

Tutors

---

Dr. Antoni Roca Vallmajor

Departament de Ciència de Materials i  
Química Física

Alfred Borràs Baldomà

Víctor García García

Coplosa, S.A.



# Treball Final de Grau

Methods of determination of lead oxides.

Mètodes de determinació d'òxids de plom.

Verónica Moreno Martín

January 2017



UNIVERSITAT DE  
BARCELONA

BKC  
Barcelona  
Knowledge  
Campus  
Campus d'Excel·lència Internacional



Aquesta obra està subjecta a la llicència de:

Reconeixement-NoComercial-SenseObraDerivada



<http://creativecommons.org/licenses/by-nc-nd/3.0/es/>



*Defensa el teu dret a pensar, perquè inclús pensar de manera errònia és millor que no pensar.*

Hipatia

Aquest projecte no s'hauria pogut dur a terme sense l'ajuda de moltes persones:

- Marco Portella (Director tècnic de l'empresa Coplosa). La seva autorització va ser crucial per al començament d'aquest projecte.
- Alfred Borràs (Cap del Departament de Qualitat de l'empresa Coplosa): Gracies per haver confiat en mi i en aquest projecte des del primer dia. Gracies per ajudar-me en tot moment i preocupar-te per mi, fins i tot en els pitjors moments. Sense ell aquest projecte no hagués estat possible.
- Dr. Antoni Roca (Departament de Ciència dels materials i Química Física) : Sense la seva col·laboració aquest projecte no s'hauria realitzat. Gracies per confiar en mi i en aquest projecte. Li he donar les gràcies per la seva paciència i dedicació. Gràcies pel temps que m'ha dedicat en dates que no tocaven i gracies també pels coneixements que m'ha aportat.
- Victor Garcia (Departament d'Investigació de l'empresa Coplosa): Gracies per involucrar-te en aquest projecte i per agafar les regnes d'aquest quan va tocar. Gràcies per la informació facilitada en tot moment i gràcies també per ajudar-me amb els teus coneixements.



# REPORT



# CONTENTS

<b>1. SUMMARY</b>	3
<b>2. RESUM</b>	5
<b>3. INTRODUCTION</b>	7
3.1. Description of Coplosa	7
3.2. Lead and lead oxides	8
3.2.1. Lead	8
3.2.2. Massicot	9
3.2.3. Litharge	11
3.2.4. Red lead	12
3.3. Transition α-β	14
<b>4. OBJECTIVES</b>	15
<b>5. METHODS FOR THE CHEMICAL AND STRUCTURAL CHARACTERIZATION</b>	16
5.1. XRD	16
5.2. DSC	19
5.3. XAS	23
5.4. Chemical characterization of metallic lead	25
5.4.1. Free lead in litharge and massicot	25
5.5. PbO <sub>2</sub> in litharge	26
<b>6. MATERIALS AND EXPERIMENTAL TECHNIQUES</b>	26
6.1. Materials	26
6.2. Experimental techniques	27
6.2.1. Free lead in massicot	27
6.2.2. Free lead in litharge	29
6.2.3. PbO <sub>2</sub> in litharge	31
6.2.4. XRD	33

---

6.2.5. Grain size distribution	34
<b>7. RESULTS AND DISCUSSION</b>	36
7.1. Free lead	36
7.2. PbO <sub>2</sub> in litharge	37
7.3. XRD	37
7.4. Grain size distribution	42
<b>8. CONCLUSIONS</b>	43
<b>9. REFERENCES AND NOTES</b>	46
<b>10. ACRONYMS</b>	47
<b>APPENDICES</b>	49
Appendix 1: XRD Quantitative diffractograms.	51
Appendix 2: Grain size reports.	53

## 1. SUMMARY

Lead oxides have been produced and used for all kinds of applications over hundreds and thousands of years. There are many types of lead oxides but, nowadays, the most common oxides in industry are Lead Monoxide ( $PbO$ ) and Red Lead ( $Pb_3O_4$ ), which can be also called Minium.

Lead Monoxide has two polymorphs, Massicot ( $\alpha\text{-PbO}$ ) and Litharge ( $\beta\text{-PbO}$ ), which have different properties such as colour or conductivity and, as a result, different industrial applications.

The determination of the distinct crystalline forms on Lead Monoxide is not simple. A specific method for the determination and quantification of lead monoxide is not established.

The main part of this project has been searching a method for the measurement of these two modifications. Subsequently an analysis of the most suitable technique for the determination of the different lead monoxide modifications has been carried out.

This project describes three different methods for the determination of lead monoxides: X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and X-Ray Absortion (XAS) and discusses if XRD is a suitable technique for the determination of lead monoxide polymorphs.

Also a chemical characterization of metallic lead and lead dioxide is realized using classical analytical methods.

Finally, a granulometric study of lead monoxides is accomplished by a grain size distribution analysis.

**Keywords:** Lead Oxides, Lead Monoxide, Red Lead, Minium, Massicot, Litharge, Polymorphism, Methods, XRD, DSC, XAS.



## 2. RESUM

Els òxids de plom s'han produït i utilitzat per a tot tipus d'aplicacions durant centenars i milers d'anys. Hi ha molts tipus d'òxids de plom, però, avui dia, els òxids més comuns en la indústria són el monòxid de plom ( $PbO$ ), i el mini ( $Pb_3O_4$ ).

El monòxid de plom té dos polimorfs, massicot ( $\alpha$ - $PbO$ ) i litargiri ( $\beta$ - $PbO$ ), que tenen diferents propietats com ara el color o la conductivitat i, com a resultat, diferents aplicacions industrials.

La determinació de les diferents formes cristal·lines al monòxid de plom no és simple. No s'ha establert cap mètode específic per a la determinació i quantificació de monòxid de plom .

La part principal d'aquest projecte ha estat buscar un mètode per a la determinació d'aquestes dues modificacions. Posteriorment s'ha dut un anàlisi de la tècnica més adequada per a la determinació de les diferents modificacions de monòxid de plom.

En aquest projecte es descriuen tres mètodes diferents per a la determinació del monòxid de plom: Difracció de Raigs X (DRX), Calorimetria diferencial d'escombrat (DSC) i Absorció de Raig-X (XAS) i s'analitza si difracció de raigs X és una tècnica adequada per a la determinació dels polimorfs de monòxid de plom .

També es realitza una caracterització química de plom metà·lic i diòxid de plom mitjançant mètodes analítics clàssics.

Finalment, es duu a terme un estudi granulomètric de monòxid de plom mitjançant una anàlisi de la distribució de la mida de gra.

**Paraules clau:** Òxids de plom, Monòxid de plom, Tetraòxid de plom, Mini, Massicot, Litargiri, Polimorfisme, Mètodes, XRD, DSC, XAS.



### 3. INTRODUCTION

The introduction is cleft in two sections.

Taking into account that this project is part of a development program pertaining to a company called Coplosa, S.A., the first part of the introduction focuses on the company, the work they do and the development program they are carrying forward.

The second part discusses some information about lead and its oxides as well as the source of lead metal and the process for obtaining massicot, litharge and minium.

#### 3.1. DESCRIPTION OF COPLOSA

Coplosa, founded in 1946, is a company specialised in the manufacture of lead oxides, activity in where it has archived a well-known prestige that has been enlarged with a range of metal oxides. Nowadays, the company main products are litharge, minium and antimony trioxide. Figure 1 is an external view of Coplosa Company.

Coplosa's factory is located in Barcelona, at the Zona Franca's industrial area; therefore their products are distributed all over Spain and in more than 20 countries worldwide.



Fig 1. Exterior view of Coplosa SA.

Coplosa keeps a strict policy of quality, holds the ISO-9001:2000, quality certifications and the environmental management certification ISO 14001:2004.

In 1994 Coplosa incorporated into Penox Group, the European leader of the lead oxide market, later on, in 1999, Penox Engineering was created. Nowadays, Penox Engineering has the best worldwide technology in lead oxide production equipment.

At the beginning of the 20th century lead was still the most important non-ferrous metal in the world but nowadays, lead consumption is being reduced due to its high toxicity and Penox has to attend a way of standing out in the industry. Accordingly, a method for the determination of lead monoxide is required to guarantee the quality of the final product and in intermediate products and to establish the best furnace parameters according to the client's specification.

### 3.2. LEAD AND LEAD OXIDES

As has been mentioned previously, Coplosa's activity is based on producing lead oxides. Lead oxides significant production began about 3000BC. The Roman Empire was the first society to use lead widely, they employed lead for numerous applications including additive for wine. Nowadays, lead oxides most important uses are batteries of lead-acid, ceramics, pigments and insulator for wires, among others.

#### 3.2.1. Lead

Lead is a soft, grey and dense metal that is usually found as lead(II) sulphide, which is also known as Galena. Figures 2 and 3 illustrate galena and metallic lead, respectively.

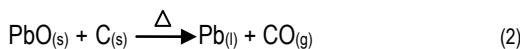
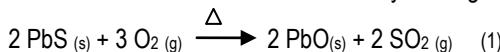


Fig 2. Galena (James St. John, 19/12/16, Creative commons Attribution 2.0 Generic)



Fig 3. Lead (Hi-Res Images of Chemical Elements, 19/12/16, CC by 3.0)

In order to obtain Lead from Galena the compound is heated in air to oxidize the sulphide ions into sulphur dioxide. Lead monoxide can be reduced by heating in carbon atmosphere.



This process used for the obtaining of Lead contributes to the atmospheric pollution by producing sulphur dioxide and, nowadays, fifty per cent of the lead production comes from recycling of lead oxides.

The main use of lead is the production of lead oxides although it can be also used in accumulators or in welding alloys.

### 3.2.2. Massicot

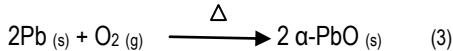
Massicot is the “ $\alpha$ ” lead monoxide modification which is thermodynamically stable at low and medium temperatures. This term can be confusing considering that its common name is “Litharge”. Even though in science its common name is Litharge, this term is often used for commercializing the  $\beta$  modification. Since in Coplosa the commercial name of the  $\alpha$  modification is Massicot and for the  $\beta$  is litharge, we will refer to the the  $\beta$  modification as Litharge and to the  $\alpha$  modification as Massicot, which exhibits a brown/reddish colour. Figure 4 illustrates a portion of massicot.



Fig 4. Massicot

To obtain massicot firstly lead metal has to be melt, this is accomplished on a melting pot at 450°C. Afterward, liquid lead metal is oxidised. In order to obtain  $\alpha\text{-PbO}$  two different processes can be executed: the Ball Mill Process and the Barton Pot Process. Both of these mechanisms are used in Penox group: Colonia's plant uses Ball Mill process and Coplosa uses Barton Pot

Process. Using the Ball Mill process it can be obtained a pure massicot with almost non litharge content while employing the Barton Pot Process a Litharge portion is always obtained. (1)



Massicot is the  $\alpha$ -phase of PbO which acquires a tetragonal crystalline form. Each lead atom is bound to four oxygen atoms forming a square pyramid with a lead atom at the apex (2), as can be observed in figure 5.

It has a well-defined layered structure; the bonds between the layers are a result of Pb-Pb interactions which are caused by Van der Waals forces. The layers are arranged in a sandwich Pb-O-Pb structure with covalent Pb-O bondings. (3)

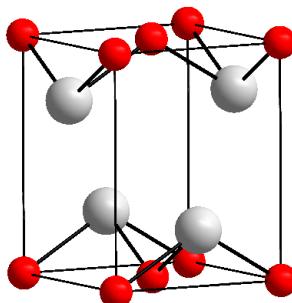


Fig 5.  $\alpha$ -PbO Crystalline structure. The red balls are oxygen atoms and the grey balls are lead atoms. ([American-Mineralogist-Crystal-Structure-Database Litharge, 19/12/16 via Wikimedia Commons, CC by-SA 3.0, 2.5, 2 and 1.0](#))

The lattice parameters for the tetragonal PbO are  $a=3.9749\text{\AA}$ ,  $b=3.9748\text{\AA}$  and  $c=5.0227\text{\AA}$ . Each Pb-O-Pb layer has a thickness of  $2.396\text{\AA}$  while the distance between the layers is  $2.6627\text{\AA}$ . (2) Due to the distribution of the electrons the specific resistivity perpendicular to the layers is  $10^{12}\Omega\cdot\text{cm}$  and along the layers is  $10^{11}-10^{10}\Omega\cdot\text{cm}$ .

Massicot has a bandgap of 1.92 eV which make it a good photoactive semiconductor (5).

Other important properties of  $\alpha$ -PbO are:

- Molecular weight: 223.19 g/mol.
- Density: 9.14 g/cm<sup>3</sup>.

-  $\Delta H_{298}$ :  $-219,000 \pm 800$  J/mol.

- Melting point:  $885^\circ\text{C}$ .

Due to the characteristics exposed above massicot main use is battery oxides.

### 3.2.3. Litharge

Litharge is the “ $\beta$ ” lead monoxide modification which is metaestable at room temperature and stable at temperatures above  $488^\circ\text{C}$  (2). Litharge exhibits yellow colour, as we can observe in figure 6.



Fig 6. Portion of litharge

In Coplosa litharge is manufactured in a furnace at  $702-4^\circ\text{C}$ . First, massicot is obtained and then it is propelled to the litharge furnace, where it reacts from  $\alpha$  to  $\beta$   $\text{PbO}$ .

The  $\beta\text{-PbO}$  is the lead monoxide modification which acquires an orthorhombic crystalline structure. It has two oxygen sublayers that are sandwiched between two lead sublayers. The layers, that are parallel to the bc plane are made up  $-\text{Pb-O-Pb-O}-$  zig zag chains. The lead atoms are in a distorted square-pyramidal coordination. (2) Figure 7 exhibits the litharge structure.

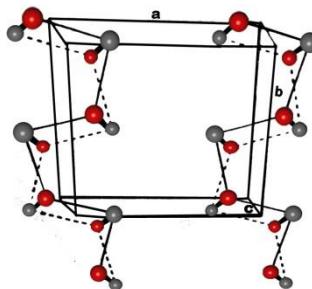


Fig 7.  $\beta$ -PbO Crystal structure. The red balls are oxygen atoms and the grey balls are lead atoms. (Picture extracted from reference 20.)

The lattice parameters for  $\beta$ -PbO are  $a=5.8931\text{\AA}$ ,  $b=5.4904\text{\AA}$  and  $c=4.7528\text{\AA}$ . The thickness of the Pb-O chains is  $2.707\text{\AA}$  and the distance between Pb adjacent layers is  $3.186\text{\AA}$ . (2)

As in massicot in litharge the bonds between the layers are a result of Pb-Pb interactions which are caused by Van der Waals forces. The resistivity of litharge is  $8 \cdot 10^{13} \Omega \cdot \text{cm}$ .

Litharge has a bandgap of 2.7 eV and it is also a good semiconductor and photoconductor.

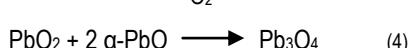
Other important  $\beta$ -PbO characteristics are (2):

- Molecular weight: 223.19 g/mol.
- Density: 9.56 g/cm<sup>3</sup>.
- $\Delta H_{298}$ : -217,700 J/mol.
- Melting point: 885°C.

Considering the characteristics exposed above litharge can be applied in a lot of fields, the most important ones are: glass and ceramics industries, pigments, rubbers and PVC stabilizer, among others applications.

### 3.2.4. Red Lead

Red lead ( $\text{Pb}_3\text{O}_4$ ) is originated as a combination of two different lead oxides,  $\alpha$ -PbO and  $\text{PbO}_2$ .



Minium exhibits a red/orange colour, which can be observed in figure 8, and it can be obtained at a temperature range of 450°C up to 480°C.



Fig 8. Red Lead

Red lead owns a tetragonal structure. The latter contains  $\text{PbO}_6$  octahedra with  $\text{Pb}^{4+}$  ion in the center and  $\text{O}_2^-$  ions at the peaks which are bonded only at opposite edges and divalent  $\text{Pb}^{2+}$  are coordinated with three oxygen ions, as is shown in figure 9. The  $\text{Pb}^{2+}\text{-O}$  bond is predominantly covalent with a 22-50% ionic character. (5)

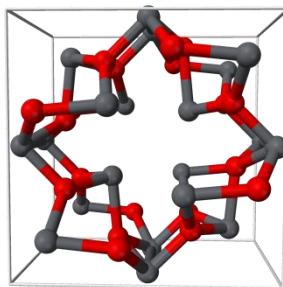


Fig 9. Red Lead Crystal Structure. Red balls are oxygen and grey balls are lead. (Benjah-bmm27, 19/12/16, Via Wikimedia Commons, Public Domain)

When  $\text{Pb}_3\text{O}_4$  is heated to  $550^\circ\text{C}$  this is converted to  $\beta\text{-PbO}$ .

Some of the most important properties of red lead are:

- Molecular weight: 685.57 g/mol
- Density: 8.94 g/cm<sup>3</sup>.
- $\Delta H_{298}$ :  $-734,000 \pm 17,000 \text{ J/mol}$ .
- Melting point:  $885^\circ\text{C}$ .

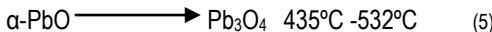
### 3.3. TRANSITION ( $\alpha$ - $\beta$ ).

The reported thermodynamic phase transition temperature is 488°C. This transition exhibits small enthalpies and free energies.



$$\Delta G = 0.632 \text{ kJ/mol}$$

Thermal analysis studies (6) have suggested that massicot oxidizes in air to form minium and afterwards reduces to form litharge phase at 532°C. The reaction sequences observed are summarized as follows:



Massicot to litharge transition is enantiotropic and depends on pressure and temperature.  $\beta$ -PbO has been proved to be high-temperature as well as high-pressure phase at the same time even though at room temperature compressive strain leads to transformation into the stable  $\alpha$  phase. (7)

Although temperature and pressure are the fundamental cause of the massicot-litharge transition there are other aspects that influence in this conversion as water, light or friction.

It seems probable that water promotes the  $\beta \rightarrow \alpha$  transformation through interaction of the polar molecule with the particle surface, resulting in relief of strain in the metastable orthorhombic layers. (8) The effect of light can be observed when litharge is exposed to daylight in clear glass bottles. After only few days the surfaces exposed to light already take on a red colour while the center of the bottles still remains yellow. (7)

It is proved that, with grinding, the litharge phase is mostly transformed into the red modification.

Other factors like impurities (9), micro stresses and grain size determine the transformation rate.

## **4. OBJECTIVES**

This project procures several objectives. This study is part of a development program of Coplosa SA, thus the first objective of this project is to find information about the different lead oxides: massicot, litharge and minium.

Coplosa's development program consist on establish new methods for the determination and characterization of lead oxides. These methods will guarantee the quality of its intermediate product (massicot) and its final products (litharge and red lead).

Considering what is exposed above the main purpose of this project is to search methods of chemical determination and structural characterization of lead oxides through a bibliographic research.

Afterwards the bibliographic study is done the most suitable technique will be carried out and its results will be discussed.

Another purpose of this project is to compare the results of the technique chosen with the classical methods for the chemical characterization of metallic lead content in lead oxides.

Finally, although the main objective of this project is to search a method for the chemical determination of lead oxides, a physical characterization of the products is also interesting, so a secondary objective of this work is carry out a grain size distribution characterization.

## 5. METHODS FOR THE CHEMICAL AND STRUCTURAL CHARACTERIZATION OF LEAD AND LEAD OXIDES.

In Coplosa massicot is used as intermediate product for the production of the final products, litharge and red lead, so guarantee the quality of its intermediate product is very important for the company.

Having information of the chemical composition of their intermediate product is not only useful to ensure the quality of the final products but to know the most influent parameters of reaction in the furnace. Therefore lead monoxide determination techniques will be studied.

### 5.1 X-Ray Diffraction

X-Ray Diffraction or XRD is an identification and characterization technique for crystalline substances. Crystalline substances have regular periodic arrangement and atoms are arranged in a three dimensional frame of points, translation vectors  $a$ ,  $b$  and  $c$  (lattice parameters). A basic repeating atoms' arrangement is called unit cell. The lattice parameters describe the size of unit cell.

A diffraction phenomenon is the interference between waves that is generated when there is an object in their path. Although there are two types of X-Ray Diffractometers, Single Crystal XRD and Powder XRD, through the characteristics of our samples Powder XRD is studied. In Powder XRD a monochromatic beam (just one frequency) of X-Rays is directed to the sample, which is dispersed in a support. Considering that monochromatic radiation can be treated geometrically like reflection, the intensity of diffraction will be measured as the detector is moving in different angles, following Bragg's law (10):

$$n \lambda = 2d \sin\theta$$

(1)

$n$  is an integer.

$\lambda$  is the wave length of the X-Ray.

$d$  is the distance between crystalline planes.

$\Theta$  is the angle between incident beams.

Bragg's law calculates the angle where constructive interference from X-ray scattered by parallel planes of atoms will produce a diffraction peak. Peaks are associated with planes of atoms and Miller indices  $d(hkl)$  are used to identify those planes. In figure 10 Bragg's Law is represented.

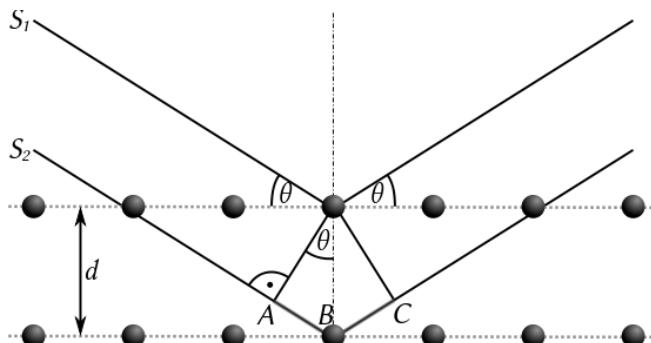


Fig 10. Representation of Bragg's law.

(Freundchen, 19/12/16, Via Wikimedia Commons, CC0 1.0 Universal Public Domain Dedication.)

Powder XRD is a very capable method considering that is a direct method, the sample is not destructed and we can operate with few quantity of sample. Nevertheless there are some disadvantages (9):

- No peaks are obtained for amorphous samples.
- There are problems with new products since there are no files in the ICDD (International Center of Diffraction Data).
- Substances with preferential orientation have different diffraction patterns than the model.
- The presence of minority substances is not guaranteed.

### 5.1.1. Applications of XRD

As has been mentioned XRD is a good technique for crystal phase identification nevertheless quantitative and semiquantitative analysis can be done to determine the relative amounts of compounds or phases in a sample.

Qualitative analysis of a diffraction spectrum is based on the intensity of the diffraction peaks of a particular crystalline phase. Intensity is not only the height of the peak, background must be subtracted and peaks must be integrated. Three basic types of peaks can be detected when facing quantitative analysis (11):

1. Peak height is proportional to peak area. This is a very simple situation that permits us estimate the area of the peak through the measurement of the peak height. An example of this type of peak can be observed at fig 11.
2. Peak height is not proportional to peak area. This situation is very common; the area of the peak requires to be integrated. Peak number 2 of figure 11 is an example of this situation.
3. Peak area is overlapped by other peaks. These types of peaks occur when we have a mixture of different crystals and the peaks that they exhibit are overlapped. In this case refinement methods have to be used for the integration of the peaks. This can be seen in example 3 of figure 11.

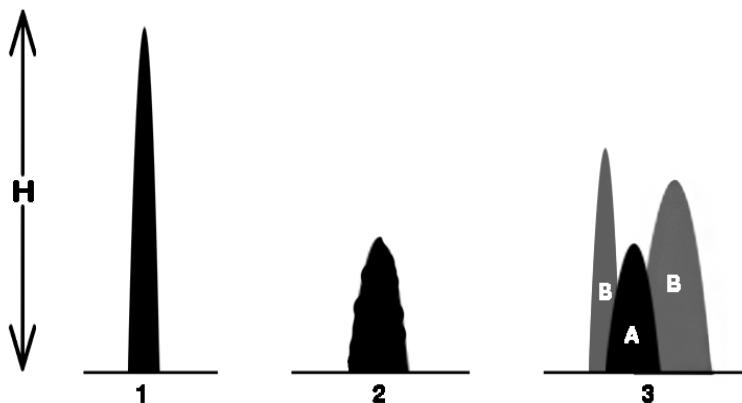


Fig 11. Peaks explained above. (Verónica M.Martín)

Considering that we pretend to do a quantitative analysis of our samples and that presumably our samples are a mixture of species and phases a refinement method will be required.

Rietveld's Refinement Method (12) is the most used method for the quantification of crystal species. The Rietveld method can be described as a theoretical adjustment (least square model) of the diffraction pattern. This model includes both structural and experimental factors.

Although it is a very reliable method there are some factors that can affect the intensity of the diffraction peaks and implicitly the Rietveld's results:

1. Structural factors: Position of the atoms in the cell, temperature, light polarization...
2. Instrumental factors: Intensity of the scatter of X-Ray, efficiency of the diffractometer...
3. Sample factors: Absorption, size of the crystals and preferential orientation of the crystals.

A preferential orientation was found out in our samples so Rietveld method could not be applied in order to quantify the different lead oxides contained in our samples. As a consequence RIR (Reference Intensity Ratio) method was needed for a general semiquantitative analysis implemented at the informatics program X'Pert HighScore (Plus) from Panalytical (13)(14)(21).

## 5.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a thermal analysis. Thermal analysis is based on material reactions to thermal energy flow, these reactions are called thermal events. This instrument measures heat flow difference between sample and reference. There are two types of DSC: The heat flux DSC and the Power-compensate DSC.

*The heat flux DSC* measures the temperature difference and then converts it into heat flow. This DSC system is also called DTA (Differential Thermal Analysis).

*Power-compensate DSC* measures directly the enthalpy change of a sample during the experiment. In picture 12 individual sample heaters from power-compensate DSC are represented.

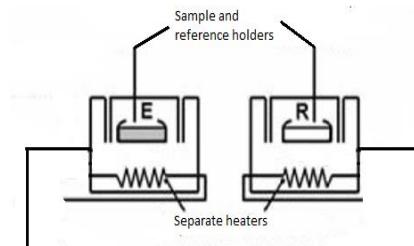


Fig 12. Power-compensate DSC.  
(Aboalbiss, 19/12/16, Via Wikimedia Commons, CC Attribution 1.0 Generic)

The enthalpy change of transformation can be directly measured from the corresponding peak area of a DSC curve. The total enthalpy change ( $\Delta H$ ) should be proportional to the peak area ( $A_p$ ) where  $K_c$  is a calibration factor that includes contributions from the experimental conditions and the thermal conductivity of the system (11):

$$\Delta H/\text{mass} = K_c A_p \quad (2)$$

A DSC instrument always maintains a thermal null state ( $\Delta T=0$ ). If there is a thermal event in the sample, the instrument registers a difference in the temperature between the reference and the sample and the power of the heating element has to change in order to maintain the thermal null state. The reference sample should have a very well defined heat capacity over the range of temperatures to be scanned.

An endothermic event causes an increase in power to heat the sample oppositely an exothermic event a reduction in the power needed to heat the sample.

In a DSC curve heat flow is plotted versus temperature. Heat flow standardally is expressed in W/g. Figure 13 represents an example of a DSC curve where an endothermic event is registered.

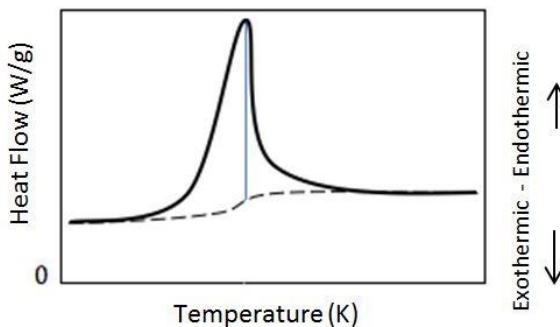


Fig 13. Illustration of a DSC curve.

(Original: Schmin, 19/12/16, Via Wikimedia Commons, Public Domain).

Although DTA and DSC measure the same thermal events using different measurement methods they differ in some points. DTA is a qualitative technique on account of measured temperature differences do not provide any quantitative data for energy. On the other hand DSC is a quantitative technique because measured heat flow provides enthalpy change in the sample during a thermal event. Also DTA can reach temperatures greater than 1500°C while the power-compensated DSC's maximum temperature is 750°C.

There are some experimental aspects that we have to take into account before doing a DSC measurement (11):

- Sample requirements: The sample must be arranged in dense powder or small discs and should have low mass due to the fact that a low mass sample can quickly reach temperature equilibrium throughout its volume.
- Baseline determination: There are two baselines the instrument baseline (zero), which is taken without the sample over the range of temperatures that the measures will be taken, and the sample baseline, which is the line that connects the sample curve before and after a peak appears.
- Scanning rate: It can change the curve shape and characteristics. The Scanning Rate is a more relevant aspect to take on account in cooling than in heating.

Most common applications of DSC are:

- Determination of heat capacity.

- Thermal Stability of polymers.
- Phase transformation and phase diagrams.

Solid state phase transformations are first-order transitions, which exhibits an enthalpy change, that could be measured with a DSC equipment.

Considering that Massicot to Litharge transition is a phase transformation transition it is possible considering the DSC technique for the determination of lead monoxide.

Previous thermal analysis suggested that Massicot oxidizes in air to form Red Lead and subsequently reduces to form Litharge phase at 532°C (6). This is confirmed in Munsons and Rimann experiment (15). In this experiment a DSC analysis of a massicot sample is performed. It is detected a broad exotherm centred at 510°C, characteristic of a slow reaction, followed by a sharp endotherm, centered at 580°C, characteristic of a rapid reaction (fig14).

These results are in accordance with previous work (6) where oxidation was reported to occur from 435°C to 532°C and reduction from 532°C to 578°C.

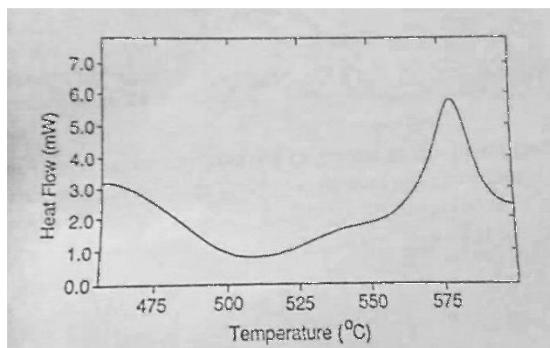


Fig 14. DSC trace of massicot powder. (ref15.)

Also it has been observed that massicot oxidizes at 470°C when heated in air.(16).

All of these experiments are made in an air atmosphere, so we observe the oxidation-reduction of lead oxides, for the observation of a PbO –  $\beta$  PbO transition a N<sub>2</sub> atmosphere would be required.

### 5.3. X-Ray absorption spectroscopy.

X-Ray absorption spectroscopy (XAS) is a powerful tool for the structural study of solids. In XAS an X-Ray beam is directed to the sample and a core electron is excited into unoccupied atomic/molecular orbitals above the Fermi level. Every element absorbs a characteristic X-Ray radiation and, consequently will produce a characteristic absorption pattern from atomic-like electric dipole transitions (change of angular momentum  $\Delta l \pm 1$ ). XAS information is obtained by tuning the photon energy using a crystalline monochromator to a range where core electrons can be excited (0.1-100 keV photon energy). Depending of which core electron is excited, it has been determined different edges and principal quantum numbers  $n=1, 2$  and  $3$  correspond to the K, L and M edges, respectively (17). Figure 15 illustrate the K, L and M edges.

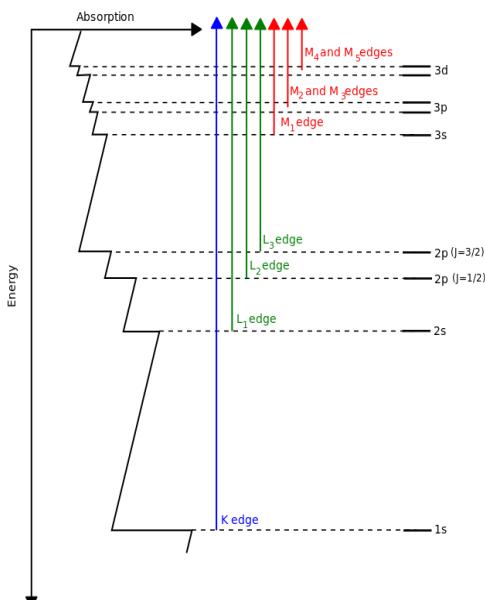


Fig 15. Transitions that contribute to XAS edges  
 (Atenderholt, 19/12/16, via Wikimedia Commons, CC by-SA 3.0)

There are three relevant regions on a XAS generated spectrum (17):

1. Absortion thereshold: The energy at which the open continuum channel for photo-electric absorption becomes available. It is determined by the transition to the lowest occupied states.
2. XANES (X-Ray Absorption Near Edge Structure): Gives information of the oxidation state.
3. EXAFS (Extended X-ray Absorption Fine Structure): Provides information about the local environment around the absorbing ions including distances between atoms and coordination numbers of surrounding shells.

In figure 16 the three parts of the spectrum can be appreciated.

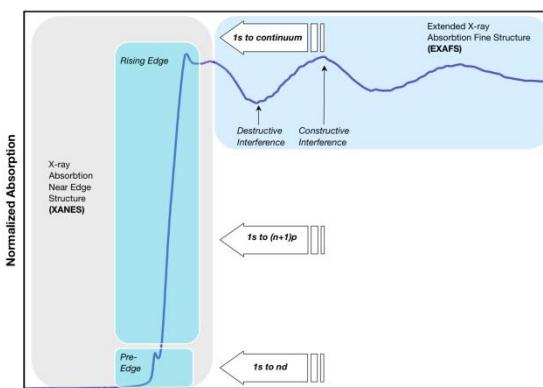
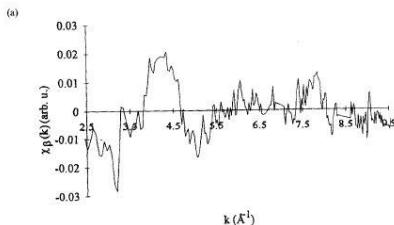
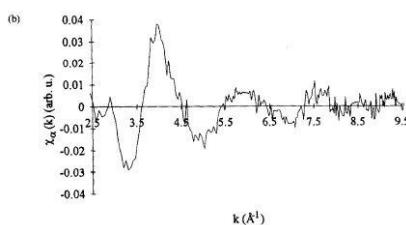


Fig 16. Three regions of XAS data.  
(Munzarin, 19/12/16, via Wikimedia Commons, CC BY-SA 3.0)

Although XAS is a widely-used technique for determining the local, geometric and/or electronic structure of matter it counts with a big disadvantage; It needs a synchrotron radiation source (to provide intense and tunable X-Ray beams)(18).

XAS can be used for determining oxidation state of atoms in minerals, oxides and mixed-metal systems, determining structural changes of metals during alloying processes, local environment around doped atoms in a metal and identification of metal in geological samples.

Previous XAS analysis of lead monoxide illustrates the possibility to study solid state mechanisms such as phase transition. As has been mentioned, EXAFS is the region of the XAS data which provides information about the local environment of the atoms. It is possible to distinguish two different EXAFS curves for  $\alpha$  and  $\beta$  PbO (fig 17 and 18).(19)

Fig 17. EXAFS curve of  $\alpha$ -PbO. (Ref 19)Fig 18. EXAFS curve of  $\beta$ -PbO (Ref 19)

XAS is also a fast technique and allows *in situ* observations of quick phenomena, so a time resolved XAS study will give information not only about  $\alpha$  and  $\beta$  PbO but about the transition between the two polymorphs (fig 20).

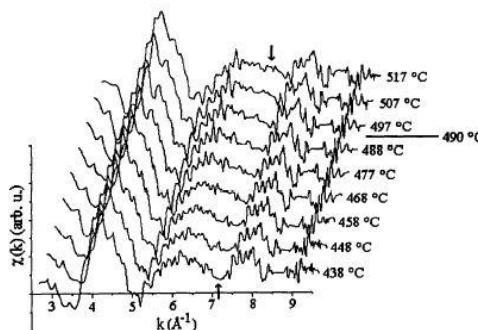


Fig 19. EXAFS curve profile of lead monoxide in the temperature range 438-517°C. The expected phase transition temperature 490°C is shown by a straight horizontal line. (ref 19).

## 5.4 Chemical characterization of metallic lead contained in lead oxides.

### 5.4.1. Free lead in massicot and litharge.

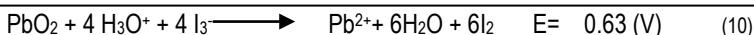
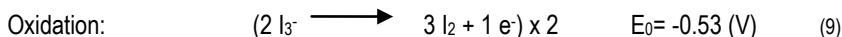
For the analysis of free lead in massicot and litharge standard UNE-EN ISO 13086 can be followed. Metallic lead is practically unaffected by diluted acetic acid whereas lead monoxide is a basic oxide and it can be easily diluted in acetic acid to give lead (II) in dissolution.



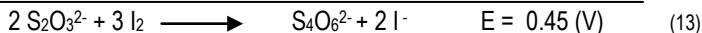
Therefore, we can obtain the free lead content by solving massicot in diluted acetic acid.

### 5.5. Determination of PbO<sub>2</sub> in litharge.

As has been mentioned in section 3.3, before the formation of litharge red lead is produced. It is important to guarantee that the entire final product obtained is litharge. In order to do that a determination of PbO<sub>2</sub> in litharge is required. For the determination of PbO<sub>2</sub> in litharge standard UNE-EN 13086:2000 can be followed. Lead dioxide content on litharge can be measured by a back titration. First of all lead dioxide has to be reduced in an attack reaction by triiodide.



Subsequently a titration of iodine with sodium thiosulfate is possible:



Finally, we can calculate stoichiometrically the PbO<sub>2</sub> content in PbO.

## 6. MATERIALS AND EXPERIMENTAL TECHNIQUES.

### 6.1. Materials

#### OXIDES ORIGIN

For the accomplishment of the experiments five samples have been selected. Considering that they are manufactured in four different reactors at four different temperatures the presumed

$\alpha$ - $\beta$  PbO content is different for all of them. Samples 1, 4 and 5 (table1) are basically massicot and samples 2 and 3 are basically litharge.

As has been mentioned Penox Group employs two different methods for the production of massicot, consequently, samples manufactured with different processes were chosen. Sample 1 was produced with a Ball-mill reactor and samples 4 and 5 were produced with two different Barton reactors. Sample number 5 was extracted from the TOPF2 reactor and sample number 4 was extracted from TOPF3, which includes a recirculation system that returns to the furnace the big particles.

Samples 2 and 3 (table 1) were produced in a LE-3 reactor at 702/4 °C the difference between these two samples is that sample 3 was taken from the furnace way out and sample 2 was taken after milling the product.

Sample number	Reference	Presumed $\alpha$ - $\beta$ PbO content	Reactor	Temperature of the furnace (°C)
1	ROBMG	$\alpha$	Ball-Mill	420
2	ROLE3S1	$\beta$	LE-3	702/4
3	ROLE3S2	$\beta$	LE-3	702/4
4	ROT3S	$\alpha$ - $\beta$	TOPF 3	404/6
5	ROT2S	$\alpha$ - $\beta$	TOPF 2	408/20

Table 1. Samples chosen and short description of them.

## 6.2. Experimental techniques

### 6.2.1. Free lead in massicot.

For analyze free lead in massicot standard UNE-EN ISO 13086 is followed.

#### REAGENTS

- Glacial Acetic Acid
- Distilled water

### EQUIPMENT

- Erlenmeyer 250 ml
- Stirring plate
- Drying paper
- Analytical balance (0.01 g accuracy)
- Muffle furnace
- Watch glass

### PROCEDURE

1. Weight 5gr of massicot sample in an Erlenmeyer and add 50ml of distilled water and 5ml of acetic acid.



Fig 20. Solution of massicot and acetic acid.

2. Warm at the stirring plate until the solution boils. Cool to room temperature.



Fig 21. Solution of massicot and acetic acid boling.

3. Decant solution and clean the residue twice with distilled water and dry obtained lead with drying paper.



Fig 22. Pb residue after the analysis.

4. Place lead in a watch glass and introduce it in the muffle furnace at 150°C 10minutes and cool sample to room temperature.

5. Weight lead in the balance.

## RESULTS

$$\% \text{ Pb free} = (\text{W} / \text{S}) \times 100$$

where:

W : weight of the lead residue

S : quantity of sample

### **6.2.2. Free lead in litharge**

#### REAGENTS

- Glacial acetic acid.
- Distilled water.

#### EQUIPMENT

- 250ml beaker.
- Glass rod.

- Stirring plate.
- Magnetic core.
- Precision balance.
- Standard table of equivalent concentrations.

### PROCEDURE

1. Weight 20 gr of litharge with a precision of 0.01 gr in a 250ml beaker, add 75-80 ml of distilled water and stir.
2. Add 25ml of glacial acetic acid and maintain stirring until litharge dissolves completely.
3. Leave the solution repose for 4-5 minutes and remove the solution with a glass rod.



Fig 23. Removing of the solution with a glass rod.



Fig 24. Result of removing the solution.

4. Compare the result with the standard table of equivalent concentrations.

### RESULTS

For obtaining results we compare the stain obtained at the bottom of the baker with the following table (fig 25):

$\approx 0'3\%$	$\approx 0'1\%$	$\approx 0'075$	$\approx 0'037$
$\approx 0'017$	$\approx 0'006\%$	$\approx 0'003\%$	$\approx 0'0015\%$
			$< 0'001\%$

Fig 25. Table of comparison of the free Pb in litarge.

### 6.2.3. $\text{PbO}_2$ determination in litharge.

For the determination of  $\text{PbO}_2$  in litharge standard EN 13086:2000 is followed.

#### REAGENTS

- Litharge.
- Metaleurop solution (5L):
  - 300 g sodium acetate 3-hidrate.
  - 12 g potassium iodide.
  - 160 ml acetic acid solution 100%.
  - Starch solution (1,25 g starch in 100 ml water, boil during 2 or 3 minutes).
  - Fill with water until 5 lts.
- Sodium thiosulfate solution 0.02N
- Acetic acid.

#### EQUIPMENT

- Balance, accuracy 0,01 g.
- Magnetic stirrer.
- Erlenmeyer flask with stopper, volume 250 ml.
- Microburette, volume 2 ml, graduation 0,01 ml.

### PROCEDURE

1. Place 10 g of the sample into an Erlenmeyer flask, add 100 ml of attack solution and 5 ml of acetic acid.
2. Close the flask and stir the solution until all the litharge is dissolved.
3. Finally titrate the solution with the sodium thiosulfate solution, changing the colour from violet to colourless.



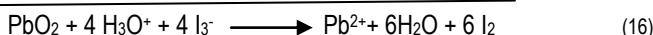
Fig 26. Solution before the titration.



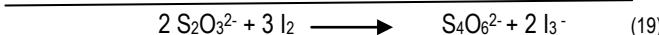
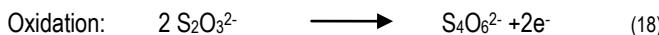
Fig 27. Solution after the titration.

### RESULTS

Attack reaction:



Titration reaction:



$$V (\text{ml}) \times \frac{0.02 \text{ eq } 2 \text{S}_2\text{O}_3^{2-}}{1000 \text{ ml}} \times \frac{1 \text{ mol } \text{S}_2\text{O}_3^{2-}}{1 \text{ eq } \text{S}_2\text{O}_3^{2-}} \times \frac{4 \text{ mol } \text{I}_3^-}{2 \text{ mol } \text{S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mol } \text{PbO}_2}{4 \text{ mol } \text{I}_3^-} \times \frac{239.2 \text{ g } \text{PbO}_2}{1 \text{ mol } \text{PbO}_2} \times \frac{100\%}{10 \text{ g}} =$$

$$\% \text{ PbO}_2 = V \times 0.02 \times 1.196 \times F$$

where:

**V** : volume of sodium thiosulfate solution

**0.02N** : sodium thiosulfate solution concentration

**1.196** : (g. of PbO<sub>2</sub> per eq. of sodium thiosulfate solution) × 100

**F** : sodium thiosulfate solution factor

#### 6.2.4. XRD Analysis.

This technique permits the obtainance of a semiquantitative analysis of every oxide proportion by means of RIR refinement.

As has been mentioned previously, X-Ray power diffraction is the adequate equipment for the analysis of our samples, accordingly our five samples are examined by this technique in the Centres Científics i Tecnològics (CCiT). (21)

#### SAMPLE PREPARATION METHODOLOGY:

First, a manual pressing of the received powder materials is done, by means of a glass plate to get a flat surface. Then the samples are disposed in cylindrical standard sample holders of 16 millimetres of diameter and 2.5 millimetres of height. In figure 29 we can see instruments needed for the preparation of the 5 samples.



Fig 28. Materials needed for the preparation of the samples.

#### INSTRUMENT AND EXPERIMENTAL CONDITIONS:

- PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in Bragg-Brentano  $\theta/2\theta$  geometry of 240 millimetres of radius
- Cu K $\alpha$ 1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ).
- Work power: 45 kV – 40 mA.
- Focalizing Ge (111) primary monochromator
- Sample spinning at 2 revolutions per second
- Variable automatic divergence slit to get an illuminated length in the beam direction of 10 millimetres.
- Mask defining a length of the beam over the sample in the axial direction of 12 millimetres
- Diffracted beam 0.04 radians Soller slits
- X'Celerator Detector: Active length = 2.122 °.
- $\theta/2\theta$  scan from 4 to 100°  $2\theta$  with step size of 0.017° and measuring time of 100 seconds per step.

#### **6.2.5. Grain size distribution.**

To determine the particle size distribution in the oxide samples Beckman Coulter LS 13 320 equipment has been used. The measures have been taken in liquid environment using the

Universal Liquid Module and isopropanol as dispersant. The optical model selected has been PbO.rf780d, with an R.I. of 1.377 for isopropanol.

### EQUIPMENT

- Ultrasounds bath
- Beaker 120ml
- Spatula
- Pasteur Pipette
- Beckman Coulter LS 13 320 Particle Size analyser.

### REAGENTS

- Isopropanol
- Litharge
- Massicot

### PROCEDURE

1. An small quantity of sample (spatula tip) is dispersed in 20ml of isopropanol, then this mixture is introduced in an ultrasound bath for 2 minutes.



Fig 29. Litharge simple at the ultrasound bath.

2. When the equipment is ready, a portion of sample is taken with a Pasteur pipette, without removing it from the bath, and, finally, the sample is introduced in the equipment for its analysis.



Fig 30. Introduction of a litharge sample at the gran size distribution measuring equipment with the universal liquid module using a pioette.

## 7. RESULTS AND DISCUSSION

### 7.1. Free lead.

The following table (table2) shows the results obtained for the lead determination in massicot and litharge attending the UNE-EN ISO 13086 standard:

Sample number	Reference	Main product	% Free Pb
1	ROBMG	Massicot	21
2	ROLE3S1	Litharge	0.0015
3	ROLE3S2	Litharge	0.0015
4	ROT3S	Massicot	4
5	ROT2S	Massicot	5.2

Table 2. Results obtained for the lead determination in massicot by UNE-EN ISO 13086.

### Pb content in massicot

As we can see in the table 2 sample number 1 has a 21% of free Pb and samples number 4 and 5 have a 4% and 5.2% free Pb content, respectively. These results are coherent, as long as, sample 1 was produced with the Ball-mill process and samples 3 and 4 with the Barton Pot process in two different reactors and, as has been explained before, a higher content of metallic lead is expected for a sample manufactured by the Ball-Mill process.

### Pb content in litharge

As demonstrated, samples 2 and 3 have, both, 0.0015% of free Pb. This result was also expected. Since massicot is an intermediate product and litharge is obtained at 702-4°C it is scheduled a lower metallic lead content.

## 7.2. PbO<sub>2</sub> in litharge

The following table (table 3) shows the results obtained for the PbO<sub>2</sub> determination in litharge; the analysis was made attending the UNE-EN ISO 13086 standard:

Sample number	Reference	% PbO <sub>2</sub>
2	ROLE3S1	0.0069
3	ROLE3S2	0.0074

Table 3. Results obtained for the PbO<sub>2</sub> determination in litharge attending the UNE-EN ISO 13086 standard.

Litharge is formed from red lead at 532°C-578°C. Since the temperature of LE-3 furnace is 702/4 °C it is logical to observe a very low percentage of lead dioxide in our litharge samples.

## 7.3. XRD

Firstly, a quantitative and complete semi-quantitative analysis by Rietveld's method of our five samples was attempted. Due to the strong preferential orientation of the principal crystalline phases it hasn't been possible to execute. A general semi-quantitative analysis was carried out

by the RIR (Reference Intensity Ratio) method, implementing at the informatics program X'Pert HighScore (Plus) of Panalytical(13)(14). All analysis were made at the CCiT (21).

On the subsequent figures qualitative diffractograms from all samples are exposed. Quantitative diffractograms are included on the appendix1.

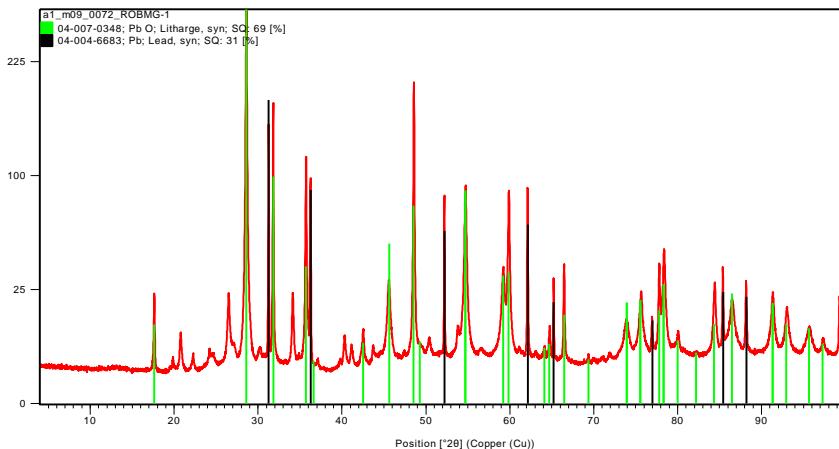


Fig 31. Qualitative diffractogram of sample 1 ROBMG.

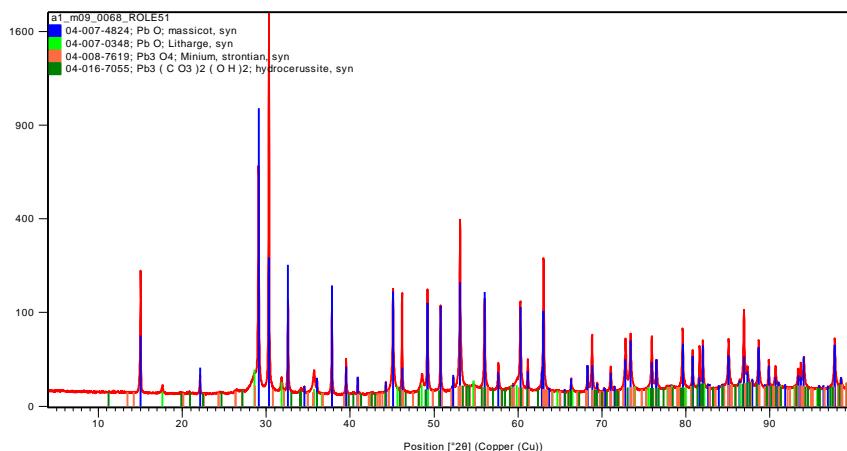


Fig 32. Qualitative diffractogram of sample 2 ROLES1.

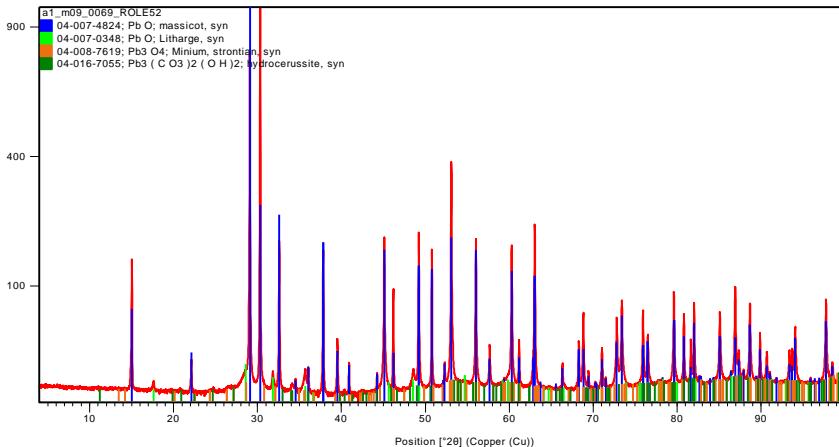


Fig 33. Qualitative diffractogram of sample 3 ROLES2.

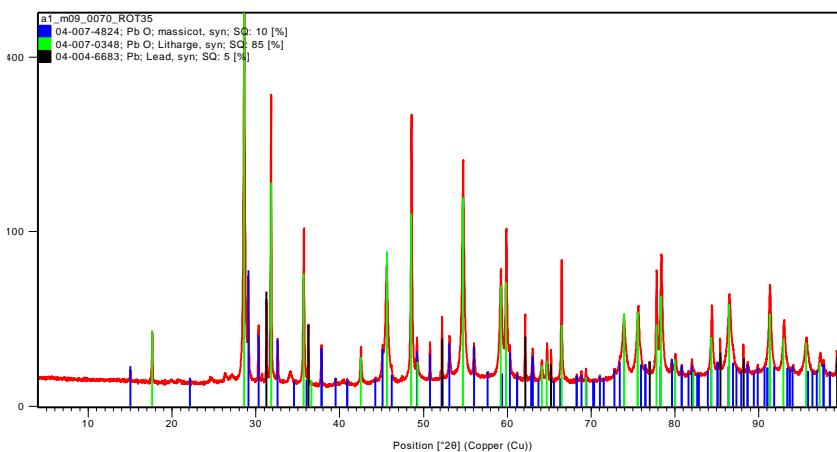


Fig 34. Qualitative diffractogram of sample 4 ROT3S.

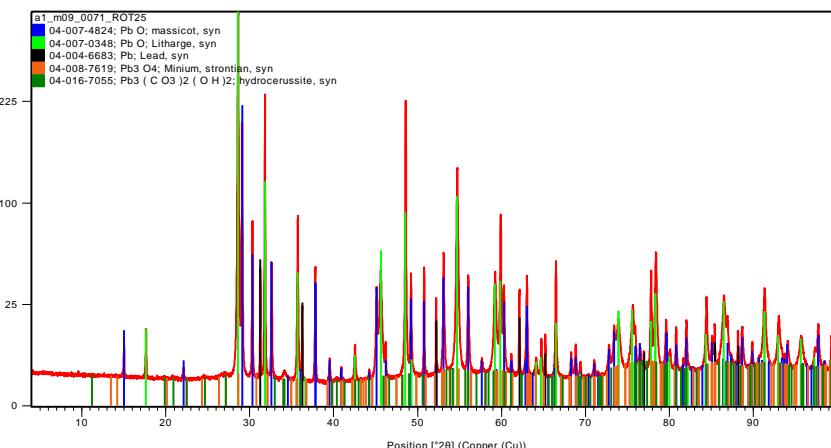


Fig 35. Qualitative diffractogram of sample 5 ROT2S.

In the subsequent table (table 4) there is a resume of the results that were extracted from the XRD analysis of our samples. Since these results are extracted from an incomplete semi-quantitative analysis the results are expressed in relative quantity. In some cases small traces of some components are detected, due to the small peaks that they generate and to the overlap of them with other compound peaks it was not possible to determine in which proportion they are in the samples.

Also the presence of two unexpected compounds, hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ) and plumbonacrite ( $\text{Pb}_5(\text{CO}_3)_2\text{O}(\text{OH})_2$ ), is detected in a very low proportion. These two lead carbonates could have been formed at the furnace exit, when the product is exposed to the atmosphere at very high temperatures.

Sample number	Reference	$\alpha\text{-PbO}$	$\beta\text{-PbO}$	$\text{Pb}_3\text{O}_4$	Pb	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$	$\text{Pb}_5(\text{CO}_3)_2\text{O}(\text{OH})_2$
1	ROBMG	54	-	-	24	6	16
2	ROLE3S1	1	99	NP	NP	NP	-
3	ROLE3S2	1	99	NP	NP	NP	-
4	ROT3S	73	8	13	5	2	-
5	ROT2S	59	35	NP	6	NP	-

(a) NP means that it was not possible to quantify this compound but it was detectable.

(b) All the numbers are expressed in percentage.

Table 4. Resume of the results that were extracted from the XRD analysis of our samples.

Analyzing sample by sample we can discern that the results are coherent with the description of the samples given in section 6.1.

### MASSICOT SAMPLES

Sample number 1: No litharge was expected since the sample comes as a result of the Ball-mill process. A 21% of metallic lead content was also expected for that sample and with the XRD technique a 24% is observed.

Samples number 4 and 5: Accordingly to the manufacture process of these two samples (Barton Pot process) a small portion of litharge was expected, as well as, a 5-6% of metallic lead. Clearly this is in concordance with the XRD results. A lower proportion of litharge, as well as, a higher proportion of red lead was expected for sample 4 because it was produced with TOPF3, which includes a recirculation cyclone. So it is also coherent observing that for sample 4 the litharge content is 8% and the minium content is 13% while for sample number 5 the litharge content was 35% and the minium content was not possible to measure.

### LITHARGE SAMPLES

For litharge samples a very low proportion of massicot and an utterly low quantity of Pb and  $PbO_2$  were expected. The XRD technique confirms the expectations about litharge sample samples, giving a 1:99  $\alpha$ - $\beta$  proportion.

Comparing these results with the ones obtained at the laboratory we can observe (table 5) that they are very similar, fact that confirms too XRD results are coherent.

	Reference	Main product	% Free Pb UNE-EN ISO 13086	% Free Pb XRD
1	ROBMG	Massicot	21	24
2	ROLE3S1	Litharge	0.0015	NP
3	ROLE3S2	Litharge	0.0015	NP
4	ROT3S	Massicot	4	5
5	ROT2S	Massicot	5.2	6

Table 5. Comparison of the results obtained by UNE-EN ISO 13086 standard procediment and XRD.

## 7.4. Grain size distribution

The results of the grain size distribution are not relevant for the determination of the  $\alpha$ - $\beta$  proportion in lead monoxides but it is interesting for the furnace parameters improvement.

On table 6 we can see the results of these analyses.

Sample	Reference	D <sub>10</sub>	D <sub>50</sub>	D <sub>90</sub>
1	ROBMG	-	-	-
2	ROLE3S1	2.03	4.483	7.862
3	ROLE3S2	-	-	-
4	ROT3S	2.148	3.849	6.459
5	ROT2S	3.749	5.704	8.691

Table 6. Results of the grain size distribution analysis.

For sample 1 two curves were observed since it has a 21-24% of metallic lead. On Fig 36 we can observe the graphic that represents the grain size distribution of sample 1.

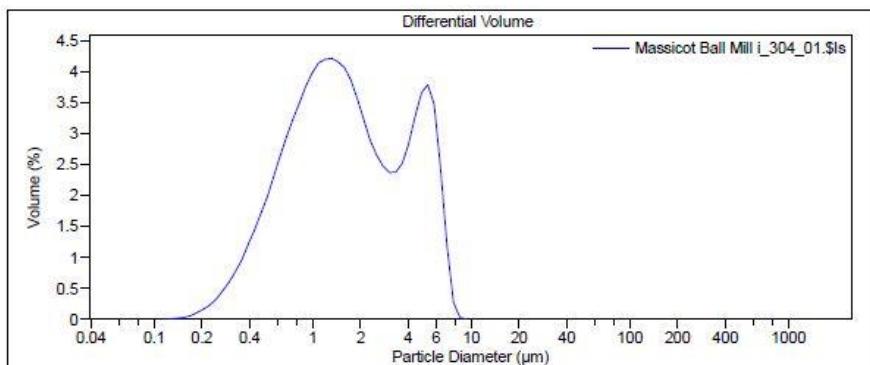


Fig 36. Curve generated from the analysis size distribution analysis of sample 1.

For sample number 3 no grain size distribution was possible since the sample is not milled and the analysis cannot be executed.

The rest of the samples show a standard distribution curve (fig 37) and the indicators given and exposed in table 6, the complete reports of the analysis are attached at appendix 2.

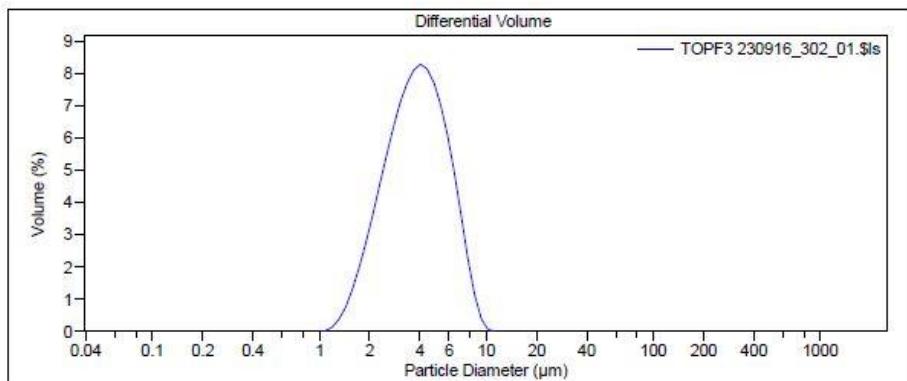


Fig 37. Curve generated from the analysis size distribution analysis of sample 2.



## 8. CONCLUSIONS

- In this project a bibliographic research of a method of determination of the different polymorphs of lead monoxide has been carried out. Three different methods have been found out; X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and X-Ray Absorption (XAS). All of these techniques are capable of distinguishing between the two lead monoxide polymorphs but the best technique for the quantification of both  $\alpha$  and  $\beta$  PbO is XRD.
- Consequently, XRD technique has been tested with five different samples including different proportion of both modifications. For the quantification of both polymorphs first, Rietveld's refinement was tried but due to the preferential orientation of our samples this method could not be accomplished. Finally RIR method was applied and we could obtain a semi-quantitative analysis of our five samples.
- These results were compared with standard techniques for the determination of metallic lead in litharge and massicot and we can notice that the results are in concordance. There is also a relation between XRD results and the way the samples were manufactured.
- According to that, XRD can be considered a good technique for the determination of lead monoxide polymorphs.
- Even though it has been proved that XRD is a good technique for the determination of lead monoxide polymorphs evaluation by another of the two methods found would put these results on firmer ground.

## 9. REFERENCES AND NOTES

1. D.P.Boden Improved oxides for production of lead/acid battery plates. *Journal of Power Sources*. **1998**, 73, 56-59.
2. Yonggang Wang, Xiaohuan Lin,a Hao Zhang, Ting Wen, Fuqiang Huang, Guobao Li, Yingxia Wang, Fuhui Liao and Jianhua Lin Selected-control hydrothermal growths of  $\alpha$ - and  $\beta$ -PbO crystals and orientated pressure-induced phase transition. *CystEngComm*, **2013**, 15, 3513.
3. Dickens, B. The bonding in Red PbO. *J.Inorg.Nucl.Chem.*, **1965**, 27, 1507.
4. D.L. Perry, T.J. Wilkinson Syntesis of high-purity  $\alpha$ - and  $\beta$ -PbO and possible applications to synthesis and processing of other lead oxide materials. *Appl. Phys. A*, **2007**, 89, 77-80.
5. Pavlov, Detchko. Lead-Acid Batteries. Oxford : Elsevier, **2011**, 225.
6. S. Nordyke. Lead in the world of ceramics, American Ceramic Society, Columbus, OH 1984, p.5.
7. Marx, Reinhard. Lead Oxides : Developements in the 20th Century. Zellerfeld : GDMB, 2000.
8. Sorrell, Charles A. PbO Transformation Induced by Water. *Journal of American Ceramics*, **1972**, 55, iss1, 47.
9. Ballester, A., Verdeja. F.L., Sancho., J. Metalúrgia extractiva. Vol. 1 Química Básica.
10. Atkins, Peter. Jones, Loretta. Principios de química: los caminos del descubrimiento., Editorial Medica Panamericana, 3<sup>a</sup> edición, 2<sup>a</sup> reimpresión. Buenos Aires, Argentica, 2009. PX.
11. Leng, Yang Materials Characterization, John Wiley & Sons, Asia, 2009.
12. Susana Petrick Casagrande a, Ronald Castillo Blanco. Método de Rietveld para el estudio de estructuras cristalinas. Laboratorio de Datación, Facultad de Ciencias, Universidad Nacional de Ingeniería. **15 de noviembre de 2004**
13. Chung, F.H. "Quantitative interpretation of X-ray diffraction patterns. I. Matrix-flushing method of quantitative multicomponent analysis", *J. Appl. Cryst.* Vol. 7 **1974**, p. 519-525.
14. Chung, F.H. "Quantitative interpretation of X-ray diffraction patterns. II. Adiabatic principle of X-ray diffraction analysis of mixtures", *J. Appl. Cryst.* Vol. 7 **1974**, p. 526-531.
15. Munson, Riman. Observed Phase Transformations. *J. Thermal Anal*, **1991**, 37, 2555-2565.
16. C.A. Sorrell. *J.Amer.Cerm.Soc.* 1971, 54, 501.
17. École nationale supérieure de chimie de Paris.X-Ray absorption for begginers.  
[http://www.iucr.org/\\_data/assets/pdf\\_file/0004/60637/IUCr2011-XAFS-Tutorial\\_-Ascone.pdf](http://www.iucr.org/_data/assets/pdf_file/0004/60637/IUCr2011-XAFS-Tutorial_-Ascone.pdf)  
(Accesed Nov,7,2016)
18. X-Ray absorption spectroscopy  
[http://photon-science.desy.de/users\\_area/industrial\\_users/methods\\_techniques/x\\_ray\\_absorption\\_spectroscopy/index\\_eng.html](http://photon-science.desy.de/users_area/industrial_users/methods_techniques/x_ray_absorption_spectroscopy/index_eng.html) (Accesed Nov 7, 2016)
19. L. Douillard †, M. Gautier-Soyer †, J.P. Durraud §, A. Fontaine , F. Baudelet , Time resolved XAS study of a phase transition: The polymorphic transformation of tetragonal to orthorhombic PbO, *J.Phys. Chem. Solids*, **1996**, 57, 495-501.
20. Terpstra HJ, de Groot RA, Haas C. Electronic structure of the lead monoxides: Band-structure calculations and photoelectron spectra. *Physical Review B*. **1995**, vol 52, number 16, 690-696.
21. Informe proporcionat CCI.T. **Diciembre 2016**

## 10. ACRONYMS

Pb	Lead
PbO	Lead monoxide
PbO <sub>2</sub>	Lead dioxide
Pb <sub>3</sub> O <sub>4</sub>	Minium/ Red lead
XRD	X-Ray Diffraction
DSC	Differential Scanning Calorimetry
XAS	X-Ray Absortion Scanning
CCiT	Centres Científics i Tecnològics



# APPENDICES



## APPENDIX 1: QUALITATIVE DIFFRACTOGRAMS

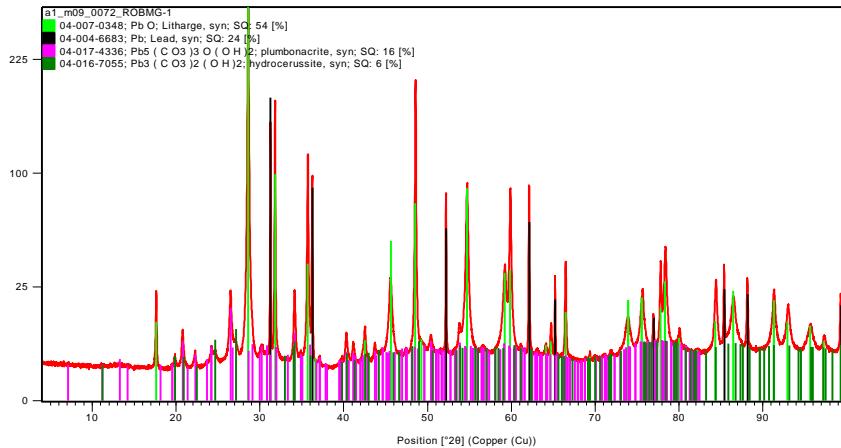


Fig 1. Quantitative diffractogram of sample 1 ROB MG.

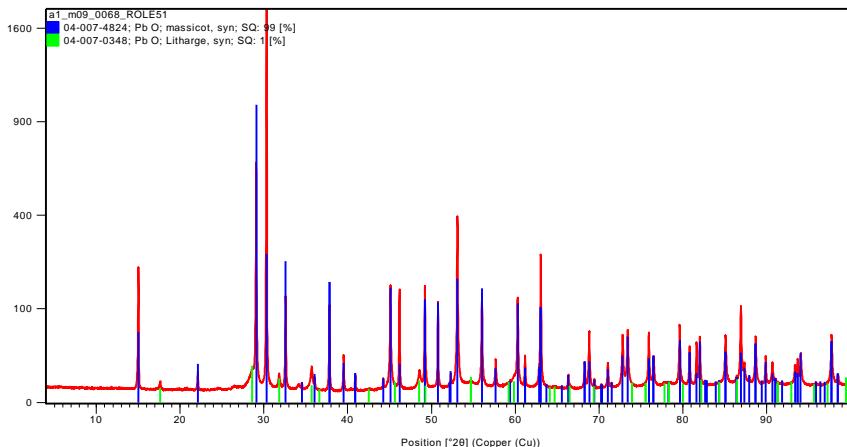


Fig 2. Quantitative diffractogram of sample 2 ROLES1.

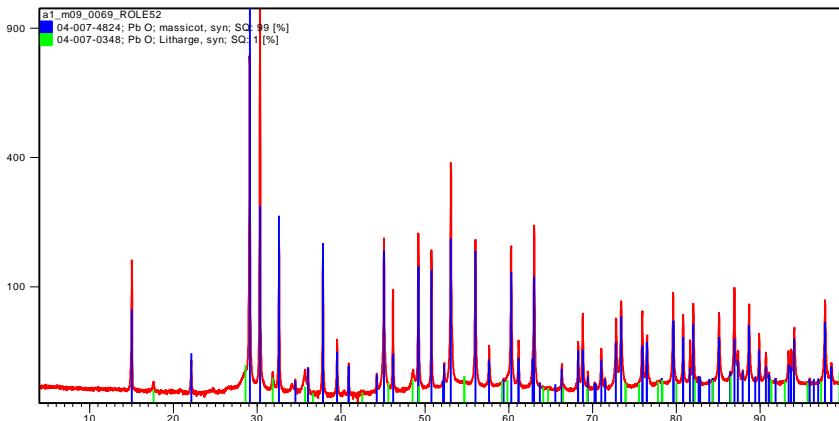


Fig 3. Quantitative diffractogram of sample 3 ROLES2.

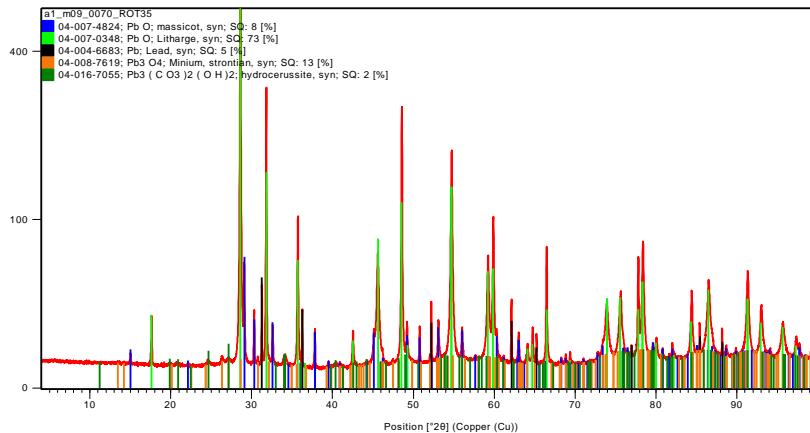


Fig 4. Quantitative diffractogram of sample 4 ROT3S.

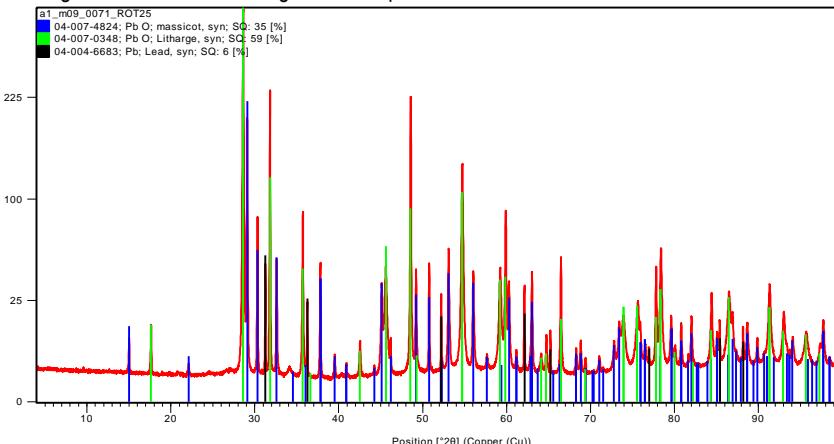


Fig 5. Quantitative diffractogram of sample 5 ROT2S.

## APPENDIX 2: GRAIN SIZE REPORTS

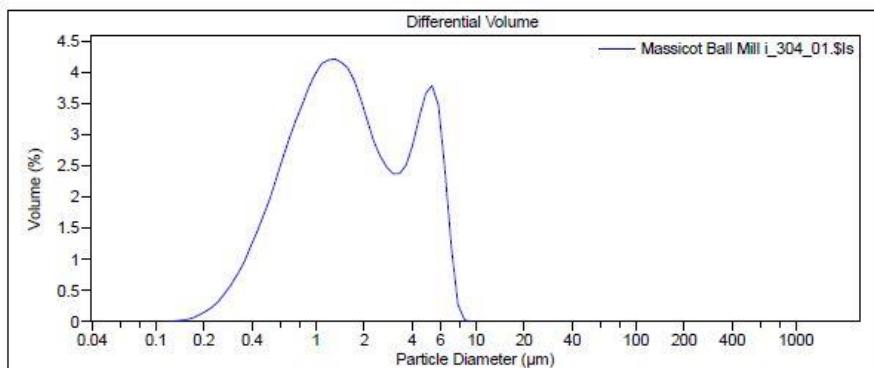


LS Particle Size Analyzer

Beckman Coulter LS 13 320

25 Nov 2016 11:11

File name:	M:\ICP-OES OPTIMA 8000\Beckman Coulter\TFG\Massicot Ball Mill i_304_01.xls	
File ID:	Massicot Ball Mill i_304_01.xls	
Run number:	304	
Comment 1:	ultrasons	
Optical model:	PbOrf780d PIDS included	
Fluid R.I.:	1.377	Sample R.I.: 2.5 i0
Residual:	0.60%	
LS 13 320	Universal Liquid Module	
Start time:	11:59 28 Oct 2016	Run length: 51 seconds
Pump speed:	58%	
Obscuration:	9%	PIDS Obscur: 52%
Fluid:	isopropanol	
Software:	6.01	Firmware: 4.00



Volume Statistics (Arithmetic)		Massicot Ball Mill i_304_01.xls		
Calculations from 0.040 $\mu\text{m}$ to 2000 $\mu\text{m}$				
Volume:	100%			
Mean:	2.257 $\mu\text{m}$	S.D.:	1.803 $\mu\text{m}$	
Median:	1.555 $\mu\text{m}$	Variance:	3.249 $\mu\text{m}^2$	
Mean/Median ratio:	1.451	C.V.:	79.9%	
Mode:	1.321 $\mu\text{m}$	Skewness:	1.053 Right skewed	
		Kurtosis:	0.013 Leptokurtic	
<10%	<25%	<50%	<75%	<90%
0.544 $\mu\text{m}$	0.877 $\mu\text{m}$	1.555 $\mu\text{m}$	3.318 $\mu\text{m}$	5.266 $\mu\text{m}$

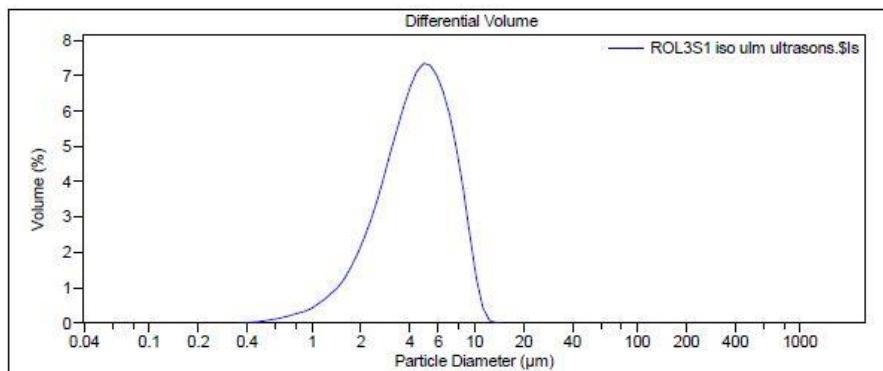


## LS Particle Size Analyzer

25 Nov 2016 11:07

Beckman Coulter LS 13 320

File name:	M:\CP-OES OPTIMA 8000\Beckman Coulter\TFGIROL3S1 iso ulm ultrasons.\$ls	
File ID:	ROL3S1 iso ulm ultrason.	
Run number:	305	
Comment 1:	ultrasons	
Optical model:	PbO.Rf780d	PIDS included
Fluid R.I.:	1.377	Sample R.I.: 2.5 i0
Residual:	0.49%	
LS 13 320	Universal Liquid Module	
Start time:	12:10 28 Oct 2016	Run length: 52 seconds
Pump speed:	58%	
Obscuration:	10%	PIDS Obscur: 48%
Fluid:	isopropanol	
Software:	6.01	Firmware: 4.00



Volume Statistics (Arithmetic)		ROL3S1 iso ulm ultrasons.\$ls		
Calculations from 0.040 $\mu\text{m}$ to 2000 $\mu\text{m}$				
Volume:	100%			
Mean:	4.737 $\mu\text{m}$	S.D.:	2.209 $\mu\text{m}$	
Median:	4.483 $\mu\text{m}$	Variance:	4.879 $\mu\text{m}^2$	
Mean/Median ratio:	1.056	C.V.:	46.6%	
Mode:	4.877 $\mu\text{m}$	Skewness:	0.492 Right skewed	
		Kurtosis:	-0.235 Platykurtic	
<10%	<25%	<50%	<75%	<90%
2.034 $\mu\text{m}$	3.057 $\mu\text{m}$	4.483 $\mu\text{m}$	6.196 $\mu\text{m}$	7.862 $\mu\text{m}$

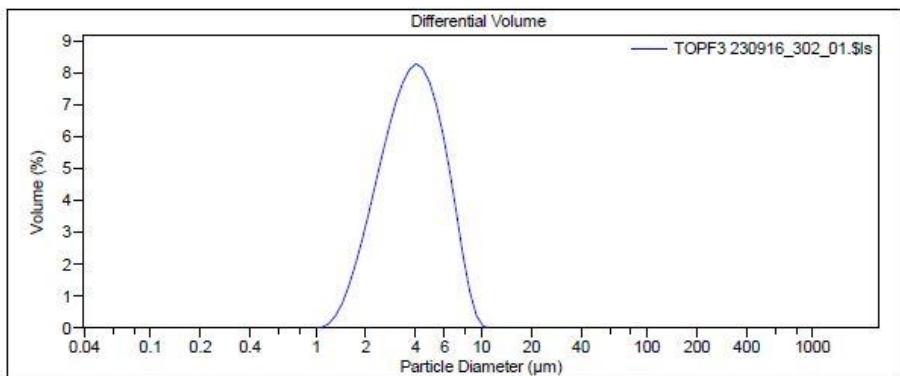


## LS Particle Size Analyzer

25 Nov 2016 11:10

Beckman Coulter LS 13 320

File name:	M:\ICP-OES\OPTIMA 8000\Beckman Coulter\TGF\TOPF3 230916_302_01.xls		
File ID:	TOPF3 23/09/16		
Run number:	302		
Comment 1:	ultrasons		
Optical model:	PbO.rf780d	PIDS included	
Fluid R.I.:	1.377	Sample R.I.:	2.5 i0
Residual:	0.56%		
LS 13 320	Universal Liquid Module		
Start time:	11:34 28 Oct 2016	Run length:	52 seconds
Pump speed:	58%		
Obscuration:	8%	PIDS Obscur:	44%
Fluid:	isopropanol		
Software:	6.01	Firmware:	4.00



Volume Statistics (Arithmetic)		TOPF3 230916_302_01.xls		
Calculations from 0.040 μm to 2000 μm				
Volume:	100%			
Mean:	4.099 μm	S.D.:	1.647 μm	
Median:	3.849 μm	Variance:	2.712 μm <sup>2</sup>	
Mean/Median ratio:	1.065	C.V.:	40.2%	
Mode:	4.047 μm	Skewness:	0.658 Right skewed	
		Kurtosis:	-0.023 Platykurtic	
<10%	<25%	<50%	<75%	<90%
2.148 μm	2.819 μm	3.849 μm	5.149 μm	6.459 μm

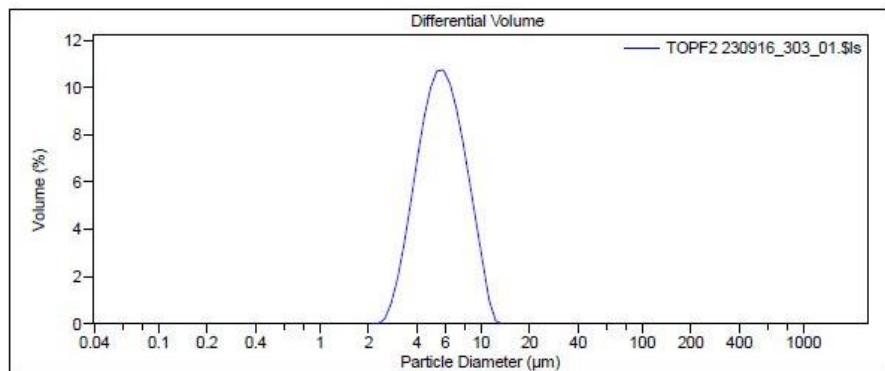


## LS Particle Size Analyzer

25 Nov 2016 11:09

Beckman Coulter LS 13 320

File name:	M:\ICP-OES\OPTIMA 8000\Beckman Coulter\TFG\TOPF2 230916_303_01.xls		
File ID:	TOPF2 23/09/16		
Run number:	303	Sample R.I.:	2.5 i0
Comment 1:	ultrasons	Run length:	52 seconds
Optical model:	PbO.rf780d PIDS included	Pump speed:	58%
Fluid R.I.:	1.377	Obscuration:	6%
Residual:	0.30%	Fluid:	isopropanol
LS 13 320	Universal Liquid Module	Software:	6.01
Start time:	11:46 28 Oct 2016	PIDS Obscur:	43%
		Firmware:	4.00



Volume Statistics (Arithmetic)		TOPF2 230916_303_01.xls		
Calculations from 0.040 $\mu\text{m}$ to 2000 $\mu\text{m}$				
Volume:	100%	S.D.:	1.877 $\mu\text{m}$	
Mean:	5.981 $\mu\text{m}$	Variance:	3.524 $\mu\text{m}^2$	
Median:	5.704 $\mu\text{m}$	C.V.:	31.4%	
Mean/Median ratio:	1.049	Skewness:	0.619 Right skewed	
Mode:	5.878 $\mu\text{m}$	Kurtosis:	-0.119 Platykurtic	
<10%	<25%	<50%	<75%	<90%
3.749 $\mu\text{m}$	4.537 $\mu\text{m}$	5.704 $\mu\text{m}$	7.189 $\mu\text{m}$	8.691 $\mu\text{m}$

