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ESCALA/ESPECIALIDAD: Escala Facultativa Superior, Facultativos Superiores Especialistas, Químicos.

TURNO: Libre.

CONVOCATORIA: BOA 11/07/2014

EJERCICIOS: Primero, tercero y cuarto.

# CUERPO SUPERIOR DE LA ADMINISTRACIÓN DE LA COMUNIDAD AUTÓNOMA DE ARAGÓN, ESCALA FACULTATIVA SUPERIOR, FACULTATIVOS SUPERIORES ESPECIALISTAS, QUIMICOS

## OFERTA COMPLEMENTARIA 2011

## PRIMER EJERCICIO

14/02/2015

1. El procedimiento administrativo como cauce de actuación de la administración pública. El ciudadano, situaciones activas y pasivas en general y su manifestación en el procedimiento. Los principios del procedimiento sancionador.

2. El análisis químico en el sector agrícola. Implicaciones ambientales y productivas. Parámetros y técnicas espectroscópicas.

# PRUEBAS SELECTIVAS PARA INGRESO EN EL CUERPO DE FUNCIONARIOS SUPERIORES DE LA ADMINISTRACIÓN DE LA COMUNIDAD AUTÓNOMA DE ARAGÓN, ESCALA FACULTATIVA SUPERIOR, FACULTATIVOS SUPERIORES ESPECIALISTAS, QUÍMICOS.

## EJERCICIO Nº 3.

Tiempo de ejecución: 3 horas.

## SUPUESTO PRÁCTICO 1

Una industria de fabricación de productos derivados de la madera ubicada en Aragón tiene una capacidad de producción de 350 toneladas/día de tablero conglomerado y tablero contrachapado con una densidad promedio de 750 kg/m3. Presenta los siguientes consumos en su último año civil de funcionamiento:

Materia prima

| | |
|---|---|
| Madera, serrín, virutas de madera | 225.000 t |
| Ceras | 600 t |
| Resinas | 4.050 t |
| Productos ignífugos no clorados | 500 t |
| Colas | 10.000 t |
| Sulfato amónico | 100 t |
| Agua | 40,000m$^3$ |

Combustibles

| | |
|---|---|
| Gas Natural | 473 TJ |
| Residuos del proceso de fabricación de los tableros | 20.000 t |

y genera los siguientes residuos:

| Residuos peligrosos | Código LER | Cantidad (t/año) |
|---|---|---|
| Envases que contienen restos de sustancias peligrosas o están contaminados por ellas | 150110 | 5 |
| Líquidos acuosos de limpieza | 120301 | 1 |
| Productos químicos inorgánicos desechados que consisten en, o contienen, sustancias peligrosas. | 160507 | 19 |
| Residuos que contienen hidrocarburos | 160708 | 1 |
| Agua aceitosa procedente de separadores de agua/sustancias aceitosas | 130507 | 1 |
| Envases metálicos, incluidos los recipientes a presión vacíos, que contienen una matriz porosa sólida peligrosa (por ejemplo, amianto) | 150111 | 10 |
| Absorbentes, materiales de filtración (incluidos los filtros de aceite no especificados en otra categoría), trapos de limpieza y ropas protectoras contaminados por sustancias peligrosas | 150202 | 6 |

| | | |
|---|---|---|
| Residuos de adhesivos y sellantes que contienen disolventes orgánicos u otras sustancias peligrosas | 080409 | 1 |
| Otros aceites de motor, de transmisión mecánica y lubricantes | 130208 | 20 |
| Equipos eléctricos y electrónicos desechados, distintos de los especificados en los códigos 200121 y 200123, que contienen componentes peligrosos | 200135 | 2,5 |
| Baterías de plomo | 160601 | 0,5 |
| **Residuos industriales no peligrosos** | | |
| Envases de papel y cartón | 150101 | 85 |
| Envases de plástico | 150102 | 14 |
| Hierro y acero | 170405 | 320 |
| Serrín, virutas, recortes, madera, tableros de partículas y chapas distintos de los mencionados en el código 030104 (recortes y barreduras y polvo de lijado) | 030105 | 9.680 |
| Cenizas de hogar, escorias y polvo de caldera (excepto polvo de caldera especificado en el código 100104) | 100101 | 2.349 |
| Lodos del tratamiento de aguas residuales urbanas | 190805 | 163 |
| Residuos no especificados en otra categoría (Lijas y bandas) | 030199 | 37 |

La industria tiene tres focos de emisiones de combustión, y cada foco recoge las emisiones de los siguientes dispositivos:

Foco 1. Caldera de vapor alimentada por Gas Natural de 15,0 MW de potencia nominal térmica.
Foco 2. Caldera de vapor de alimentada por Gas Natural 15,0 MW de potencia nominal térmica.
Foco 3. Incineradora con recuperación de energía mediante caldera de vapor que se alimenta con los residuos provenientes del proceso de fabricación de los tableros, con una capacidad de tratamiento de 15 t/día.

En el curso de un muestreo llevado a cabo en la salida de la chimenea correspondiente al Foco 2 por un Organismo de Control Autorizado (OCA) según lo establecido en el Real Decreto 100/2011, se recoge una masa de 67 mg de partículas para un volumen de gases de emisión de 2,35 $m^3$. El gas en el punto de muestreo está a 68°C y 1,03 atm y tiene una humedad relativa del 12,5 %. El análisis Orsat (con absorción alcalina y en base seca) de estos gases da un 10,03 % de $O_2$ y un 10,20% de $CO_2$. El OCA realiza la medición en las mismas condiciones de CO obteniendo un resultado de 92 ppmv.

Los valores límite de emisión (VLE) establecidos para ese foco son:

| Contaminante | VLE |
|---|---|
| Partículas | 50 mg/$m^3$N expresado a un 7% de $O_2$ y en base seca |
| CO | 150 mg/ $m^3$N en base seca |

Responder a las siguientes cuestiones

1. Cumplen los valores medidos por el OCA los VLE? Razone su respuesta.

2. Una estación de medición de calidad del aire de la RRICAA, a 20 km de la instalación, se considera adecuada para evaluar la calidad del aire de la zona donde se ubica la instalación, y proporciona los siguientes valores para el último año civil de funcionamiento de la fábrica de tableros:

| **Contaminante** | **Parámetro** | **Valor** | **% datos válidos** |
|---|---|---|---|
| PM10 | Percentil 90,4 de los valores medios diarios | 50 µg/m³ | 100 |
| PM10 | Media anual de un año civil | 40 µg/m³ | 100 |
| CO | Media octohoraria | 10 ppmv* | 95 |

* el volumen está referido a una temperatura de 293 K y a una presión de 101,3 kPa.

Con esta información determine si se están cumpliendo los valores límite de protección para la salud, establecidos en la normativa vigente. Razone su respuesta

# SUPUESTO PRÁCTICO 2

La determinación de sulfitos en muestras de alimentos se realiza trasformando los compuestos de sulfitos en dióxido de azufre en medio clorhídrico concentrado y en caliente. El dióxido de azufre producido se dirige, por arrastre con gas nitrógeno, hacia una solución de peróxido de hidrógeno. Esta solución se valora con disolución valorada de hidróxido de sodio 0,01 N, utilizando rojo de metilo como indicador.

Se recibe en el laboratorio una muestra de marisco para el análisis de sulfitos. Se pesan 50,32 gramos y se analiza mediante el método descrito anteriormente, utilizando 23,4 ml de disolución valorada de hidróxido de sodio 0,01 N en la valoración de la solución final obtenida.

Datos:

Factor de la disolución valorada de hidróxido de sodio 0,01 N = 1.

El ácido clorhídrico concentrado utilizado es de 37 %, con una densidad de 1,3 kg/L.

Cuestiones:

1.- Describir todas las reacciones que se producen y definir los procesos.

2.- Junto con el dióxido de azufre, el nitrógeno arrastra también vapor de agua debido al calentamiento de la disolución acuosa de la muestra. Este vapor es necesario evitar que pase a la disolución de peróxido de hidrógeno para que no la diluya e incluso la desborde del recipiente que la contiene. ¿Cómo se puede evitar su paso al recipiente de recogida de gases?

3.- ¿Qué tipo de valoración es la utilizada para medir la disolución de peróxido de hidrógeno? Indicar el color de indicador citado antes del punto final de la valoración y después de él.

4.- Establecer la expresión para el cálculo de la cantidad de sulfitos en las muestras y calcular la concentración de sulfitos en la muestra indicada en el enunciado. La concentración de sulfitos en las muestras se expresa como miligramos de dióxido de azufre por kilogramo de muestra analizada.

# SUPUESTO PRÁCTICO 3

En un laboratorio de análisis químico se desea validar un método para determinar cobre en purín de cerdo. El método consiste en la digestión ácida de la muestra y posterior determinación del cobre mediante la técnica de absorción atómica de llama ( longitud de onda 324,75 nm, llama aire/acetileno)

Se construye una recta de calibrado con patrones de cobre con bajas concentraciones, y se obtienen las absorbancias dadas en la siguiente tabla:

| Concentración de Cu (mg/L) | 0 | 0,1 | 0,2 | 0,4 | 0,8 | 1,0 |
|---|---|---|---|---|---|---|
| Absorbancia (UA) | 0 | 0,010 | 0,017 | 0,038 | 0,077 | 0,095 |

A continuación se realiza la lectura de absorbancia de 10 blancos, siendo los resultados obtenidos:
0,002; 0,002; 0,004; 0,002; 0,003; 0,003; 0,002; 0,002; 0,003; 0,002
Determinar:

1. Concentración correspondiente al límite de cuantificación
2. Concentración correspondiente al límite de detección
3. Concentración característica para la determinación de cobre en las condiciones dadas de la determinación con absorción atómica.
4. Determinar la sensibilidad del método y el coeficiente de correlación

**Pruebas selectivas para ingreso en el Cuerpo de Funcionarios Superiores de la Administración de la Comunidad Autónoma de Aragón, Escala Facultativa Superior, Facultativos Superiores Especialistas, Químicos.**

**EJERCICIO Nº 4.**

Traducir directamente al idioma castellano el siguiente texto:

# The Monitoring and Reporting Regulation (MMR) – Guidance on Sampling and Analysis

## 1 OVERVIEW

### 1.1 Overview of this document

Note: This document is only relevant for installations which determine calculation factors by analyses, or – regarding the competence requirements of laboratories – apply on-line gas analysers or continuous emission measurement systems (CEMS).

This document provides an overview of the importance of sampling and analysis and how this topic is treated in the MRR. In particular, the MRR uses the term "analyses in accordance with Article 32 to 35" on several occasions where calculation factors are to be determined by analysis (usually in the context of high tier approaches). Section 2.2 provides an introduction to this topic, and explains also how those requirements relate to situations where the MRR allows the use of "industry best practice". Section 2.3 then gives a more detailed summary of the MRR's requirements for analyses.

Chapter 3 gives guidance on the requirements of Article 32 for preparing a sampling plan. Chapter 4 discussed how to determine the appropriate frequency of analyses based on Article 35.

Thereafter the requirements for laboratories used to carry out analyses for the determination of calculation factors as laid down in Article 34 are elaborated in Chapter 5. This focusses particularly on the possibilities to demonstrate equivalence to an accreditated service, if the laboratory is not accredited in accordance with EN ISO/IEC 17025.

### 1.2 Calculation factors – Principles

Calculation factors are the focus of this paper. These factors are:

- In the case of the standard methodology for combustion of fuels, or fuels used as process input: Emission factors, net calorific values, oxidation factors and biomass fractions;
- In the case of the standard methodology for process emissions (in particular decomposition of carbonates): Emission factors and conversion factors;
- For mass balances: Carbon contents and, if applicable, the biomass fractions and net calorific values.

The following formula shows how the calculation factors relate to the calculation of emissions. The example relates to the most common case, i.e. emissions from the combustion of fuels, using the standard calculation method in accordance with Article 24(1):

Example: Calculation-based monitoring of combustions of fuels

$$Em = AD \cdot NCV \cdot EF \cdot OF \cdot 1(-BF)$$

Where:

Em ...... Emissions [t CO2]

AD ....... Activity data (= fuel quantity) [t or Nm3 ]

Calculation factors:

NCV .... Net Calorific Value [TJ/t or TJ/Nm3 ]

EF ....... Emission factor [t CO2/TJ, t CO2/t or t CO2/Nm3 ]

OF ....... Oxidation factor [dimensionless]

BF ....... Biomass fraction [dimensionless]

According to Article 30(1) of the MRR, these factors can be determined by one of the following principles:

- from default values (see section 6.2.1 of guidance document 1);or
- by laboratory analyses.

The applicable tier will determine which of these options is used. Lower tiers allow for default values, i.e. for values which are kept constant throughout the years, and updated only when more accurate data becomes available. The highest tier defined for each parameter in the MRR is usually the laboratory analysis, which is more demanding, but of course more accurate. The result of the analysis is valid for the very batch from which the sample has been taken, while a default value is usually an average or conservative value determined on the basis of big quantities of that material. For example, emission factors for coal as used in national inventories might be applicable to a country-wide average of several (or even many) coal types as used also in energy statistics, while an MRR analysis will be valid for the particular batch analysed (one coal type).

Important note: In all cases the operator must ensure that activity data and all calculation factors are used consistently. Where a fuel's quantity is determined in the wet state before entering the boiler, the calculation factors must also refer to the wet state. Where analyses are carried out in the laboratory from the dry sample, the moisture must be taken into account appropriately, for arriving at calculation factors applicable for the wet material.

Operators must also be careful not to mix up parameters of inconsistent units. Where the amount of fuel is determined per volume, also the NCV and/or emission factor must refer to volume rather than mass.

## 1.3 General requirements for laboratory analyses

Where the MRR refers to determination "in accordance with Article 32 to 35", this means that a parameter must be determined by (chemical) laboratory analyses. The MRR imposes relatively strict rules for such analyses, in order to ensure a high quality level of the results. In particular, the following points need consideration:

- The laboratory must demonstrate its competence. This is achieved by one of the following approaches:
    - An accreditation in accordance with EN ISO/IEC 17025, where the analysis method required is within the accreditation scope; or
    - Demonstrating that the criteria listed in Article 34(3) are satisfied. This is considered reasonably equivalent to the requirements of EN ISO/IEC 17025. Note that this approach is allowed only where use of an accredited laboratory is shown to be technically not feasible or involving unreasonable costs.
- The way samples are taken from the material or fuel to be analysed is considered crucial for receiving representative results. Therefore the MRR puts considerably more emphasis on this topic than the MRG 2007. Operators have to develop sampling plans in the form of written procedures (see Chapter 3) and get them approved by the competent authority. Note that this applies also where the operator does not carry out the sampling himself, but treats it as an outsourced process.
- Analytical methods usually have to follow international or national standards.

Note that the above is usually related to the highest tiers for calculation factors. Therefore, these more demanding requirements are more rarely applicable to smaller installations. In particular operators of installations with low emissions may use "any laboratory that is technically competent and able to generate technically valid results using the relevant analytical procedures, and that provides evidence for quality assurance measures as referred to in Article 34(3)". In fact, the minimum requirements would be that the laboratory demonstrates that it is technically competent and "capable of managing its personnel, procedures, documents and tasks in a reliable manner", and that it demonstrates quality assurance measures and corrective actions, if needed, for calibration and test results . However, it is in the operator's interest to receive reliable results from the laboratory. Therefore operators should strive to comply with the requirements of Article 34 to the highest degree feasible.

Furthermore it is important to note that the MRR, in the activity specific requirements of Annex IV, allows the use of "industry best practice guidelines" for some lower tiers. In some cases this is the lowest tier where no default values are applicable. In such cases, where despite approval to apply a lower tier methodology analyses are still required, it may not be appropriate or possible to apply Articles 32 to 35 in full. However, the competent authority should deem the following as minimum requirements:

- Where the use of an accredited laboratory is technically not feasible or would lead to unreasonable costs, the operator may use any laboratory that is technically competent and able to generate technically valid results using the relevant analytical procedures, and that provides evidence for quality assurance measures and corrective actions, if needed, as referred to in Article 34(3).
- The operator should submit a sampling plan in accordance with Article 33.
- The operator should determine the frequency of analysis in accordance with Article

## 1.4 Procedures for analytical methods

Annex I of the MRR requires that a monitoring plan shall contain, if applicable, a list of the analytical methods to be used for the determination of all relevant calculation factors for each source streams, and a description of the written procedures for those analyses. How such procedures can be described in the monitoring plan is shown by the following example.

Example of the required MP summary for an analysis procedure:

| **Item according to Article 12(2)** | **Possible content (examples)** |
|---|---|
| Title of procedure | Analysis of NCV of solid and liquid fuels. |
| Reference for procedure | Solid fuels: ANA 1-1/UBA; Liquid fuels: ANA 1-2/UBA; Comparison by external (accredited) laboratory: ANA 1-3 ext |
| Diagram reference (where applicable) | N.A. |

| | |
|---|---|
| Brief description of procedure | Bomb calorimeter method is used. Appropriate amount of sampleis based on experience from earlier measurements of similar materials. Samples are used in dry state (dried at 120°C for at least 6h). NCV is corrected for moisture content by calculation. Solid fuels: as in standard. Liquid fuels: Only slightly adapted from standard; samples are not dried. |
| Post or department responsible for the procedure and for any data generated | Company's Laboratory - Head of department. Deputy: HSEQ manager. |
| Location where records are kept | Hardcopy: Laboratory Office, shelf 27/9, Folder identified “ETS 01-ANA-yyyy” (where yyyy is the current year). Electronically: “P:\ETS*MRV\labs\ETS*01-ANA-yyyy.xls” |
| Name of IT system used (where applicable). | Internal log of the lab (MS Access database): sample numbers and origin/name of sample are tracked together with the results. |
| List of EN or other standards applied (where relevant) | EN 14918:2009 with modifications for using also for non-biomass and liquid fuels. |

# 2 SAMPLING PLAN

## 2.1 Introduction to sampling

“Frequency of Sampling” versus “Frequency of Analyses”

The MRR refers to “Frequency of Analyses” (see Chapter 4) in Article 35. Depending on the specific situation the resulting requirement in the approved monitoring plan for the operator may be e.g. that the minimum frequency of analyses of the emission factor of a certain source stream is four times a year. This term “Frequency of Analyses” must not be confused with the “Frequency of Sampling”, i.e. the frequency of taking samples or increments from a batch or delivery of a fuel or material. In general a lot more samples/increments than four have to be taken over the year to obtain representative results. This Chapter 3 and its sections only deal with the frequency of taking samples.

The following example should help to clarify.

Example: A coal firing plant is burning 500,000 tonnes of coal a year. In accordance with Annex VII (also see section 4.1) the operator is required as a minimum to analyse every 20,000 tonnes of coal. This will at least result in 25 different laboratory samples that are analysed each year. The main objective of the sampling plan, which also includes the frequency of sampling, is to prepare (at least) 25 laboratory samples that are representative for each of the 20,000 tonne batches. In order to have representative laboratory sample more than just one sample/increment will have to be taken from each 20,000 tonne batch.

Sampling is a very important task wherever something is to be analysed in a laboratory. It is crucial to develop and apply a reproducible methodology (the sampling plan) which ensures that the sample taken is representative of the whole batch or delivery from which the sample is taken. The sampling plan describes the overall aims and objectives; it includes specific and practical instructions on what is going to be sampled, how it will be sampled, at what frequency, what the sample will be analysed for and by whom. An appropriate sampling plan provides transparency to all users and will not only improve the reliability of the results and the level of assurance; it may also help to reduce costs for analyses and verification. The complexity of the sampling plan will to a large extent depend on the degree of heterogeneity of the fuel or material. In general, it might be useful in complex cases to put some effort into the preparation of an elaborate sampling plan. However, it should also be noted that the use of highly heterogeneous materials is not a very common practice in EU ETS installations. Therefore few installations will have to develop sophisticated sampling plans. In many cases it may happen that sampling used for other purposes (such as quality or process control) can be used (as it is) without further adaptation, as the examples show.

The development of a sampling plan is explained in section 3.3. Sampling is more complicated the more heterogeneous the material is. For a very homogeneous material (e.g. a liquid fuel which is homogenised in a tank by stirring) a simple sample of 50 ml may well be representative for the whole 500 tonnes in the tank. At the other end of the spectrum, some waste fractions (e.g. electronic scrap) may consist of items each beyond 50kg mass, while a laboratory analysis usually needs only samples of some grams or even in some cases micrograms (µg).

The aim of every sampling exercise is that the final sample in the aboratory is as representative of the whole delivery period or batch of fuel or material as possible. It is a statistical exercise to determine how many "increments" (smaller samples which are combined into a bigger sample) must be picked from a batch, and how big the increments must be, in order to obtain a reasonably representative "composite sample". The increments must be considerably bigger than the particle size, and the locations of sampling should be spread over the whole area to be sampled. The number of increments must be high enough to allow a meaningful average.

Example 1: An installation is burning clay delivered by storage tanks on trucks. To determine the properties of this source stream, e.g. the EF, of each delivery is sampled and treated according to industry best practise.

Example 2: A power plant is firing coal. Sampling is done by an automatic sampler from the onsite coal stockpile.

In both examples, the provision of a written procedure for the sampling plan may well be an exercise of documenting what is already being done in the past rather than implementing any new process steps.

Example 3: A cement clinker producing installation is exclusively firing petcoke. The operator intends to additionally burn waste tyres and other solid recovered fuels.

In this case the operator is well advised to carefully study relevant standard documents (see below) to prepare a transparent sampling plan accompanied by the underpinning procedure. The accredited laboratory that will be engaged for the analyses may also be consulted for the purpose of preparing an appropriate sampling approach.

Generally all standards containing provisions for preparing sampling plans are suitable, in particular those related to the specific type of source stream e.g. coal. The following standards and technical reports may be considered when preparing a sampling plan, in particular for more complex cases:

EN 932-1: Tests for general properties of aggregates - Part 1: Methods for sampling

EN ISO 10715: Natural gas - Sampling guidelines

ISO 13909-2: Hard coal and coke -- Mechanical sampling -- Part 2: Coal -- Sampling from moving streams

EN 14899: Characterization of waste – Sampling of waste materials – Framework for the preparation and application of a Sampling Plan

CEN/TR 15310: Characterization of waste – Sampling of waste materials This technical report consisting of five parts assists and supplements EN 14899

EN 15442: Solid recovered fuels – Methods for sampling

EN 15443: Solid recovered fuels – Methods for laboratory sample preparation

EN 14778: Solid biofuels - Sampling

Some of these standards and technical reports focus on waste materials. However, solid waste materials are often very heterogeneous. Therefore the approaches for preparing a sampling plan related to waste materials presented in the standards and technical reports can be considered to cover even the most complex non-waste cases as well. In the absence of a suitable standard for the specific fuel, considerable simplifications may be possible if the fuel or material is more homogeneous.

In some cases analytical results may show that the heterogeneity of the fuel or material significantly deviates from the information on heterogeneity on which the original sampling plan for that specific fuel or material has been based. In such cases Article 33(2) requires the operator to adapt the relevant elements of the sampling plan. Those adaptations shall be in agreement with the laboratory carrying out the analysis for the respective fuel or material (see Chapter 5) and subject to the approval of the competent authority.

## 2.2 Sampling plan requirements of the MRR

For putting the above into practice in a practical and consistent manner, Article 33 requires the operator to submit a sampling plan to the competent authority for approval for each fuel or material for which calculation factors are to be determined by analyses. If only tiers using default values or purchasing records are applied for the determination of calculation factors, this requirement (and consequently this guidance document) is not relevant.

The sampling plan shall be in form of a written procedure containing the following information:

- Methodologies for the preparation of samples
- Responsibilities
- Locations
- Frequencies
- Quantities
- Methodology for the storage and transport of samples.

Furthermore, the MRR contains provisions that the sampling plan has to be updated regularly if any changes of source streams or of the properties of source streams occur over time. This is achieved by requiring that the operator puts in place a procedure attached to the monitoring plan related to the revision of the appropriateness of the sampling plan.

The ultimate goal of a sampling plan in the MRR is to ensure that samples analysed are representative for the relevant batches and that the cumulated results of analytical values thereof allow the determination of representative calculation factors, e.g. that sampling and analysis of the carbon content8 of a source stream is representative for that material over the whole reporting period.

In many cases the requirement to have sampling plan and an underpinning procedure in place does not impose any additional requirements to current practice at the installation. In any case the MRR requires that relevant elements of the sampling plan shall be agreed with the laboratory carrying out the analysis for the respective fuel or material, and evidence of that agreement shall be included in the sampling plan. This is in particular relevant in cases of rather heterogeneous material having properties that vary spatially and temporally.

In some cases sampling itself may be carried out by a third party, e.g. the fuel/material supplier. In such a case it is still the operator's responsibility to demonstrate compliance with the requirements in the MRR for sampling plans. This may be achieved by obtaining information and evidence about the sampling plan by the third party. In any event the operator is responsible for correct sampling defined in an appropriate sampling plan in accordance with Article 33 regardless whether sampling or analysis is carried out by the operator or by third parties.

Example for a relatively simple sampling plan procedure:

| **Item according to Article 12(2)** | **Possible content (examples)** |
|---|---|
| Title of the procedure | Sampling Plan for waste oil |
| Traceable and verifiable reference for identification of the procedure | ETS 01-SP |
| Post or department responsible for implementing the procedure and the post or department responsible for the management of the related data (if different) | Head of the waste department of the installation's laboratory |
| Brief description of the procedure | 1000 ml samples are taken from each truck's storage tank (about 250 trucks a year).<br>Responsible person makes arrangement that sampling is supervised (weekly spot checks) by the responsible shift manager or a representative nominated by the manager.<br>Samples are collected in tight bottles clearly marked with date and time, fuel supplier ID, and name of the person who took the sample.<br>Samples are stored in room LA-007 of the laboratory (at room temperature).<br>When 10 samples have been collected, they are mixed |

| | |
|---|---|
| | and homogenised to give “a composite sample”.<br>This results in approximately 6 composite samples each quarter. Once per quarter the composite samples are sent to the accredited laboratory identified in the Monitoring plan. |
| Location of relevant records and information | Hardcopy: Laboratory Storage Room, shelf 27/9, Folder identified “ETS 01-SP”. Electronically: “P:\ETS*MRV\Analyses\ETS*01-SP.xls” |
| Name of the computerised system used, where applicable | N.A. (Normal network drives) |
| List of EN standards or other standards applied, where relevant | EN 1489 |

## 2.3 Preparing a sampling plan

The following section outlines a step-by-step approach for preparing a sampling plan, including a brief description of the steps. This approach is taken from CEN/TR 15310-1

**1.Specify the objective of the Testing Programme**

This should be a general statement on the overall purpose and this is an essential first step. However, it will usually be at a rather high-level and too non-specific to lead directly to detailed instructions for a sampling plan.

In most cases this objective will simply be something like “to determine the average carbon content” or “to determine the average emission factor of a material over the whole reporting period”

**2.Develop the Technical Goals from the objective**

(a) Define the population to be sampled

Population is a statistical term for defining the total volume of material about which information is required through sampling. This should be one of the first steps. In the most general case the population will refer to the total amount of material or fuel consumed within a reporting period. Sub-populations may, for example, be defined as single batches (e.g. each delivery, or as a volume as given by the analysis frequency in Annex VII of the MRR) or as fuel consumed each month in case of a continuous source stream.

Reliability refers to "bias", "precision" and "confidence". Choices must be made on the confidence level, and to the extent that random and systematic errors in sampling can be minimised.

### 3.Determine the practical instructions

(a) Choose the sampling pattern

The sampling pattern defines when, where and how samples are selected.

(b) Determine the increment/sample size

An increment is the amount of material that is obtained through one single sampling action. It is not analysed as an individual unit, but is combined with other increments to form a composite sample. A simple "sample" is defined as a lot that is analysed individually. The increment/sample size should depend on properties like heterogeneity or particle size.

(c) Determine the use of composite or individual samples

This selection depends inter alia on costs and the statistical parameter. As in general the mean value will be of particular interest, usually composite samples will be used

### 4.Determine required number of samples

This is a statistical exercise taking into account any standard deviations between increments, samples, composites, etc. This point is relevant for the reliability of results but also for cost-efficiency.

After all relevant decisions have been made the sampling plan can be put down on paper. At least the following elements should be covered:

- Who is responsible for each step?
- Where and when are samples taken?
- How are the samples taken? E.g. it might be necessary to first clean pipes where residues from previous samples might still be contained, etc.
- Which instruments are used, if relevant? Describe automatic sampling equipment, but also describe the tools for manual sampling. It might also be important how samples can be picked out from sufficiently deep in a pile of several metres height.
- How will the identity of the samples be ensured?
- How are the samples stored (dry, cool, dark, inert atmosphere, etc.)?
- How and when are increments combined?
- When are the samples analysed, are remaining samples stored after analysis, etc.?

As further help for the development of a sampling plan, the Annex of this document contains an example of a template for a sampling plan.

(b) Assess variability Variability can be distinguished between

Spatial variability

This term refers to the heterogeneity of a material depending on the location, e.g. the heterogeneity within one single batch

Temporal variability

This term takes into account changes of properties over time, e.g. the variability of the net calorific values between a batch consumed in March and a batch consumed in November

(c) Select the sampling approach

This can be distinguished between

Probabilistic sampling

This means that each element within the population to be assessed has an equal chance of being selected. This approach is therefore preferable to obtain representative results and eliminates one source for committing systematic errors.

Judgmental sampling

Due to practical or costs reasons a probabilistic sampling is not always possible. Judgmental sampling will result in sampling sub-populations, e.g. due to technical reasons only samples from the top of a storage tank are being taken.

(d) Identify the scale

The scale defines the minimum quantity of material below which variations are judged to be unimportant.

(e) Choose the required statistical approach

The relevant statistical parameters will be the mean values as well as the standard deviation. Although only the mean value over the whole reporting value is to be reported and no specific uncertainty thresholds are mentioned in the MRR for those mean values, the deviation provides information about the appropriateness of the sampling plan to improve the level of assurance.

(f) Choose the desired reliability