) is low. It is easier when the material is moving (for example, on a conveyor belt, or being loaded into or unloaded from transport equipment). Hence sampling from moving materials is to be preferred wherever possible. It is important to regularly ensure that the equipment in use is properly cleaned and maintained. If the equipment show signs of not functioning in accordance with the intended use, action shall be taken to test and repair or replace it. The integrity of the sampled material shall be ensured, e.g. avoiding loss or gain of moisture, fines etc. All sampling equipment shall be handled according to the described use, and it is important to ensure uniform extractions in repeated use. One shall always be ensured that all extracted material is transferred from the sampling device to a sample container, without loss or gain.

EN 14780: Solid biofuels – sample preparation

Two basic methods are used during the sample preparation. These methods are:

- sample division;
- particle size-reduction of the sample.

Methods for sample division include riffling, strip mixing, long pile-alternate shovel method, rotary divider, coning and quartering and handful sampling. Methods for reducing laboratory samples to subsamples include mixing, initial sample division, pre-drying, coarse cutting (particle size reduction to < 31.5 mm), sample division of < 31.5 mm material, particle size reduction of < 31.5 mm material to < 1 mm, sample division of < 1 mm material and finally particle size reduction of < 1 mm material to < 0.25 mm. Requirements of apparatus both for the sample division (riffle boxes, rotary sample dividers, shovels and scoops) and for the sample size reduction (coarse cutting mill or wood crusher, cutting mill, axe, hand saw, sieves, balance) are described in the given standard as well.

Because of the risk of changes in the moisture content (loss of moisture), a sub-sample (moisture analysis sample) shall be separated at the earliest possible stage of the sample preparation procedure. As an alternative, a separate moisture analysis sample may be taken. The sample reduction shall be carried out by a procedure that does not conflict with requirements of EN 14774-1 or EN 14774-2. For materials that have to be examined for moisture content, care shall be taken to avoid any significant heat build-up and risk of drying. A possible loss of moisture and fine particles during milling and other operations should be avoided.

For every sample division stage to be carried out it is important that a sufficient mass of material is retained, otherwise the sub-samples produced or the test portions to be taken may not be representative of the original sample. Table 1 gives a guideline for minimum masses to be retained after each sample division stage, depending on the nominal top size of the material. In addition to the minimum masses stated in EN 14780 (Table 1), it shall be ensured that the mass after a sample division stage is sufficiently large for the actual test or tests to be performed. Supplementary requirements concerning the masses of the test portions are given in European standards for test methods of solid biofuels.
Combined samples may be divided into two or more laboratory samples and laboratory samples are in general further divided in sub-samples (test-portions). This clause describes the methods and procedures for sample division. For every division step the mass of retained material given in Table 1 shall be taken into account.

Table 1 Guideline for minimum masses to be retained during sample division stages

Nominal top size	Minimum mass
millimetres	grams
200	120000
150	50000
100	15000
63	4000
50	2000
45	1500
40	1000
30	500
10	150
5	100
1	50
0,25	10

If the initial mass of the laboratory sample exceeds the minimum mass given in Table 1, the laboratory sample shall be divided using one of the methods described in Clause 8 of the standard.

CEN/TS 15442: Solid recovered fuels – methods for sampling

In this Technical Specification, sampling procedures and the procedure for the development of a sampling plan are provided for a range of process streams and common storage conditions. After a sampling plan has been prepared the sampling of solid recovered fuels itself can be implemented. The sampling objectives, along with the sequence of operations required to fulfil them are detailed in an overall sampling plan. From a pre-defined lot of solid recovered fuel, samples shall be taken representatively on the basis of a sampling plan that shall be drawn up before the sampling takes place. The sampling technique adopted depends on a combination of different characteristics of the material and circumstances encountered at the sampling location. The determining factors are: the type of solid recovered fuel; the situation at the sampling location / the way in which the material occurs (e.g. in a stockpile, on a conveyor belt, in a lorry); the (expected) degree of heterogeneity (e.g. mono-streams, mixed fuels, blended fuels).

The main principle stays the same: every particle in the lot or sub-lot to be represented by the sample should have an equal probability of being included in the sample. When this principle cannot be applied in practice, the sampler shall note the limitations in the sampling plan.
The main requirements for the determination of the effective increment size and for the effective sample size are the following: the effective increment size shall be at least as large as the minimum increment size; the effective increment size shall be large enough in order to obtain a sample of the minimum sample size with the selected number of increments; the effective increment size shall be large enough in order to obtain a sample sufficiently large enough for the analysis in the laboratory.

The effective sample size shall be at least as large as the minimum sample size; the effective sample size shall be large enough in order to equal at least the minimum increment size multiplied by the number of increments; the effective sample size shall be large enough for the analysis in the laboratory. Only if the nominal top size is more than 40 mm the effective sample size may be reduced in order to downscale the sample size to realistic proportions.

The reduction of the particle size and the sample size shall be done according to EN 15443, but the sampling report and the analyses report shall clearly mention this deviation and state that therefore the testing results are less representative.

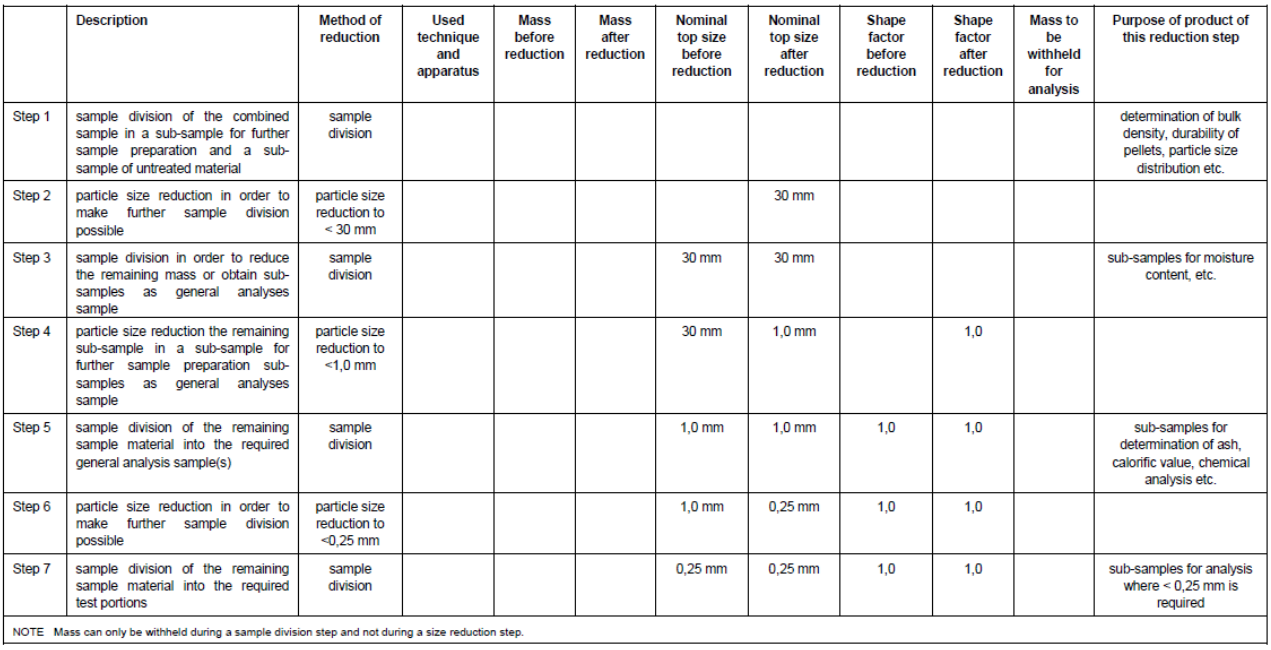
Additionally to the above listed standards for sampling of solid biofuels and solid recovered fuels, the following standards may be used for sampling coal and coke, but they will not be discussed here, due to the fact that they consist of only fossil components:

- ISO 13909: Hard coal and coke – mechanical sampling. Par4: Coal – preparation of test samples. Part 6: Coke – preparation of test samples
- ISO 18283: Hard coal and coke – manual sampling.
- ISO 20904: Hard coal – sampling of slurries

EN 15443: Solid recovered fuels – methods for the preparation of the laboratory samples
This standard specifies methods for reducing combined samples to laboratory samples and laboratory samples to sub-samples and general analysis samples. The methods described in this standard may be used for sample preparation, for example, when the samples are to be tested for bulk density, biomass determination, durability, particle size distribution, moisture content, ash content, ash melting behaviour, calorific value, chemical composition, and impurities. The methods are not intended to be applied to the very large samples required for the testing of bridging properties.

The main principle of correct sample preparation and two basic methods that are used during the sample preparation remain the same as in EN 14780. Apparatus both for the sample division (riffle boxes, rotary sample dividers, shovels and scoops) and for the sample size reduction (coarse cutting mill or wood crusher, cutting mill, axe, hand saw, sieves, balance) and the requirements for them are described in the given standard as well. These requirements are the same as the requirements present in EN 14780. Methods of the sample division and methods for reducing laboratory sample to sub-sample are listed in the standard and do not differ from EN 14780. The quantitative difference in the procedure described in these two standards is that one step-size before reduction is 30 mm in EN 15443 and not 31.5 mm as in EN 14780. Complete sample preparation plan is summarized in EN 15443 (Table 2).

Table 2 Sample preparation plan



	Description	Method of reduction	Used technique and apparatus	Mass before reduction	Mass after reduction	Nominal top size before reduction	Nominal top size after reduction	Shape factor before reduction	Shape factor after reduction	Mass to be withheld for analysis	Purpose of product of this reduction step
Step 1	sample division of the combined sample in a sub-sample for further sample preparation and a sub-sample of untreated material	sample division									determination of bulk density, durability of pellets, particle size distribution etc.
Step 2	particle size reduction in order to make further sample division possible	particle size reduction to < 30 mm					30 mm				
Step 3	sample division in order to reduce the remaining mass or obtain sub-samples as general analyses sample	sample division				30 mm	30 mm				sub-samples for moisture content, etc.
Step 4	particle size reduction the remaining sub-sample in a sub-sample for further sample preparation sub-samples as general analyses sample	particle size reduction to <1,0 mm				30 mm	1,0 mm		1,0		
Step 5	sample division of the remaining sample material into the required general analysis sample(s)	sample division				1,0 mm	1,0 mm	1,0	1,0		sub-samples for determination of ash, calorific value, chemical analysis etc.
Step 6	particle size reduction in order to make further sample division possible	particle size reduction to <0,25 mm				1,0 mm	0,25 mm	1,0	1,0		
Step 7	sample division of the remaining sample material into the required test portions	sample division				0,25 mm	0,25 mm	1,0	1,0		sub-samples for analysis where < 0,25 mm is required

NOTE Mass can only be withheld during a sample division step and not during a size reduction step.

For granular materials generally the principle of the third-power law is accepted and shall be respected at each sample division step. The equation for this third power law is shown in Equation (1):

$$m > \alpha \times (d_{95})^3 \qquad (1)$$

Where m is the mass retained after each sample division step in g;
d_{95} is the nominal top size in mm;
α is a constant over the whole sample preparation procedure for a particular material in g/mm^3. The value and unit of constant α is fixed by the nominal particle size, d_{95}, and the sample size, m, of the sample before sample preparation.

In EN 15443 (Table 3) the resulting reduction factors for the minimum (sub-)sample size are given, if a certain reduction of the nominal top size is chosen and the third-power law is respected. The reduction factor of the nominal top size can be calculated by dividing the current nominal top size by the proposed nominal top size after size reduction. In EN 15443 (Table 4) the resulting reduction factors for the minimum nominal top size are given, if a certain reduction of the (sub-)sample size is chosen and the third-power law is respected. The reduction factor of the minimum (sub-)sample size can be calculated by dividing the current minimum (sub-) sample size by the proposed minimum (sub-)sample top size after size reduction. Equation (1) can be used to calculate the exact values for each specific situation.

Table 3 Common values for desired reduction factor minimum (sub) sample size

Chosen reduction factor of the nominal top size	Resulting reduction factor for the minimum (sub-)sample size
1,5	3,4
2	8
3	27
4	64
5	125
6	216
7	343
8	512
9	729
10	1 000
20	8 000
30	27 000

Table 4 Common values for desired reduction factor nominal top size

Desired reduction factor for the minimum (sub-)sample size	Necessary reduction factor of the nominal top size
2	1,3
3	1,4
4	1,6
5	1,7
10	2,2
20	2,7
50	3,7
80	4,3
100	4,6
200	5,8
500	7,9
1 000	10,0

For SRF, however, many materials turn out to be far from granular. For example in fluff the particles turn out to be predominantly flat. Therefore, for solid recovered fuels, a correction can made for non-granular materials. Care is needed to avoid loss of fine particles and volatile components such as moisture and mercury during milling and other operations.

Besides, if a sub-sample is required for the determination of moisture content, then the sample preparation shall be carried out by a procedure that does not conflict with the requirements of CEN/TS 15414-1, CEN/TS 15414-2 or EN 15414-3. It is recommended that, if moisture content of the material (as sampled) is to be determined, a separate moisture analysis sample is taken (as there is a risk of reducing the moisture content by sample preparation operations). If a sub-sample is required for the determination of mercury content, then the sample preparation shall be carried out by a procedure that does not conflict with the requirements of EN 15297. It is recommended that, if mercury content of the material (as sampled) is to be determined, a separate mercury analysis sample is taken (as there is a risk of reducing the mercury content by sample preparation operations). For materials that have to be examined for moisture and mercury content, care shall be taken for any significant heat build-up and risk of loss of moisture and mercury.

3.1.3.1 American standards

ASTM D7026: Standard guide for sampling and reporting of results for determination of bio-based content of materials via carbon isotope analysis

This guide provides a framework for collecting and handling samples for determination of bio-based content of materials by means of the carbon isotope method described in Test Methods given in ASTM D6866. Bio-based materials often represent sampling problems specific to a given material, such as heterogeneity, and so forth, which require employment of material-specific sampling methods. The use of specialized sampling methods already accepted and validated by industries that manufacture and/or use the biomaterial is encouraged. However, all sampling techniques, especially non-standard techniques developed for specific materials must be reported in sufficient detail to allow critical assessment of the techniques used.

This guide is designed for materials that can be classified either as solids or liquids. Sample collection, determination of number of required samples and sample preparation are discussed in the frameworks of this guide. Analogically to the requirements of the European sampling standards, here also the primary requirements are that the sample be representative of the material to be tested and that the quantity or weight of sample be accurately established.

ASTM D7026 is in most cases linked to Test Methods described in ASTM D6866. The latter presents two methods for determining biobased carbon content: LSC (Liquid Scintillation Counting), a relatively widely available method, with presently established maximum error (range) of 15% (which is expected to be reduced as more data is accumulated), and AMS/IRMS (Accelerated Mass Spectrometry, coupled with Isotope Ratio Mass Spectrometry) with maximum error of about 1 to 2%, but which can be performed by only a few laboratories in the United States. Since the ASTM D6866 present two methods for the determining the bio-based carbon content, sample size requirements for both of these methods are mentioned. LSC requires a sample that contains 1.0 to 2.0 g of carbon. AMS/IRMS requires a sample that contains 0.5 to 1.0 g of carbon.

Samples should be taken from the most homogenous subunit of an object or material. If there are suspected gradual trends in the sample, the material should be subdivided to a set of smaller units or sub lots that can be considered essentially homogenous, except for possible small-scale graininess in some materials, such as particle board and so forth, and these sub lots treated as independent units or lots. The sampling should be performed in accordance with the probability sampling methods described in Practice E 105. The lot should be divided into sample size elements. These elements should be assigned numbers and the samples (elements) collected using random numbers, as described in Practice E 105. Representative sampling requires that either the material be homogenous on scale of sampling, or the initial sample taken is large enough to encompass inhomogeneities in a representative way, as described above.

The biobased content normally is to be reported based on dry weight. Moisture content of the sample must be controlled carefully. If feasible, the sample should be dried prior to weighing and the sample subsequently kept in dry, controlled environment, such as a desiccator. If there is a possibility of sample decomposition during drying, the sample may be sealed to retain constant moisture level, the water content determined by an appropriate, accepted analytical method and the dry weight of the sample calculated.

The estimate of the biobased carbon content of the material is the average of several independently analysed samples. The number of samples to be included in the average depends on the desired accuracy. The determination of the required number of samples assumes that the variability of results arises primarily from a single source and that the error is randomly distributed. The number of independent samples to be analysed depends on the maximum acceptable error *E* in estimation of the biobased content, the desired degree of certainty regarding the correctness of the answer, and the standard deviation s(0) of the analysis procedure. The procedure for estimating the number of samples needed is given in

Practice E122. Assuming that the analytical error is randomly distributed, the number of samples needed for a desired *E* is given by:

$$n(k) = (k \times \frac{\sigma(0)}{E})^2 \qquad (2)$$

where *k* is the factor defining the probability of the deviation of the average of *n* samples exceeding *E*; that is, the degree of certainty of correctness of the estimate. Some *k*-values and the corresponding levels of uncertainty are presented in Practice E122:

- *k* = 1.64 for 10% chance of the error exceeding *E*,
- *k* = 2 for 5.5% chance of the error exceeding *E*, and
- *k* = 3 for 0.3% chance (practical certainty) of the error exceeding *E.*

These numbers are derived from the properties of the random distribution curve.

3.1.3.2 Other standards

There are a number of standards from China and Australia dealing with this sampling:

- GB/T 28730 (Chinese): Method of preparation of solid biofuels sample.
- AS 2646.7 (Australian): Sampling of solid mineral fuels.
- AS 4264 (Australian): Coal and coke. Sampling – sampling procedures.
    - Part 1: Higher rank coal.
    - Part 2: Coke.
    - Part 3: Lower rank coal.

The objective of AS 4264 is to provide a set of rules for sampling coal that will ensure that the subsequent testing of the coal is representative of the full quantity of coal being sampled. In preparing this standard, reference was made to ISO 13909 (parts 1 to 4) and includes tables and information obtained from those standards. This standards sets out the methods for the sampling of coal from moving streams and stationary situations, including stopped-belt sampling (the reference method against which other sampling procedures are compared), for both routine and special purposes, to provide samples for general analysis and for the determination of total moisture content. Although this standard is intended to cover all coal sampling from moving streams, the procedures recommended may not be applicable in cases of extreme segregation of materials, as found with very wet coal owing to moisture run-off, or with very dry coal with generation of dust. In such cases, it may be necessary to revert to stopped-belt sampling.

3.1.3.3 Comparison

While European standards listed in this sub section are suitable for sampling solid bio-fuels and solid recovered fuels, American ASTM D7026 standard can be used both for solids and liquids.

The main principle of correct sampling is to obtain a representative sample from the whole lot concerned. Every particle in the lot or sub-lot to be represented by the sample should have an equal probability of being included in the sample. In order to do so a sampling plan is needed.
For sample preparation (EN 14780, EN 15443 and partly ASTM D7026), the main purpose is that a sample is reduced to one or more test portions that are in general smaller than the original sample. The main principle for sample reduction is that the composition of the sample

as taken on site shall not be changed during each stage of the sample preparation. Each sub sample must be representative of the original sample. Methods of the sample division and methods for reducing laboratory sample to sub-sample are listed in the standards EN 14780 and EN 15443 and do not differ from each other. The quantitative difference in the procedure described in these two standards is that one step-size before reduction is 30 mm in EN 15443 and not 31.5 mm as in EN 14780.

ASTM D7026 that is used in most cases, gives a link to Test Methods described in ASTM D6866. The latter presents two methods for determining biobased carbon content: Liquid Scintillation Counting and Accelerated Mass Spectrometry, coupled with Isotope Ratio Mass Spectrometry.

3.1.4 Natural products: rubber / paper / structural wood and wood-based products

For sampling of natural products (rubber, paper and wood-based products the standards mentioned below can be used.

3.1.4.1 International / European standards

ISO 1795: Rubber, raw natural and raw synthetic – sampling and further preparative procedures

This International standard specifies a method for the sampling of raw rubber in bales, blocks or packages and further procedures carried out on the samples to prepare test samples for chemical and physical tests.

The greater the number of bales in the sample, the more representative is the sample of the lot, but in most cases practical considerations impose a limit on what is possible. The number of bales to be chosen at random shall be agreed between customer and supplier. If applicable, a statistical sampling plan chosen from ISO 3951-2 shall be used.

The preferred method of taking a laboratory sample from each of the selected bales is the following: Remove the outer wrapping sheets, polyethylene wrapping, bale coating or other surface material from the bale and make two cuts, without the use of lubricant, through the entire bale, normal to the bale faces of largest surface area, so that a cross-sectional slice is removed from the middle of the bale. For referee purposes, this preferred method shall be used. Alternatively, a laboratory sample may be taken from any convenient part of the bale. In each case, the total mass of the laboratory sample shall be between 350 g and 1500 g, depending on the tests to be carried out. If the rubber is in chip or powder form, a similar quantity shall be taken at random from the package. Unless the laboratory sample is used immediately, it shall be placed in a light-proof and moisture-proof container or package of not more than twice its volume until it is required.

ISO 7213: Pulps – sampling for testing

This standard applies to all kinds of pulp delivered in bales or rolls, and is recommended for use when sampling for all kinds of testing purposes except for the determination of saleable mass. If the pulp is to be tested for saleable mass, in addition to other properties, the gross sample obtained according to the appropriate International standard for sampling saleable mass may also be used for the other pulp property test.

ISO 186: Paper and board – sampling to determine average quality

This International standard specifies a method of obtaining a representative sample from a lot of paper or board, including solid and corrugated fibre-board (see ISO 4046:1978), for testing to determine whether or not its average quality complies with set specifications. It defines the conditions which apply when sampling is carried out to resolve disputes between buyer and seller relating to a defined lot of paper or board, which has been or is being delivered. Note, that if less than 50% of the lot is available for sampling, then sampling in terms of this International standard will be considered as invalid in the absence of agreement to the contrary. The method is unsuitable for determining the variability within a lot. In cases where International standards make reference to sampling according to this standard but where such sampling is impossible, impractical or inappropriate, and where no dispute is involved, guidance is given in normative annex of ISO 186.

3.1.4.2 American standards

ASTM D1485: Standard practice for rubber from natural sources. Sampling and sample preparation

This practice outlines a procedure for sampling and sample preparation of natural rubber. A statistical method for determining a quality index and lot acceptability is given. The sampling plan is optional for quality control or production, but may be used when needed for referee purposes. This practice, intended for referee purposes, covers a uniform procedure for sampling lots of solid natural rubber. Natural rubber generally is marketed in bales or packages of various sizes. A procedure for determining the acceptability of lots of natural rubber is given. This procedure is based on a variable sampling plan. The sample size is based on the assumption of a visually homogeneous material. If obvious heterogeneity exists, the number of samples shall be increased.

ASTM D6085: Standard practice for sampling in rubber testing. Terminology and basic concepts

This practice covers a standardized terminology and some basic concepts for testing and sampling across the broad range of chemical and physical testing operations characteristic of the rubber and carbon black manufacturing industries. In addition to the basic concepts and terminology, a model for the test measurement process is given. This serves as a mathematical foundation for the terms and other testing concepts. It may also find use for further development of this practice to address more complex sampling operations.

ASTM D2915: Practice for sampling and data analysis for structural wood and wood-based products

This practice covers sampling and analysis procedures for the investigation and evaluation of allowable properties of specified populations of stress-graded structural wood and wood-based products.

This practice generally assumes that the population is sufficiently large so that, for sampling purposes, it may be considered infinite. Where this assumption is inadequate, that is, the population is assumed finite, many of the provisions of this practice may be employed but the sampling and analysis procedure must be designed to reflect a finite population. The statistical techniques embodied in this practice provide procedures to summarize data so that logical judgments can be made. This practice does not specify the action to be taken after the results have been analysed. The action to be taken depends on the particular requirements of the user of the product.

The population shall be clearly defined where it may be necessary to specify the following:

1) trade name and description,
2) geographical area over which sampling will take place,
3) species or species group,
4) time span for sampling,
5) lumber size, and
6) moisture content.

Two statistical techniques are described under this practice, namely: parametric and nonparametric analysis. The sampling methods include: random sampling, sampling with unequal probabilities, and sequential sampling.

Selection and method of determining sample size are described more detailed in the standard.

3.1.4.3 Other standards

TAPPI (Technical Association of the Pulp and Paper Industry) standard, T 400sp: Sampling and accepting a single lop of paper, paperboard, containerboard or related products (sp - standard practice)

This method describes procedures for obtaining a representative sample for testing. In ideal situation the samples selected should represent a lot of paper or paperboard, container board or related product, including converted paper products. However, in some situations the sample may be as small as a single sheet of paper provided to a laboratory for testing and may not represent the lot from which it is obtained. Procedures for establishing the lot of paper to be sampled and the rules for selecting a representative sample for testing from this lot are described. Specific sampling procedures are described for large rolls or skids. Procedures for sampling a single roll of containerboard, for sampling and testing a continuous strip of paper and procedures for handling a sample are described too in the standard.

3.1.4.4 Comparison

Subsection 3.1.3 covers standard practices for sampling rubber, paper, structural wood and wood-based products. In the subsection above the standards that can be used for sampling of the above mentioned products or materials are listed. Solid biofuels should be treated accordingly to EN 14778 and EN 14780. If sampling of a solid material or product is not mentioned above, then in general EN 15443 can be used for the preparation of the laboratory sample. An appropriate method for sampling then can be decided accordingly to CEN/TS 15442.

There are similar American and International/European standards mentioned in this subsection that cover rubber-based materials: rubber, raw natural and raw synthetic is covered by ISO 1795; standards practice of sampling rubber from natural sources is described in ASTM D1485. ASTM D6085 introduces terminology and basic concepts for sampling in rubber testing.

Procedures for sampling pulps, paper and board are given in ISO 7213 and ISO 186. More general is American ASTM D2915 practice, that describes sampling procedures and data analysis for structural wood and wood-based products.
There is also document T 400sp of Technical Association of the Pulp and Paper Industry (TAPPI), which describes standard practice for sampling and accepting a single lop of paper, paperboard, containerboard or related products.

3.2 Liquid materials and products

Sampling procedures of liquid materials should meet common criteria for sampling and should aim to obtain a smaller sample which is representative for the whole amount of material. For liquids this requirement can be reformulated into a demand of having either single phase or relatively homogeneous liquid material. The inhomogeneity, if it is temporary, in many cases can be removed by stirring or centrifuging of a liquid material before sampling. The most challenging sampling is done for mixtures of liquids, containing a volatile component.
More detailed approaches and procedures for sampling different liquid materials are described in the standards below.

3.2.1 Fuels: petroleum and petroleum products

3.2.1.1 International / European standards

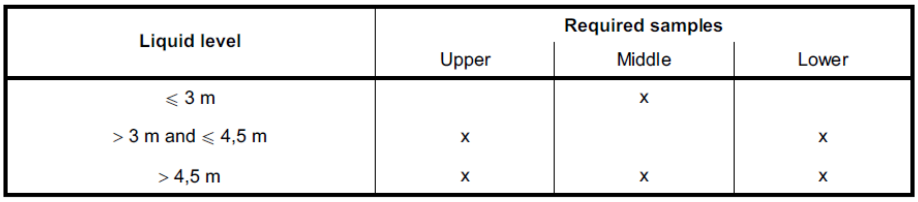
ISO 3170: Petroleum liquids. Manual sampling
This International standard specifies the manual methods to be used for obtaining samples of liquid or semiliquid hydrocarbons, tank residues and deposits from fixed tanks, railcars, road vehicles, ships and barges, drums and cans, or from liquids being pumped in pipelines. It applies to the sampling of petroleum products, crude oils and intermediate products, which are stored in tanks at or near atmospheric pressure, or transferred by pipelines, and are handled as liquids at temperatures from near ambient up to 200°C. The sampling procedures specified are not intended for the sampling of special petroleum products which are the subject of other International standards, such as electrical insulating oils (IEC 60475), liquefied petroleum gases (ISO 4257), liquefied natural gases (ISO 8943) and gaseous natural gases (ISO 10715).

If the hydrocarbon to be sampled is of non-homogeneous character showing significant variations in composition or containing sediments and water, samples taken manually should not be expected to be representative, but may enable the degree of non-homogeneity to be assessed and estimates of quality and quantity to be made.

To ensure that samples submitted for examination are as representative as possible of the liquid being sampled, the necessary precautions are given. These depend on the characteristics of the liquid, the tank, container or pipeline from which the sample is being obtained, and the nature of the tests to be carried out on the sample. Generally, two basic manual sampling methods are available: tank sampling (static sampling) and pipeline sampling (dynamic sampling).

The general procedures that shall be applied for sampling homogeneous liquids are specified within the standard. Additional procedures for sampling crude oil and non-homogeneous liquids are described in Clause 8 of the standard. Unless otherwise specified, multiple-spot samples shall be collected using the detailed procedure relevant to the particular application. Typically they are upper, middle and lower; or, upper, middle and suction (outlet) samples. The minimum number of samples shall be in accordance with ISO 3170 (Table 5).

Table 5 Spot samples – Minimum requirements



Liquid level	Required samples		
	Upper	Middle	Lower
⩽ 3 m		x	
> 3 m and ⩽ 4,5 m	x		x
> 4,5 m	x	x	x

When taking samples of volatile crude oils and products, if it is necessary to avoid the loss of light ends, for example for determination of density, vapour pressure or distillation, composite or bulk oil shall not be transferred from the original sample container(s). Transportation and storage of the sample shall be done an inverted position to avoid loss of light ends through the closure.

A composite sample may be prepared from representative subsamples of spot samples obtained from within a single tank (e.g. by combining subsamples from the upper, middle and lower spot samples), or may be prepared by combining subsamples representative of individual tanks to provide a composite for a larger oil quantity (e.g. several ship or barge tanks of the same product). Composite samples shall include all the material collected in the primary sampling device without subdivision. The volume collected in the primary sampling device shall be chosen to allow the entire contents of the device to be added to the volume of the other subsamples in the transport container. Compositing of subsamples smaller than the entire contents of a subsample shall only be performed in a laboratory with facilities to assure adequate mixing and measurement of the subsamples. To prepare either type of composite sample, transfer subsamples of representative individual samples into a composite-sample container, and mix them together gently. The subsamples shall be volume weighted in proportion to the quantity that each represents. When the subsamples that are to be combined originate from a tank of non-uniform cross-sectional area (or from multiple tanks), the compositing operation shall require careful calculation and measurement of the subsamples to maintain the representative nature of the sample. These operations shall, if practical, be conducted under controlled laboratory conditions.

Besides, procedures to minimize or eliminate losses of light ends from samples are described in the standard. Such losses can occur during handling or transfer of samples, thereby making them non-representative of the bulk. The procedures specified are intended to provide samples for the following purposes:
a) the determination of the liquid/hydrocarbon quality;
b) the determination of the water content;
c) the determination of other contaminants that are not considered to be part of the liquid transferred.

If the sampling conditions for purposes a), b) and c) are in conflict, separate samples are required.

Sampling procedures for tank contents that are not homogeneous are specified that enable the degree of non-homogeneity to be assessed and estimates of quality and quantity to be made.

ISO 3171: Petroleum liquids. Automated pipeline sampling

ISO 3171 recommends procedures for crude oil and liquid petroleum products being conveyed by pipeline. Does not apply to liquefied petroleum gases and liquefied natural gases. The principal purpose is to give guidelines for specifying, testing, operating, maintaining and monitoring crude oil samples.
The purpose of collecting a sample of the material flowing through a pipeline is to determine the mean composition and quality of the bulk quantity. Samples of the bulk quantity in the line may be analysed to determine composition, water and sediment content or density, viscosity, vapour pressure.

Manual methods of pipeline sampling are adequate for homogeneous liquids whose composition and quality do not significantly vary with time. If this is not the case, the automated sampling is recommended, since the continuous or repetitive extraction of small samples from the pipeline ensures that any changes in the bulk content are reflected in the collected sample. To have the sample as representative as possible is essential to meet the recommendations of this standard regarding the homogeneity of the liquids and regarding the sampling location.

Sometimes consideration should be given to provide a sample by manual method in case automatic sampler fails to perform properly. However, manual sampling will be a subject to uncertainty if the pipeline conditions are varying.

The equipment and techniques described have generally been used for sampling stabilized crude oil, but may also be applied to un-stabilized crude oil and refined products provided that a consideration is given to the difficulties of sample handling and safety precautions.
Representative sampling of crude oil for density and water and sediment content is a critical process. Extensive studied have shown that in crude oil transfers four distinct steps are required for having representative values:

1) adequate steam conditioning of the pipeline contents;
2) reliable and effective sampling, ensuring proportionality between sampling ratio and flow rate in the line;
3) proper conservation and transporting of the sample;
4) proper conditioning and dividing into parts for accurate laboratory analysis.

ISO 4257: Liquefied petroleum gas – method of sampling

This International standard specifies the procedure to be used for obtaining samples of unrefrigerated liquefied petroleum gases (LPG). It is suitable for sampling from bulk containers, to provide samples for laboratory testing of products covered by ISO 9162.This International standard is applicable for the provision of samples for compositional analysis by ISO 7941. It is not applicable for the provision of samples for trace analysis of low-boiling components. If trace analysis of low boiling components is required, a variable-volume receiver such as that described in ASTM D3700 should be used.

Principle: a liquid sample is transferred from the source into a sample container through a transfer line by purging the container and filling it with liquid, then providing a liquid ullage so that 80% of the container volume remains filled with liquid.
Great care is required to obtain a representative sample, especially if the material to be sampled is a mixture of liquefied gases. The following factors shall be taken into account: samples should be taken from the liquid phase only; sampling from the bottom of a vessel should be avoided. In general, the contents of tanks can be non-homogeneous. Homogeneity can be improved by circulating the contents prior to sampling. A waiting period of 30 min is recommended after circulation before sampling to permit settling of any aqueous material and to allow dissipation of any static charge that may have developed.
When sampling from pipelines under flow conditions, the pressure in the line needs to be above vapour pressure to avoid two-phase conditions.

General safety precautions, safety at the sampling point, safety of the container and safety during transport are mentioned in the standard as well. Requirements for the apparatus to use while sampling are given too.

ISO 8943: Sampling of liquefied natural gas. Continuous and intermittent methods
In the studies of the liquefied natural gas (LNG), it is common practice to determine the quantity transferred on a calorific-content basis. The total calorific content of quantities of LNG quoted in the custody transfer is determined by the liquid volume, liquid density and gross calorific value of the LNG delivered. A knowledge of the composition of the LNG is required in order to calculate the density and the calorific content of quantities of LNG. Therefore, precise sampling is a prerequisite for precise analysis. LNG is a complex mixture of low-molecular-weight hydrocarbons with nitrogen as a principal inert impurity. Typically, methane is the major component. Minor-component concentrations vary with the source of the raw gas, the liquefaction pre-treatment, the liquefaction process and the storage conditions.

3.2.1.2 American standards

ASTM D4057: Standard practice for manual sampling of petroleum and petroleum products
Representative samples of petroleum and petroleum products are required for the determination of chemical and physical properties, which are used to establish standard volumes, prices, and compliance with commercial and regulatory specifications. The objective of manual sampling is to obtain a small portion (spot sample) of material from a selected area within a container that is representative of the material in the area or, in the case of running or all-level samples, a sample whose composition is representative of the total material in the container. A series of spot samples may be combined to create a representative sample. Manual sampling may be applied under all conditions within the scope of this practice, provided that the proper sampling procedures are followed. In many liquid manual sampling applications, the material to be sampled contains a heavy component (such as free water) which tends to separate from the main component. In these cases, manual sampling is appropriate under the following conditions: sufficient time must have elapsed for the heavy component to adequately separate and settle; it must be possible to measure the level of the settled component in order to stay well above that level when drawing representative samples, unless all or part of the heavy component will be included in the portion of the tank contents to be identified; when one

or more of these conditions cannot be met, sampling is recommended and is accomplished by means of an automatic sampling system (see Practice D4177 (API MPMS Chapter 8.2)).

This practice covers procedures for manually obtaining representative samples of petroleum products of a liquid, semi-liquid, or solid state whose vapor pressure at ambient conditions is below 101 kPa. If sampling is for the precise determination of volatility, use Practice D5842 (API MPMS Chapter 8.4) in conjunction with this practice. For sample mixing and handling of samples, refer to Practice D5854 (API MPMS Chapter 8.3). The practice does not cover sampling of electrical insulating oils and hydraulic fluids. The procedures described in this practice may also be applicable in sampling most noncorrosive liquid industrial chemicals, provided that all safety precautions specific to these chemicals are strictly followed. The procedure for sampling liquefied petroleum gases is described in Practice D1265; the procedure for sampling fluid power hydraulic fluids is covered in ANSI B93.19 and B93.44; the procedure for sampling insulating oils is described in Practice D923; and the procedure for sampling natural gas is described in Test Method. The procedure for special fuel samples for trace metal analysis is described in an appendix to Specification D2880.

ASTM D4177: Standard practice for automated sampling of petroleum and petroleum products

Representative samples of petroleum and petroleum products are required for the determination of chemical and physical properties.
This practice covers information for the design, installation, testing, and operation of automated equipment for the extraction of representative samples of petroleum and petroleum products from a flowing stream and storing them in a sample receiver. Petroleum products covered in this practice are considered to be a single phase and exhibit Newtonian characteristics at the point of sampling. This practice is applicable to petroleum and petroleum products with vapour pressures at sampling and storage temperatures less than or equal to 101 kPa. Reference to D5842 (API MPMS Chapter 8.4) can be made when sampling for Reid vapour pressure (RVP) determination. Petroleum products whose vapour pressure at sampling and sample storage conditions are above 101 kPa and liquefied gases (that is, LNG, LPG etc.) are not covered by this practice.

While the procedures covered by this practice will produce a representative sample of the flowing liquid into the sample receiver, specialized sample handling may be necessary to maintain sample integrity of more volatile materials at high temperatures or extended residence time in the receiver. Such handling requirements are not within the scope of this practice. A theoretical calculations for selecting the sampler probe location, accepted methodologies for sampling systems and components, performance criteria for permanent installations, also the criteria for portable sampling units are listed in the Annexes of the standard.

ASTM D233: Standard test methods for sampling and testing turpentine

The test procedures described in this standard were developed when the chief use for turpentine was as a solvent. Currently however, the chief use for turpentine (and pinenes) is as raw materials for the production of resins and synthetic organic chemicals. Thus the chemical composition of turpentines and pinenes is extremely important and tests, in addition to the ones described in these test methods, are required in order to fully characterize turpentines and pinenes. The most widely used technique for determining the chemical composition of turpentines (and pinenes) is gas chromatography (see Test Methods D6387).

These test methods described in the standard cover procedures for sampling and testing turpentine and are also used for the sampling and testing of pinenes, the major components of most turpentines. These test methods primarily measure the physical rather than the chemical properties of turpentines and pinenes. As turpentines and pinenes are currently used chiefly as chemical raw materials for the production of resins and synthetic organic chemicals, chemical composition is also very important. Consequently, testing the chemical composition of turpentines and pinenes by gas chromatography has displaced these test methods to a large extent (See for example Test Methods D6387).

ASTM D5854: Practice for mixing and handling of liquid samples of petroleum and petroleum products (API MPMS Chapter 8.3)

Representative samples of petroleum and petroleum products are required for the determination of chemical and physical properties. The treatment of samples from the time of collection until they are analysed requires care and effort to maintain their compositional integrity. This practice covers the handling, mixing, and conditioning procedures that are required to ensure that a representative sample of the liquid petroleum or petroleum product is delivered from the primary sample container/receiver into the analytical test apparatus or into intermediate containers. Selection of sample containers, acceptance test criteria for power mixer and sample container combinations and acceptance tests for mixing systems are covered by this practice.

Sampling procedures are referred to in Practices D4057 (API MPMS Chapter 8.1) and D4177 (API MPMS Chapter 8.2). Practice D5842 (API MPMS Chapter 8.4) covers sampling and handling of light fuels for volatility measurement.

ASTM D7026: Standard guide for sampling and reporting of results for determination of bio-based content of materials via carbon isotope analysis

The sampling described in 3.1.2.2 of this standard is also applicable for sampling of liquids. This guide is designed for materials that can be classified either as solids or liquids. Sample collection, determination of number of required samples and sample preparation are discussed in the frameworks of this guide.

ASTM D5842: Practice for sampling and handling of fuels for volatility measurement (API MPMS Chapter 8.4)

This practice covers procedures and equipment for obtaining, mixing, and handling representative samples of volatile fuels for the purpose of testing for compliance with the standards set forth for volatility related measurements applicable to light fuels. The applicable dry vapour pressure equivalent range of this practice is 13 to 105 kPa.

This practice is applicable to the sampling, mixing, and handling of reformulated fuels including those containing oxygenates.

3.2.1.3 Other standards

Not found.

3.2.1.4 Comparison

Generally, manual methods for sampling of liquids are applicable for homogeneous liquids whose composition and quality are not significantly time-dependent. However, automated sampling is recommended, since the continuous extraction of small samples from the pipeline ensures that any changes in the bulk content are reflected in the collected sample. Sometimes consideration should be given to provide a sample by manual method in case automatic sampling fails to perform properly. However, manual sampling will be a subject to uncertainty if the pipeline conditions are varying.
ISO 3071 and ISO 3171, as well as ASTM D4057 and ASTM D4177 describe the sampling procedures and requirements for both manual and automated sampling of petroleum liquids. ISO 3071 distinguishes two basic manual sampling methods: tank sampling (static sampling) and pipeline sampling (dynamic sampling). Both ISO 30171 and ASTM D4057 (manual sampling) aim to obtain a small portion (spot sample) of material from a selected area within a container that is representative of the material in the area or, in the case of running or all-level samples, a sample whose composition is representative of the total material in the container. A series of spot samples then may be combined to create a representative sample. ASTM D4057 also provides a special instruction how to deal with heavy or volatile compounds of liquids to be sampled. ISO 3071 is applicable at or near atmospheric pressure and starting from ambient to 200°C temperature range. American standards both for manual and automated sampling have the same applicability range: material to sample has to be at ambient conditions with vapour pressure at or below 101 kPa.

Both European and American standards on automated sampling of petroleum products cover information for the design, installation, testing, and operation of automated equipment for the extraction of representative samples of petroleum and petroleum products. Standard test methods for sampling and testing turpentine are described in a separate standard (ASTM D233).

Standard practice and sample preparation of petroleum and lubricant products for elemental analysis is described in ASTM D7455 in the next subsection.

3.2.2 Paints/ Varnishes / Solvents / Volatile solvents / Lubricants

3.2.2.1 International / European standard

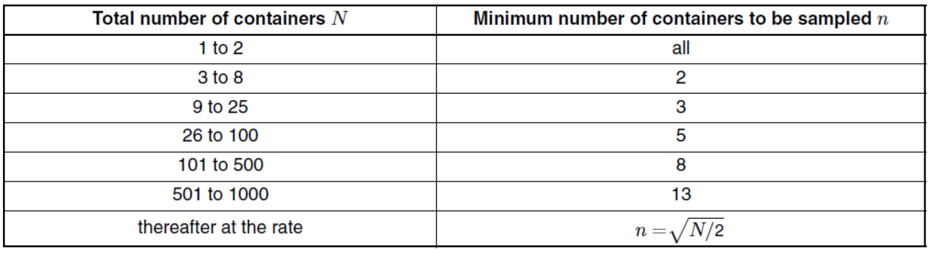
ISO 15528: Paints, varnishes and raw materials for paints and varnishes – sampling
This International standard describes manual methods of sampling paints, varnishes and raw materials for paints and varnishes. Such products include liquids and materials which, without undergoing chemical modification, are capable of being liquefied when heated up, and also powdered, granulated and pasty materials. Samples may be taken from containers, e.g. cans, drums, tanks, containers, tank wagons or ships' tanks, as well as from barrels, sacks, big-bags, silos or silo wagons, or from conveyor belts. The minimum size of a sample shall be or three to four times the quantity needed to carry out the required tests.

Before sampling is carried out, the material, the container and the sampling point shall be inspected for abnormalities. If any abnormalities are observed, they shall be recorded in the sampling report. The operator shall then decide whether a sample shall be taken and if so what type of sample.

- For homogeneous materials, a single sample is sufficient.
- For inhomogeneous materials, there is a distinction between two types of non-homogeneity; temporary and permanent.
  - Temporary inhomogeneity may result from insufficient mixing, foaming, crystallization, etc., which may results in different density or viscosity. Such materials may be homogenized by stirring or warming before sampling is carried out.
  - In case of materials which are neither miscible nor soluble in each other (permanent inhomogeneity), it shall be decided whether and for what purpose a sample is to be taken.

Container sizes are also of importance:
For small containers, samples shall be taken by means of a sampling tube. For small containers, the number of samples to be taken, is given in ISO 15528 (Table 6):

Table 6 Minimum number of containers to be sampled



Total number of containers N	Minimum number of containers to be sampled n
1 to 2	all
3 to 8	2
9 to 25	3
26 to 100	5
101 to 500	8
501 to 1000	13
thereafter at the rate	$n = \sqrt{N/2}$

For liquids, in small containers, individual samples may be taken by means of a scoop. Samples from each level, composite samples or bottom samples may also be taken by means of sampling tubes.

If large containers are to be sampled, at least two samples are to be taken. The upper phase shall be sampled by means of a scoop, and the lower phase by means of a zone sampler, or a suitable dipping bottle, or dipping can (with a stopper that can be removed at the desired depth if suitable), or at the bottom valve if there is one. When preparing a sample, the relative sizes of the two phases shall be taken into account.
In large containers, for liquids, a top sample may be taken from a liquid or liquefied product by means of a scoop. For sampling at other levels, the dipping can is the most suitable, and the zone sampler is particularly suitable for taking a bottom sample. Other possible sampling procedures include taking an individual sample from a bleed point, taking care to allow sufficient liquid to run off first, or in the case of pumped liquids by means of a branch pipe during circulating, discharging or loading. In case of pumping operations, a continuous sample may be taken from a bypass lien by using a suitable branch pipe.

For products in paste form, for large and small containers, a top sample may be taken by using a spatula, a scoop, or in a certain cases a sampling tube.

For solids in powdered form as granules or rough grains, for small and large containers, it is generally only possible to take a top sample by means of a scoop, spatula or shovel. Intermittent samples may be taken when containers are being filled or emptied, using a conveyor belt or worm conveyor for instance. A sampling tube may also be used in certain cases.

3.2.2.2 American standards

ASTM D268: Standard guide for sampling and testing volatile solvents and chemical intermediates for use in paints and related coating and material

A brief discussion of each test method is given with the intent of helping the user in the selection of the most applicable procedure where more than one is available. This guide covers procedures for the sampling and testing of volatile solvents used in the manufacture of paint, lacquer, varnish, and related products. The test methods are listed in ASTM D268 (Table 7):

Table 7 List of Test Methods

Test Method	Section in ASTM D268	ASTM Method
Acidity in:		
Aromatic hydrocarbons	11	D847
Volatile solvents	11	D1613
Acid wash colour of aromatics	23	D848
Alcohols in ketones	18	D2804, D3329
Alkalinity in acetone	12	D1614
Aromatics in mineral spirits	25	D3257
Colour, platinum cobalt scale	6	D1209
Copper corrosion test:		
Aromatic hydrocarbons	14	D849
Mineral spirits	14	D130
Distillation range:		
Aromatic hydrocarbons	7	D850
Mineral spirits, turpentine	7	D86
Volatile organic liquids	7	D1078
Ester value	13	D1617
Esters, purity	13	D3545
Flash point:		
Pensky-Martens closed cup	17	D93
Tag closed cup	17	D56
Tag open cup	17	D1310
Setaflash tester	17	D3278
Method surveys:		
Ethylene and propylene glycols	22	E202
Methanol	21	E346
Nonaromatics in aromatics	24	D2360
Nonvolatile matter	8	D1353
Odour	9	D1296
Paraffins in aromatics	24	D2360
Permanganate time for acetone and methanol	16	D1363
Purity of ketones	18	D2192, D2804, D3329, D3893
Sampling	4	E300
Solvent power evaluation:		
Aniline point and mixed aniline point of petroleum products and hydrocarbon solvents	19	D611
Kauri-butanol value of hydrocarbon solvents	19	D1133
Dilution ratio in cellulose nitrate solution for active solvents, hydrocarbon diluents, and cellulose nitrates	19	D1720
Specific gravity	5	D891, D2935, D3505, D1555
Sulphur as hydrogen sulphide and sulphur dioxide	15	D853
Water:		
Fischer reagent titration method	10	D1364, E203
Turbidity method	10	D1476
Water miscibility of water-soluble solvents	20	D1722

ASTM D7455: Standard practice and sample preparation of petroleum and lubricant products for elemental analysis

Crude oil, petroleum, petroleum products, additives, and lubricants are routinely analysed for their elemental content such as chlorine, nitrogen, phosphorus, sulphur, and various metals using a variety of analytical techniques. Some of these test methods require little to no sample preparation; some others require only simple dilutions; while others require elaborate sample decomposition before the product is analysed for its elemental content. Fairly often it can be shown that the round robin results by a co-operator are all biased with respect to those from other laboratories. Presumably, the failure to follow good laboratory practices and instructions in the test methods can be a causal factor of such errors. A further consequence is an unnecessarily large reproducibility estimate or the data being dropped from the study as an outlier. Uniform practice for sample preparation is beneficial in standardizing the procedures and obtaining consistent results across the laboratories.

This practice covers different means by which petroleum product and lubricant samples may be prepared before the measurement of their elemental content using different analytical techniques. This practice includes only the basic steps for generally encountered sample types. Anything out of the ordinary may require special procedures. There are individual test methods mentioned in the standard for instructions to handle such situations. This practice is not a substitute for a thorough understanding of the actual test method to be used, caveats the test method contains, and additional sample preparation that may be required.
This practice may also be applicable to sample preparation of non-petroleum based bio-fuels for elemental analysis.

ASTM D7718: Standard practice for obtaining in-service samples of lubricating grease

This practice covers the method to obtain a trendable in-service lubricating grease sample from the following configurations including motor-operated valves, gearboxes, pillow-block bearings, electric motors, exposed bearings, open gears, or failed grease-lubricated components. In some cases, it may be necessary to take more than one sample from a piece of equipment to obtain more trendable results. Examples of this could be a large bearing that does not fully rotate, such as a slew bearing, or one in which sufficient mixing does not otherwise occur. Samples taken in the above manner may need to be mixed to form a more homogeneous sample. This may also be true of other samples such as those taken from open face bearings.

ASTM D460: Standard test method for sampling and chemical analysis for soap and soap products

Soap and soap products are widely used. The test methods presented in the standard are suitable for setting specifications and performing quality control on soap and soap products. These test methods cover the sampling and chemical analysis of cake, powdered, flake, liquid, and paste soaps, and soap products.

ASTM E300-03: Standard practice for sampling industrial chemicals (simple liquids, solids, slurries)

This practice covers procedures for sampling several classes of industrial chemicals. It also includes recommendations for determining the number and location of such samples, to ensure their being representative of the lot in accordance with accepted probability sampling principles. Although this practice describes specific procedures for sampling various liquids, solids, and slurries, in bulk or in packages, these recommendations only outline the principles to be observed. They should not take precedence over specific sampling instructions contained in other ASTM product or method standards.

ASTM D3437: Standard practice for sampling and handling liquid cyclic products
This practice covers procedures for sampling and handling several liquid cyclic products. These specifically cover liquids at ambient temperature and include benzene, toluene, xylenes, cyclohexane, styrene, pyridine, ethyl benzene, isopropyl benzene, and alpha-methyl styrene. Any person sampling and handling these products should have specific first aid instructions and equipment available for use in the event of personal contact or exposure.

ASTM D802: Standard test methods for sampling and testing pine oils
The testing procedures described in these test methods have been in use for many years and emphasize the physical properties of pine oil rather than its chemical composition. Test Methods D 6387 describe a capillary gas chromatography method which is suitable for determining both the major and minor components found in pine oils. Test methods of the given standard cover procedures for sampling and testing pine oils, and are applicable to both natural pine oils derived from pine stumps either by the steam and solvent process or by destructive distillation, and also to synthetic pine oils obtained by the chemical hydration of terpene hydrocarbons. Procedures for sampling, appearance, colour and specific gravity determination, also composition and moisture determination are described in the standard.

3.2.2.3 Other standards

EPA 340/1-91-010: Standard procedure for collection of coating and ink samples for analysis by reference methods 24 and 24A
This standard procedure recommends step-by-step activities for proper sampling.
Firstly, coatings or inks and the processes from which they are to be sampled are to be identified. The location in the operation where samples can best be obtained has to be identified. The sample should be taken at the point of application of coating or ink, or as close to that point as possible, in order for the sample to be representative of the coating material "as applied" to then web or substrate.

Multi-component coatings that harden upon mixing and application to the substrate must be sampled differently since a representative "as applied sample cannot be obtained in the field. Examples of these coatings are the two and three part catalysed polyurethane coatings. Each component of these coatings must be sampled separately and submitted for laboratory analysis as a multi-part sample. The component mix ratio must be obtained from the facility at the time of sampling and submitted to the analytical laboratory. This will enable the laboratory to mix the components using the same proportions as in the actual coating operation prior to the analysis.
The coating should be thoroughly mixed before sampling. During operation of the coating application equipment, the coatings may be shaken technically or stirred with various agitators or circulation systems. Lacquers and other coatings containing highly volatile solvents should be agitated in closed containers to avoid evaporation. Water-thinned coatings tend to incorporate air bubbles if stirred too vigorously, so they should be stirred slowly. The risk of stratification or separation of components into a non-homogeneous mixture depends on the type of coating and is also directly proportional to the size of the reservoir being sampled. To

ensure that a representative sample is obtained, it is essential that it be taken during steady process operation and at the point of application to the web or substrate (or as close to it as possible).
Special plastic containers or glass sample bottles have been used for corrosive substances. If a plastic container is used it must be impermeable to diffusion through the walls of the plastic container. Sample containers, caps, and inner seal liners must be inert to the chemically reactive compounds in the sample and must therefore be selected on a special case-by case basis by the agency affected.

According to the standard procedure described in the document, only one sample is required for each coating to be characterized. The sample can be used in the analytical laboratory for a number of repeat analyses as required. One field replicate sample should be taken for every 10 samples collected. A minimum of one field replicate sample should be taken for each facility visit, even if less than 10 samples are taken. This provides a means to check the accuracy of the methods used. If a company requests a set of samples for its own analysis, an entirely separate set of samples should be taken concurrently using new sample containers. A fresh new sample should be taken if a repeat or follow-up sample is required for any reason.

3.2.2.4 Comparison

To have the sample as representative as possible it is necessary to meet the condition of having a liquid sample as homogeneous as possible. In practice there is no difficulty with sampling and obtaining a representative sample of uniform pure liquids. Liquid materials which are not homogeneous can introduce some practical differences. If the inhomogeneity is temporary and is removed after applying some mechanical effects (mixing, etcetera), then such material can be sampled in a usual way after its homogeneity is achieved. In case it is not practically possible, then samples should be taken from different parts (layers) of material. The latter approach can be used for instance in sampling paints. Additionally, mixed systems where liquid matrix consists of solid inclusion of possibly different sizes can introduce a challenge in obtaining a representative sample and demands special consideration. The sampling of the latter case can possibly partially be resolved by applying the same sampling methods as for solids in powdered form in paints (see ISO 15528), but generally it demands more careful consideration.

Subsection 3.2.2 covers the sampling procedures for testing of volatile solvents and chemical intermediates used in paints and related coatings and materials; sample preparation of petroleum and lubricant products for elemental analysis; practice for obtaining in-service samples of lubricating grease materials; sampling and chemical analysis for soap and soap products; sampling industrial chemicals (simple liquids, solids, slurries); sampling and testing pine oils. These materials or products are covered by ASTM standards.

ASTM D268 gives a guide for sampling and testing volatile solvents and chemical intermediates for use in paints and related coating and material. This guide covers procedures for the sampling and testing of volatile solvents used in the manufacture of paint, lacquer, varnish, and related products. Various test methods are listed within ASTM D268 standard. The question of sampling of materials that involve volatile compounds is also partially discusses in ISO 3170, in contest of sampling volatile crude oils and products: when sampling volatile crude oils and products, it is necessary to avoid the loss of material. A sample shall not be transferred from the original sample container. Transportation and storage of the sample should be done in an inverted position to avoid loss of light ends through the closure.

Test methods given in ASTM D802 standard cover procedures for sampling and testing pine oils: these methods are also applicable to both natural pine oils derived from pine stumps either by the steam and solvent process or by destructive distillation, and also to synthetic pine oils.
Sampling procedures for paints, varnishes and raw materials for paints and varnishes are described in details in ISO 15528.
Standard procedure for collection of coating and ink samples is given in technical report EPA 340/1-91-010.

3.3 Gaseous materials and products: natural gas/liquefied petroleum gas/flue gas/methane

3.3.1 International / European standards

ISO 13833: Stationary source emissions -- Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination
This standard specifies sampling methods and analysis methods for the determination of the ratio of biomass and fossil derived CO_2 in the CO_2 from exhaust gases of stationary sources, based on the radiocarbon (^{14}C isotope) method. The lower limit of application is a biogenic to total CO_2 fraction of 0.02. The working range is a biogenic to total CO_2 fraction of 2 – 100%. The measurement of the presence of the ^{14}C isotope in flue gas / stack gas enables the determination of the biogenic and fossil fractions of the CO_2 that is emitted.

The determination of the biogenic CO_2 fraction in flue gas/stack gas consists of:

(1) representative sampling of CO_2,
(2) the measurement of the sampled ^{14}C and
(3) the calculation of the biogenic CO_2 fraction in the stack gas emitted during the sampling period.

Procedures for collection of whole gas samples and absorption of CO_2 in liquid or solid alkaline media are given. The three ^{14}C determination procedures that can be used are described. The biogenic fraction is calculated using the measured ^{14}C value. From the calculated biogenic CO_2 fraction the emitted amount of biogenic and fossil CO_2 can be calculated. Sampling of CO_2 in stack gas is in principle not different from sampling of other acid gaseous substances like SO_2 or HCl. The CO_2 present in a representative stack gas sample is absorbed in an alkaline medium or transferred to a gas bag or lecture bottle and after sampling the collected CO_2 is prepared for ^{14}C analysis.

Standard equipment used for other gaseous components can be applied. As CO_2 is present in relative high concentrations compared to other acid gaseous substances, the capacity of the absorption media used must be considered, an excess of alkaline media must be used to ensure complete absorption during the sampling period. In case the stack gas is to be collected in a gas bag, canister or gas cylinder, accepted procedures for the collection of gas in gas bags, canisters or gas bottles shall be used. Only gas bags impenetrable for CO_2 shall be used. Most aluminum lined gas bags will comply.

When liquid or solid absorbers are used, the CO_2 is sequestrated in a medium containing alkaline reagents. For sampling with liquids, alkaline solutions of e.g. 2 - 4 M KOH or equivalent (NaOH) are suitable. For solid absorbers commercial products for the absorption of CO_2 are available. After collection of the sample, the absorbers shall be closed and stored gas-tight, in order to prevent adsorption of atmospheric CO_2.

The ^{14}C content of the collected samples can be determined using the following techniques: AMS (Accelerator Mass Spectrometer); BI (Beta Ionization measurement) (gas proportional counter); LSC (Liquid Scintillation Technique).Depending on the ^{14}C analysis technique different amounts of sampled CO_2 are required. For AMS measurements the minimum amount of CO_2 is 4 ml. For BI measurements 2 – 10 litre CO_2 is required. For LSC measurements the required amount of CO_2 depends on the way the sample is prepared for measurement, but at least a few gram will be required.

In order to be able to obtain the performance characteristics as given in this standard, the following requirements shall be met: mass flow controller should have accuracy at least 2% of reading; solid adsorber should contain more than 90% NaOH; capacity left after sampling should remain more than 25% of the total capacity of the adsorber.

ISO 10715: Natural gas – sampling guidelines

These guidelines cover sampling strategy, details of sampling methods and sampling equipment. This document also contains guidelines for sampling strategy, probe location and the handling and design of sampling equipment. It considers spot, composite (incremental) and continuous sampling equipment. A consideration to constituents like oxygen, hydrogen sulphide, air, nitrogen and carbon dioxide in the gas steam are given. Sampling of liquid steams and steams with multiphase flow are not included in the document.

The main function of sampling is to take an adequate sample that is representative of the gas. The main distinction in sampling is between direct and indirect sampling methods. In direct sampling method, the sample is drawn from a stream and directly transferred to the analytical unit. In the indirect sampling method, the sample is stored before it is transferred to the analytical unit. The main indirect sampling methods are spot sampling and incremental sampling. The information needed from the analysis of natural gas is divided into two basic categories: averaged (for example, calorific value) and limit values (like limits on composition).
Sampling frequency in the most cases is the matter of common sense. Information on the properties of the gas stream in the past and on expected (systematic) future changes determines the sampling frequency. Generally, pipeline gas composition can have daily, weekly, monthly, semi-annual and seasonal variations. Compositional variations also occur due to gas treatment equipment and reservoir changes. All these variations have to be considered when selecting a sampling interval. In this content, the required sampling frequency is the number of sample to be taken in a certain period of time in order to obtain meaningful results.
The number of samples can be calculated according to the formula:

$$\sqrt{N} = t \cdot s/d \qquad (3)$$

Where $\sqrt{N}$ is the square root of the number of samples,
s is the standard deviation,
d is the error margin required,
t is Student's factor.

This equation has to be solved by iterations: an initial value of t is estimated and used to calculate N, which in turn is used to calculate a new value of t. the error margin, the number of samples and the standard deviation shall be taken over the same period of time.

Equipment to sample shall be designed to meet relevant sampling conditions (pressure, temperature, resistance to corrosion, flow, chemical compatibility, vibration, thermal expansion)
When sampling and transporting a natural gas, all flammability precautions and personal protective measures should be guaranteed.
A method for sampling turbulent flow and two-phase flow is described within the standard as well.

ISO 10396: Stationary source emissions — Sampling for the automated determination of gas emission concentrations for permanently-installed monitoring systems

This standard specifies procedures and equipment that permits up to certain limits representative sampling for the automated determination of gas concentration of effluent gas streams. The application is limited to the determination of oxygen, carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen monoxide, nitrogen dioxide or the sum of nitrogen monoxide and dioxide as nitrogen oxides.

CEN/TS 15439: Biomass gasification. Tar and particles in product gases. Sampling and analysis

This European Technical Specification gives methods for sampling and analysis of tars and particles in order to determine the load of these contaminants in flowing biomass gasification product gases. The Technical Specification is applicable to sampling and analysis of tars and particles in the concentration range typically from 1 mg/m_n^3 to 300 g/m_n^3 (tars) and from 20 mg/m_n^3 to 30 g/m_n^3 (particles) at all relevant sampling point conditions (0°C to 900°C and 60 kPa to 6000 kPa). Particle concentrations lower than 20 mg/m_n^3 are outside the scope of this Technical Specification and can be measured according to EN 13284-1. Application of this Technical Specification allows determination of concentration of gravimetric tar in mg/m_n^3 and concentration of individual organic compounds in mg/m_n^3.

This Technical Specification gives data on repeatability and reproducibility for the compounds listed in Annex B. The Technical Specification is also applicable for other organic compounds (e.g. those mentioned in Annex A), but repeatability and reproducibility have not been assessed for compounds other than those in Annex B.

3.3.2 American standards

ASTM D7459*: Standard practice for collection of integrated samples for the specification of biomass(biogenic) and fossil-derived carbon dioxide emitted from stationary emission sources.

*Remark: *ISO 13833 mentioned in 3.3.1 also covers the procedure for the determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide via Radiocarbon sampling method. ISO 13833 is the dominant standard.*

Greenhouse gases are reported to be a major contributor to global warming. Since "biomass CO_2" emitted from combustion devices represents a net-zero carbon contribution to the atmosphere (that is, plants remove CO_2 from the atmosphere and subsequent combustion returns it), it does not contribute additional CO_2 to the atmosphere. The measurement of biomass (biogenic) CO_2 allows regulators and stationary source owners/operators to determine the ratio of fossil-derived CO_2 and biomass CO_2 in developing control strategies and to meet federal, state, local and regional greenhouse gas reporting requirements. The distinction of the two types of CO_2, biogenic and fossil-derived, has financial, control and regulatory implications.
This practice defines specific procedures for the collection of gas samples from stationary emission sources for subsequent laboratory determination of the ratio of biomass (biogenic) carbon to total carbon (fossil derived carbon plus biomass or biogenic carbon) in accordance with ASTM D6866. This practice applies to stationary sources that burn municipal solid waste or a combination of fossil fuel (for example, coal, oil, natural gas) and biomass fuel (for example, wood, wood waste, paper, agricultural waste, biogas) in boilers, combustion turbines, incinerators, kilns, internal combustion engines and other combustion devices. This practice applies to the collection of integrated samples over periods from 1 hour to 24 hours, or longer. Representative gas samples are collected at a constant rate from stationary emission sources into portable containers for shipment to off-site analytical facilities performing ASTM D6866 analysis. Equipment to use and how to describe a sampling procedure, how to record a sampling flow and how to perform a quality control in described within the Practice.

Special limitations are mentioned to the sampling devices and for the amount of pure CO_2 in the subsample: the capacity of the sample container must be large enough to contain at least 2 cm^3 of CO_2 (sample container capacity (litres) x $\%CO_2$ x 10 >= 2 cm^3) at the end of the sampling period. If sub-samples are used for shipment to the laboratory, then determine the size of the sub-sample container such that it will contain at least 2 cm^3 of pure CO_2.
During the sampling period, the date and time, the sample flow rate (including temperature and pressure), should be recorded accordingly to the following frequencies:

For sampling time which equals or is longer than 6 hours the recording should be done every hours: for 3, 4, or 5 hours sampling time the recording should be done every 30 minutes; for 2 hours sampling time — every 20 minutes and for 1 hour sampling time - every 10 minutes.

ASTM D5503: Standard practice for natural gas sample-handling and conditioning systems for pipeline instrumentation

A well-designed sample-handling and conditioning system is essential to the accuracy and reliability of pipeline instruments. Approximately 70% of the problems encountered are associated with the sampling system. This practice covers sample-handling and conditioning systems for typical pipeline monitoring instrumentation (gas chromatographs, moisture analysers, and so forth). The selection of the sample-handling and conditioning system depends upon the operating conditions and stream composition. This practice is intended for single-phase mixtures that vary in composition. A representative sample cannot be obtained from a two-phase stream.

ASTM D1265: Standard practice for sampling liquefied petroleum gases. Manual method
Samples of liquefied petroleum gases are examined by various test methods to determine physical and chemical characteristics and conformance with specifications. Equipment described by this practice may be suitable for transportation of liquefied petroleum samples, subject to applicable transportation regulations.

This practice covers equipment and procedures for obtaining a representative sample of specification liquefied petroleum gas, such as specified in Specification ASTM D1835 and comparable international standards. This practice is suitable for obtaining representative samples for all routine tests for liquefied petroleum gases required by Specification ASTM D1835. In the event of a dispute involving sample integrity when sampling for testing against Specification ASTM D1835 requirements, Practice ASTM D3700 shall be used as the referee sampling procedure. Practice ASTM D3700 describes a recommended practice for obtaining a representative sample of a light hydrocarbon fluid and the subsequent preparation of that sample for laboratory analysis when dissolved gases are present. Use of Practice ASTM D1265 will result in a small but predictable low bias for dissolved gases due to the liquid venting procedure to establish the 20% minimum ullage.

This practice may also be used for other natural gas liquid products that are normally single phase (natural gas liquid mix, field butane, etc.), defined in other industry specifications or contractual agreements. It is not intended for non-specification products that contain significant quantities of un-dissolved gases (N_2, CO_2), free water or other separated phases, such as raw or unprocessed gas/liquids mixtures and related materials. The same equipment can be used for these purposes, but additional precautions are generally needed to obtain representative samples of multiphase products (see Practice ASTM D3700).

Recommendations for the location of a sample point in a line or vessel are also included in the Practice. It is the responsibility of the user to ensure that the sampling point is located so as to obtain a representative sample.

3.3.3 Other standards

JIS K0095 (Japanese): Method for sampling of flue gas
This Japanese Industrial Standard specifies methods for absorbing and non-absorbing sampling of flue gas to analyse specific gaseous components exhausted into flues, chimneys and ducts. This standard has been prepared based on the first edition of ISO 10396 standard published in 1993. Some items and contents are added while some parts are not adopted.
Items and contents that are added are listed here: components of target gas; flue gas sampling hole; equipment (fitting metal, catching part, air-liquid separating part, safety trap, vacuum gauge, sampling gas distributing tube and collecting tube); sampling for chemical analysis (manual measurement).

Items and contents that are not adopted are listed here too: normative references; collecting particle size of primary filtering material; heat resisting temperature of some materials; collecting particle size of secondary filtering material, operation temperature of suction pump; sample gas piping to analyser; calibration method; advance check of concentration; flow speed and temperature of gas and apparatus for non-absorbing collecting method.

AFS (American Foundry Society) report 2007: Sampling and measurement of methane from metal foundry process emissions.

Chemically, CH_4 is considered a volatile organic compound, but is excluded from this category in the Code of Federal Regulations (40 CFR 51.100(s)) by definition. The regulatory definition states that volatile organic compounds (VOC) are any compound of carbon excluding certain compounds such as carbon monoxide (CO) and CO_2, which may participate in atmospheric photochemical reactions, or other such organic compounds such as CH_4 and C_2H_6, which have been determined to have negligible photochemical reactivity.

Methane is a permanent and low molecular weight gas. Compared with other straight chain hydrocarbons (alkanes), CH_4 has an unusually high carbon-hydrogen (C-H) bond strength, which means that it is normally the least reactive alkane in reactions. Because of its low mass and non-reactivity, the simplest sampling and measurement techniques are limited to the gas phase.

The report mentioned here is written to document the methodology for sampling and measurement of methane (CH_4) emitted from metal casting operations. The determination of methane is of interest to stationary sources for compliance with VOC permitting limits. Since methane is not considered a VOC by regulatory definition, subtraction of this compound from stack gas emissions ensures that only non-methane hydrocarbons are reported. While not regulated as VOCs, methane and other non-photo chemically reactive compounds may also need to be estimated for certain modelling inventories or to meet certain state inventory requirements.

ESML Analytical (USA): Methane. Sampling guide

This document lists three methods whose can be used for sampling methane.

In Tedlar bag sampling, a sample is collected in a 1literTedlar bag using Tedlar bag pump. The Tedlar bag fills 1-3 minutes using the standards sampling kit.

In canister sampling, a time-integrated sample can be taken using a SUMMA-type evacuated canister and a pre-calibrated flow controller o regulator. Typical sampling durations are 1 hour, 2 hours, 8 hours and 24 hours.

In mini-canister sampling, a mini-canister (400 ml) can be used to take a grab sample to determine methane concentration. Methane is analysed by ASTM D1946 using gas chromatography/flame ionization detection.

Detection limit are typically 5 ppm for the Tedlar and 10 ppm for the canister and mini-canister.

3.3.4 Comparison

Among ISO standards, ISO 13833 and ISO 10715 are applicable for sampling of natural gas and for the determination of the ratio of biomass (biogenic) and fossil-derived carbon dioxide. Both ISO 13833 (Stationary source emissions - Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination) and ASTM D7459

(Standard practice for collection of integrated samples for the specification of biomass(biogenic) and fossil-derived carbon dioxide emitted from stationary emission sources) are devoted to the same problem of sampling collection to specify the biogenic or fossil-derived content of carbon dioxide.

As it is mentioned in ASTM D7459, the final sample must contain at least 2 cm^3 of pure CO_2. In this Practice, there is a requirement that the capacity of the sample container must be large enough to contain at least 2 cm^3 of CO_2 (sample container capacity (litres) x %CO_2 x 10 >= 2 cm^3) at the end of the sampling period. ISO 13833 distinguishes between three different ^{14}C analysis techniques, and depending on the technique, different amount of sampled CO_2 is needed.

3.4 Conclusions

In Section 3, the main sampling standards that can be used or referred to when sampling of some specific classes of solid materials are mentioned. The main purpose of sample preparation is that a sample is reduced to one or more test portions that are in general smaller than the original sample. The main principle for sample reduction is that the composition of the sample as taken on site shall not be changed during each stage of the sample preparation. Each sub sample shall be representative of the original sample. To reach this goal every particle in the sample before sample division shall have an equal probability of being included in the sub-sample following sample division.

Both ISO 13833 and ASTM D7459 give some sampling guides and cover determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide using radiocarbon sampling and analysis. For the conversion of the carbon present in solids, liquid and/or gaseous samples to a suitable sample for ^{14}C determination the standard test method ASTM D6866 can be applied. This method is applicable to any product containing carbon-based components that can be combusted in the presence of oxygen to produce CO_2 gas. The overall analytical method is also applicable to gaseous samples, including flue gases from electrical utility boilers and waste incinerators.

Solid materials in most cases introduce no practical difficulties in obtaining a representative sample. Usually combustion method and CO_2 trapping is used to sample CO_2 and to determine the carbon content subsequently. However, practical difficulties can occur when sampling materials that are partially combustion resistant and therefore cannot be combusted completely (ceramics for example), or materials containing volatile components. Such materials are quite peculiar due to their inhomogeneity which cannot be removed by simple mechanical effects (crushing, shaking, centrifuging, mixing, etc) and determination of their CO_2 and then the carbon content demands a different approach which sometimes is not given in the standards. Then a method of sampling and testing has to be developed first on a laboratory scale.

When sampling, all liquids should be either single phase or relatively homogeneous. The homogeneity in many cases can be achieved by stirring of a sample. Another approach is to separate the clear liquid and the sediment by centrifuging and then to examine them separately. In case of viscous liquids or materials with volatile components the transfer problems exaggerate weighing problems. Effort should be made to obtain the sample weight in the combustion tube, rather than transferring a previously weighed sample to the oxidation tube.

Generally, independently of solid, liquid or gaseous state of a material or product to sample, attention should be paid to representativeness of a sample, its required minimal size, its homogeneity and pre-treatment procedure. The latter is discussed in the next section of this document.

4 (Pre-)Treatment and Chemical Analysis

The key issue in sample pre-treatment is that there is no universal method which can be applied to all types of materials. Following the scope of the project, we focus on the pre-treatment of different kinds of materials and products which is aimed to convert all available carbon for further analysis of the ^{14}C content. Each sample submitted for the ^{14}C analysis has its own specific preparation history. The variety of samples is reflected in the variety and complexity of pre-treatment procedures that for some particular materials are laid down in separate International, European or American standards.

The standards listed below cover pre-treatment methods and procedures for some selected materials or products. This section is divided into three subsections representing standards on pre-treatment and chemical analysis for three classes of materials or products: solid materials and products, liquid material and products, gaseous materials and products. Generally, if there is no existing standard for some specific solid, liquid or gaseous material for its pre-treatment, it can be pre-treated accordingly to ASTM D6866.

In this chapter, we also list known standardized methods and pre-treatment procedures for general chemical analysis of some solid, liquid or gaseous materials. Although such methods do not describe the conversion of carbon into carbon dioxide, they might be helpful and provide the scheme for sample pre-treatment in general.

4.1 Solid materials and products

This subsection lists European, American and other standards that can be used for sample pre-treatment of some specific materials or products which can be classified as “Solid materials and products”. The solid materials and products mentioned in this subsection comprise of

- biomass (wood based materials)
- solid recovered fuels
- organic-based materials
- ceramics
- inorganic materials (textiles, natural and synthetic rubber, polymer matrix composite materials, paper)

4.1.1 Biomass

4.1.1.1 International / European standards

EN 15104: Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods

Instrumental methods for the analysis of carbon, hydrogen and nitrogen are now widespread and in regular use, often in preference to formerly developed chemical methods for which international standards exist.

The reliable determination of carbon, hydrogen and nitrogen is important for quality control and the results can be used as input parameters for calculations applied to the combustion of solid biofuels. The environmental importance of the nitrogen content is linked to emissions of NO_x (formation of fuel NO_x). Hydrogen content is important for calculation of the net calorific value. Carbon content is required for the determination of CO_2-emissions.

A known mass of sample is burnt in oxygen, or in an oxygen /carrier gas mixture, under conditions such that it is converted into ash and gaseous products of combustion. These consist mainly of carbon dioxide, water vapour, nitrogen and/or oxides of nitrogen, oxides and oxyacids of sulphur and hydrogen halides. The products of combustion are treated to ensure that any hydrogen associated with sulphur or halides products of combustion are liberated as water vapour. Oxides of nitrogen are reduced to nitrogen, and those products of combustion which would interfere with the subsequent gas-analysis procedures are removed. The carbon dioxide, water vapour and nitrogen mass fractions of the gas stream are then determined quantitatively by appropriate instrumental gas- analysis procedures.

EN 15289: Solid biofuels — Determination of total content of sulphur and chlorine.

Sulphur and halogens (fluorine, chlorine, bromine and iodine) may be found in materials in various forms. During the combustion of these materials, corrosive and harmful compounds may be released. The determination of sulphur and halogens by oxygen combustion may be used to assess the suitability of waste for incineration.

4.1.1.2 American standards

ASTM E1757: Standard practice for preparation of biomass for compositional analysis

There are three methods for preparation of biomass for compositional analysis mentioned in the standard and referred to as methods A, B and C.

Preparation Method A is suitable for the preparation of large quantities (>20 g) of field collected samples into a form appropriate for compositional analysis. Woody samples must first be available as chips of a nominal 5 cm by 5 cm by 0.6 cm or less and twigs not exceeding 0.6 cm diameter. Herbaceous materials may be processed as whole straw. It is recommended that wastepaper should be shredded into pieces less than 1 cm wide. Furthermore, it is recommended that twigs, straw and wastepaper should not exceed 61 cm (24 in.) in length to facilitate handling.

Preparation Methods B and C are suitable for very moist feed stocks, samples that would not be stable during prolonged exposure to ambient conditions, or for drying materials when room conditions deviate from the ambient conditions described in 3.1.1. These test methods are also suitable for handling small samples of biomass (<20 g). The drying step is done in a convection oven at 45°C (Test Method B) or by lyophilization (Test Method C).

This practice is not intended for materials that will already pass through a 20 mesh sieve or cannot be dried by the described methods to a total solids content of greater than 85%, based on an oven dried weight. This practice will separate the milled material into two fractions, a −20/+80 mesh fraction and a −80 mesh fraction. Extraneous inorganic materials will accumulate in the -80 mesh fraction and it should be analysed independently from the -20/+80 mesh fraction. Weighted results from the two fractions can then be combined to obtain results for materials on an "as received" basis. It is noted in the standard that during analysis, the very fine consistency of the -80 mesh fraction may cause problems in filtering operations and should be handled appropriately.

This practice covers a reproducible way to convert hardwoods, softwoods, herbaceous materials (such as switch grass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), feed stocks pre-treated to improve suitability for fermentation and fermentation residues into a uniform material suitable for compositional analysis. During pre-treatment, milling and sieving actions both produce large amounts of dust. This dust can be a nuisance hazard and irritant. Therefore an appropriate respiratory protection as needed and dust control measures are needed.

ASTM E1755: Standard test method for ash in biomass
The ash content is an approximate measure of the mineral content and other inorganic matter in biomass. The ash content is used in conjunction with other assays to determine the total composition of biomass samples.
This test method covers the determination of ash, expressed as the mass per cent of residue remaining after dry oxidation (oxidation at 575 ± 25°C), of hard and soft woods, herbaceous materials (such as switch grass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), acid and alkaline pre-treated biomass, and the solid fraction of fermentation residues. All results are reported relative to the 105°C oven-dried mass of the sample. For particulate wood fuels, Test Method E 1534 should be used.

ASTM D1762: Standard test methods for chemical analysis of wood charcoal
Low quality wood and wood residues are used for wood charcoal. This test method is used for evaluating the charcoal to assess the methods of production and assist in developing new methods. This test method covers the determination of moisture, volatile matter, and ash in charcoal made from wood. The test method is applicable to lumps and briquettes and is designed for the evaluation of charcoal quality. The test method employs apparatus that is found in most laboratories and is adapted to routine analyses of a large number of samples.

4.1.1.3 Other standards

Not found.

4.1.1.4 Comparison

Instrumental methods for the determination of carbon, hydrogen, nitrogen, for the total content of sulphur and chlorine are covered by European norms EN 15104 and EN 15289. Both standards refer to the combustion of a known mass of a sample for further analysis on carbon, hydrogen, nitrogen, sulphur or chlorine content. American ASTM E1757 standard describes standard practice for preparation of biomass for compositional analysis and distinguishes between three different methods depending on sample size. This practice covers such materials as hardwoods, softwoods, herbaceous materials, agricultural residues, wastepaper and describes a reproducible way to convert them into a uniform material suitable for compositional analysis. Additionally, standard test methods for chemical analysis of wood charcoal are given in ASTM D1762 and standards test method to analyse ash in biomass is described in ASTM E1755.

4.1.2 Solid recovered fuels

4.1.2.1 International / European standards

For analysis of solid recovered fuels (SRF) the below mentioned standards shall be used:
- EN 15400: Solid recovered fuels – Determination of the calorific value.
- EN 15403: Solid recovered fuels – Determination of ash content.
- EN 15440: Solid recovered fuels – Method for the determination of biomass content.
- EN 15443: Solid recovered fuels – Methods for the preparation of the laboratory samples.

EN 15400 specifies a method for the determination of the calorific value in solid recovered fuel. A weighed portion of the analysis sample of the solid recovered fuels is burned in high-pressure oxygen in a bomb calorimeter under specified conditions.

EN 15440 specifies the methods for the determination of biomass content in solid recovered fuels. This standard specifies three normative methods for the determination of the biomass fraction in solid recovered fuel, and when to use each method. Sampling, transport, storage of the solid recovered fuel and sample preparation in the field shall be conducted according to EN 15442 (Solid recovered fuels – Methods for sampling) and EN 15443 described in the previous section 3. Preparation of the test sample shall be conducted according to EN 15413 (Solid recovered fuels. Methods for the preparation of the test sample from the laboratory sample)

In EN 15440, there are three methods mentioned for the determination of biomass content:
1) the determination of the biomass content based on the selective dissolution method (SDM) (described in Annex A of the standard). The determination of the biomass content is based on the property of biomass that it can be dissolved in a sulphuric acid / hydrogen peroxide mixture;
2) the determination of the biomass content based on the manual sorting method (MS). The manual sorting method is based on the separation of different fractions by visual inspection. This method is suitable for samples with a particle size > 10mm (the method is described in Annex B of the standard);
3) the determination of the biomass content based on the ^{14}C method. The determination of the biomass content using the ^{14}C method is based on the well-established analytical procedures that are used for the determination of the age of carbon containing objects. This method is suitable for samples of all types of fuel.

The influence of the physical shape and composition of materials/particles affects the manual sorting method, because it is based on differences in the physical appearance and properties of biomass or non-biomass materials. Three sources of error exist that affect the performance of the manual sorting method. These sources of error are:
1) the potential presence of mixed materials that are not feasible to separate manually. These mixed materials are particles which are made of both biomass and non-biomass indistinguishably connected together;
2) minimum particle size, below which effective manual separation is impossible without using a microscope;
3) the presence of materials which mimic the physical appearance or properties of the complementary material class, such as biodegradable plastics.

The quantitative implications of these sources of error are difficult to predict and therefore the selective dissolution method prevails as the main sorting method.

4.1.2.2 American standards

Not found.

4.1.2.3 Other standards

Not found.

4.1.2.4 Comparison

In this subsection, our focus is made on solid recovered fuels and methods for their preparation, determination of the calorific value and for determination of the biobased content. These items are covered by corresponding European norms: EN 15400 specifies a method for the determination of the calorific value, EN 15440 describes the method for the determination of biomass content. Methods for the preparation of the laboratory samples are covered by EN 15443. Methods for the preparation of the test sample from the laboratory sample are mentioned in EN 15413.
No American or other standards were found.

4.1.3 Organic based materials

4.1.3.1 International / European standards

CEN/TS 16137: Plastics – Determination of bio-based carbon content.
This Technical Specification specifies the calculation method for the determination of bio-based carbon content in monomers, polymers, plastics materials and products using the ^{14}C method. This calculation method is based on the well-established analytical test methods used for the determination of the age of objects containing carbon and is applicable to monomers, polymers and plastic materials and products and to any polymers containing organic carbon, including bio-composites.

The document also specifies three test methods to be used for the determination of the ^{14}C content from which the biobased carbon content is calculated: Liquid scintillation-counter method (LSC); Beta-Ionisation (BI); Accelerator mass spectrometry (AMS).

ISO 1928: Solid mineral fuels – Determination of gross calorific value by the bomb calorimetric method.
This standard specifies a method for the determination of the gross calorific value of a solid mineral fuel at constant volume and at the reference temperature of 25°C in a bomb calorimeter calibrated by combustion of certified benzoic acid. The result is the gross calorific value of the analysis sample at constant volume with all the water of the combustion products as liquid water. In practice, fuel is burned at constant (atmospheric) pressure and the water is not condensed but is removed as vapour with the flue gases. Under these conditions, the operative

heat of combustion is the net calorific value of the fuel at constant pressure. The net calorific value at constant volume can also be used; equations are given for calculating both values.

General principles and procedures for the calibrations and the fuel tests are presented in the main text, whereas those pertaining to the use of a particular type of calorimetric instrument are described in annexes. Checklists for performing calibration and fuel tests using specified types of calorimeters and examples illustrating some of the calculations are also given.

4.1.3.2 American standards

Not found.

4.1.3.3 Other standards

Not found.

4.1.3.4 Comparison

Analysis of solid mineral fuels to determine gross calorific value can be done the bomb calorimetric method, as it is mentioned in ISO 1928 standard in this subsection. Gross calorific value is determined at constant volume and at the reference temperature of 25°C in a bomb calorimeter calibrated by combustion of certified reference material (benzoic acid). No similar American or other standards were found on this specific item.

Technical Specification CEN/TS 16137 is widely used for the determination of bio-based carbon content in plastics. The documents list three test methods to determine ^{14}C content, namely liquid scintillation-counter method; beta-ionisation; accelerator mass spectrometry. No analogous standard specifically on plastics was found among American standards; however American ASTM D6866 is applicable to any product containing carbon-based components that are combustible. CEN/TS 16137 refers to the same methods as ASTM D6866.

4.1.4 Ceramics

4.1.4.1 International / European standards

ISO 21068: Chemical analysis of silicon carbide containing raw materials and refractory products. Part 1: general information and sample preparation. Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon

Here, the second part of ISO 21068 is referred to. This part of ISO 21068 is applicable to the analysis of all refractory products classified in ISO 10081 [2] to [5] (shaped) and ISO 1927 [1] (unshaped) and raw materials containing carbon and/or silicon carbide.

This part covers the full range of analysis from pure silicon carbide to oxidic refractory composition with a low content of silicon carbide and/or nitrides. Primarily, this part of ISO 21068 provides methods to distinguish between different carbon-bound types like total carbon (C_{total}) and free carbon (C_{free}) and derives from these two the silicon carbide content.

The method for chemical analysis of SiO_2, total Si, oxygen and nitrogen and other oxidic-bound metals which typically occur in the materials is also described within the standard. This part of ISO 21068 represents a listing of analytical methods which is approximately structured according to material composition, however, it is still the user who should prove the applicability of the method, depending on the material and analytical requirements.

The total carbon content can be determined by the following combustion methods and detection techniques:

- Combustion method using:
  - resistance furnace
    - in oxygen and lead borate as decomposing agent
    - in oxygen and tin powder as decomposing agent
  - induction furnace
    - in oxygen and metallic powder as decomposing agent

- By detection method using:
  - coulometry
  - gravimetry
    - using resistance furnace
    - using high-frequency induction furnace
  - conductometry
    - infrared absorption method and resistance furnace combustion
    - thermal conductivity method and induction furnace combustion

<u>Combustion and detection techniques and reagents to use are described below:</u>

- Resistance furnace in oxygen and lead borate as decomposing agent.
  Principle
  The sample is heated together with lead borate in a stream of oxygen in a resistance tube furnace to convert the carbon to carbon dioxide by combustion. The combustion gases are conducted through a tube containing percarbamide to absorb the oxidation products of the sulphur contained in the sample. The carbon dioxide is absorbed in an alkaline medium.

- Resistance furnace in oxygen and tin powder as decomposing agent
  Principle
  The sample is burned with accelerator in an oxygen atmosphere inside a resistance heating furnace and the yielded carbon dioxide is collected in an alkaline medium.

- Induction furnace (IF) in oxygen and metallic powder as decomposing agent
  Principle
  The sample is heated together with a base metal additive in a stream of oxygen using a high-frequency induction furnace. The carbon dioxide gas formed shall be collected in a 4M sodium hydroxide solution.

4.1.4.2 American standards

Not found.

4.1.4.3 Other standards

Not found.

4.1.4.4 Comparison

ISO 21068 standardizes the methods and procedures for chemical analysis of silicon carbide containing raw materials and refractory products. Part 1 of this standard gives general information and guides for sample preparation. Part 2, that is described in the given subsection, covers the determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon. These methods and procedures can applicable to the analysis of all refractory products classified in ISO 10081 [parts 2-5] (shaped) and ISO 1927 [part 1] (unshaped) and raw materials containing carbon and/or silicon carbide.
Among American standards, ASTM D6866 is applicable to any product containing carbon-based components that are combustible, but no analogous American or other standards were found specifically on ceramics, except ISO 21068.

4.1.5 Inorganic materials: textiles / rubber / composite materials / paper

4.1.5.1 International / European standards

ISO 1833: Textiles – Quantitative chemical analysis
In general, the methods described in the different parts of ISO 1833 are based on the selective solution of an individual component. After the removal of a component, the insoluble residue is weighed, and the proportion of soluble component is calculated from the loss in mass. This part of ISO 1833 gives the information which is common to the analyses, by this method, of all fibre mixtures, independently of their composition. This information should be used in conjunction with the other parts of ISO 1833; these parts contain the detailed procedures applicable to particular fibre mixtures.

Mixtures of fibres during processing and, to a lesser extent, finished textiles may contain fats, waxes or dressings, either occurring naturally or added to facilitate processing. Salts and other water-soluble matter may also be present. Some or all of these substances would be removed during analysis, and calculated as the soluble-fibre component. To avoid this error, non-fibrous matter should be removed before analysis. A method of pre-treatment for removing oils, fats, waxes and water-soluble matter is given in Annex A of part 1 of this standard.

In addition, textiles may contain resins or other matter added to bond the fibres together or to confer special properties, such as water-repellence or crease-resistance. Such matter, including dyestuffs in exceptional cases, may interfere with the action of the reagent on the soluble component and/or it may be partially or completely removed by the reagent. This type of added matter may also cause errors and should be removed before the sample is analysed. If it is impossible to remove such added matter, the methods of analysis are no longer applicable. Dye in dyed fibres is considered to be an integral part of the fibre and is not removed.

Most textile fibres contain water, the amount depending on the type of fibre and on the relative humidity of the surrounding air. Analyses are conducted on the basis of dry mass, and a procedure for determining the dry mass of test specimens and residues is given in this part of the standard. The result is therefore obtained on the basis of clean, dry fibres.
If it is practicable to separate the components manually (the method described in Annex B of ISO 1833 should be used in preference to the chemical methods of analysis given in the individual parts of the standard).

After the identification of the components of a mixture, one component is removed, usually by selective solution, the insoluble residue is weighed, and the proportions of soluble component are calculated from the loss in mass. Where relevant, the fibre in the larger proportion is removed first.

Only analytical grade reagents or recognized reagents should be used, like light petroleum, re-distilled, distilling between 40°C and 60°C or distilled or deionized water. Requirements for the apparatus are also given in the standard. Because dry masses are determined, it is unnecessary to condition the specimen. The analysis is carried out under ordinary room conditions.

A laboratory test sample shall be taken as described ISO 5089. The sample must be representative of the laboratory bulk sample and sufficient to provide all the specimens, each of at least 1 g, that are required. Fabrics may contain yarns of different composition and account should be taken of this fact in the sampling of the fabric.
Pre-treatment should be done in the following way: the air-dry sample should be extracted in a Soxhlet apparatus with light petroleum for 1 h at a minimum rate of six cycles per hour. The light petroleum should be let to evaporate from the sample. Then the specimen should be soaked in cold water for 1 h, and then in water at (65 ± 5)°C for a further 1 h. In both cases, a liquor/specimen ratio of 100/1 shall be used and the liquor should be agitated from time to time. Then the excess water has to be removed from the sample by squeezing, suction, or centrifuging and then allow the sample to become air-dry. Where non-fibrous matter cannot be extracted with light petroleum and water, it shall be removed by a suitable method that does not substantially alter any of the fibre constituents. However, for some unbleached, natural vegetable fibres (for example, jute, coir), it has to be noted that normal pre-treatment with light petroleum and water does not remove all the natural non-fibrous substances; nevertheless, additional pre-treatment is not applied unless the sample contains finishes which are insoluble in both light petroleum and water.
Drying, cooling and weighting of the sample should be done as is described in details in the standard.

4.1.5.2 American standards

ASTM D629: Standard test method for quantitative analysis of textiles

This standard may be used for acceptance testing of commercial shipments but caution is advised since information on between-laboratory precision is lacking. In case of a dispute arising from differences in reported test results using Test Methods D 629 for acceptance testing of commercial shipments, the purchaser and the supplier should conduct comparative tests to determine if there is a statistical bias between their laboratories. Competent statistical assistance is recommended for the investigation of bias. As a minimum, the two parties should take a group of test specimens which are as homogeneous as possible and which are from a lot of material of the type in question. The test specimen should then be randomly assigned in equal numbers to each laboratory for testing. The average results from the two laboratories should be compared using Student's t-test and an acceptable probability level chosen by the two parties before the testing began. If a bias is found, either its cause must be found and corrected or the purchaser and supplier must agree to interpret future test results in the light of the known bias.

The effects of the various reagents used in the chemical methods on the residual fibres in a blend depend upon the history of the fibres and, unless otherwise stated, are generally too small or too uncertain to warrant the application of correction factors.

Fibre composition is generally expressed either on the oven-dry mass of the original sample or the oven-dry mass of the clean fibre after the removal of non-fibrous materials. If non-fibrous materials are not first removed from the textile before the fibre analysis is carried out, or if the treatments described in Section 8 are incapable of removing them, any such materials present will increase the percentage of the fibre constituent with which they are removed during the analysis, assuming they are soluble in the solvent used.

The analytical methods are intended primarily for the separation of binary mixtures of fibres. These procedures may also be used for the analysis of mixtures containing more than two types of fibres by selecting the best combination of methods to use. Since a sequence of solvents on a given fibre may produce different results than the expected results from a single solvent, it is advisable to determine the results of such sequential effects when testing multiple fibre blends. It is sometimes more convenient to separate mechanically the yarns in a textile which are of similar types, and then use the appropriate chemical method to analyse each of the components. The solubilities of the various fibres in different chemical reagents is listed in ASTM D629.

These test methods cover procedures for the determination of the fibre blend composition, also for mixtures of fibres. Procedures for quantitative estimation of the amount of moisture and certain non-fibrous materials in textiles are also described, for use in the analysis of mixtures, but these are not the primary methods for the determination of moisture content for commercial weights.

ASTM D4762: Standard guide for testing polymer matrix composite materials

This guide summarizes the application of ASTM standard test methods (and other supporting standards) to continuous-fibre reinforced polymer matrix composite materials. The most commonly used or most applicable ASTM standards are included, emphasizing use of standards of Committee D30 on Composite Materials. This guide does not cover all possible standards that could apply to polymer matrix composites and restricts discussion to the documented scope. Commonly used but non-standard industry extensions of test method scopes, such as application of static test methods to fatigue testing, are not discussed. A more complete summary of general composite testing standards, including non-ASTM test methods, is included in the Composite Materials Handbook (MIL-HDBK-17). Additional specific recommendations for testing textile (fabric, braided) composites are contained in Guide D6856.

ASTM D6370: Standard test method for rubber compositional analysis by thermogravimetry (TGA)

This test method is intended for use in quality control, material screening, and related problem solving where a compositional analysis or comparison to a known material is desired. The parameters described are guidelines and may be altered to suit the analysis of other rubber compounds. This test method is not suitable for rubber compounds containing filler materials which decompose in the temperature range of 50 to 800°C, for example, $CaCO_3$, $Al(OH)_3(3H_2O)$, etc. Analysis of compounds containing fillers of this type requires knowledge of the filler type and some correction for mass loss. This test method provides a thermogravimetric analysis (TGA) technique to determine the amounts of organics (oil, polymer), carbon black and ash (filler) in a rubber compound. The amount of plasticizer/oil may be determined separately using Test Method D 297. This test method utilizes previously calibrated, manual or computer assisted TGA instrumentation.

ASTM D4678: Standard practice for rubber preparation, testing, acceptance documentation and use of reference materials

This practice and the IRM program described here are being developed to replace a standardization program conducted by the National Institute of Standards and Technology (NIST) that was begun in 1948 and is being phased out. The standard materials developed by the NIST program are referred to as Standard Reference Materials or SRM.

This practice covers materials used on an industry-wide basis as reference materials, which are vitally important to conduct product, specification, and development testing in the rubber and carbon black industry. This practice describes the steps necessary to ensure that any candidate material, that has a perceived need, can become a Reference Material. The practice sets forth the recommendations on the preparation steps for these materials, on the testing that shall be conducted to permit acceptance of any candidate material, and on how the documentation needed for the acceptance shall be recorded for future use and review.

Reference materials are vitally important in product and specification testing, in research and development work, in technical service work, and in quality control operations in the rubber and carbon black industries. They are especially valuable for referee purposes.

Reference materials are divided into two categories: Industry Reference Materials (IRM) — Materials that have been prepared according to a specified production process to generate a uniform lot; the parameters that define the quality of the lot are evaluated by a specified measurement program.
Common-Source Reference Materials (CRM) — materials that have been prepared to be as uniform as possible but do not have established property (parameter) values; the knowledge of a common or single source is sufficient for certain less critical applications.

ASTM D297: Standard test methods for rubber-products chemical analysis

These test methods cover the qualitative and quantitative analyses of the composition of natural and synthetic crude rubbers. These methods are divided into general and specific test methods. General test methods shall be performed to determine the amount and type of some or all of the major constituents of a rubber product, and shall include determination of rubber polymer content by the indirect method, determination of density, and extract, sulphur, fillers, and ash analyses. Specific test methods, on the other hand, shall be performed to determine specific rubber polymers present in a rubber product such as crude, un-vulcanized, reclaimed, and vulcanized rubbers. These test methods cover the qualitative and quantitative analysis of the composition of rubber products of the "R" family. Many of these test methods may be applied to the analysis of natural and synthetic crude rubbers. Part A of the standard consists of general test methods for use in the determination of some or all of the major constituents of a rubber product. Part B covers the determination of specific polymers present in a rubber product.

ASTM D1278: Test methods for rubber from natural sources – chemical analysis

These test methods are intended for quality control acceptance of natural rubber and may be used for referee purposes. These test methods cover the sampling and chemical analysis of solid natural rubber in the forms supplied to the rubber industry. The analytical procedures mentioned in the standard cover sampling, volatile matter, dirt, ash, copper (referee colorimetric method, alternative colorimetric method, alternative flame atomic absorption method), manganese (colorimetric method, alternative flame atomic absorption method), iron (colorimetric method), acetone extract, rubber hydrocarbon and hydrogen.

Besides the standards that are briefly described above, the following standards may also be of use in rubber (pre)treatment and sample preparations.

- ASTM D5667: Standard test method for rubber from synthetic sources - total and water-soluble ash
- ASTM D5668: Standard test methods for rubber from synthetic sources - volatile matter
- ASTM D1417: Standard test methods for rubber lattices - synthetic
- ASTM D1485: Standard practice for rubber from natural sources - sampling and sample preparation (described in Section 3 of this document)

4.1.5.3 Other standards

TAPPI (Technical Association of the Pulp and Paper Industry) standard, T 264 cm: Preparation of wood for chemical analysis

Wood for chemical analysis should be ground to a fine particle size to permit complete reaction of the wood with a reagent. TAPPI norm T257 specifies that the wood should be ground to 0.4 mm (40 mesh) screen. Chemical methods for analysis of wood typically call for utilization of the entire amount of material without further fractionation. The fine material might contain a disproportional quantity of some wood constituents and its removal could alter the chemical composition. In some chemical methods the fine material interferes with the analysis. Comminuted wood samples need to have fines removed by fractionation.

Wood extractives are materials that are soluble in neutral solvents and they are not generally considered as parts of wood substance. These materials should be removed before any chemical analysis of wood substance, except where the extraction process and subsequent washing could interfere with certain chemical analysis. The acetone removes mainly wood resin materials, including fatty and resin acids, sterols, waxes and fats. Hot water is used to extract tannings, gums, sugars, starches and colouring matter.

4.1.5.4 Comparison

Quantitative chemical analysis of textiles is well covered both by International ISO 1833 standard and American ASTM D629 standard. Methods described in different parts of ISO 1833 are based on the selective solution of an individual component. After the removal of a component, the insoluble residue is weighed, and the proportion of soluble component is calculated from the loss in mass. This approach is common to the analyses of all fibre mixtures, independently of their composition. Similarly, ASTM D629 describes the analytical methods that are intended primarily for the separation of binary mixtures of fibres. These procedures may also be used for the analysis of mixtures containing more than two types of fibres by selecting the best combination of methods to use. ASTM D629 mentions the solubility's of the various fibres in different chemical reagents.

Despite that sampling and further preparative procedures for rubber, raw natural and raw synthetic are given in ISO 1795, no International/European standards were found to describe rubber compositional analysis. The latter is covered by ASTM D6370 (determination of rubber composition by thermogravimetry). standards test methods for rubber-product chemical analysis are given in ASTM D297. Test methods for chemical analysis of rubber from natural sources are mentioned in ASTM D1278.
For testing of polymer matrix composite materials American ASTM D4762 standard can be applicable.

Among others, non-American and non-International standards, we can mention classical method for preparation of wood for chemical analysis that is described in T 264cm document of Technical Association of the Pulp and Paper Industry (TAPPI).

4.2 Liquid materials and products

4.2.1 International / European standards

Not found.

4.2.2 American standards

Among American standards, there are two that are the most relevant to the pre-treatment procedures of liquid materials and products: ASTM D7455 and ASTM D5291.

ASTM D7455: Standard practice and sample preparation for petroleum and lubricant products for elemental analysis, and is briefly mentioned also in Chapter 3 of this document.
This practice covers different means by which petroleum product and lubricant samples may be prepared before the measurement of their elemental content using different analytical techniques. This practice includes only the basic steps for generally encountered sample types. Anything out of the ordinary may require special procedures. There are individual test methods mentioned in the standard for instructions to handle such situations. This practice is not a substitute for a thorough understanding of the actual test method to be used, caveats the test method contains, and additional sample preparation that may be required.

ASTM D5291: Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants.

This standard covers the simultaneous determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants. Carbon, hydrogen, and particularly nitrogen analyses are useful in determining the complex nature of sample types covered by this test method. The carbon, nitrogen and hydrogen results can be used to estimate the processing and refining potentials and yields in the petrochemical industry. The concentration of nitrogen is a measure of the presence of nitrogen containing additives. Knowledge of its concentration can be used to predict performance. Some petroleum products also contain naturally occurring nitrogen. Knowledge of hydrogen content in samples is helpful in addressing their performance characteristics. Hydrogen to carbon ratio is useful to assess the performance of upgrading processes.

The standard is applicable to samples such as crude oils, fuel oils, additives, and residues for carbon and hydrogen and nitrogen analysis. These test methods were tested in the concentration range of at least 75 to 87 mass% for carbon, at least 9 to 16 mass% for hydrogen, and <0.1 to 2 mass% for nitrogen.

The nitrogen test method is not applicable to light materials or those containing <0.75 mass% nitrogen, or both, such as gasoline, jet fuel, naphtha, diesel fuel, or chemical solvents. These test methods are not recommended for the analysis of volatile materials such as gasoline, gasoline-oxygenate blends, or gasoline type aviation turbine fuels.

Besides, ASTM D4209 can be also of use for determining volatile and non-volatile content of cellulosic, emulsions, resin solutions, shellac and varnishes.

ASTM D4209: Standard practice for determining volatile and non-volatile content of cellulosic, emulsions, resin solutions, shellac and varnishes

The non-volatile content of raw materials may be used to determine the total non-volatile content (solids) of paint and related coatings. Such information may be useful to coatings producers and users for the determination of the total solids available for film formation and for the estimation of the volatile organic content. This practice is intended to serve as a guide to the selection of the proper ASTM test method for determining the volatile and non-volatile content of cellulosics, emulsions, resin solutions, shellac, and varnishes. This practice does not cover methods for determining the composition of the volatile fraction.

Other related ASTM standards that can be of interest are listed here:

- ASTM D29: Test Methods for Sampling and Testing Lac Resins
- ASTM D1259: Test Methods for Non-volatile Content of Resin Solutions
- ASTM D1490: Test Method for Non-volatile Content of Urea-Formaldehyde Resin Solutions
- ASTM D1644: Test Methods for Non-volatile Content of Varnishes
- ASTM D1650: Test Methods for Sampling and Testing Shellac Varnish
- ASTM D2369: Test Method for Volatile Content of Coatings
- ASTM D4758: Test Method for Non-volatile Content of Latexes

Note, that despite sampling of paints is well covered by ISO 15528, up to our knowledge there is no standard that would cover the pre-treatment and chemical analysis of paints in order to determine the CO_2 content. If paints are to be analysed, than the pre-treatment shall be done accordingly to ASTM D6866.

4.2.3 Other standards

Not found.

4.2.4 Comparison

Up to our knowledge, there are no European/International standards to cover the pre-treatment and chemical analysis of liquids. Within American standards, there are two that are the most relevant to the pre-treatment procedures of liquid materials and products: ASTM D7455 and ASTM D5291. ASTM D7455 describes standard practice and sample preparation for petroleum and lubricant products for elemental analysis and ASTM D5291 introduces standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants.

For determination of volatile and non-volatile content of cellulosic, emulsions, resin solutions, shellac and varnishes American ASTM D4209 standard can be also of use.
Despite sampling of such type of materials like paints is well covered by ISO 15528, no standards were found that would cover the pre-treatment and chemical analysis of paints.

4.3 Gaseous materials and products

4.3.1 International / European standards

ISO 13833: Stationary source emissions -- Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination
This standard specifies sampling methods and analysis methods for the determination of the ratio of biomass and fossil derived CO_2 in the CO_2 from exhaust gases of stationary sources, based on the radiocarbon (^{14}C isotope) method.
More detailed description of the standard in given in Chapter 3 (sampling of gaseous materials) and Chapter 5 (^{14}C content determination) of this report.

For natural gas analysis, the following standards may be of use:

- ISO 6974: Natural gas – determination of composition and associated uncertainty by gas chromatography
- ISO 6975: Natural gas – Extended analysis – Gas chromatographic method
- ISO 6976: Natural gas – calculation of calorific values, density, relative density and Wobbe index from composition

4.3.2 American standards

Despite there is known American standard ASTM D7459 (described in Chapter 3 in the subsection describing the sampling of gaseous materials) on standard practice for collection of integrated samples for the specification of biomass(biogenic) and fossil-derived carbon dioxide emitted from stationary emission sources, no American standards were found on pre-treatment of gaseous materials or products.

4.3.3 Other standards

Not found.

4.3.4 Comparison

Several European standards were found that can be applied for natural gas analysis. ISO 6974 describes methods that can be used for the determination of composition and associated uncertainty by gas chromatography. ISO 6975 also refers to gas chromatographic method in extended analysis of natural gas. ISO 6976 described the methods for calculation of calorific values, density, relative density and Wobbe index from natural gas composition.

ISO 13833 specifies methods for the determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide from stationary source emissions. ASTM D7459 describes standard practice for collection of integrated samples for the specification of biomass (biogenic) and fossil-derived carbon dioxide emitted from stationary emission sources. ASTM D7459 is described more detailed in Chapter 3 in the subsection describing the sampling of gaseous materials.

4.4 Conclusions

Generally, to make all carbon free, material needs to be completely combusted, irrespectively of solid, liquid, or gaseous state of material. After combustion procedure, all available carbon is gathered as CO_2 in a suitable absorber: the CO_2 present in a representative stack gas sample is absorbed in an alkaline medium or transferred to a gas bag or lecture bottle. After sampling, the collected CO_2 is prepared for ^{14}C analysis.

Sampling of CO_2 in stack gas is in principle not different from sampling of other acid gaseous substances and can be found in Chapter 3 of this report. As CO_2 is present in relatively high concentrations compared to other acidic gaseous substances, the capacity of the absorption media requires careful consideration and excess of alkaline media shall be used to ensure complete absorption during the sampling period.

Below we list the standards that can be used for sample preparation procedures for different samples depending of their state:

- For solid sample preparation procedures the following standards can be used:
  - ➢ EN 15104: Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods.
  - ➢ EN 15400: Solid recovered fuels – Determination of the calorific value.
  - ➢ EN 15440: Solid recovered fuels – Method for the determination of biomass content.
  - ➢ EN 15443: Solid recovered fuels – Methods for the preparation of the laboratory samples.
  - ➢ EN 15413: Solid recovered fuels – Methods for the preparation of the test sample from the laboratory sample.
  - ➢ CEN/TS 16137: Plastics – Determination of bio-based carbon content.
  - ➢ ISO 1928: Solid mineral fuels – Determination of gross calorific value by the bomb calorimetric method.

- For liquid sample preparation procedures the standards mentioned below can be used:
    - ASTM D7455: Standard practice and sample preparation for petroleum and lubricant products for elemental analysis.
    - ASTM D5291: Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants.

- For gaseous sample preparation procedures the standards mentioned below can be used:
    - ISO 13833: Stationary source emissions - Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination.
    - ASTM D7459: Standard practice for collection of integrated samples for the specification of biomass (biogenic) and fossil-derived carbon dioxide emitted from stationary emission sources.

Irrespectively of solid, liquid, or gaseous state of materials or products, the American ASTM D6866 standard can be applied if there is no other standardized pre-treatment procedure for a specific material or product.

5 ^{14}C Content Determination

5.1 Introduction

Accurate data on the emission of biogenic carbon dioxide (CO_2) is needed for carbon emission trading. When combusting mixtures of fuels from fossil and biogenic origin, it is often difficult to determine the exact ratio of biogenic and fossil CO_2 in the total CO_2 that is emitted through the stack gas, because the biogenic/fossil composition of the combusted fuels is not always known or cannot be determined with sufficient accuracy. The contribution of solid, liquid and gaseous bio fuels to energy production is constantly increasing. In relation to this, a reliable and robust method for the determination of the ratio of fossil and biogenic CO_2 in the total emitted CO_2 of stack gas is needed.

The amount of bio-based carbon is proportional to the ^{14}C content. The ^{14}C present in chemicals is originating from recent atmospheric CO_2. Due to its radioactive decay, it is almost absent from fossil products older than 20 000 years to 30 000 years (the half-life of ^{14}C is 5730 years). The ^{14}C content may thus be considered as a tracer of chemicals recently synthesized from atmospheric CO_2 and particularly of recently produced bio-based products.

If there is a standard sampling procedure for the material or product to be evaluated that is widely accepted by the different parties, such a procedure may be used and the details of sampling must be recorded. For any sampling procedure, the samples shall be representative of the material or product and the quantity or mass of sample shall be accurately established. Sampling is described in Section 3 of this document.
After sampling has been performed, the samples need to be treated in order to obtain all available carbon in either as pure carbon or as carbon-dioxide. All available data on treatment is described in Section 4 of this document.

With respect to the determination of the biobased content of solid, liquid and gaseous samples using radiocarbon analysis the American ASTM D6866 standard is most often referred to. The standard describes the standard techniques and procedures to be used. These test methods are applicable to any product containing carbon-based components that can be combusted in the presence of oxygen to produce carbon dioxide and will be mentioned in this Chapter. The overall analytical method is also applicable to gaseous samples, including flue gases from electrical utility boilers and waste incinerators.
Besides the techniques that can be used for the ^{14}C content determination, also already known methods for making a distinction between material of organic and inorganic origin will be presented.

This section will also list other standards that describe the determination of the total carbon content of some particular materials and may be interesting in the content of further carbon analysis.
Finally, it should be noted that in this section no distinguishing is made between solid, liquid and gaseous materials since all standard methods mentioned below can be used for solids, liquid and gaseous materials.

5.2 Bio-based carbon determination methods

There are two standard methods for the determining the bio-based content of solid, liquid and gaseous samples mentioned in ASTM D6866 standard of 2012, and an additional method is described in ISO 13833.

5.2.1 Accelerator mass spectroscopy (AMS) / isotope ratio mass spectrometry (IRMS)

This technique allows to quantify the biobased content of a given product. Sample preparation methods include the production of CO_2 within a vacuum manifold system where it is ultimately distilled, quantified in a calibrated volume, transferred to a quartz tube, and torch sealed. This method represents a commonly used procedure to quantitatively combust the carbon fraction within product matrices of varying degrees of complexity. In this technique, sample atoms are ionized, accelerated to high energies, then separated on basis of their momentum, charges and masses.

Principle

$^{14}C/^{12}C$ and $^{13}C/^{12}C$ isotopic ratios are determined using AMS. The AMS method determines the presence of the ^{14}C isotope directly. The atoms in the sample are converted into a beam of ions. The ions formed are accelerated in an electric field, and subsequently deflected in a magnetic field, and finally detected in ion detectors, resulting in the determination of the relative isotope abundances of these ions. AMS uses a high potential electrostatic field, which serves not only to accelerate but also to specifically form only C^{n+} ions ($n = 1 ... 4$) that are allowed into the spectrometer, excluding all other ionic species.

This greatly enhances sensitivity without compromising selectivity. In most AMS systems, the ^{14}C is currently determined from graphite (carbon) sample targets. To obtain graphite sample targets, it is necessary to convert the CO_2 in each sample into graphite before analysing.

With AMS the amount of ^{14}C atoms is measured relative to the amount of (one of) the more abundant carbon isotopes ^{12}C and/or ^{13}C. This measured $^{14}C/^{12}C$ or $^{14}C/^{13}C$ ratio is calculated relative to the measured isotope ratio in a reference material with standardized ^{14}C amount, to obtain standardized and normalized ^{14}C content (in pMC) for each sample.

Sample analysis

A percentage ^{14}C of zero represents the entire lack of ^{14}C atoms in a material thus indicating a fossil (for example, petroleum based) carbon source. One hundred percentage ^{14}C, after correction for the post-1950 bomb injection of ^{14}C into the atmosphere, likewise indicates an entirely bio-based carbon source. The percentage modern carbon can be slightly greater than 100% due to the continuing, but diminishing, effects of the 1950s nuclear testing programs.

However, all certified laboratories refer to pMC value determined from the atmosphere every year. Because all recent biomass is harvested within three years this yearly adopted value is used.

All percentage modern carbon (pMC) values obtained from radiocarbon analyses must be corrected for isotopic fractionation using stable isotope data ($^{13}C/^{12}C$ ratios) obtained on CO_2 derived from combustion of the sample.

5.2.2 Liquid scintillation counting (LSC)

This technique allows us to quantify the biobased content of a product. LSC determines the isotope abundance of ^{14}C indirectly, through its emission of beta-particles due to the radioactive decay of the ^{14}C isotope. The beta-particles are observed through their interaction with a scintillator. This test method determines the biobased content of a sample with a maximum total error of ±3%. The test method directly discriminates between product carbon resulting from contemporary carbon input and that derived from fossil-based input.

Principle

There are two methods that can be used for the preparation of the collected CO_2 for activity measurement.

- CO_2 extracted from the flue gas is converted to benzene. This benzene is mixed with an organic solution containing a scintillator (described in the current version of ASTM D6866-12).
- CO_2 extracted from the flue gas is trapped in an amine solution thus forming carbamates. This solution is mixed with the organic solution containing the scintillation reagent (present in previous versions, but omitted in the current version of ASTM D6866-12, as the precision of this method is considered to be too low).

The ^{14}C activity of the mixture is measured in a liquid scintillation counter in Bq. This measured activity of the sample is calculated relative to the known ^{14}C activity of a standard reference material to obtain standardized and normalized ^{14}C content (in pMC) for each sample.

Sample analysis

Significantly lower ^{14}C counts indicate the presence of ^{14}C-depleted carbon. The lack of any ^{14}C counts in a material indicates a fossil (for example, petroleum based) carbon source. A sample that has the same ^{14}C activity level (after correction for the post-1950 bomb injection of ^{14}C into the atmosphere) as the oxalic acid standard is 100% biobased and signifies an entirely modern carbon source. The inherent assumption is that all of the organic components within the analysed material are either fossil or present day in origin.

5.2.3 Beta-Ionization technique (BI)

This procedure for ^{14}C determination is not described by ASTM D6866 but is referred to in ISO 13833 for ^{14}C determination in the CO_2 and exhaust gas samples collected at the stationary source.

Principle

The BI method determines the isotopic abundance of ^{14}C indirectly. This method employs the emission of beta-particles by ^{14}C due to the radioactive decay of the ^{14}C isotope. It detects beta-particles by means of discharge current pulses between high-voltage electrodes in a proportional gas counter. Those pulses are initiated by the beta-particles. The detection principle resembles the way a Geiger-Müller (GM) counter works, the difference being details of the electron avalanche in the counter.

To use this method, the sample has to be in the form of CO_2 or converted to CO_2. The CO_2 extracted from the stack gas is purified to be suitable as a counting gas in a proportional gas counter, e.g. by removal of electron negative impurities, e.g. oxygen, SO_2, water vapour, and radon. The purity of the gas is critical (e.g. O_2 levels need to be kept well below a few micro-litres per litter). The sample is counted for several days in a low-level counting system to reach the number of counts desired for statistical precision. The CO_2 is held under pressure in the central tube (typically at 0.2 MPa to 0.3 MPa) and a high voltage is introduced between the central wire and the counter wall. An ionizing event, such as a β^- particle produced by ^{14}C decay, creates an ionization trail and an avalanche of electrons. This avalanche is measured as an electrical pulse. Any impurities in the gas quench the multiplication of electrons, leading to some decay events being undetected. The number of counts per minute, the activity of the sample, is detected with the proportional gas counters. This measured activity of the sample is calculated relative to the measured activity of a reference material with standardized ^{14}C amount to obtain standardized and normalized ^{14}C content (in pMC) for each sample.

5.3 Bio-based determination methods

Additionally, there are two methods mentioned in EN 15440 for the determination of the biomass content. However, it should be noted that these methods are related to the material types (organic and inorganic products) and not related to the biomass content of the material. Especially when more biomass is becoming present in materials like e.g. plastics, the error by selecting material on their appearance is increasing.

5.3.1 Selective dissolution method (SDM)

The selective dissolution method is based on the fact that biomass oxidizes significantly more quickly than non-biomass.

Principle

The selective dissolution method for the determination of the biomass content expressed in per cent by weight involves the treatment with concentrated sulphuric acid topped with hydrogen peroxide. The biomass in the solid recovered fuel will selectively dissolve and the non-biomass will remain in the residue. For the determination of the biomass content expressed in per cent by weight, the sample shall be weighed before and after selective dissolution. The biomass content by weight is corrected for the content of carbonates by measuring the ash content (according to EN 15403) before and after dissolution.

The determination of the biomass content by calorific value consists of two procedures. The first procedure determines the calorific values of the total sample and non-biomass fraction. The second procedure calculates the biomass content by energy content. Depending on the use of the results, the biomass content may be calculated in per cent by net calorific value or by gross calorific value.

The determination of the biomass content by carbon content involves the determination of the TC content before and after the selective dissolution of the biomass fraction. The results are used for the calculations of the biomass content expressed in percentage by TC. The maximum relative error for the biomass content by TC is 0.4% per 1.0 per cent by weight of the ash fraction. Therefore, a correction for carbonate present in the ashes is made if the ash content in the original sample (as determined in this annex is larger than 10% by weight on a dry basis.

5.3.2 Manual sorting (MS) method

In the manual sorting method, a sample of the solid recovered fuel is sorted by hand into sub-fractions, such as plastics, paper/cardboard, wood, vegetable, fruit, garden waste and inert matter.

Principle

The manual sorting method for the determination of the biomass content in per cent by weight involves the separation of the components into a number of fractions which are either (mostly) biomass or (mostly) non-biomass. The manual sorting error is determined for the specific type of SRF with the selective dissolution method. This method is not applicable for solid recovered fuels with a maximum particle size smaller than 10 mm and/or SRF that is pelletized.

5.4 Conclusions

Generally, there are three methods known for the determination of the bio-based content of materials or products:

a) selective dissolution method (SDM)
b) manual sorting method (MS).
c) biogenic carbon (^{14}C) determination method.

Within the ^{14}C determination method, three techniques are distinguished:
1) AMS - accelerator mass spectrometry
2) LSC - liquid scintillation counting
3) BI - beta-ionization technique

These three techniques are considered to be equivalent and are discussed in this Chapter. Each of these techniques requires different amount of the CO_2: for AMS measurements the minimum amount of CO_2 is 4 ml, for BI measurements 2 – 10 litre CO_2 is required, and for LSC measurements the required amount of CO_2 depends on the way the sample is prepared for measurement, but at least a few gram will be required.

While the selective dissolution and the manual sorting methods allow us only the distinguishing between organic and inorganic content of materials or products, the ^{14}C method and the techniques involved distinguish the ^{14}C and the ^{12}C isotopes and thus allow us the biogenic content determination.

To summarize, the ^{14}C isotope method is applied in a variety of samples to determine the ratio of biogenic and fossil carbon. Biogenic and fossil carbon can be distinguished based on the measured amount of the ^{14}C isotope in the sample.

Complete combustion is carried out in a way to comply with the requirements of the subsequent measurement of the ^{14}C content and shall provide the quantitative recovery of all carbon present in the sample as CO^2 in order to yield valid results. The calculation of the bio-based carbon content includes the following steps:

- determination of the total carbon content of the sample expressed as a percentage of the total mass or the determination of the total organic carbon content of the sample expressed as a percentage of the total mass;

- calculation of the bio-based carbon content by mass using the ^{14}C content value, determined by calculation from one of the test methods mentioned in ASTM D6866.
- calculation of the bio-based carbon content as a fraction of the total carbon content or as a fraction of the total organic carbon content.

5.5 List of standards

Finally, a list of standards that can be helpful for the biogenic carbon content determination is presented:

ISO 13833	Stationary source emissions -- Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination
CEN/TS 16137	Measuring the bio-based carbon content of plastics and other polymers
CEN/TR 15591	Solid recovered fuels – determination of the biomass content based on the C^{14} method
EN 15440	Solid recovered fuels – method for the determination of biomass content
EN 15104	Solid biofuels – determination of total content of carbon, nitrogen and hydrogen
ISO DIS 16948	Solid biofuels – determination of total content of carbon, nitrogen and hydrogen
ISO 29541	Solid mineral fuels – determination of total carbon, hydrogen and nitrogen – instrumental methods
ISO 21068	Chemical analysis of silicon carbide containing raw materials and refractory products. Part 2: determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon
ASTM D5291	Standard test methods for instrumental determination of carbon, hydrogen and nitrogen in petroleum products and lubricants
EN 1484	Water analysis -- Guidelines for the determination of total organic carbon and dissolved organic carbon
EN 13137	Characterization of waste. Determination of total organic carbon content in wastes, sludge and sediments