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Treball Final de Grau

Feasibility study for the preparation of reference materials for the physico-chemical characterisation of solid wastes.
Estudi de viabilitat per a la preparació de materials de referència per a la caracterització físico-química de residus solids.

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"Si supiese qué es lo que estoy haciendo, no lo llamaría investigación, ¿verdad?"

Albert Einstein

REPORT

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1. SUMMARY

Nowadays, waste management is a very important aspect, so minimizing waste is vital. When waste cannot be recycled or reused, it is disposed in controlled landfills. European Decision 2003/33/EC establishes the criteria and procedures for the admission of waste to controlled landfills, which are based on a previous physico-chemical characterization of the waste. In Catalonia, its management is the responsibility of Agència de Residus de Catalunya (ARC). The ARC monitors the analytical behavior of the laboratories that participate in proficiency test for the characterization of waste.

Since 2003, Mat Control organise proficiency tests for the characterization of solid wastes from soil matrices. For the correct operation of a proficiency test, the reference material sent to the participant, must be homogenous and stable over time and it has to allow to check the analytical performance of participants for the list of parameters of interest. For achieving the best conditions, a feasibility study must be performed, that has as objective quantify in aqueous leachate the established parameters decided in the campaign with the difficulties that this may cause. The parameters established for the analysis, and according to the present legislation, are some metals, some anions, phenol index and total organic carbon.

In this work, the physico-chemical properties of the initial soil will be analysed and a fortification process will be established to obtain the reference material used in the proficiency test for the 2022 campaign that achieves the mentioned objectives.

Keywords: Waste, reference material, proficiency test, feasibility study, Mat Control.

2. RESUM

Actualment, la gestió de residus és un aspecte molt rellevant, d'aquesta manera la minimització dels residus, és vital. Quan el residu no es pot reciclar o reutilitzar es disposa en abocadors controlats. La Decisió Europea 2003/33/EC estableix els criteris i procediments per l'amissió d'aquests residus als abocadors controlats mitjançant una caracterització fisico-química prèvia del residu. A Catalunya, la seva gestió és competència de l'Agència de Residus de Catalunya (ARC). L'ARC controla el comportament analític dels laboratoris que participen en assajos d'aptitud per la caracterització de residus.

Des del 2003, Mat Control organitza assajos d'aptitud per a la caracterització de residus a partir de matrius de sòl. Pel bon funcionament d'un assaig d'aptitud, el material de referència enviat als participants, ha de ser homogeni i estable en el temps, i ha de permetre als laboratoris comprovar el seu comportament analític per la llista de paràmetres d'interès. Per assolir les millors condicions s'ha de realitzar un estudi de viabilitat, que té com a objectiu que els paràmetres establerts en la campanya, d'acord amb la legislació vigent, siguin quantificables en el lixiviat aquós amb les dificultats que això pot provocar. Els paràmetres establerts per l'anàlisi són alguns metalls, alguns anions, índex de fenol i el contingut de carboni orgànic total.

En aquest treball, s'analitzaran les propietats fisico-químiques del sòl de partida i s'establirà un procés de fortificació per obtenir el material de referència utilitzat en l'assaig d'aptitud de la campanya 2022 que assoleixi els objectius citats.

Paraules clau: Residus, material de referència, assaig d'aptitud, estudi de viabilitat, Mat Control.

3. INTRODUCTION

Nowadays, many analytes are determined in different matrices in an analytical laboratory every day. This process is very important for the different environmental compartments as water, air, soil, plants, wildlife, among others with different objective such as control, identification, knowledge studies or behavioral studies.

To make reliable decisions, the laboratories need to have tools to control their results and their performance. One tool is to participate in an interlaboratory comparison (ILC).

3.1 INTERLABORATORY COMPARISON

ILC is the organization, performance and evaluation of a test on the same or similar test items by two or more laboratories in accordance with predetermined conditions [1].

According to ISO/IEC 17025 [2] the laboratory shall have a procedure for monitoring the validity of the test or measurement undertaken. The laboratory shall monitor its performance by comparison with the results of other laboratories. Laboratories can participate in proficiency tests (PTs) or/and participate in ILC other than PT.

ILC is for the external control of the laboratories, they can participate with one or both of these uses:

- External use with the aim of demonstrating their analytical performance to an accreditation body or a certifying organisation.
- Internal use with the purpose of continuous improvement and detection of potential analytical problems.

Among the benefits that laboratories can obtain participating in an ILC the following can be highlighted:

- Increases the confidence of a method throughout the comparison of accuracy and present results.

- Determinate systematic errors in methods.

Some of the aims of ILC are the establishment of the effectiveness and comparability of testing or measurement methods, identification of interlaboratory differences or among others the provision of additional confidence to laboratory customers. The organisers then share the results and inform the participants of the outcome. [**3**]

There are three types of ILC because not all interlaboratories have the same purpose:

- PT: the objective is to know if the method that the laboratory used gives accurate and precise results along the time.

- Certification exercise: the purpose is to certify a reference material (RM).

- Collaborative exercise: the aim is to validate a method that a laboratory uses frequently.

This work is going to be focused in the design of a PT for the characterization of a solid waste.

3.1.1 Proficiency test

A PT is an objective evaluation of the technical competence of the laboratory participant according to a predefined condition and it involves the use of ILC.

ISO/IEC 17043:2010 defines it as an organisation, performance and evaluation of measurement or test on the same or similar items by two or more laboratories in accordance with predetermined conditions [**4**].

PT involves several laboratories performing the same measurement on the same sample and report the results to the organizer by a deadline. Then the organiser performed a statistical treatment of their results, and the laboratories can know if their measurement of the sample was correct.

The steps involved in the organization of a PT are presented in Figure 1.
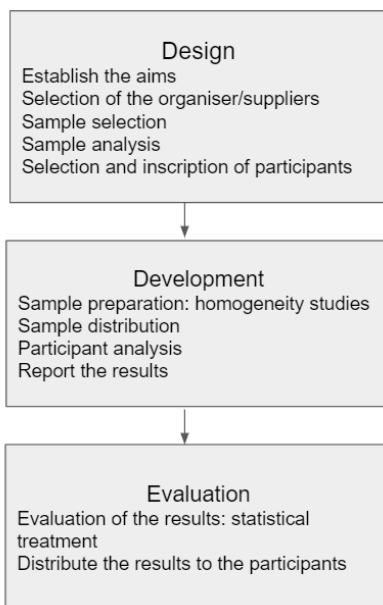
Figure 1: Steps involved in the organisation of a PT.

The PT is classified according to the aim, type of organisation or type of sample.

According to the objective:

- Qualitative scheme: identification of the sample characteristics.

- Quantitative scheme: quantification of more than one analyte in a sample.

- Sampling.

According to the type of organisation there are:

- Single occasion exercise is organized only once without continuity.

- Continuous scheme where PT items are provided in regular intervals.

And finally, according to the type of sample used, there are step-by-step scheme, two-level scheme and two identique samples.

Monitoring of laboratory performance is usually achieved by participating in a continuous and quantitative PT scheme, when is available. The sample used for a successful PT organisation has to accomplish the requirements of a RM.

3.1.2 Reference material

According to the ISO/IEC Guide 30 [**5**], a RM is a material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or the assignment of values to materials.

RMs are widely used in analytical chemistry, and according to ISO/IEC Guide 33 [**6**] RMs are used for calibration of apparatus, establish traceability of the measurement and for method validation.

RMs have to follow certain rigorous criteria before being accepted for its intended use. The following conditions are prerequisites for preparing a RM that is acceptable for organizations around the world [**7**].

1. Homogeneity: this assures that the subsequent analysis of the subsamples taken for measurement in different laboratories will produce the same analytical result.

2. Stability: the material has to be stable under a variety of transport, conditions and storage. For this reason, it's necessary to assess the stability during a long term.

3. Similarity to the sample: the RM should be similar as close as possible to the matrix of the test, it has to be representative.

4. Accuracy, uncertainty and traceability

The general steps to prepare RMs are presented in Figure 2 [**8**].
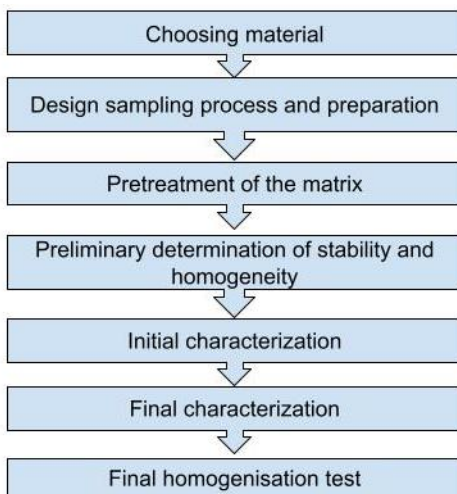
Figure 2: General steps to prepare RMs.

The preparation process is made in small-scale with the aim that the material has the establish objective, this is a feasibility study (FS).

There are three different strategies of RMs preparation: natural matrix where all the target analytes are present, fortification where it is necessary to add the analytes in form of anions or cations to the matrix and the last blending. The ideal situation is to find a natural matrix to prepare a RM, but not always is possible and any of the other strategies must be followed.

3.2 PROFICIENCY TEST FOR CHARACTERIZATION OF WASTES

3.2.1 Waste and waste management

A waste that can be defined as the useless by-product of human activity which physically contains the same substance that is available in the useful product [3]. It can be classified into three main types based on their physical states in liquid, solid and gas.

But one of the most important environmental issues is waste management.

Waste management [1] is the collection, transport, processing, recycling or disposal, and monitoring of waste materials.

Once the waste is generated, its reuse, recycling and/or recovery is addressed, and only when none of these methods are available, the waste is disposed in landfills.

In Spain the waste management is transferred to the autonomous communities.

The European Decision 2003/33/ EC establishes the criteria and procedures for the admission of waste into controlled landfills, which are based on a physico-chemical characterization according also to the Real Decreto 69/2009 of Diari Oficial de la Generalitat de Catalunya (DOGC) [**9**]. This characterization provides basic information about the residue such as origin, composition, leachability among others.

According to its hazard, the residues are classified in inert residues, non-special residues they are not dangerous, and special residues they are dangerous not only for human and animals also to the environment and they will be deposited in the corresponding landfills.

A very important aspect is the leachate formed inside the controlled landfill due to the filtration of water or the moisture of solid.

For this reason and depending on the classification of the residue, the limit value in an aqueous leachate for a long list of parameters (for exemple, As, Cd, Cr, Cu, sulphates, total organic carbon, among others) will vary.

As an example, the As limit value in the leachate for admissible residue in landfill for inert residues, non-special residues and special residues are shown in Table 1.

	$mg \cdot kg^{-1}$ dry matter
Inert residues	0,5
Non-special residues	2
Special residues	25

Table 1: Limit value for leachable arsenic in the different type of residues

In Catalonia, waste management is under the responsibility of the Agència de Residus de Catalunya (ARC), which monitors the analytical behavior of the laboratories that characterize wastes through their participation in PT.

Since 2003, ARC monitors their collaborating laboratories through their participation in the PT organized by Mat Control.

3.2.2 Mat Control laboratory

Mat Control is a laboratory specialist in the preparation of RMs, principally for the campaigns of food or environmental fields and, since 2003 and for the requirement of the ARC, organize PT for the characterization of residues.

Actually, they organized PT for the characterization of solid waste, cereals, organic elemental analysis and one program focused to teaching laboratories.

The laboratory has an internal quality management system based on the ISO/IEC 17043 for organizers of PT that included the requirements of the ISO/IEC 17025 for the analytical activities.

In this work, is going to prepare a multicomponent waste soil that allows to the laboratories participant in the ILC campaign 2022 quantify heavy metals, anions, cations, phenol and TOC. However, finding a soil that naturally has all these elements in large quantity when leachate in water, is so difficult. First, because water has a very weak extraction power and then all these elements have different physical-chemical proprieties.

So Mat Control with their experience decided to follow a fortification process for the preparation of the item, that is one of the strategies for the preparation of a RM.

4. OBJECTIVES

As I explained the ILC is a good tool for the laboratories for the establishment of the effectiveness, identification of interlaboratory differences, detect errors in their methods, among others.

In this work, it is going to design a ILC for the campaign of characterization of multicomponent solid waste 2022.

As all the parameters agreed within the Mat Control team following the present legislation for waste characterisation must be quantifiable in the aqueous leached fraction, the purposes of this work are:

-   Determinate the pysico-chemical property of a soil used as bulk material, such as pH, percentage humidity, field capacity and organic matter.
-   Establish the process of fortification to obtain a suitable RM to be used in the PT.

5. EXPERIMENTAL SECTION

5.1 MATERIAL, REAGENTS, STANDARD SOLUTION AND EQUIPMENT

Material

The most important materials are electronic pipettes, volumetric material, weighing bottles, crucibles, crushing and sieving material, plastic bottles with stoppers and paper filter.

Reagents

The most important reagents used in this work are several nitrate salts, chlorine salts, $Na_2HAsO_4 \cdot 7H_2O$, Na_2SeO_4, $C_4H_4KO_7Sb \cdot 1/2H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, NaF and phenol all the salts with analytical quality.

Moreover, reagents like acetic acid, glycerol, hydrochloride acid, salts such as NaCl, NaF, 4-aminoantipyrine, $K_3Fe(CN)_6$, among others.

Also, double deionized water with a conductivity 18 $M \cdot \Omega \cdot cm^{-1}$ and COMPO universal fertilizer.

Standard solution

Standard solution of Cd, Cr, Cu, Ni, Pb and Zn HNO_3 2% quality certipur® with a concentration 1000 $mg \cdot L^{-1}$ of two differents providers one for calibration process and the other for control sample.

Instrument and equipment

- Rotor mill RETSCH SR 200
- Roller table MOTOVARIO NMRV/063
- Oven MEMMERT UPL-800

- Kneader KENWOOD

- Balance AND GX-2000

- Stirring system Heidolph REAX 2018.

- Filtration system OM100 Millipore

- Flame atomic absorption spectrophotometer Perkin-Elmer 1100B

- Inductively coupled plasma atomic emission spectrophotometer Perkin-Elmer Optima 3200RL

- Analytical balance Salter HR-200

- pHmetre SENSION

- End-over-end shaker SELECTA

- Desiccator

- Centrifuge HETTICH ROTINA 420

- Muffle CARBOLITE

- Potentiometer SENSION with fluoride selective electrode

- UV-Visible spectrophotometer Agilent Cary 60

5.2 SOIL MATRIX PRETREATMENT

The first step was mixing different soils coming from the same geographic area. Then, the sample was sieved through a 1 mm mesh sieve following PNT/MAT/EQP/04/01 [**10**]. It was homogenized during a week following PNT/MAT/EQP/0X/01 [**11**].

The solid was fertilized with a natural fertilizer, each kilogram of solid was mixed in the kneader with a solution of 150 mL of double deionized water and 150 mL of the natural fertilizer.

Then the solid stayed at 40 ºC in the oven until was completely dried. Afterwards, the sample was milled and homogenized during a week.

5.3 CHARACTERIZATION OF THE WASTE SOIL

The characterization of the waste soil starts with leaching process, this process has been realized following PNT/MAT/MET/02/02 [**12**].

Leaching is the process that involves the use of a solvent to remove a solute from a solid mixture.

The process started weighing 100 g of the solid into a 2L plastic bottle. It was necessary to ensure that the pH of deionized water was around 6, then a liter was added. The bottles were closed with a stopper and parafilm and were introduced in the agitator shaken at 5 rpm during 24 hours at room temperature.

When the leaching process was finished, the process of filtration started through OM100 Millipore with a 0,45 µm filter of nitrocellulose.

In this point the leaching process finished and start the measuring step.

Determination of Cd, Cr, Cu, Ni, Pb and Zn in soil solution has been realized by flame atomic absorption spectroscopy (FAAS). The linearity interval is shown in Table 2.

	Cd	Cr	Cu	Ni	Pb	Zn
Interval $[mg \cdot L^{-1}]$	0,16-2,00	0,20-5,50	0,20-6,00	0,20-5,50	1,00-16,00	0,08-1,50

Table 2: Linearity interval of analysed heavy metals.

Determination of Cd, Cr, Cu, Ni, Pb, Zn, Mo, Se, Sb, Hg, As and Ba in soil solution has been also realized by inductively coupled plasma atomic emission spectroscopy (ICP-OES). This determination has been realized in the Scientific and Technological centers of UB (CCiTUB).

5.4 DETERMINATION OF SOIL PROPERTIES

All the determinations have been carried out in triplicate.

5.4.1 Preparation of standard solution, control samples, stock solution and added samples

All the process was realized following PNT/MAT/MET/04/01 [**13**].

All the calculation has been realized from the weight of the volumes, with the aim of realizing fewer errors. The weights were registred in a template included in the laboratory management system following ISO 17025 and ISO 17043 (Appendix 1).

Stock solutions

The volume shown in Table 3 was added from the commercial standard solution of 1000 mg·L^{-1} Cd, Cr, Cu, Ni and Zn, not Pb because for working standards, it was taken directly from the commercial dissolution.

Stock solutions	Cd	Cr	Cu	Ni	Zn
Volume [mL]	10	25	25	25	5
Theoretical concentration [mg·L^{-1}]	100	250	250	250	50

Table 3: Preparation of the stock solution of each metal.

Standard solutions

The volumes added from the intermediate stock solution to prepare the standard solution are shown in Table 4. Then it was completed to a weight of 50 g with double deionized water.

Standard solutions	Volume from diluted solution [μL]
P1	50(Cr,Cu,Ni,Pb); 80(Cd,Zn)
P2	200
P3	600
P4	800 (Pb); 1000 (Cd,Cr,Cu,Ni,Zn)

Table 4: Preparation of standard solution from stock solution.

Control samples

The volumes added from standard solution from a different supplier are shown in Table 5. Then it was completed to a weight of 50 g with double deionized water.

	Volume [μL]					
	Cd	Cr	Cu	Ni	Pb	Zn
Low concentration [mg·L^{-1}]	10	15	15	15	100	8
High concentration [mg·L^{-1}]	80	200	200	200	700	40

Table 5: Preparation control sample.

Added samples

The volumes added from standard solution from a different supplier are shown in Table 6. Then it was completed to a weight of 50 g with the leachate of one sample.

Fortified sample	Cd	Cr	Cu	Ni	Pb	Zn
Volume [μL]	2.5	25	25	25	75	10

Table 6: Preparation added samples.

5.4.2 Determination of pH

Figure 3: Determination of pH

This process has been realized following UNE 77308(2001) [**14**].

The process started weighing 20 g of solid, 100mL of double deionized water was added and then for 30 minutes stayed in a shaker. After that, rest for another 30 minutes.

To determinate pH, first the samples were filtered with a paper filter of 110 mm diameter and then the measure was performed by means of a pH-metre.

5.4.3 Determination of field capacity

This process has been realized following PNT/MAT/MET/YY/01 [**15**].

The process started weighing 15 g of solid in a cylinder. The cylinders were placed in a tray with 1 cm of height of water, it was allowed to rise by capillarity.

The cylinders were put in the centrifuge for 30 minutes at 1000 rpm.

Meanwhile, the weighting bottles were weighted. When the centrifuge process finished, 5 g of each cylinder was added to the weighting bottles. For 3 hours stayed in the oven and all night in the desiccator. The last step was weighting.

5.4.4 Determination of humidity

This process has been realized following UNE-EN 14774-3(2010) [**16**].

The weighting bottles with cover stayed during 3 hours in the oven at 105ºC, afterwards stayed in the desiccator all night at room temperature. Then, 5 g of solid was added.

Stayed for 2 hours in the oven at 105 ºC and all night in the desiccator. The process was repeated, 30 min in the oven at 105 ºC and 20 min in the desiccator and weighed.

5.4.5 Determination organic matter

Figure 4: Determination organic matter

This process has been realized following UNE-EN 15169 [**17**]. The organic matter was determined through the calcination losses and was expressed in weight percentage of dry matter.

The first step was weighed the crucible and 3 g of solid. It was introduced in the muffle at 150ºC, each hour the temperature will increase 50ºC until 550ºC. Then the crucibles with the remaining solid were introduced in the desiccator and were weighed.

5.4.6 Determination of F⁻ by potentiometry with fluoride selective electrode

For that determination the reagents needed were the following:

- Dissolution of TISAB made of NaCl 0,1 M, CH_3COOH 0,25M, CH_3COONa 0,75 M and sodium citrate 0,001M, that is necessary to adjust ionic strength and pH.

- From standard solution of 1000 mg·L⁻¹ F⁻, four standard solutions for the calibration line with a concentration between 1 and 10 mg·L⁻¹ and with a proportion 1:1 water:TISAB are prepared. It was important prepare all solutions in plastic volumetric flask.

5.4.7 Determination of Cl⁻ by Mohr method

The volumetric determination of chlorides with silver nitrate is based on a precipitation reaction (1).

Mohr's method consists in using potassium chromate as indicator, that reacts with the excess of silver (2).

$Cl^- + Ag^+ \rightarrow AgCl\ (s)$ (1)

$CrO_4^- + 2Ag^+ \rightarrow Ag_2CrO_4\ (s)$ (2)

Figure 5: Determination of Cl⁻
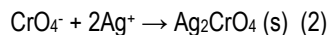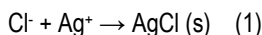
It was necessary:

- Dissolution of potassium chromate 5%
- Dissolution of silver nitrate 0,1M

To do the titration with $AgNO_3$ of the samples, 20 mL of sample was added with 100 mL double deionized water. It was important to check the pH and if it is below 6,5, $NaHCO_3$ was added until reaching this value. Then a 1 ml of indicator was added.

To do the titration of the blank:

To a 100 ml of double deionized water a spatula tip of $CaCO_3$ is added. It's important to check the pH and if it is below 6,5, $NaHCO_3$ was added until reaching this value. Then a 1 ml of indicator was added.

5.4.8 Determination turbidimetric of sulfate

For the determination of the transmittance the reagents needed are the following:

- NaCl/HCl solution, prepared from 60 g NaCl and 5 mL HCl in 250 mL.

- Glycerol/ethanol solution proportion 1:3.

- Standard solution 100 $mg \cdot L^{-1}$ sulfates.

Six standard solutions and a blank were prepared within the linearity range 5-30 $mg \cdot L^{-1}$ sulfates.

To prepare the samples it was necessary to add the reagents in this order: an aliquot of sample, 10 mL NaCl/HCl, 20 mL glycerol/ethanol and 0,3 g $BaCl_2$.

5.4.9 Determination phenol index

For that determination is necessary:

- Phosphate buffer solution: 10,4 g K_2HPO_4 with 7,2 g KH_2PO_4 in 100 mL.

- 4-aminoantipyrine solution: 1 g 4-aminoantipyrine in 50 mL.

- Potassium ferricyanide solution: 4 g $K_3Fe(CN)_6$ in 50 mL.

Four standard solutions were prepared within the linearity range 1-5 $mg \cdot L^{-1}$ of phenol.

To determine the absorbance of the standard solution was added in the volumetric flask 100 μL 4-aminoantipyrine solution, 100 μL potassium ferricyanide solution, 10mL phosphate buffer solution and 10 mL standard solution.

To determine the absorbance of the samples was added in the volumetric flask 100 μL 4-aminoantipyrine solution, 100 μL potassium ferricyanide solution, 10mL phosphate buffer solution and 10 mL sample.

6. RESULTS AND DISCUSSION

Mat Control as organizer of ILC, following the list of parameters as described in the present legislation, decided the following parameters to be analysed in the multicomponent solid waste item: As, Ba, Cd, Cu, Cr, Hg, Ni, Pb, Zn, Mo, Sb, Se, chloride, sulphate, fluoride, phenol index, pH, field capacity, humidity, organic matter and TOC.

6.1 MULTICOMPONENT SOLID WASTE ITEM

To begin with the preparation of the item, it is going to mix different soils coming from different sampling points of a contaminated area after a pyrite slurry spill.

Then the soils were milled through a 1 mm mesh sieve in the rotor mill and during a week it was homogenized in the roller table.

After, three samples of 100 g that were collected from the bottom, middle and upper part of the drum and the leaching process started, following the procedures described in 5.2.

For the initial characterization, it is going to analyse on the one hand the metals present in the soil by FAAS and ICP-OES. For the characterization by FAAS it is necessary to prepare different solutions explained in 5.4.1. And on the other hand, pH, humidity, field capacity and organic matter as explained in 5.4 were also analysed.

The results of the initial characterization of the metals are shown in Table 7 and the results of the properties are shown in Table 8.

	[mg·Kg^{-1}]
Cd	<LOQ
Cu	0,4±0,3
Pb	<LOQ
Zn	3±1
Mo	<LOQ
Ni	<LOQ
Se	<LOQ
Sb	<LOQ
Hg	<LOQ
Cr	<LOQ
As	<LOQ
Ba	1,4±0,7

Table 7: Results of the initial characterization of metals.

pH	Field capacity [%]	Humidity [%]	Organic matter [%]
6,95±0,06	30±14	4,0±0,1	4,7±0,3

Table 8: Results of the soil properties.

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As the results show, the metals Cd, Pb, Mo, Ni, Se, Sb, Hg, Cr and As not leach in aqueous medium, the causes may be due to the low extraction power of water, the possible interaction with other metals and/or with the organic matter or that they are not naturally present in the soil.

For this reason and based on the last studies realized in Laboratory Mat Control, it was decided to fertilize the soil with a universal fertilizer as a previous step to the fortification. In a previous study of the research group on a different soil matrix it was concluded that the fertilization process made that the field capacity, humidity and organic matter increased and the pH decreased. Consequently, when fertilizing the soil, the metals availability in aqueous solution was higher except for Ba [18].

For all these advantages and that the fertilization process is not difficult and not very time consuming, this strategy was followed with the aim of increase the concentration of the metals above the LOQ.

The availability of the metals in aqueous solution depends on the characteristics of the soil where it is and the physical-chemical process as absorption and desorption for the interaction metal-soil. The most important factors that affect metal solubility from soil are [**19**]:

- pH: except As, Mo, Se and Cr, the other heavy metals are more available in acidic pH.
- Organic matter: the organic matter can react with the metals forming complexes and chelates, and this can decrease the availability of the metals.
- Texture: the clay soil retains more heavy metals by absorption.
- Salinity: an increase of salinity, increase the mobility and retention of the metals.

Considering that the field capacity of the soil was about 30%, this indicated that 100g of soil can accept about 30 g of water. So, each kilogram of solid was fertilized with a solution of 150 mL fertilizer and 150 mL double deionized water (factor dilution 1:1 as indicated for the application of fertilizer).

The solid was mixed in the kneader with the solution and dried in the oven at 40-50ºC for 4 days. When the soil was completely dried, the sample was milled and homogenized during a week.

All the soil proprieties described in 5.4 were determined and their results are shown in Table 10. The results of the metals after that process are shown in Table 9.

The concentration in mg·Kg^{-1} of fluorides is 0,9±0,1, chlorides 8315±831, sulfates 4477±720 and the phenol index 34,2±0,4 .

	[mg·Kg^{-1}]
Cd	<LOQ
Cu	17,4±0,3
Pb	<LOQ
Zn	22,4±0,3
Mo	2±1
Ni	3,4±0,3
Se	<LOQ
Sb	<LOQ
Hg	<LOQ
Cr	<LOQ
As	<LOQ
Ba	0,6±0.3

Table 9: Extracted metals on aqueous solution after fertilization.

pH	Field capacity [%]	Organic matter [%]	Humidity [%]
6,80±0,06	26±5	8,0±0,1	3,4±0,4

Table 10: Results of soil proprieties after fertilization.

As the results show, some of the metals increase their concentration after fertilization process such as Cu, Zn, Mo, Ni and Ba but for most of them their concentration was still below the LOQ.

If the soil properties are compared, the pH decrease without importance but the humidity and field capacity decrease more and the percentage of organic matter double the initial value. The fact that the organic matter increased can cause interference with the metals forming complex or chelate.

As a 58% of the metals were below LOQ, fluorides and phenol index provided a little concentration in soil, a feasibility study (FS) for establishing the fortification process to be undertaken were

realized. Sulfates and chlorides provided a high concentration in soil and for this reason they won't be fortified.

6.2 FEASIBILITY STUDY FOR THE PREPARATION OF A SOLID WASTE ITEM

With the aim of increasing the concentration of Cd, Cr, As, Cu, Ni, Pb, Zn, Se, Sb, Mo, F⁻ and phenol index is necessary to do a feasibility study on small-scale, that is on portions of 1 Kg of the bulk material.

Initially, it was decided to do three fortification tests called A, B and C. Each test is separated in three portions called 1,2 and 3, and each one was fortified with the selected elements, as Figure 6 shown.
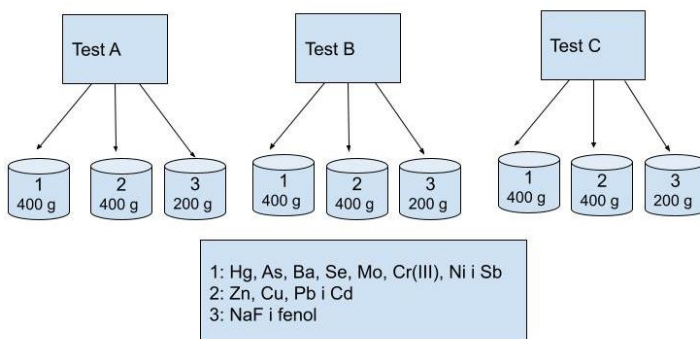

Figure 6: Scheme of the elements in each test.

To decide the element of each portion with the purpose of decreasing the interaction between them, the Mat Control team was based on the one hand in a study of mobility of heavy metals in soils that show that Pb, Cu and Zn competed with Ca, element present in high concentration in the soil, for sorption sites [20]. On the other hand, the results of FS from previous editions were also taken into account.

To prepare the fortification solution for each portion, the gram of each element salt must be calculated. The grams needed were calculated from the multiplication of different fortification factors to the theoretical grams of salt needed according to the concentration values included in

the Decreto 69/2009 [9] (Appendix 2). The fortification factors chosen by the team are shown in Table 11.

Parameters	Salt	Test A	Test B	Test C	Test D	Test E
As	$Na_2HAsO_4 \cdot 7H_2O$	60	80	120	290	290
Ba	$BaCl_2 \cdot 2H_2O$	2	4	4	5	10
Cd	$Cd(NO_3)_2 \cdot 4H_2O$	8	8	8	8	10
Cr	$Cr(NO_3)_3 \cdot 9H_2O$	20	40	40	80	80
Cu	$Cu(NO_3)_2 \cdot 3H_2O$	12	12	20	20	20
Ni	$Ni(NO_3)_2 \cdot 6H_2O$	12	12	12	15	15
Pb	$Pb(NO_3)_2$	120	120	120	250	250
Zn	$Zn(NO_3)_2 \cdot 6H_2O$	4	6	6	5	5
Hg	$HgCl_2$	200	200	200	300	500
Se	Na_2SeO_4	40	80	80	100	100
Sb	$C_4H_4KO_7Sb \cdot 1/2 \ H_2O$	80	120	120	150	150
Mo	$(NH_4)_6Mo_7O_{24} \cdot 4 \ H_2O$	11	11	17	200	300
F^-	NaF	0,6	0,6	0,6	0,5	0,5
Phenol	Phenol	10	10	20	25	25

Table 11: Summary of the fortification factors established in each test realized.

According to the field capacity and working 2% below, each 100 g of soil can accept about 28 mL of water. For this reason and taking account the grams of soil of each portion, the fortification solution 1 and 2 were mixed with 112 mL of double deionized water and the portion 3 with 56 mL.

The corresponding grams of salt were weighted in the balance and stirred for a day. Afterward, the solutions were mixed with the corresponding portion of soil in the kneader.

Then stayed during a day in the oven at 40ºC and when was totally dried the three portions of each test were milled together and homogenized for two days.

After the leaching process, the samples of each test were analysed in duplicate and the results of the FS on small-scale with the corresponding technique used are shown in Table 12.

Parameters [mg·kg^{-1} soil]	Test A	Test B	Test C	Technique
As	<LOQ	<LOQ	<LOQ	ICP-OES
Ba	2,5±0,5	2,2 ±0,2	2,0 ±0,6	ICP-OES
Cd	10,63±0,07	10,52±0,08	6,93±0,03	FAAS
Cr	<LOQ	<LOQ	<LOQ	FAAS
Cu	37,78±0,07	25,0±0,5	35,22±0,05	FAAS
Ni	378±24	262±24	345±70	FAAS
Pb	<LOQ	<LOQ	<LOQ	FAAS
Zn	220±9	278±8	277±92	FAAS
Hg	9,8±0,9	7,0	10,45±0,07	ICP-OES
Se	122±2	238±1	277±2	ICP-OES
Sb	30,6±0,6	23,4±0,8	31,2±0,9	ICP-OES
Mo	<LOQ	<LOQ	<LOQ	ICP-OES
F$^-$	40±2	58,42	45,46	IES
Phenol	112±9	146±4	150±12	UV-Vis

Table 12: Results of each test.

Unfortunately, although there were some metals able to be leachated in the aqueous solution of the soil, about 29% of the parameters are not able to be leachated in the aqueous solution of the soil and Hg, Cd and Ba, provided a low concentration.

If the results of these tests are compared with the results after fertilization process Cd, Hg, Se and Sb that before were below LOQ, now are quantifiable in leachate. And Mo that before was quantifiable after fortification process not.

Consequently, it was decided to realize two more tests called D and E, increasing the fortification factors of the salts except for fluorides because there were in concentration higher enough, with the aim that all the element leach in aqueous solution. The new factors assayed are shown in Table 11.

As in the other three tests the concentration of salt in portion 1 were very high and there were problems to dissolve Mo, As and Cr because a precipitate was formed, in these tests it has been decided to added these metals at the end of the process on the 1 Kg of soil mass.

Firstly, the process done with the other tests without Mo, As and Cr in the fortification solution 1 was repeated as shown Figure 7.
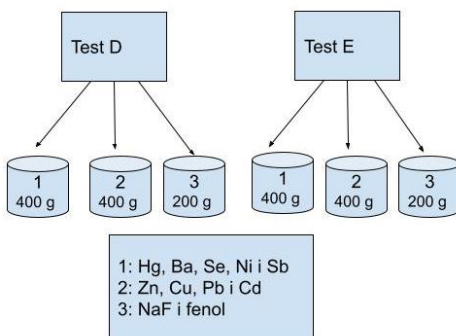
Figure 7: Scheme of the elements in each test.

After the homogenized process of the soil, a solution that contain Mo, As and Cr was prepared from the grams of its salts calculated from the fortification factors shown in table 11 and diluted in 270 mL of double deionized water, according to the field capacity.

Then, the fortification solution was mixed with the soil that has been previously fortified with the other elements and the process of drying and homogenization was repeated.

When the leaching process finished, the samples of each test were analysed in duplicate and the results of the FS on small-scale with the corresponding technique used are shown in Table 13.

[mg·Kg⁻¹ soil]	Test D	Test E	Technique
As	<LOQ	<LOQ	ICP-OES
Ba	2,3±0,6	3,4±0,3	ICP-OES
Cd	6,0±0,1	10,17±0,06	FAAS
Cr	<LOQ	<LOQ	FAAS
Cu	14,8±0,1	20,36±0,02	FAAS
Ni	366±57	453±5	FAAS
Pb	<LOQ	<LOQ	FAAS
Zn	89±2	156±20	FAAS
Hg	32,5±0,7	4,6±0,5	ICP-OES
Se	603±3	302±2	ICP-OES
Sb	65,4±0,7	27,4±0,4	ICP-OES
Mo	<LOQ	<LOQ	ICP-OES
F⁻	38,5±1	40±1	IES
Phenol	104,2±0,9	173±1	UV-Vis

Table 13: Results of each test.

As the results shown, the four metals that in the initial tests were below the LOQ and for this reason the fortification factor in these tests were increased continue below the LOQ.

Leaving aside that these metals cannot be quantified in the leachate, for this FS the results shown that test D provides better results that test E due to Hg in test E is very close to the LOQ that are 4 mg·Kg⁻¹.

Considering that a 71% of the parameters are able to be leachated in the aqueous solution of the soil in the five tests realized in small-scale and that in the initial tests there were problems with the solubility of the salts, test D is chosen as the best sample preparation strategy for the PT campaign 2022.

Therefore, next step of the study will be the preparation of the RM at big-scale. Additionally to the soil, the participants in the ILC will receive a vial with a solution containing As, Pb, Cr and Mo and a procedure for fortifying the leachate once obtained. In that way, they will be able to check their analytical performance also for those elements.

7. CONCLUSIONS

During these months of work, the aim was preparing a multicomponent waste soil that allows to the participants of the Mat Control ILC characterization of solid waste 2022 quantify metals as As, Ba, Cd, Cu, Cr, Hg, Ni, Pb, Zn, Mo, Sb and Se, anions like F^-, Cl^- and SO_4^{2-}, phenol and TOC. It may seem easy, but the analysis of the elements must be in aqueous leachate and it is so difficult due to the low extraction power of water, the possible interaction with other metals presents in the soil and/or with the organic matter or the natural absence of this elements in the soil.

Feasibility studies for the preparation of sample carried out in this work, allowed Mat Control to settle the best fortification strategy to be closer to the objective (test D): 71 % of parameters needed to be analysed by participants will be able to be quantified in the aqueous leachate. For the quantification of the remaining four elements, a vial will be provided to participants for fortification of the leachate once obtained.

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9. ACRONYMS

Acronyms	Meaning
ILC	Interlaboratory Comparison
ISO	Internacional Organization for Standardization
IEC	International Electrotechnical Commission
PT	Proficiency Test
RM	Reference material
FS	Feasibility Study
DOGC	Diari Oficial de la Generalitat de Catalunya
ARC	Agència de Residus de Catalunya
TOC	Total Organic Carbon
FAAS	Flame Atomic Absorption Spectroscopy
ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
TISAB	Total Ionic Strenght Adjustmen Buffer
CCiTUB	Scientific and Technological Centers UB
PNT	Standard Operation Procedures (SOP)
LOQ	Limit of Quantification

APPENDICES

APPENDIX 1: TEMPLATE OF THE PREPARATION STANDARD SOLUTION

P1	Tara del tub de plàstic amb tap (g):	15,3434						
		Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Pes final dissolució (g)**
	Volum de solució mare a afegir (µL)	80	50	50	50	50	80	
	∑ pes alíquota solució mare (g)	0,0847	0,1392	0,1936	0,2478	0,2979	0,3814	50,4018
	Pes alíquota individual solució mare (g)	0,0847	0,0545	0,0544	0,0542	0,0501	0,0835	
	Concentració real (mg/L)	0,1714	0,2757	0,2751	0,2732	0,9930	0,0848	
	Concentració teòrica (mg/L)	0,16	0,25	0,25	0,25	1,00	0,08	
	Criteri acceptació	0,15 - 0,17	0,24 - 0,26	0,24 - 0,26	0,24 - 0,26	0,95 - 1,05	0,076 - 0,084	
		Criteri acceptació:		Concentració real = Teòrica ± 5 %				

APPENDIX 2: MULTICOMPONENT SOLID WASTE FORTIFICATION

					Informació RD			Per 1 Kg de mostra	Per assajos sobre 1 kg de residu sòlid									
									PROVA A			PROVA B			PROVA C			
Paràmetre	Sal disponible	P atòmic	P molecular	Solubilitat	Annex 6	Annex 9	Conc. Desitjada	Pes sal teòric	Factor	Pes sal	Pes real	Factor	Pes sal	Pes real	Factor	Pes sal	Pes real	Paràmetre
		g	g		mg/kg	mg/kg	mg/kg	g		g			g			g		
As	Na2HAsO4.7H2O	74,91	312,02	61g/100mL	2	25	20	0,083	150	12,50		200	16,66		300	24,99		As
Ba	BaCl2 · 2 H2O	137,33	244,28	34g/100mL	100	300	200	0,356	5	1,78		10	3,56		10	3,56		Ba
Cd	Cd(NO3)2.4H2O	112,41	308,49	127g/100mL	1	5	5	0,014	20	0,27		20	0,27		20	0,27		Cd
Cr	Cr(NO)3·9H20	52,01	400,15	810g/L	10	70	50	0,385	50	19,23		100	38,47		100	38,47		Cr (Nitrat)
Cu	Cu(NO3)2.3H2O	63,54	241,6	137,8g/100mL	50	100	75	0,285	30	8,56		30	8,56		50	14,26		Cu
Ni	Ni(NO3)2.6H2O	58,71	290,8	238,5g/100mL	10	40	30	0,149	30	4,46		30	4,46		30	4,46		Ni
Pb	Pb(NO3)2	207,21	331,23	52g/100mL	10	50	50	0,080	300	23,98		300	23,98		300	23,98		Pb
Zn	Zn(NO3)2.6H2O	65,38	297,47	184g/100mL	50	200	150	0,682	10	6,82		15	10,24		15	10,24		Zn

Hg	$HgCl_2$	200,61	271,61	7,4g/100mL	0,2	3	3	0,004	500	2,03		500	2,03		500	2,03		Hg
Se	Na_2SeO_4	78,96	188,94	840g/L	0,5	7	7	0,017	100	1,68		200	3,35		200	3,35		Se
Sb	$C_4H_4KO_7Sb \cdot 1/2H_2O$	121,76	333,93	8,3g/100mL	0,7	5	4	0,011	200	2,19		300	3,29		300	3,29		Sb
Mo	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	95,94	1235,86	43g/100mL	10	30	25	0,322	200	9,20		200	9,20		300	13,80		Mo
Clorurs	$NaCl$	35,45	58,44	36g/100mL	15000	25000				0,00			0,00			0,00		Clorurs
Florurs	NaF	19	41,99	4g/100mL	150	500	500	1,105	3	3,32		3	3,32		3	3,32		Florurs
Sulfats	K_2SO_4	96,06	174,25	111g/L	20000	50000				0,00			0,00			0,00		Sulfats
Índex fenol	Fenol	94,11	94,11	8,3g/100mL	10		10	0,010	50	0,50		50	0,50		100	1,00		Índex fenol
TOC	$C_6H_4COOHCOOK$	12	204,23	80g/L	800	1000				0,00			0,00			0,00		TOC