



## Waste Sampling – Case Studies

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### Abstract

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This work and its precursors intend to organise the administrative and practical procedures to adopt in waste sampling, in accordance with European Standard EN 14899 and its associated technical reports CN / TR 15310-1/2/3/4/5 as well as national legislation.

It is structured in line with the organization and sequence of the mentioned European Standard and Reports and includes relevant information available elsewhere. Practical examples of waste sampling conducted during inspective acts are illustrated. In these acts, the results obtained are essential as evidence, so the waste sampling must follow specific criteria regarding the procedures to be observed, as it should have probative value. The aim is usually to determine the waste characteristics and verify the compliance with the landfill admission criteria.

It also includes a practical example of sampling an industrial wastewater residue in accordance with ISO 5667 Standard (and comparison with EN 14899). Various parameters are analysed: temperature, pH, conductivity and metals present in the sample by Atomic Absorption Spectroscopy. The objective is to verify the conformity of the obtained values with the regulations of *Serviços Municipalizados de Água e Saneamento* - SMAS Almada and validate the sampling procedure performed.

**Key words:** sampling, waste, standard, procedures

### 1. Introduction

Residues are materials that the holder discards or intends to discard and which can be reused, recovered or disposed of by sending to landfill, for example. They are usually heterogeneous, so a testing program to assess its destination can be quite complex, involving multiple sampling plans.

A landfill is a space for the final disposal of solid waste generated by human activity. The landfill should have a drainage system to prevent the contamination of groundwater, leachates must be treated and the biogas resulting from the decomposition of waste must be burned or recycled for power generation. It should have a cover with a drainage system for rainwater, a system for environmental monitoring and infrastructure support systems.

When it reaches the limit of storage capacity and the conditions are fulfilled, the landfill is closed and can hold a green space or a leisure park, eliminating the negative aesthetic effect.

Only residues that meet the acceptance criteria defined in the DL 183/2009 and which have undergone treatment can be landfilled, as well as a few special cases. The waste admission process in landfill comprises three possible levels of verification or testing: Basic characterization, compliance testing and on-site verification. Where appropriate, collection and analysis of representative samples may be required to verify residue compliance [8].

## **2. Preparing a sampling plan**

There is a great variability of waste types and components that need to be investigated, so defining a sampling plan can be a complex process. A standardized process for developing a sampling plan is defined by EN 14899 and associated technical reports [1-6]. This work supports these plans development by environmental inspectors, in collaboration with other stakeholders, by providing planning, technical and administrative tools. The sampling plan summarizes all information on the sampling activity and avoids misunderstandings between experts about what to do. It must provide guidelines and procedures, elements for the Quality Assurance and suggestions and criticisms. The sampling plan has to be documented and include justifications and technical objectives, identify stakeholders and issues of health and safety, characterize the waste and identify target constituents, venue details and any restrictions on access. It should evaluate population and variability, identify the scale,

select sampling approach, choose the parameters to be analysed and the desired confidence. It sets practical guidelines regarding the sampling pattern and the size and number of increments and samples, as well as the techniques and protocols for sampling and preparation of samples. A test program can have multiple sampling plans and a sampling plan generally corresponds to a general objective, which should be translated into practical and achievable technical goals.

Population is a term referring to the total volume of material to be characterized by sampling. It is usually impractical to sample the entire population so it is defined as a representative part of the "global population" (e.g. a month of waste from a factory). The variability of population characteristics over time or space is another feature to consider in sampling and is closely related to the scale, which is another important element of the sampling plan and defines the minimum amount (mass or volume) of material below which variations are not considered important. A statistical parameter is any characteristic of a population that can be quantified, such as its mean or standard deviation. Deciding the parameter estimation is a key step in any testing program and it will have a decisive effect on the type of sampling and number of samples required. Reliability is a generic term that involves three statistical concepts: error, accuracy and confidence. The purpose of the test influences the acceptable level of reliability, but the selection criteria are always subject to a commitment to the process costs. For example, given the importance of basic characterization, it is natural that in this case the reliability has to be as high as possible. That is, the larger the number of samples, the

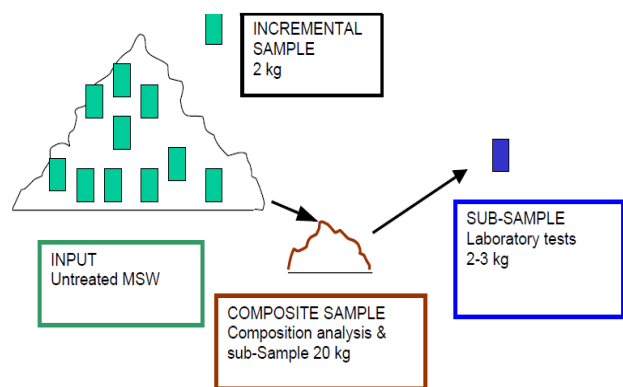
higher the costs and reliability. It all depends on the purpose and level of testing. The sampling plan should anticipate any restrictions or limitations relating to its key steps that may impact the reliability of the test data.

### Sampling and samples

Sampling is the process of selecting a portion of the material to be analysed, small enough to be conveniently carried and handled in the laboratory, but sufficiently representative of the sampled environment. Sampling and testing for basic characterization and compliance testing are carried out by independent and suitably qualified institutions and persons. There are two fundamental approaches to sampling, probabilistic and non-probabilistic. The first should be chosen whenever possible but especially if high reliability is required. The basis of this approach is that each element of the population has an equal probability to be sampled. The non-probabilistic sampling does not follow the statistical methods and implies that the samples are collected, at best, using semi-probabilistic methods. The need for its use arises when the population random sampling is impossible, given the resources or conditions. The sampling pattern defines where, when and how the samples are collected. The non-probabilistic sampling can have a multitude of sampling patterns that essentially differ in the distance that they are from probabilistic sampling. The general definition of the sampling sites must comply with the objectives and consider the heterogeneity of the system.

Samples may be individual or composite (with two or more increments). In the case of

composite sampling, proportions of each sub-sample must be respected. The size of an individual sample is dictated by the grain size, heterogeneity and the volume of sampled material. An increment is the amount of material obtained through a single act of sampling and is combined with other increments to form a composite sample. Fig. 1 shows the differences between samples, increments and sub-samples.



The importance of the sample or increment size depends on the type of material. In the case of granular materials, the minimum is dictated by the need to sample all sizes of particles present. In the case of liquids, there is no special requirement since the particle size is on the molecular scale. A sample must be large enough to minimize or exclude errors caused by the variability of the material. To get an average concentration in a waste, one or more composite samples must be collected. If the intended result is the range of variation in the concentration of the waste, at least three single samples must be collected. For heterogeneous wastes difficult to sample and which representativeness cannot be defined with a single sample, the choice of method and number of samples should be defined by the several stakeholders and registered in the sampling plan.

### 3. Sampling procedures

Before starting the sampling itself, all elements of the sampling plan should be checked. A visual description of the material should be made and the location recorded, as well as the state of the waste to be sampled, which should be complemented with photographic record. There should be no changes to the sampling plan, but if they are necessary and do not alter the sequence of the testing program, the technician may be responsible for them. If the changes affect the testing objective, should only be superiorly allowed. The EN 14899 European Standard and associated technical reports identify the preparation of sampling and the sampling procedures. These are performed according to the physical state of the material (liquid, slurry or solid), its storage (container, tank, etc.), expected heterogeneity degree and level of testing. Fig. 2 shows two of the ways to select samples collection points.

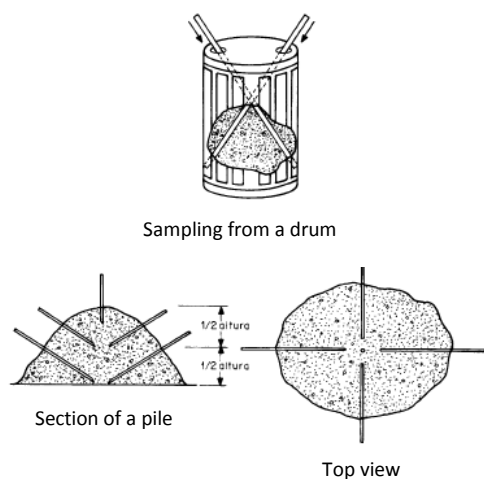


Fig. 2 – Examples of points to collect samples

### 4. Sub-sampling procedures and sample preparation

The sub-sampling methods are chosen to minimize changes in physical or chemical state of the sample and depend on the objectives of

the sampling and testing program level. The sub-sampling should only be done in the sampling location if needed for the sample to be transported. The sample integrity must be ensured, with no loss of moisture or volatile components, or cross-contamination. The methods should be documented in the sampling plan. The sub-sampling can be done with or without particle size reduction, which consists in crushing or grinding the sample, decreasing the size of the particles. These procedures should only take place in prepared places. When two or more sub-samples are required, they should be prepared so that they have identical size and expected composition.

### 5. Preservation, storage and transport procedures

The European Standard EN 14899, the associated technical report TR 15310 - 4 and *Portaria* 200/2002 describe the conditions and the proper procedures for packaging, preservation, storage and transport of samples of liquids, solids, pastes and sludge waste. There is some flexibility in the choice of approach, method and equipment but the choice of procedures must be in accordance with the laboratory analysing the samples. The transport of samples must be done ensuring its integrity and respecting the chain of custody.

The containers can be made of several materials and should be chosen to reduce the attachment to its walls or reaction of chemical species or even photosynthetic activity. If possible, all containers shall be disposable. If not, they must be properly cleaned prior to sampling. Each sample vessel should be given a readable and unique code, using labels, identifying stickers or indelible ink markers. All

the necessary information for unambiguous identification of the sample should be included. If the sample contains hazardous waste, it should be mentioned. Ideally, samples should be analysed immediately after collection, but this is rarely possible, being necessary to preserve them in the field and transport them to the laboratory. The sample stability, the components properties, its concentration and necessary storage time influence the choice of the methods to use.

To preserve the chain of custody, a company representative should witness the above procedures and, if wanted, they can keep a duplicate sample. In addition to the initial sampling plan, there are several documents, including a sampling record, which should be completed and kept.

## **6. Case studies**

Four case studies are presented and documented: Sampling static material from drum or block up to 500 kg; Sampling coarse or lumpy solid materials (I, II); Sampling a liquid from a lagoon or pit. For the last sampling example, analytical determinations were also performed.

### **Wastewater sampling - case study**

Samples were collected from Repsol wastewater streams washing LPG cylinders. The objectives were to verify the results conformity with the regulations and validate an industrial wastewater sampling procedure, using two automatic samplers. The kind of wanted samples determines each sampler programming, so that it retains the desired amount of liquid in each cylinder. The sampler automatically prepares the collection system to

prevent clogging and then begins collection of the samples. The probe has to be handled with care so it does not hit the bottom and shake the accumulated sediments. Sampler and vessels were numbered and registered. Some individual sampling was performed and the temperature was determined at the sampling site. The pH, conductivity and concentration of metals were determined in the laboratory. Concerning equipment, automatic samplers, bucket, thermometer, gloves, bottles, water heaters, thermal box were used. For composite samples (total volume = 9,6 L), each automatic sampler collected 100 ml X 4 increments in each of the 24 vials. The persons involved wore disposable gloves and suitable footwear and clothing and fulfilled the site safety rules.

The individual samples were transferred to the collection vials; the increments of the composite samples were mixed and collected in 2 x 500 ml bottles. The samples were stored in decontaminated plastic bottles, cleaned with deionized water after filling and placed in a refrigerated cabinet at about 4 °C. The bottles were completely filled to avoid the presence of air, which can adulterate the results of pH measurements.

### **Analytical determinations of wastewater sampling case study**

Temperature was measured on site for individual samples. Before use, the lab material was immersed in HNO<sub>3</sub> 2N for several days and then washed with deionized water. The pH and conductivity were measured in the laboratory on the sampling day and the samples remained chilled. Table 1 shows the temperature results and table 2 shows the pH and conductivity results.

Sample code	Sampling time	Temperature
P1	11h00m	14,0 °C
P2	11h55m	14,6 °C
P3	13h00m	15,8 °C

Table 1: Temperature results (should be  $\leq 35^{\circ}\text{C}$ )

Sample code	Sample	pH	Conductivity ( $\mu\text{S/cm}$ )
C1	Composite sample 1	7,51	669
C1d	Composite sample 1–analytical duplicate	7,61	621
C2	Composite sample 2–sampling duplicate	7,57	624
C2d	Composite sample 2–analytical duplicate	7,60	624
P1	Individual sample 1	7,65	588
P2	Individual sample 2	7,68	582
P3	Individual sample 3	7,70	575

Table 2: pH and conductivity results ( $\leq 6 < \text{pH} < 9$ )

### Microwave digestion of samples

Once determined each sample pH and conductivity, the samples were acidified to  $\text{pH} < 2$  with concentrated  $\text{HNO}_3$  and stored at  $5 \pm 3^{\circ}\text{C}$  until digestion, to preserve metals. Concentrated  $\text{HNO}_3$  should be added immediately after the arrival of the samples and one should ensure at least 16 hours of preservation before analysis, which was done. The metals are conserved like this from 3 to 6 months [7]. Samples with a single, transparent, colourless phase with turbidity  $< 1$  NTU and no odour can be directly analysed by atomic absorption spectroscopy or ICP without prior digestion. When there are particles or organic

materials, as in the case of the samples under study, digestion is necessary prior to spectroscopic analysis. This was done some weeks after sampling. Samples were microwave digested (acid digestion at high temperature and pressure). Digestion and filtration were accompanied by blanks and recovery tests were made. This procedure is based on heating the acidified samples in two steps: i) reaching  $160 \pm 4^{\circ}\text{C}$  in 10 minutes; ii) increasing to  $170^{\circ}\text{C}$  for 10 minutes [16].

The analytical procedure was done according to quality control tools, to ensure results accuracy. These include individual and composite samples, two duplicates of composite samples for evaluation of uniformity, a blank, a digestion duplicate of an individual sample, an addition duplicate of an individual sample (*spike*) + known analyte amount: in this case 25  $\mu\text{l}$  of a 1000 ppm multi-element standard, equivalent to 0.5 mg/L of Cu, Zn, Fe, Pb, Ni. An analytical duplicate was made to assess the error associated with the analytical procedure. Dilution of samples after digestion was 1:2 [16].

### Atomic Absorption Spectroscopy

In this technique, a sample solution is aspirated into a flame and atomized. It then focuses a light beam with a specific wavelength through the flame towards a monochromator and a detector measures the amount of light absorbed by the atomized element in the flame. Each metal has its own characteristic absorption wavelength so a lamp of the element to be analysed is used, which makes the method almost free from spectral or radiation interference. The absorbed radiation at the characteristic wavelength is proportional

to the element concentration in the sample, according to Beer's Law [17]. The metals determined in this study were Zn, Fe, Cu, Ni and Pb and the determination of iron in the presence of calcium (CaCO<sub>3</sub>) was also performed [16]. Table 3 shows the AAS calibration data.

Metal	Calibration curve	r	LD (mg/L)	Concent. range (mg/L)
Zn	$y = (0,62 \pm 0,05) x + (0,02 \pm 0,03)$	0,997	0,09	0,1 – 1,0
Cu	$y = (0,174 \pm 0,004) x + (0,005 \pm 0,008)$	0,9998	0,08	0,5 – 3,0
Pb	$y = (0,070 \pm 0,001) x + (0,002 \pm 0,005)$	0,9999	0,13	0,5 – 7,0
Ni	$y = (0,102 \pm 0,008) x + (0,01 \pm 0,02)$	0,998	0,28	0,5 – 4,0
Fe	$y = (0,103 \pm 0,008) x + (0,01 \pm 0,02)$	0,998	0,35	1,0 – 5,0
Fe (+ Ca)	$y = (0,085 \pm 0,003) x + (0,006 \pm 0,006)$	0,994	0,12	0,5 – 4,0

Table 3: Calibration data

## Results and conclusions

Regarding the atomic absorption spectroscopy, its sensitivity is the concentration of the metal which produces absorption of 1% (about 0.0044). The limit of detection is the concentration that produces an absorption equivalent to twice the magnitude of the fluctuation of the background (in practice is the concentration from which the equipment can distinguish white). The sensitivity and the detection limit will vary according to the instrument, the element, the complexity of the matrix and the employed technique. The optimum concentration range usually starts from the concentration of several times the detection limit and extends up to the concentration at which the calibration curve begins to show a negative bias [16]. Thus, there were used concentrations of samples

and standards within the optimum concentration range of the spectrometer. Linear regression of the concentration values as a function of the absorbance was made for each standard and calculated the concentration of the metals for each absorbance measurement. The measurements for iron were repeated in a lower concentration range, as the iron concentration determined at first was in the limit of the first range of standards.

The presence of blanks may determine possible contamination, which was not observed in this case. Duplicates allow the assessment of precision (reproducibility). The fortified samples allow determining the accuracy and verify if there was any loss of analyte in digestion – recovery essays.

Calculating recovery percent (Zn example):

$$(C_{\text{Added sample}} - C_{\text{Sample}}) / C_{\text{addition}} \times 100 = (0,9278 - 0,4646) / 0,5 \times 100 = 92,6\%$$

(in case of Fe+Ca, C<sub>addition</sub> = 0,25 mg/L)

<b>Zn</b>	92,6%
<b>Cu</b>	92,8%
<b>Pb</b>	102,0%
<b>Ni</b>	99,8%
<b>Fe</b>	69,8%
<b>Fe (+Ca)</b>	66,5%

Table 4: Recovery percentage for the several metals

Analysing AAS results it can be seen that the results for three of the studied metals were below the detection limit, which reflects in final results (table 5). In the case of the composite sample C2, the duplicate for Zn gives a value a little above the others. As there is no blank to

compare with, this may be due to the heterogeneity of the sample, or a contaminated container. Overall, the Zn and Fe values are consistent among the composite samples and individual ones, although in this case they are somewhat lower. In the case of iron, the concentration value was very close to the highest value of the calibration curve, so a dilution and new measurements were done.

Regarding recovery assays, these attacks generally get good results - no losses in the microwave attack. The differences may indicate matrix problems; one should reproduce the sample matrix patterns whenever possible. If the sample matrix is complex and components, surface tension or viscosity cannot be accurately compared to standards, one can use the standard additions method to correct matrix effects. As it can be seen in Table 4, the recovery tests results are close to 100%, except in the case of Fe. For compounds with greater atomizing difficulty the phosphate ( $\text{FePO}_4$ ) present in solution may be withheld. To check this, calcium was added to the solutions and standards. Iron + calcium standards, in the range 0.5 to 4 mg/L were prepared. Samples were diluted 1:4 and 2.5 ml of calcium was added to the new solutions, 1.25%  $\text{HNO}_3$ . Fe was determined in the presence of calcium - it was found that the introduction of calcium did not significantly alter the recovery outcome, the error persisted: the standard may have not been suitable for the present Fe concentration.

From the AAS results, considering dilution and average values, the final concentration of each element in the analysed water was calculated. In the iron case, calculations were made based on the results of the dilute solutions added with

calcium as these concentrations were within the limits of the calibration line. The results for the concentration of metals in the wastewater are shown in Table 5.

<b>Metal</b>	<b>Average metal concentration in the sample</b>
Zn	1,5 ± 0,2 mg/L
Fe	9,1 ± 0,2 mg/L
Cu	Below detection limit
Ni	Below detection limit
Pb	Below detection limit

Table 5: Metals concentrations results (Zn (5 mg/L), Fe (n. a.), Cu (5 mg/L), Ni (5 mg/L), Pb (5 mg/L))

The concentration values for the various metals in the analysed wastewater meet the quality parameters required by SMAS Almada for discharge into municipal collector. In the case of zinc, it is well below the limit (5mg/L) and in the case of other metals (Cu, Pb and Ni), the results of atomic absorption spectroscopy are below the operational detection limits, so are not quantified in the sample. Regarding iron, there is no limit set on the SMAS Almada parameters.



### 3. References

- [1] EN 14899: 2005 - Characterization of waste; Sampling of waste materials — Framework for the preparation and application of a Sampling Plan
- [2] CEN/TR 15310-1: 2006 - Characterization of waste; Sampling of waste materials — Part 1: Guidance on selection and application of criteria for sampling under various conditions
- [3] CEN/TR 15310-2: 2006 - Characterization of waste; Sampling of waste materials — Part 2: Guidance on sampling techniques
- [4] CEN/TR 15310-3: 2006 - Characterization of waste; Sampling of waste materials — Part 3: Guidance on procedures for sub-sampling in the field
- [5] CEN/TR 15310-4: 2006 - Characterization of waste; Sampling of waste materials — Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery
- [6] CEN/TR 15310-5: 2006 - Characterization of waste; Sampling of waste materials — Part 5: Guidance on the process of defining the sampling plan
- [7] ISO 5667: Water Quality – Sampling (1, 3, 10)
- [8] Decreto Lei n.º 183/2009 de 10 de Agosto
- [9] Portaria n.º 200/2002 de 5 de Março
- [10] Operating Procedure SESDPROC-302-R1 (2007) - Waste Sampling, U. S. Environmental Protection Agency, Science and Ecosystem Support Division
- [11] Guidance on monitoring MBT and other pre-treatment processes for the landfill allowances schemes (England and Wales) (2005), Environment Agency
- [12] Norma brasileira ABNT NBR 10007:2004 - Amostragem de resíduos sólidos
- [13] Standard Operating Procedure EIASOP\_SOILSAMPLING2, Revision #2 (2004) – Soil, sediment and solid waste sampling, The Office of Environmental Measurement and Evaluation, EPA New England - Region 1
- [14] Waste Sampling Draft Technical Guidance EPA530-D-02-002 (2002) - Planning, implementation and assessment, U. S. Environmental Protection Agency, Office of Solid Waste
- [15] Lapa, Nuno, J. Morais, B. Mendes e J. F. Santos Oliveira (200?), “Preparação e execução de planos de amostragem de águas” FCT-UNL, Grupo de Disciplinas de Ecologia da Hidrosfera (GDEH)
- [16] Standard Methods - For the Examination of Water and Wastewater 22<sup>ª</sup>ed, 3030K, 3111B
- [17] Gonçalves, Maria de Lurdes Sadler Simões (2001), “Métodos instrumentais para análise de soluções: análise quantitativa”, 4<sup>a</sup> ed., Fundação Calouste Gulbenkian
- [18] Guia Relacre nº13 - Validação de métodos Internos de Ensaios em Análise Química, Lisbon, 2000
- [19] Carvalho, Carla (2010), “Guia de Procedimentos de Amostragem de Resíduos”, Instituto Nacional de Administração