UNIVERSITÀ DEGLI STUDI DI PADOVA

Second Cycle Degree in Environmental Engineering
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Master Thesis
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RECOVERY OF REEs FROM EXHAUSTED FLUORESCENT LAMPS

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I dedicate my efforts on this thesis to women that use to inspire me:
my mother, my mainstay for all of my life,
my second mother, friend and life teacher Cinzia,
my Math's teacher of secondary school for the passion she spread me,
my friends around all over the world with their dreams in their pockets,
finally to the Co-supervisor of this thesis work.

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INDEX OF ABREVIATION

WEEE waste electric and electronic equipment

MA Maleic acid

OA Oxalic acid

CFL Compact Fluorescent Lamp

EDTA Etilendiamminotetracetic acid

FL Fluorescent Lamp

REO Rare Earth Ores

REEs Rare Earth Elements

ox^{2-} *oxalate ion*

X halogen

ESEM Environmental Scanning Electron Microscope

XRD X-Ray Diffraction analysis

TGA Thermo-Gravimetric Analysis

FT-IR Fourier Transform Infrared Spectrometer

1. INTRODUCTION

Rare earth elements (REEs) are continually increasing their role in the international market and connected activities (Binnemansa et al. 2013). Nowadays they must be considered *strategic material* because of their wide use in different industrial fields (Tiess, 2010,Vivoda, 2011). REEs are widely considered also as *critical material* for several reasons: the difficulty to predict fluctuations of market behavior, the difficulty to find replace and these materials, the low percentage of recycle and the sustainability in that process, the stability of the supply (Skirrow et al., 2013).

In June 2010 the European Commission published a list of 14 elements, raw metals and a group of metal considered as *critical*: 12 materials (antimony, beryllium, cobalt, fluorspar, gallium, germanium, graphite, indium, magnesium, niobium, tantalum and tungsten), PGMs (platinum group metals) and REEs group (European Commission, 2010). This action wants to highlight the difficulty to supply these elements to the industries for several reasons that are explained later. The consequence is possible commercial conflicts between the more advanced and industrialized countries (Massari and Ruberti, 2013). Integrated strategies were already proposed about this topic both in European (Commission of the EC, 2008) and American (US DoE, 2010) policies.

The REEs are 17: 15 lanthanides plus yttrium and scandium, they show similar physical and chemical properties and used independently or in mixtures, also in very little quantity, they provide superb characteristics for many advanced applications (Golev et al. 2014). They represent key-elements in many modern fields such automotive catalytic converters, fluid cracking catalysts in petroleum refining, phosphors in color television and flat panel displays (cell phones, portable DVDs, and laptops), permanent magnets and rechargeable batteries for hybrid and electric vehicles, generators for wind turbines, and numerous medical devices. Moreover REEs are essential in important defense applications, such as jet fighter engines, missile guidance systems, antimissile defense, space-based satellites and communication systems (Humphries, 2013).

Unfortunately the reserves of REEs are not equally distributed in the world (Massari and Ruberti, 2013): in Europe and many other countries no relevant sources are present, and moreover recently China's exportation of REEs (major export country, about 97% of total export in the world) is dramatically decreased, for economic and environmental reasons.

Following EU rules, in the Italian legislation the WEEE (electric and electronic waste, in Italian RAEEs: rifiuti di apparecchiature elettriche e elettroniche) rich of REEs traces is classified as special waste: the mean of the national specific cost for kg of WEEE is about 28.83 eurocent/kg, with a production of 249.325 tons per year. (Data from Ispra ambiente-rifiuti urbani, 2013).

It is estimated that 20-50 million tons of e-wastes are generated around the world each year (Zhan et al. 2014).

For all these reasons Italy and many other European countries need to understand the importance of recycling REEs from pre-consumer scrap, industrial residues and REE-containing End-of-Life products. With this purpose a cooperation group of EU countries has been established with the "Directive RAEE 2012/19/EU" to reach a well-managed recycle of 85% of the RAEE generated before 2019 against the 3.5% recycled today (Directive 2012/19/UE).

More over the absence of primary deposits pushes many countries to invest in techno-spherical mining as solution for the industrial ecosystem (Binnemansa et al., 2013).

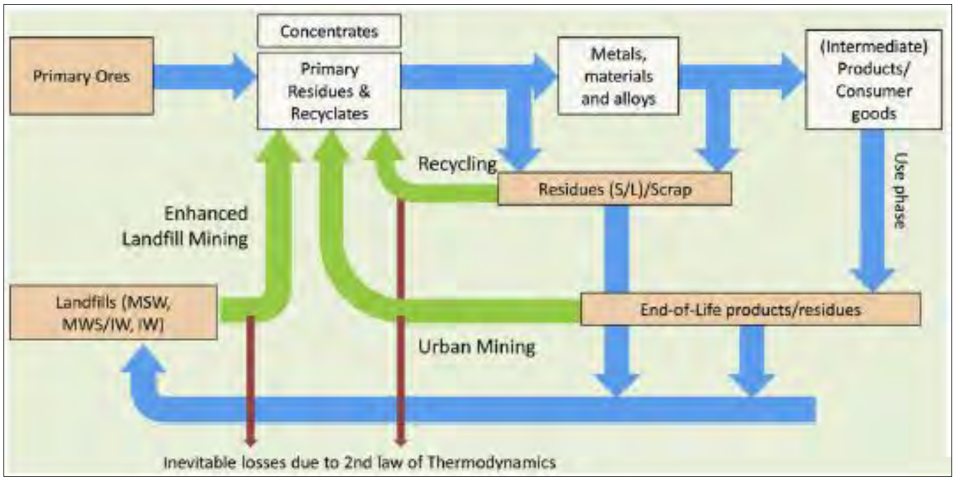


Image1:Different ways to close materials loops in a circular economy: (1) direct recycling of pre-consumer scrap and residues (e.g. slag), (2) urban mining of End-of-Life consumer goods and other products, (3) landfill mining of historically land filled pre-consumer and post-consumer waste streams. Reproduced from (Jones et al., 2011 and K. Binneamans et al.).

Summarizing the REEs must be treated in a *sustainable approach* because of their key-role in economic, environmental and social spheres.

Image2: Sustainable cycle scheme

In this thesis the attention is focused on fluorescent lamps (End-in-Life): special WEEE and rich sources of REEs traces such as Europium and Yttrium. The characteristic fineness of the REEs particles strictly attached to the other elements suggests the low efficacy of the only physical methods of separation; hydro-metallurgical methods seem to be suitable. (Belardi et al., 2014). For this reason in this thesis hydro-metallurgic process is applied following, both materials, methods and parameters found in literature. An additional mechanical sieving pre-treatment is added to the standard procedure of extraction and metal complex formation with different acids is investigated. The purpose is to decrease the Silicon content and in the meantime increasing the efficiency in the recovery of REEs. The main metals detected are: yttrium, europium, lanthanide, cerium, praseodymium, terbium, and ytterbium. The analyses to investigate the initial material and the final results are carried out with ESEM, FT-IR, XRD, thermal TGA analysis.

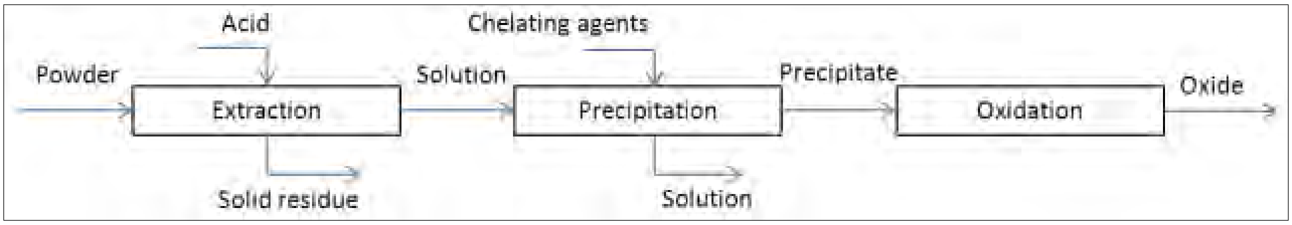
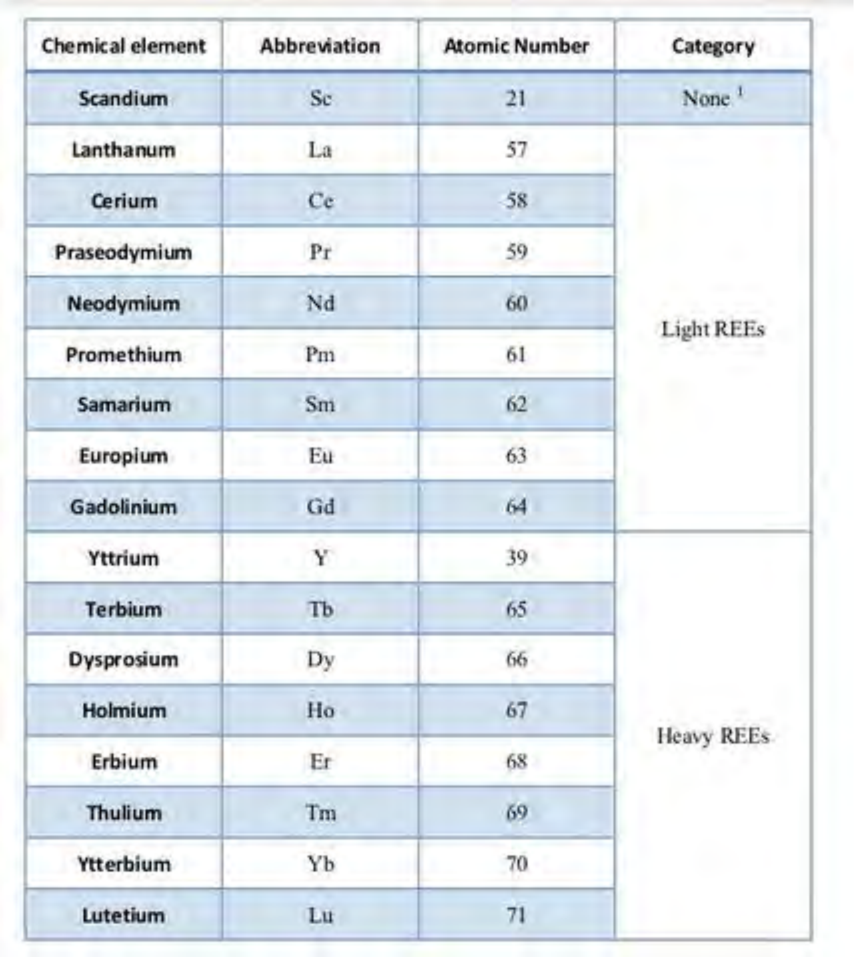


Image3: General diagram of the experimental procedure

2. REEs.: RARE EARTH ELEMENTS



Chemical element	Abbreviation	Atomic Number	Category
Scandium	Sc	21	None [1]
Lanthanum	La	57	Light REEs
Cerium	Ce	58	
Praseodymium	Pr	59	
Neodymium	Nd	60	
Promethium	Pm	61	
Samarium	Sm	62	
Europium	Eu	63	
Gadolinium	Gd	64	
Yttrium	Y	39	Heavy REEs
Terbium	Tb	65	
Dysprosium	Dy	66	
Holmium	Ho	67	
Erbium	Er	68	
Thulium	Tm	69	
Ytterbium	Yb	70	
Lutetium	Lu	71	

Image4: REEs in the periodic table (Hedric 2010)

2.1 Availability and supply – Economic sphere

The black mineral ytterbite, later renamed gadolinite was the first rare earth mineral discovered in 1787 from a Swedish Army Lieutenant Karl Axel Arrhenius, near the village of Ytterby, Sweden (Long et al., 2010).

Since the beginning the difficulty of separation was clearly visible, due to the particular characteristic of the REEs. It was 1794 when, as first, Finnish chemist Johann Gadolin isolated an impure yttrium oxide quantity (Massari and Ruberti, 2013).

The term “rare” was suggested in XVIII century when the first discover of these elements showed a low availability in the Earth crust, despite “earth” means earthly appearance because they usually have an oxidized form. On the contrary of the usual belief they are not absolutely but relative rare: the economically suitable deposits are difficult to be found, the extraction and separation procedures are complicated and moreover they show low concentrations in minerals and an attitude to associate with radioactive elements such as thorium and uranium (Xiea et al., 2014).

REEs ores, rich of REEs elements, are generally found in igneous rocks and sand or clay sediments as result of weathering processes of the primary magmatic rocks (Long et al., 2010). Many of the mineral resources show a concentration of REEs that cannot be considered economically exploitable, other deposits have complex mineralogy that further technological processing are required (Golev et al. 2014). There are about 200 known minerals containing lighter or heavier REEs, six are considered primarily sources:

Bastnaesite (cerium lanthanum and yttrium), Monazite (cerium, lanthanum, praseodymium, neodymium, gadolinium, samarium), Xenotime (yttrium, dysprosium, erbium, terbium and ytterbium), Loparite (cerium), Apatite (neodymium, dysprosium, europium, cerium), Ion-adsorption clays (yttrium, neodymium, lanthanum)

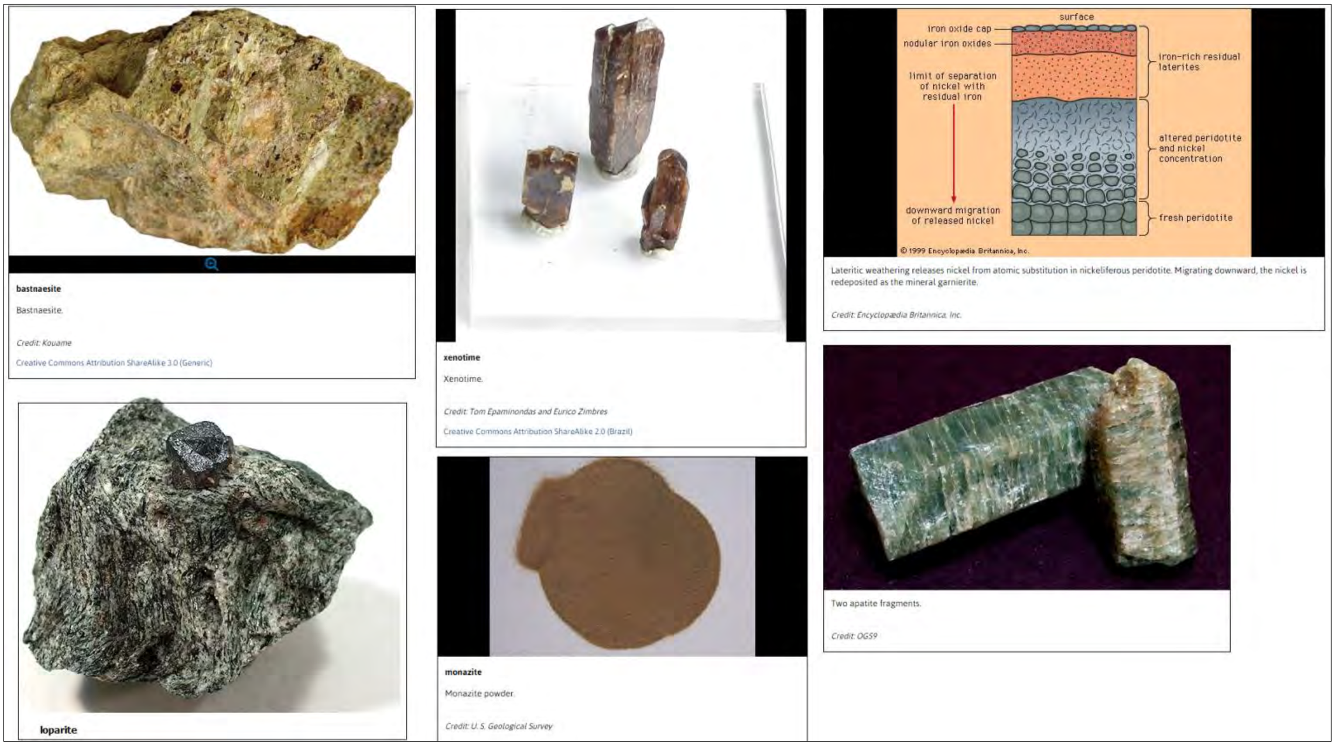


Image 5: Minerals containing REEs (http://www.britannica.com- accessed 28/02/2015)

However only the first three of the last list are considered by far the most suitable sink of REEs (about 95%) (Kanazawa and Kamitani, 2006, Jordens et al., 2013, Gupta and Krishnamurthy, 2005)

The main applications they are involved require high percentage of purity (99.99% or more 99.999%) (King, 2011).

The reserves are mainly concentrated in few countries: 6 in Europe, 14 in Asia, 10 in Africa and more in USA, Canada, Brazil and Australia (Chen, 2011). The largest reserves are in China (60%, 110million tones of REE oxides "REOs"), and this is also the largest producer with 97% of the total; follow this primacy India, Brazil and Malaysia. The larger consumers are USA, Europe, Japan, Korea and China (US Department of the interior, 2011). The demand seems to grow each year around 10% and 20% (Reuters, 2009) other experts of Goldman Sachs predict a surplus already from 2013 (Fickling, 2011).

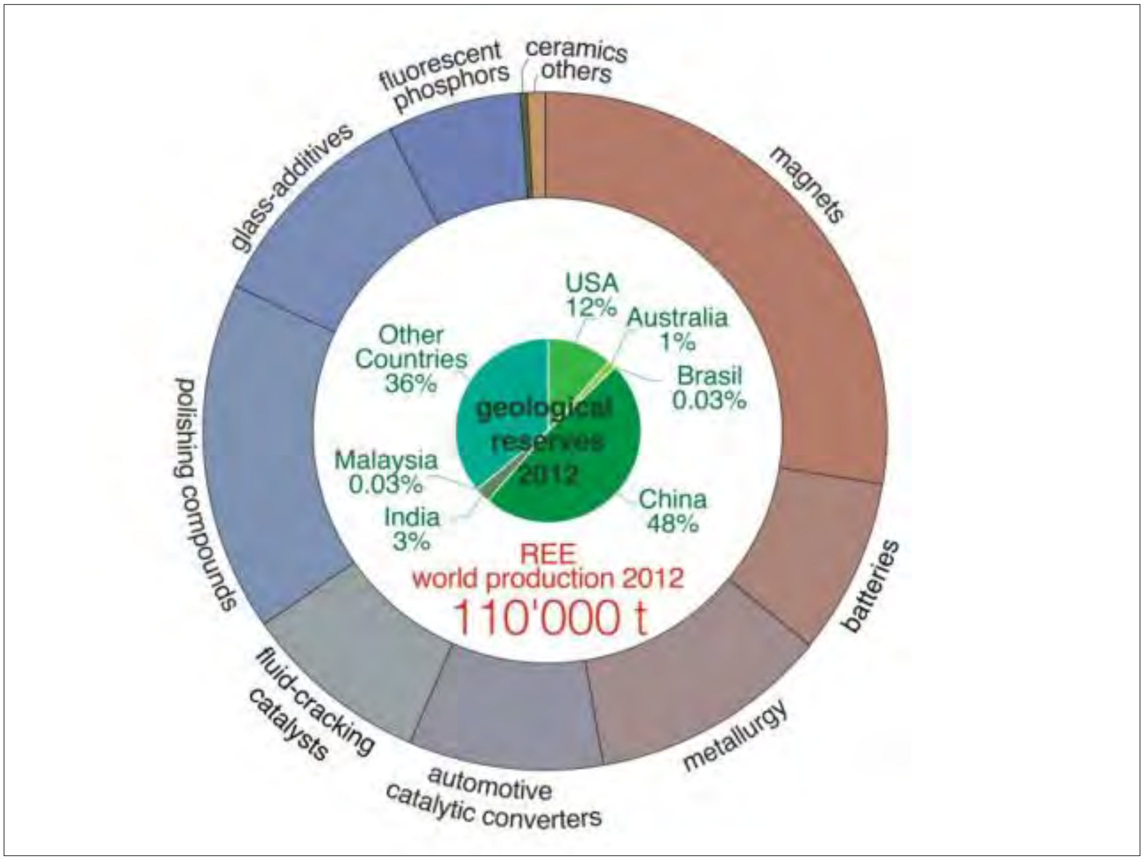


Image 6: Reported figures for the REO-reserves per country (USGS, 2013) and world production (USGS, 2013) for the year 2012; percentage shares of applications are estimates for the year 2007 for the USA, China and Japan (Du and Graedel, 2013). (Simoni, M., Kuhn, E.P., Adam, F., 2014)

The trade of REEs is developed by about twenty countries; China offers the largest number of companies (four) (Seeking Alpha, 2011). Inner Mongolia Baotou Steel Rare-Earth Hi-Tech Co., Ldt. can be recognized as the chef of all the companies for what concerns production and sale of REEs (Reuters, 2011). This small number of country involved in the trade creates a high market competition. Since 1991 the development of both produced quantities and prices are primary due to the role of China as producer and consumer of REEs and REOs, thanks that it controls market prices policies and export control quotas (Papp et al., 2008).

From September 2010 Chinese Government first stopped the exports of REEs to Japan, and then decided to decrease to the 60% also the ones to the other countries. The motivations given are the control of the illegal production and market, and the environmental care. But more reasonably seems that China is trying to develop and enhance the internal production in the hi-tech market by discourage the foreign companies (Massari and Ruberti, 2013).

Some interesting tables are reported below about the variation of price and supply of REEs. All information is supply by FOB China basis.

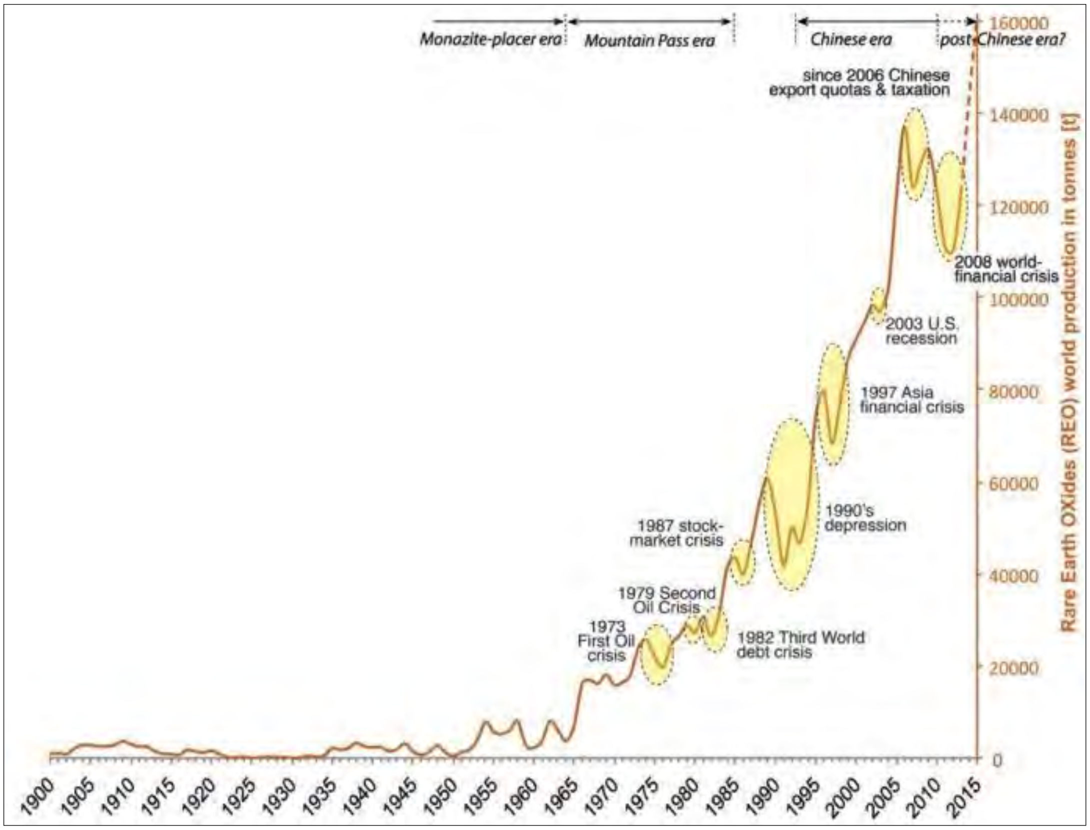


Image 7: Historical and prognosis development of the REO world production (historical: USGS, 2011a; USGS, 2013 prognosis: Kingsnorth, 2013a; Kingsnorth, 2013b). (Simoni, M., Kuhn, E.P., Adam, F., 2014)

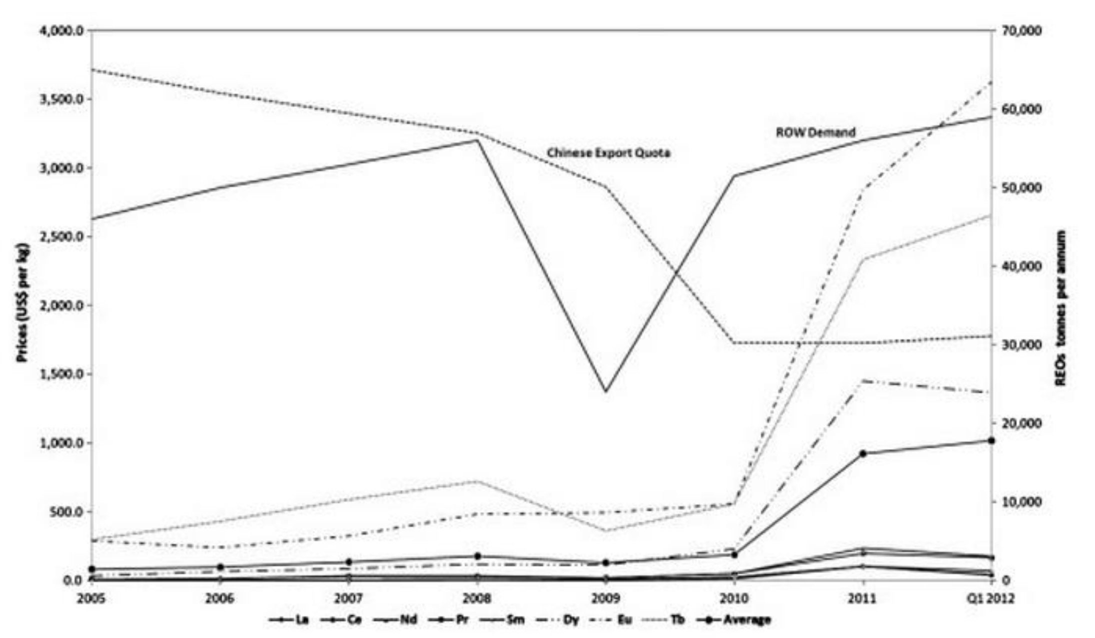
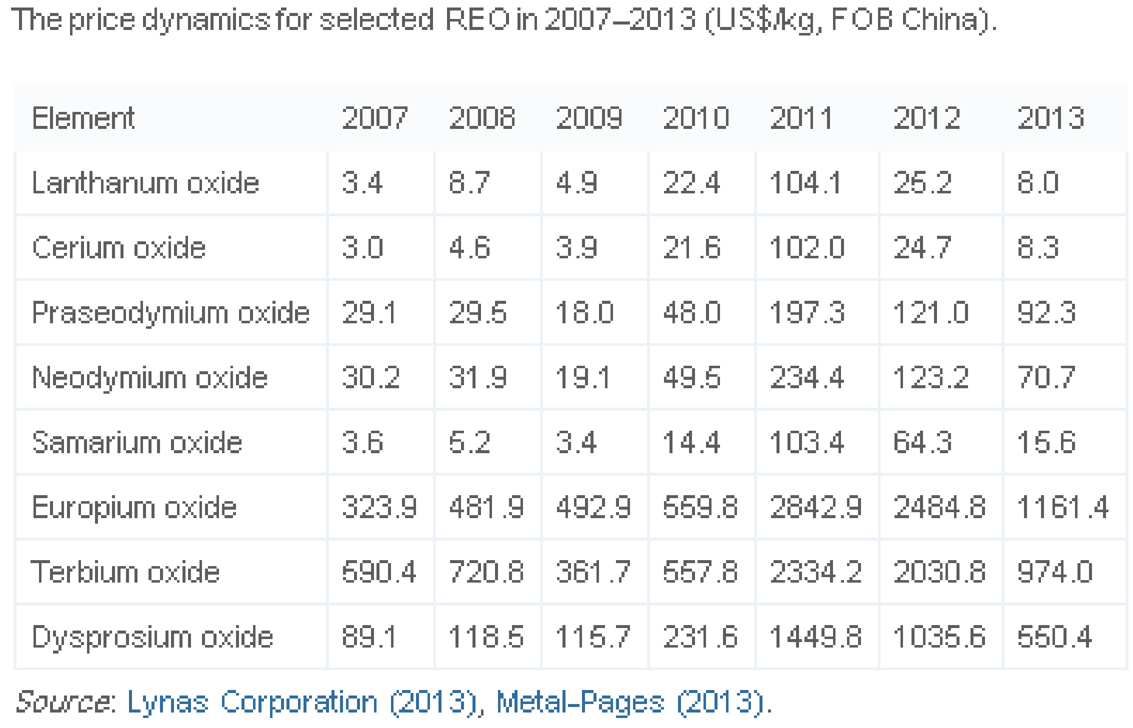


Image 8: Rare-earth oxides (purity 99% min) supply (Chinese export quota), Rest of World (ROW) demand and prices (FOB China basis).

Source: Lynas Corp. (2012), Metalpages Inc. (2011–2012), Hatch, 2011, Molycorp Inc. (2012); Frontier Rare Earths Ltd. (2012), Kingsnorth (2010b), and British Geological Survey (2011).



The price dynamics for selected REO in 2007–2013 (US$/kg, FOB China).

Element	2007	2008	2009	2010	2011	2012	2013
Lanthanum oxide	3.4	8.7	4.9	22.4	104.1	25.2	8.0
Cerium oxide	3.0	4.6	3.9	21.6	102.0	24.7	8.3
Praseodymium oxide	29.1	29.5	18.0	48.0	197.3	121.0	92.3
Neodymium oxide	30.2	31.9	19.1	49.5	234.4	123.2	70.7
Samarium oxide	3.6	5.2	3.4	14.4	103.4	64.3	15.6
Europium oxide	323.9	481.9	492.9	559.8	2842.9	2484.8	1161.4
Terbium oxide	590.4	720.8	361.7	557.8	2334.2	2030.8	974.0
Dysprosium oxide	89.1	118.5	115.7	231.6	1449.8	1035.6	550.4

Source: Lynas Corporation (2013), Metal-Pages (2013).

Image 9: REOs prices (US$ per kg).Source: Lynas Corp. (2013), Metalpages Inc. (2013)

2.2 Applications: Hi-Tech market – Social sphere

The benefit of the REEs in the everyday life can be detected by listing the market fields they belong to. The main characteristics of these elements are: ability to enhance their strength, light magnetisms by linking with metals, great optical properties such as fluorescence, and other unique features (metallurgical, chemical, electrical, optical, nuclear, catalytic and magnetic). Main applications are: metallurgic, automotive, nuclear, electric and electronic equipment, oil industry, electric and electronic equipment, green technologies and renewable energies, hi-tech civil market, military field (Xiea et al., 2014).

Rare earths phosphors are widely used in high efficiency lighting, flat display screens, plasma screens, and liquid crystal screens due to their unique luminescent properties (Ronda et al., 1988, Nazarov and Noh, 2010, Rapaport and Miliez, 2006 and Ye et al., 2011).

Despite their general similar features each REE, with its chemical properties, used to be not no-substitutable for specific application (Golev et al. 2014).

The incredibly wideness of the REEs market, both specialized but also commercial and everyday goods, permits to understand the necessary relation between the metals and the society's needs.

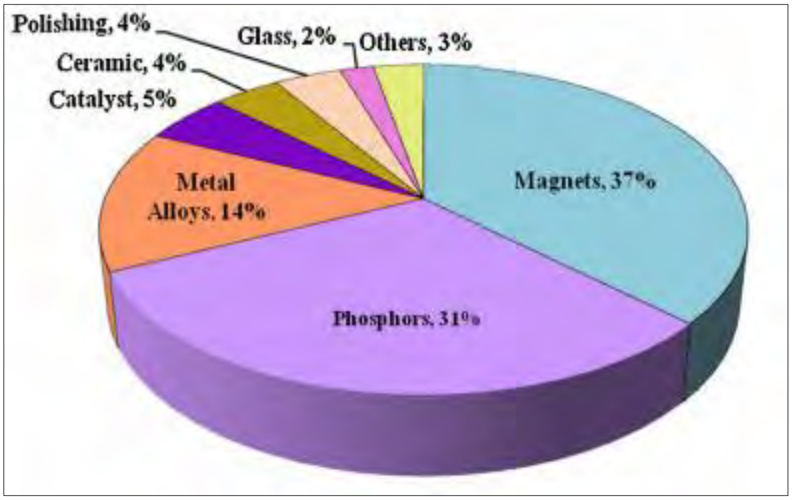


Image 10: Application of REMs (Top-targets material limited, Yahozhuang Photovoltaic Industrial Park, Jiashan, Zhejiang, China, http://www.top-targets.com/rare-earth-applications).

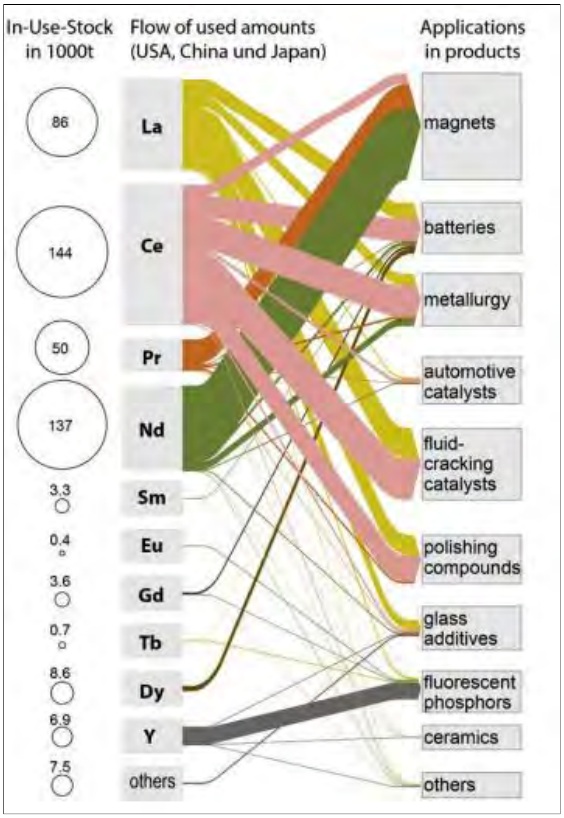
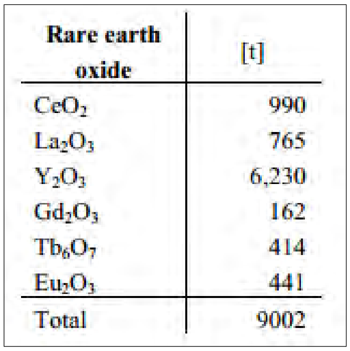


Image 11: Estimated global in-use-stocks of REE (Du and Graedel, 2011a) and flows of the respective elements in different products for the USA, Japan and China (Du and Graedel, 2013), both for the year 2007. (Simoni, M., Kuhn, E.P., Adam, F., 2014)



Rare earth oxide	[t]
CeO_2	990
La_2O_3	765
Y_2O_3	6,230
Gd_2O_3	162
Tb_6O_7	414
Eu_2O_3	441
Total	9002

Image 12: Global Rare Earth Oxide demands for phosphors in 2008 (Goonan, 2011, Zecha, G., 2014).

2.3 Recovery and alternatives – Environmental sphere

The continuous growth of REEs importance, especially Europe countries, poor in mines, highlights the importance of finding comparable alternatives but in particular the recovery and recycling of hi-tech waste (WEEE).

WEEE is a high growth rate produced waste streams in Europe: about 3 - 5% per year (Crowe et al., 2002).

The European Community directive WEEE Directive (2002/96/EC) with the RoHS Directive 2002/95/EC became an official European Law in February 2003. The purpose is to decide a minimum rate per head of population per year of recycled and recovered kg from electrical goods (Directive 2002/95/EC).

The Waste Electronic and Electrical Equipment Regulations (Directive 2012/19/EU, 2012) establishes firstly to reduce the amount of WEEE being disposed of, secondly it requires industries to pay for the reuse, recycling and recovery. It is estimated that 25% of the mass of WEEE produced is collected and processed, and the remaining 75% is not recorded (In Europe), probably because inadequate waste processing technology occurs (Kulczycka and Cholewa, 2014). The growing mass of WEEE affects firstly the developed countries; otherwise in other EU countries the system is well developed: in recent years about 16.7 kg/person of WEEE are collected in Sweden, 8.2 kg/person in the UK, and 6.5 kg/person in Austriaand 4.06 kg/person in 2012. (Raporty, 2006-2012, Cholewa et al., 2014).

The presence of hazardous substances (heavy metals and flame retardants) confers to WEEE hazardous characteristics, if it is improperly managed, may pose significant human and environmental health risks (Tsydenova et al., 2011, Falboet al, 2014)

About 32% of the value of the REE-market results from fluorescent lighting (Binnemans et al., 2013b).

Despite the existence of a vast literature about REE recycling, mostly based on lab-scale experiments, (Meyer and Bras, 2011; Tanaka et al., 2013; Anderson et al., 2012), less than 1% of the REEs was recycled in 2011. The main problems are: inefficient collection, technological difficulties and lack of incentives (Graedel et al., 2011a, 2011b; Reck and Graedel, 2012). A realistic improvement in End-of-Life recycling rates for REEs is a strategic necessity.

Table 1: WEEE classification

Class	WEEE
1	Heaters and refrigerators
2	Big household equipment
3	TV monitors
4	Small household equipment
5	Lighting equipment

Image 13: cycle recovery from waste

Toxicological studies on REEs sediment traces, about form, rate and concentration, have shown acute and chronic effects on animals (Wells and Wells, 2012).

The hazardous materials in the e-wastes including toxic metals (Pb, Cd, Hg, etc.) and non-metallic materials (epoxy resins and plastics including brominates flame retardants) are attracting attentions for their negative impact on environmental. Due to the backyard operations adopted open sky incineration and acid leaching have resulted in aquatic, terrestrial and atmospheric pollutions dramatically (Deng, et al, 2006; Leung, et al, 2008; Fu, et al, 2008).

Moreover many deposits are usually associated with radioactive elements (uranium and thorium) that require expensive safety measures during extraction and the specific treatments. During the production cycles high quantity of water, acids and electricity are required. That implies consumption of energy and production of waste to demolish or dispose and high probability and quantity of hazardous and radioactive chemicals release (EPA, 2012)

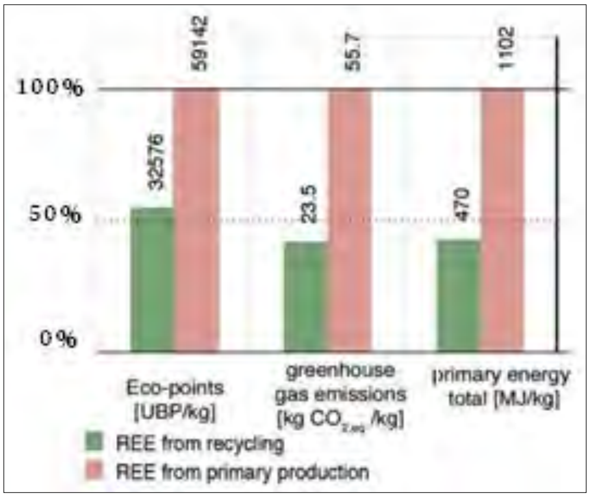


Image 14: Life cycle assessment (LCA) of the primary production of the main REEs in fluorescent lighting (Eu, Y, Tb) calculated by Werner (2013). (Simoni, M., Kuhn, E.P., Adam, F., 2014)

After the extraction from the mineral deposit, the following stages are separation of ore into REO, refining REO into metals first of all the lights from the heavies, and then the individual elements from other, forming REM into marketable product or manufacturing (Paul and Campbell, 2011).

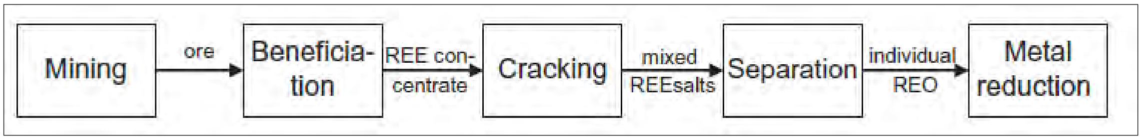


Image 15: Scheme of production Primary supply. Golev, A., Margaretha, S., Peter, E. D., Ali, S.H., Ballantyne, G. R., 2014. Rare earth supply chains: Current status, constrains and opportunities. Resources Policy 41 (2014) 52-59.

There is not a proper lack of geological resources for REEs; the proven reserves should cover the current demand for several centuries. However the monopoly of only one country (China) over several stage of the production process, from mining to separation, creates a supply risks. Diversity in the supply sources must be a key point of view in the current and future application of REEs and must include the development of green technologies.

Alternative supply chains in mining operations are developed in the USA, Australia, Russia, India, and Kazakhstan, in the processing plants in France, Malaysia, and Estonia.

Recycling and waste mining are new potentially significant sources for rare earths.

The reprocessing of existing industrial waste and recycling of end-of-life products provide diversity in the supply chain and also contribute to minimizing the environmental impacts in the REEs production.

It is important to better understanding the risks associated with rare earths mining and possessing: radioactivity issues, fair communications with stakeholder groups as critical success factors. It is equally important the minimization of environmental. Based on the economic, technical, environmental, and social factors about REEs extraction the recycling projects are the most advantageous, followed by the reprocessing of industrial waste streams. The new rare earths mining and processing facilities should take place outside of sensitive natural ecosystems, targeting low radioactive ore bodies with higher content of critical REEs. (Golev, A., Margaretha, S., Peter, E. D., Ali, S.H., Ballantyne, G. R., 2014)

Image 16: Inner Mongolia largest REEs deposit in the world

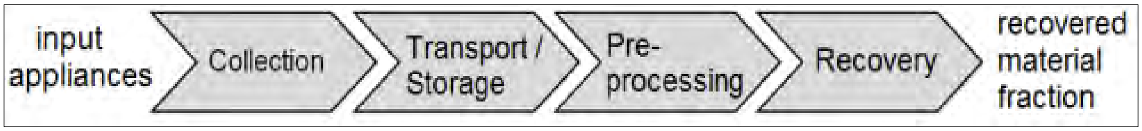


Image 17: Scheme of production Secondary supply (Zecha, g., 2014).

Some general conclusion:

In a social point of view it is essential collaboration between research institutions, industry, and communal and other authorities.

In the process of recovery key points are:

- amounts and concentrations of REE in different product components, categories and material flows
- the quality of the life cycle impact values of primary REE production
- Life cycle impact values for recycling of REE not still published for most REE
- the state-of-the-art of REE recycling, where the difficulty is the measuring of the degree of compliance and propose and the implementation of regulatory instruments
- collection and separation (disassembly) systems for circular material flow and implementation for most REE containing waste

Focusing the attention on the difference between lab scale and industrial scale:
In laboratory scale: extraction efficiencies of up to 99% of Yttrium and Europium are reported by Shimizu et al. (2005) by supercritical fluid extraction.
For *industrial scale* that conditions and basic materials might be less ideal: recovery efficiencies of 95% for the extraction of REE from fluorescent powders are reported on industrial scale in the Rhodia plant in La Rochelle, France (Walter, 2011). Moreover appropriate pre-treatment methods are performed in order to receive feed materials with high concentrations of REE. (Zecha, G., 2014)
The recycling of WEEE and in particular of fluorescent reduces the environmental impact of this waste at the end of their service life. More important they can represent an important source for secondary materials like REEs, for that reason the research must proceed from this stage of knowledge with continuous experimental activities, literature analysis and economical aspects to reduce the costs of recycling and make it economically feasible the considered hydrometallurgical processes. (Innocenzi, V. 2013)

Because a few industrial recycling REEs activities are currently implemented, there has been no large-scale recycling of rare earths from magnets, batteries, lighting and catalysts.
The recycling processes for the rare earths are quite complex and extensive if re-use is not possible and a physical and chemical treatment is necessary. For now the main post-consumer activities (the recycling) will require intensive dismantling.
The constraints for a wider recycling are:

- efficient collection system,

- adequate high prices for primary and secondary REEs compounds, losses of post-consumer goods by exports in developing countries
- A long life time of products before they enter the recycling economy.

The advantage of REEs recycling includes the utilization of European resources, independence from foreign resources and environmental benefits. (D. Schüler, M. Buchert, R. Liu, S. Dittrich, C. Merz).

3. STATE OF THE ART

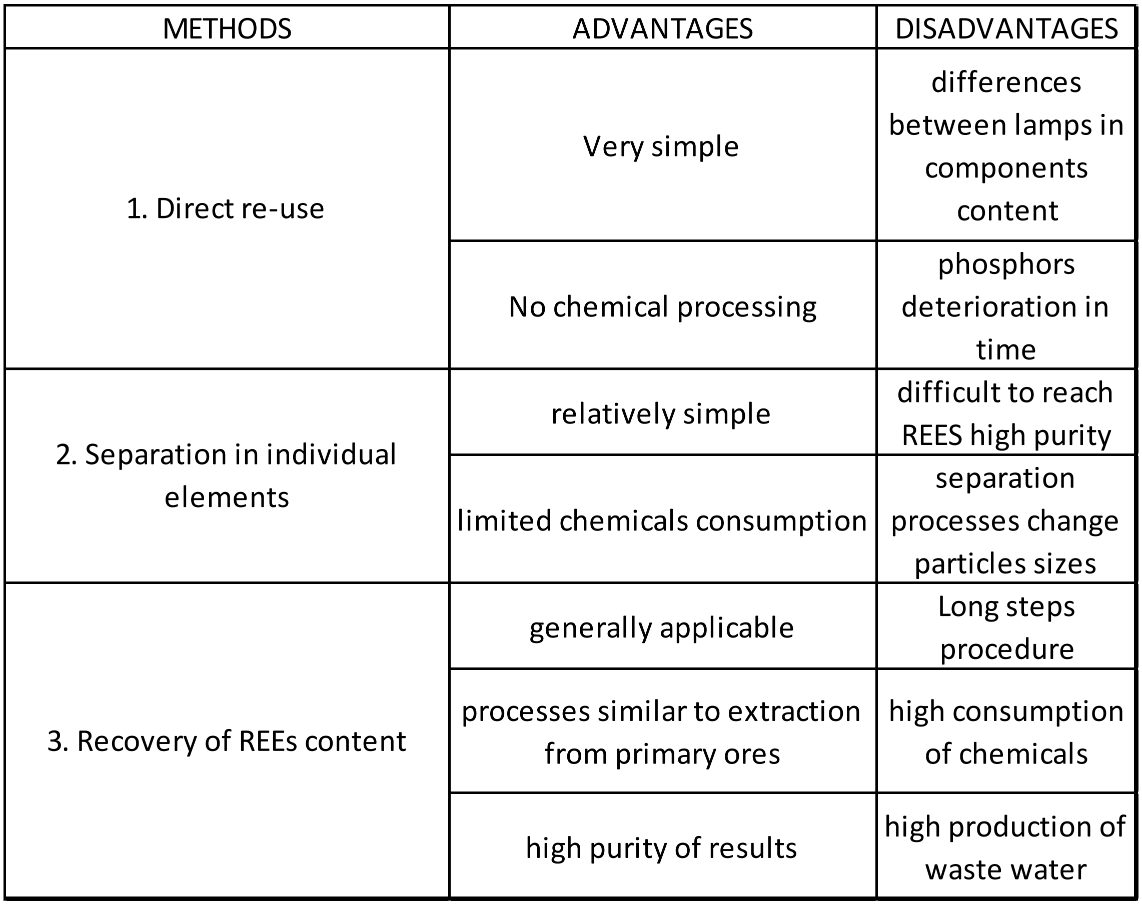
The major components of the lamp phosphors in End-of-life fluorescent lamps are: yttrium (Y), europium (Eu), and terbium (Tb).

There are three main *options for recycling* the REEs from these types of devices:

- Direct re-use lamp phosphors in new lamps,
- Recycling of individual phosphor component by physicochemical methods
- Chemical attack of the REEs contained in the raw material.

(Binnemansa et al. 2013).

The first and the second processes are used in hydrometallurgical procedures; the problem is the presence of the Mercury (Hg) that is potential hazardous.



METHODS	ADVANTAGES	DISADVANTAGES
1. Direct re-use	Very simple	differences between lamps in components content
	No chemical processing	phosphors deterioration in time
2. Separation in individual elements	relatively simple	difficult to reach REES high purity
	limited chemicals consumption	separation processes change particles sizes
3. Recovery of REEs content	generally applicable	Long steps procedure
	processes similar to extraction from primary ores	high consumption of chemicals
	high purity of results	high production of waste water

Image 18: Recycling REEs options

The principal *physicochemical methods* are: froth flotation, two liquids flotation and pneumatic separation.

a. *Froth flotation:* medium = liquid solvent; wide pH range (<4.5:9); add of anionic surfactants (SDS, DDA); the problem is that the phosphor components (phosphates, oxides, aluminates or borates) have similar hydrophobia and a really smaller size (<10μm). EFFICIENCY: DDA and SDS 70–90% 66–82%. (Hirajima et al. 2005a)

b. *Two liquids flotation:* medium = non miscible polar solvent (water or DMF) plus non polar solvent (hexane, heptanes, octane, nonane); agitation and two phase separation settlement processes. EFFICIENCY: 90%. (Otsuki et al. 2008)

c. *Other surfactants* can be used: (Otsuki at al. 2008, Mei et al. 2009b, 2009a).

d. *Pneumatic separation*: medium = air stream. The advantage is the differences in density of particles, the disadvantage is the toxicity and the high cost of the chemical used. Centrifugation, pretreatment and dense medium (diiodomethane) (Hirajima et al. 2005a). A separation of Y and Tb chemicals from Eu compounds, based on differences in magnetic susceptibility, has been proposed (Horikawa and Machida 2011).

These approaches are not recommended because of the low purity of the end products and the long-term deterioration of the phosphors in presence of Mercury. Moreover the re-arrangement of the particle during these processes gives lower quality final products. Finally these types of processes can be useful as pretreatment to remove the halo-phosphate phosphor fractions from the REEs ones.

The principals heavy REEs recoverable from reclaimed lamp phosphors are: Y, Eu and Tb, the major technique used are: precipitation and strong acids extraction. The chemicals used to attack include a large variety. They are described in the table below:

Table 2: REEs extraction treatments and extracted compounds

EXTRACTED	SOLVENT	TREATMENT	AUTHORS	EFFICIENCY & COMMENTS
Halo phosphate phosphorous	diluted acids			
Y_2O_3:EU^{3+}	diluted acids	pretreatment with mechanical activation by ball milling	(Mio et al. 2001)	
$LaPO_4$:Ce^{3+},Tb^{3+}	more resistant to	leaching adding HCl (4molL^{-1}) and	(Wang et al. 2011)	

	acids	NaOH (4.4 gL^{-1})		
		heating in molten NA_2CO_3 at1000°C	(Porob et al. 2012)	
(Ce, Tb) $MgAL_{11}O_{19}$	more resistant to acids	leaching adding HCl (4$molL^{-1}$) and NaOH (4.4 gL^{-1})	(Wang et al. 2011)	
		heating in molten Na_2CO_3 at1000°C	(Porob et al. 2012)	
$BaMgAl_{10}O10:Eu^{2+}$	more resistant to acids	heating in molten Na_2CO_3 at1000°C		
Y, Eu	H_2SO_4 or HNO_3	autoclave digestion of mixture $Y_20_3:Eu^{3+}$ and halo phosphate phosphor	(Rebah 2008)	96.4% Y, 92.8% Eu
		acidic mixture 4 hours,125°C,5MPa		
REEs	extraction with supercritical CO_2 and tri-n-butyl (TBP)	2 hours of leaching, 15MPa, 60°C	(Shimizu et al. 2005)	99.5% Y,Eu
	control experiments with $TBP/HNO_3/H_2SO_4$	atmospheric pressure		<40% Y,Eu
phosphor powders	NH_4	leaching tests with very low Y recovery	(De Michelis et al. 2011)	
	HNO_3	toxic vapors		most efficient recovery of Y
	H_2SO_4	similar to HCl		
	HCl	similar to H_2SO_4		better than HCl: less co-dissolution of Ca, Pb and Ba
phosphor mixture + high quantity of Al_2O_3	HNO_3	salting-out agent formation $Al(NO_3)_3$ brings REEs from aqueous to organic phase	(Yang et al 2012)	
all REEs:	OSEAM	mechanical separation, sieving (20-25µm), selective leaching steps	(Otto and Wojtalewicz-Kasprzac 2012)	
Halo phosphate phosphorous	HCl solution, 30°C			
$Y_2O_3:EU^{3+}$	HCl or H_2SO_4 solution, 60-90°C			
$LaPO_4:Ce^{3+},Tb^{3+}$	H_2SO_4 solution, 120-230°C			
(Ce, Tb) $MgAL_{11}O_{19}$	35% NaOH			

	solution, 150°C autoclave or in molten alkali			
BaMgAl$_{10}$O10:Eu^{2+}	35% NaOH solution, 150°C autoclave or in molten alkali			
REEs mixed with halo phosphate and RE phosphor	extraction in a flow sheet	1 step: hot HNO$_3$ or HCl	(Bracconier and Rollat 2010)	
		2 step: hot concentrate NaOH solution or molten Na$_2$CO$_3$		
		3 step: leaching for individual separation of elements		

A list of *hydro-metallurgic processes for the recovery of yttrium* from primary and secondary sources:

Table 3: Hydro-metallurgic processes for the recovery of yttrium

Authors	raw material	methods	efficiency or comment
Hirajiama et al. (2005)	**phosphors fluorescent lamps**	**centrifugation with diiomethane**	**variables: rotation speed, pulp density, adsorption sulfactant**
Shimuzuat al. (2005)	**luminescent material lamps**	**SF-CO2 and TBP complexes with HNO3 and H2O**	**100% Y, Eu**
Otshki et al. (2006)	**fluorescent powder**	**liquid liquid extraction**	**96.9,94.1% red powder 74.1,98.7% blue powder 94.6,76.0% green powder**
Rebah (2008)	**fluorescent lamps**	**leaching, precipitation, selective solvent extraction**	**99% Y 97% Eu**
De Michaeliser al. (2011) Innocenti et al. (2012)	**fluorescent lamps and CRTs**	**acid leaching, O.A. complex formation, subsequent calcinations for separation of mercury**	**99% Y purity**

A scheme of *treatment for the recovery of yttrium* from fluorescent lamps exhausted:

Table 4: Treatment for the recovery of yttrium (V. Innocenzi, 2014)

Author	Treatments
Touru et al. (2001)	Sulphuric acid leaching
	Precipitation by oxalic acid
Shimizu et al. (2005)	Extraction by supercritical carbon dioxide containing TBP complexes with HNO_3 and H_{2O}
Otsuki et al. (2007)	Hetero coagulation of fine particles in polar organic solvent
Rebah (2008)	Nitric/sulphuric acid leaching
	Thiocyanate conversion
	Solvent extraction using trimethyl-benzylammonium chloride
	Stripping by N-tributylphosphate
	Thermal reduction using hydrogen gas
Porob et al. (2011)	Fire of initial material with an alkaline material
	Acid leaching of the residues (HNO3, H2SO4 or HCl) at high temperature (i.e. 150°C)
	Solvent extraction of RE. Crystallization or precipitation process
Otto and Wojtalewicz-kasprzac (2012)	Selective leaching:
	Leaching with HCl at low temperature to leach all rare earth except the Y23:Eu3+
	Leaching with HCl or sulphuric acid at 60-90°C
	Leaching with sulphuric acid at 120-230°C to dissolve LaPO4-, Ce3+, Tb3+
	Dissolution with 35% of NaOH solution at 150°C to dissolve (Ce,Tb)MgAl11O19 and BaMgAl10
Yang et al (2013)	Leaching with acid
	Solvent extraction using ionic liquids N,N-dioctyldiglycol amic acid (DODGAA)
De Michelis et al. (2011)	Nitric/chloridric and sulphuric acid leaching
	Precipitation with oxalic acid
Innocenzi et al. (2013a,b)	Sulphuric acid leaching
	Purification with sodium hydroxide and sulphide
	Precipitation with oxalic acid

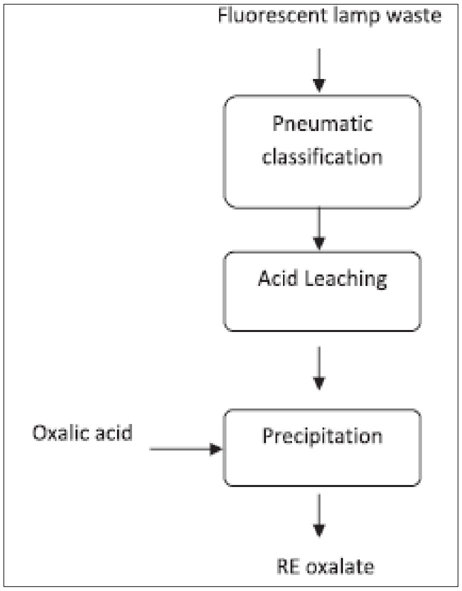


Image19: Treatment block diagram (Tooru et al., 2001)

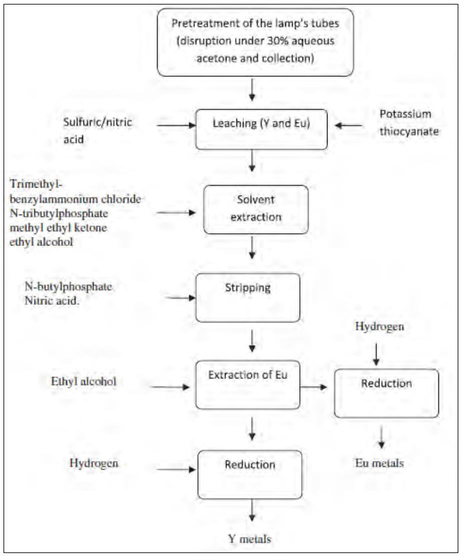


Image20: Treatment block diagram (Rahab, 2008)

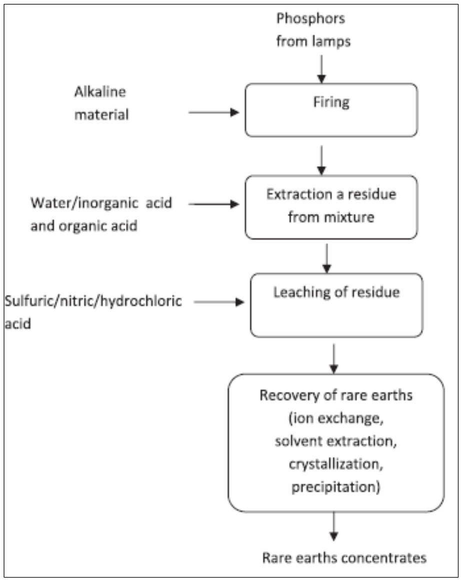


Image21: Treatment block diagram (Porob et al. 2011)

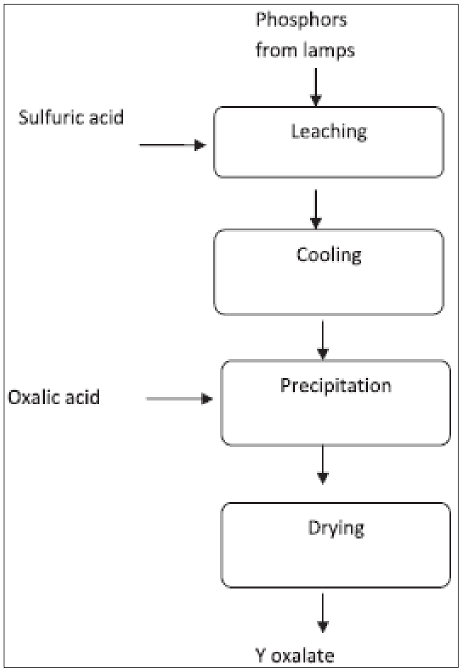


Image22: Treatment block diagram (De Michaelis et al.2011)

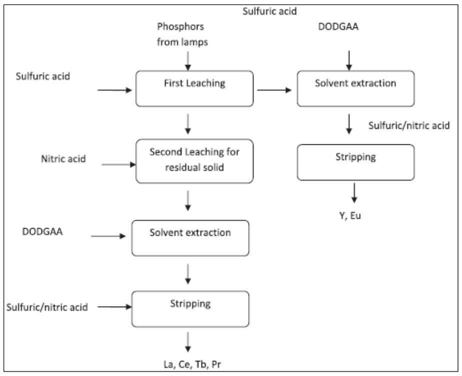


Image23: Treatment block diagram (Yang et al. 2013)

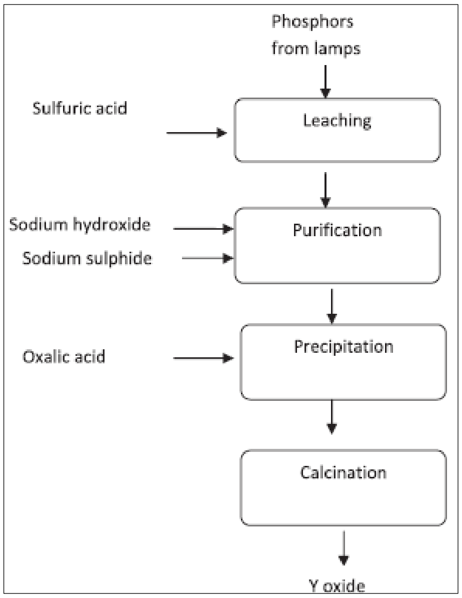


Image24: Treatment block diagram (Innocenzi et al. 2013)

INPUT:

FLUORESCENT LAMPS POWDER

9% Si	*8.12% Y*
13% Ca	*0.64% Eu*
	0.26% Tb
	0.60% Ce
	0.57% La

OUTPUT

LABSCALE:

Coumpond	**%**
Y2O3	80-88
Eu2O3	4-5.26
Gd2O3	0.35
CaO	0.71 -2.39
Hg	14.49 ppm + 2.54 ppm
Other	4-14.9

MOBILE PILOT SCALE:

Coumpond oxalate	**Average (%)**	**Max (%)**
Yttrium	~58.7	~73
Europium	~4.9	~6
Terbium	~0.5	~0.8
Gadolium	~3.2	~5.1
Lanthanum	~0.03	~0.03
Cerium	~0.5	~1.1

Image25: Scheme of the HydroWEEE pilot plant

General approach on the recycling fluorescent lamp (Wu, Y. et al., 2014) is presented:

- **Pre-treatment and physical processes**
  - **Dismantling**

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-Beijing Eco-island science and technology Co., Ltd Disposal system for waste containing mercury (2013) Retrieved from http://www.bbmgbest.com/_d1479.htm.

-Integrated Pollution and Control (IPPC) Additional Information submitted during the information exchange on Waste Treatments Industries Institute for Prospective Technological Studies, Seville, Spain (2005).

  - **Crushing**

- M.A. Rabah. Recovery of aluminum, nickel-copper alloys and some salts from spent fluorescent lamps. Waste Management, 24 (2004), pp. 119–126.

- W.K. Qi, Y.H. Sun, J.M. Nan Recovery processing method and Countermeasure of waste fluorescent lamp Environ Pollut Control, 31 (9) (2009), pp. 95–102.

- Nomura Kosan. Recycling system of used fluorescent lamps (2013) Retrieved fromhttp://www.nomurakohsan.co.jp/business/disposal_fluorescent.html.

- Fluorescent Lamp Recyclers Technologies Inc (2013). Retrieved from http://www.flr.ca/Recycle lamps.htm.

- AERC-Recycling Solutions, Lamp Recycling. (2013). Retrieved from http://www.aerc.com/.

- Lampcare-Lamps (2013). Retrieved from http://www.lampcare.com/.

- M. Jang, S.M. Hong, J.K. Park. Characterization and recovery of mercury from spent fluorescent lamps. Waste Management, 25 (2005), pp. 5–14

- S.W. Rhee, H.H. Choi, H.S. Park. Characteristics of mercury emission from linear type of spent fluorescent lamp. Waste Management (2013). http://dx.doi.org/10.1016/j.wasman.2013.07.029.

- E.J. Dos Santos, A.B. Herrmann, F. Vieira, C.S. Sato, Q.B. Correa, T.A. Maranhao, et al.

-Determination of Hg and Pb in compact fluorescent lamp by slurry sampling inductively coupled plasma optical emission spectrometry. Microchem J, 96 (2010), pp. 27–31.

- **<u>Dissolution of the rare earth</u>**
  - **Acid leaching**

- I. De Michelis, F. Ferella, E.F. Varelli, F. Vegliò. Treatment of exhaust fluorescent lamps to recover yttrium: experimental and process analyses. Waste Manage, 31 (12) (2011), pp. 2559–2568.
-H.M. Li. Recovery of rare earths from phosphor sludge by acid leaching. Chin J Rare Met, 34 (6) (2010), pp. 899–904.
- S. Luidold, A. Poscher, H. Antrekowitsch. Concepts for the extraction of rare earths from spent phosphors. Proceedings of the 51st annual conference of metallurgists of CIM (COM 2012), Rare earths 2012 Niagara, ON, Canada (2012), pp. 435–446.

  - **Alkali fusion**

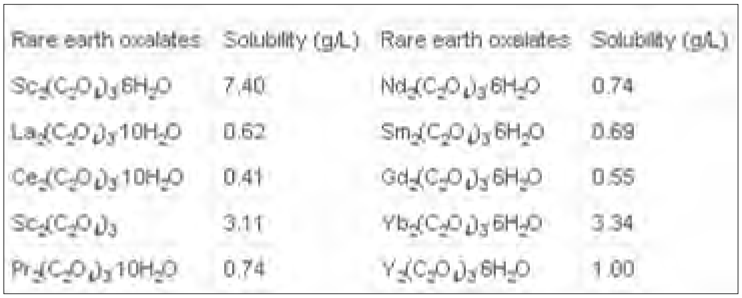
- F. Paulino, J.C. Afonso, J.L. Mantovano, C.A. Vianna, J.W.S.D. Cunha. Recovery of tungsten by liquid–liquid extraction from a wolframite concentrates after fusion with sodium hydroxide. Hydrometallurgy, 127–128 (2012), pp. 121–124.
- A.J. Manhique, W.W. Focke, C. Madivate. Titania recovery from low-grade titano-ferrous minerals. Hydrometallurgy 109 (2011), pp. 230–236.
-X.H. Wang, S.L. Zheng, H.B. Xu, Y. Zhang. Leaching of niobium and tantalum from a low-grade ore using a KOH roast—water leach system. Hydrometallurgy, 98 (2009), pp. 219–223.
- Y.B. Tang, X.Z. Zhu, H.B. Wang, F.X. Qi. Progress in research on barium magnesium aluminates. Mater Rev, 20 (S1) (2006), pp. 335–338.
- Z.H. Wu, A.N. Cormack. Defects in BaMgAl10O17:Eu2+ blue phosphor. J Electroceram, 10 (2003), pp. 179–191.

- Porob DG, Srivastava AM, Nammalwar PK, Ramachandran GC, Comanzo HA. Rare Earth. Recovery from Fluorescent Material and Associated Method. Patent US 20120152060 (2012).
- R.Q. Li, Y.F. Wu, Q.J. Zhang, W. Wang. Extraction of rare earth from waste three primary colors fluorescent powder in high temperature alkali fusion method. Proceedings of CCATM'

2012 international conference & exhibition on analysis & testing of metallurgical process & materials, 32 (2012), pp. 795–799.

- <u>**Recovery of rare earth**</u>
  - **Chemical precipitation**

- Y. Iwata, H. Imura, N. Suzuki. Selective pre-concentration of rare earth elements by sub-stoichiometric precipitation of calcium oxalate and its application to the neutron activation analysis of biological material. Anal Chim Acta, 239 (1990), pp. 115–120.
- J.C. Kirk, H.B. Robert. Rare earth element complex formation by carbonate and oxalate ion. Geochim Cosmochim Acta, 51 (3) (1987), pp. 597–605.



Rare earth oxalates	Solubility (g/L)	Rare earth oxalates	Solubility (g/L)
$Sc_2(C_2O_4)_3 6H_2O$	7.40	$Nd_2(C_2O_4)_3 6H_2O$	0.74
$La_2(C_2O_4)_3 10H_2O$	0.62	$Sm_2(C_2O_4)_3 6H_2O$	0.69
$Ce_2(C_2O_4)_3 10H_2O$	0.41	$Gd_2(C_2O_4)_3 6H_2O$	0.55
$Sc_2(C_2O_4)_3$	3.11	$Yb_2(C_2O_4)_3 6H_2O$	3.34
$Pr_2(C_2O_4)_3 10H_2O$	0.74	$Y_2(C_2O_4)_3 6H_2O$	1.00

Image 26: Solubility hydrated REEs in water at 25°C

- **Extraction**

- E. Bou-Maroun, H. Chebib, M.J.F. Leroy, A. Boos, G.J. Goetz-Grandmont. Solvent extraction of lanthanum (III): europium (III) and lutetium (III) by bis (4-acyl-5-hydroxypyrazoles) derivatives. Separ Purif Technol, 50 (2) (2006), pp. 220–228.
- H. Narita, T. Yaita, S. Tachimori. Extraction of lanthanides with N: N′-dimethyl-N, N′-diphenyl-malonamide and -3,6-dioxaoctanediamide. Sol Extract Ion Exchange, 22 (2) (2004), pp. 135–145.
- W. Li, X.L. Wang, H. Zhang, S.L. Meng, D.Q. Li. Solvent extraction of lanthanides and yttrium from nitrate medium with CYANEX 925 in heptane. J Chem Technol Biotechnol, 82 (4) (2007), pp. 376–381.
- T. Nakamura, S. Nishihama, K. Yoshizuka. Separation and recovery process for rare earth metals from fluorescence material wastes using solvent extraction. Sol Extract Res Develop Jpn, 14 (2007), pp. 105–113.

- Y. Baba, F. Kubota, N. Kamiya, M. Goto. Recent advances in extraction and separation of rare-earth metals using ionic liquids. J Chem Eng, 44 (2011), pp. 679–685.
- H.L. Yang, W. Wang, H.M. Cui, D.L. Zhang, Y. Liu, J. Chen. Recovery of rare earth elements from simulated fluorescent powder using bi-functional ionic liquid extract-ants (Bif-ILEs). J Chem Technol Biot, 87 (2012), pp. 198–205.
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- O. Tomioka, Y. Enokida, I. Yamamoto, T. Takahashi. Cleaning of materials contaminated with metal oxides through supercritical fluid extraction with CO_2 containing TBP. Prog Nucl Energy, 37 (2000), pp. 417–422.
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- R. Shimizu, K. Sawada, Y. Enokida, I. Yamamoto. Supercritical fluid extraction of rare earth elements from luminescent material in waste fluorescent lamps. J Supercrit Fluids (33) (2005), pp. 235–241.

- **<u>Example of combined processes</u>**
  - **Dismantling, acid leaching and solvent extraction**

- M.A. Rabah. Recyclables recovery of europium and yttrium metals and some salts from spent fluorescent lamps. Waste Manage, 28 (2008), pp. 318–325.

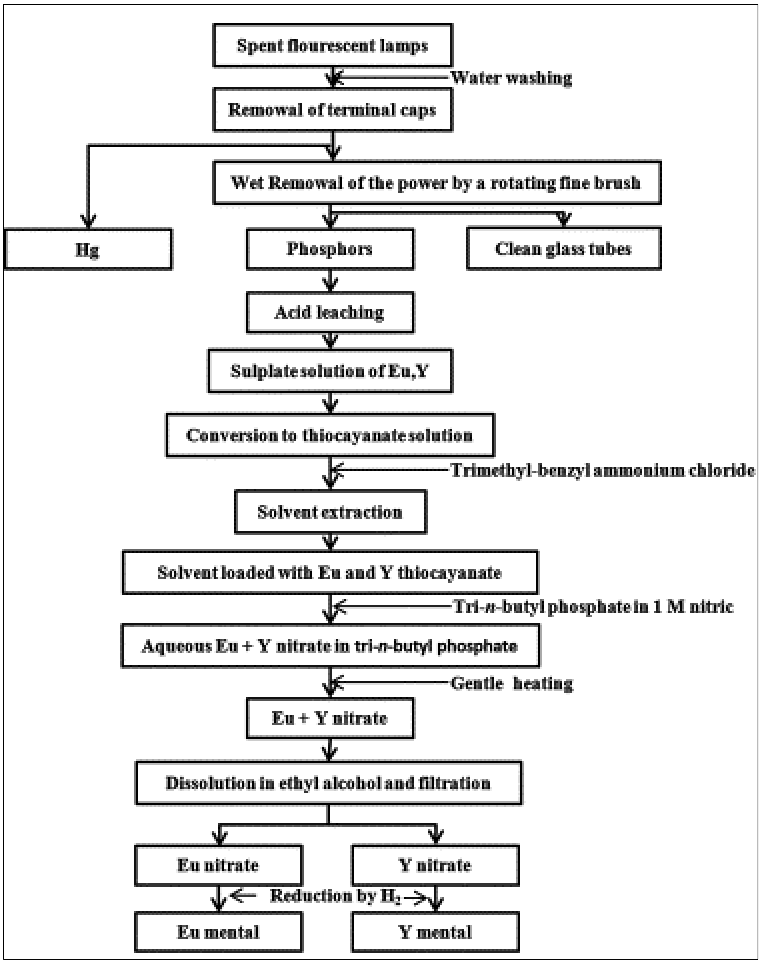

Image 27: Dismasting, leaching and solvent extraction

- J. Bussi, C.M. Noel, J. Chiazzaro, C. Canel, S. Veiga, C. Florencio, *et al.* The recovery and recycling of mercury from fluorescent lamps using photo-catalytic techniques. J Chem Technol Biotechnol, 85 (4) (2010), pp. 478–484.

○ **Crushing, acid leaching and chemical precipitation**

- G.J. Mei, Y.G. Lei, K.F. Xie. Study on the recovery of Y_2O_3 from waste fluorescent powder. The first academic conference proceedings of Chinese comprehensive utilization of rare earth resources conference and the Fifth Chinese Rare Earth Society of Selective Professional Committee. (2009)
- G.J. Mei, P. Rao, M. Mitsuaki, T. Fujita. Separation of red (Y_2O_3:Eu^{3+}): blue ((Sr, Ca, Ba)$_{10}$(PO_4)$_6$$Cl_2$:$Eu^{2+}$) and green ($LaPO_4$:$Tb^{3+}$, Ce^{3+}) rare earth phosphors by liquid/liquid extraction. J Wuhan Univ Technol Mater Sci Ed, 24 (3) (2009), pp. 418–423.

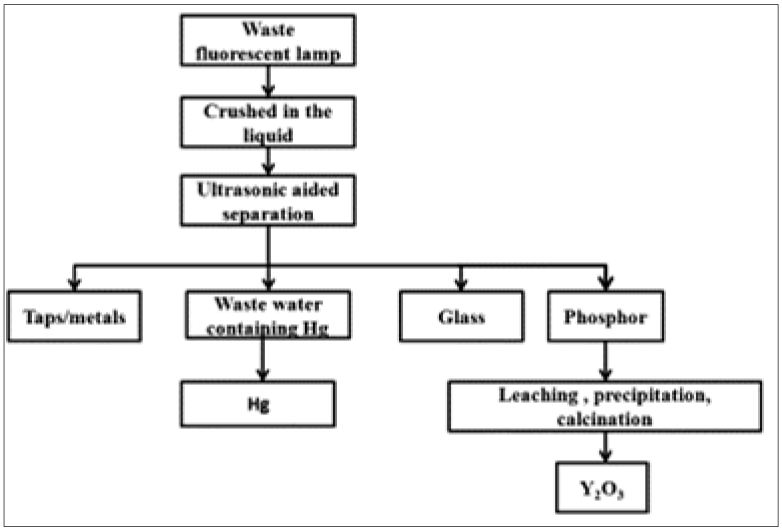

Image 28: Recycling process from waste of fluorescent lamps (Mei et al. 2009a,b)

○ Two-step acid leaching and extraction by ionic liquid

- F. Yang, F. Kubota, Y. Baba, N. Kamiya, M. Goto. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system. J Hazard Mater, 254–255 (2013), pp. 79–88.

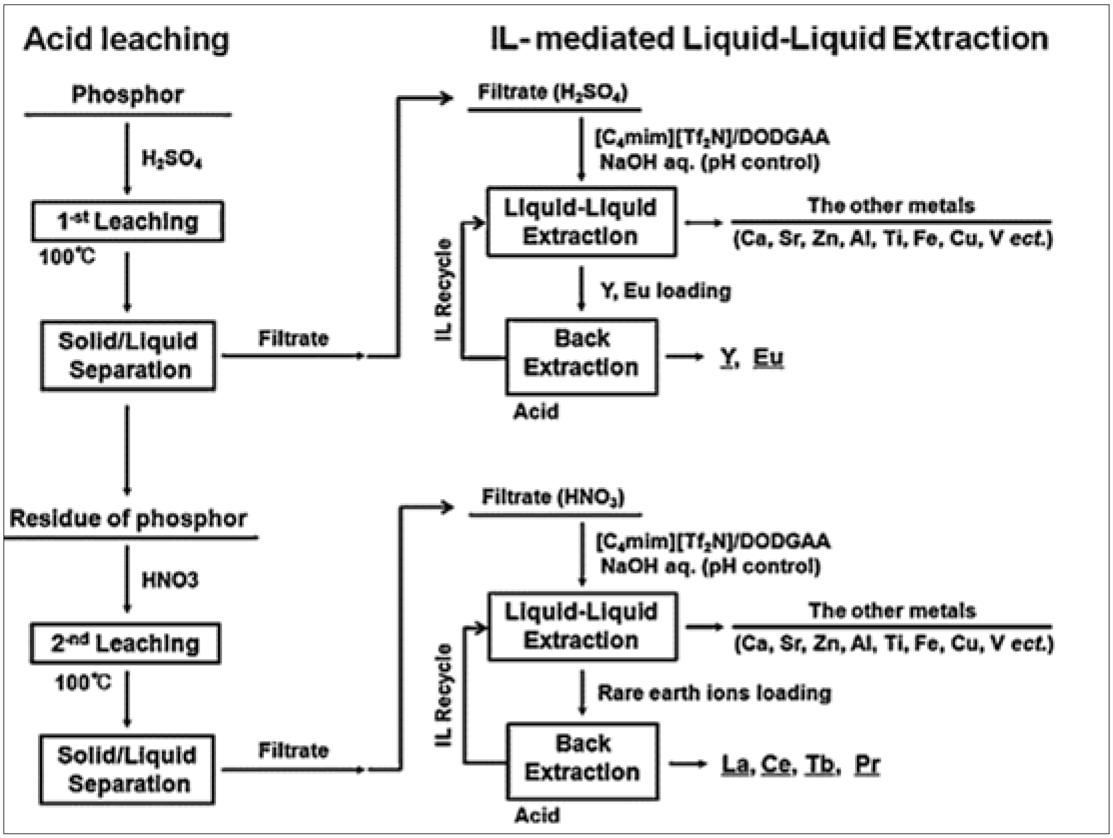

Image 29: Recovery of REEs flow-sheet from waste phosphor powders in spent fluorescent lamps by ionic liquid extraction (Yang et al. 2013)

○ Alkali fusion, acid leaching and chemical precipitation

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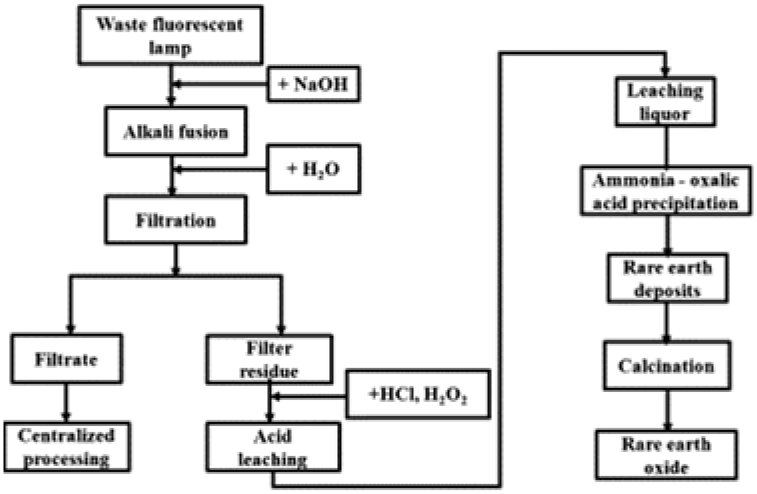


Image 30: Recovery combining process

In the following tables are reported the main *patents* concerning the recovery of REEs from fluorescent lamps:

Table 5: List of some patents about recovery of REEs

Patents	Name of Patent	Raw materials	Products
US 4858833 (1989)	Process for recycling fluorescent and television tubes	Television and fluorescent tubes	Glass and Yttrium compounds
US 005160663A (1992)		Fluorescent lamps	Reconstituted phosphors to reuse for lamps
US 5403403 (1995)	Method for processing fluorescent material	Fluorescent material of coating screen	Fluorescent material for reuse
EP 1138741 A2 (2001)	Method of recycling fluorescent substance for fluorescent lamp, recycled fluorescent lamp and lighting apparatus using thereof	Fluorescent lamps	Glass material and recover fluorescent material for reuse
WO 2007/003722 A1 (2007)		Cathode ray tubes	Glass and fluorescent powder
EP 1817437 (2007)	Method of extracting europium(iii) and yttrium(iii) from concentrate of lumino-phore dust or sludge	Screens of color TV or monitors	Yttrium and Europium oxides
US 2010/0062673 (2010)	Method For Integral Recycling For Cathode Ray Tubes	Cathode ray tubes	Glass and fluorescent powder
US 7976798 B2 (2011)	Method for recovery of rare earths from fluorescent lamps	Fluorescent lamps	RE compounds
DE19961017942 19960429	Reprocessing rare earth phosphor mixtures from used fluorescent lamps		
DE19991018793 19990426	Three-band phosphor, from scrap discharge lamps, is recycled by oxidative mineral acid leaching for impurity removal and carbonate leaching for selective yttrium-europium oxide dissolution		
RSP20100479 20101108	Recovery of Basic and Precious Metals from the Fluorescent Powders and Plant for Recovery Thereof		

Some conclusion:

Fluorescent lamps are produced and used all over the world. That fact implies a considerable number of waste rare earth fluorescent lamps are produced every year. The recycling of this type of waste is necessary through the research and investigation of the recycling technologies it is highlight that the hydrometallurgical process are suitable for the recovery purpose. A reasonable selection of extract-ant can make efficient recovery of rare earths.

Some key points in the recovery process of REEs from fluorescent lamps are reported below:

The majority of the researches are focused on extraction and recovery of Y, Eu in the red powder Y_2O_3: Eu^{3+}, it are easily dissolved in acid. Other REEs such as Ce, Tb are ignored due to the stable chemical structures of BAM and CAT, which has serious effects on the recovery efficiency of rare earths from waste tricolor fluorescent powders.

Standards concerning the recycling of waste rare earth fluorescent power must be establishing including determination of the total rare earths species and their relative contents in the waste material. The standards aim is to provide a suggestion in the method for recycling, suggesting efficient leaching technology and scientific basis for further utilization of secondary REEs resources.

A first problem is that most of the methods showed good results in the stage of the laboratory and they do not seem to be considerable in economic point of view or their applications on a larger scale. More over in some publication waste material used in the experiments is artificial waste powders synthesized by pure samples, arising out of production, or got from clean lamps, that is different from the actual waste powders which has more complex components and more impurities. That fact implies an impurity removal step as pre-treatment before carrying out the extraction reactions.

It is necessary also to pay attention to contamination during processes procedure and to the purity of secondary REEs resources by considering the different recycling technology and equipment in relation to the efficient utilization of secondary resources, environmental pollution emission standards, and quality of recycled products. The standards on the recycling of REEs from abandoned fluorescent lamps is established by the Green Eco-Manufacturer (2013) in China, it specifies a series of requirements about recycling process, storage, performance of powders, test methods, prevention of secondary pollution, and relevant contingency plans. The intent of the standard is to regulate market order and enterprise management behavior, moreover to promote the recovery of REEs from waste phosphors in fluorescent lamps efficiently.

Sometimes could be confined to pay also attention to the extraction of other elements with relatively higher contents, such as Sr, Al, and Ba, fluorescent lamps can be useful source of also these elements.

The acids, organic reagents and other chemicals used during experimental processes, produce massive waste of liquid, gas and residue, which must be recycled rationally and utilized comprehensively. It is fundamental to evaluate if the recovery processes are economically feasible, if there is a relative advantage compared to ore mining and if the technological process is suitable for industrial production. Life cycle analysis (LCA) and Material flow analysis (MFA) (Binder et al., 2001, Streicher-Porte et al., 2005 and Streicher-Porte, 2006) are useful decision-support tools in resource, waste and environmental management. The LCA study is applied to analyze quantitatively and evaluate material transfer and environmental influence in the whole product service life from raw materials acquisition, production until the disposal of products after abandoned. (Innocenzi, V., et al. 2014)

4. MATERIALS AND METHODS

4.1 Equipment:

- Sieve *Filtra, N°50316/1*
- Rotary evaporator *Buchi-Rotavapor R-114, Water-bath B-48O*
- ESEM*XL-30 (Philips)*
- Magnetic stirred
- FT-IR spectrum *PerkinElmer Spectrum 100*
- Microwave *Ethos 1600 Milestone*
- Centrifugation *MF 20 AWEL Centrifugation*
- Filter paper *WhatMan 595, 15cm*
- Solvent extraction
- TGA Thermal analysis

4.1.1 Leaching and hydrometallurgical treatments

Physical beneficiation treatments are not very successful (Girgin and Gunduz, 1996), for this reason REEs are more effectively recovered through hydrometallurgical processes that include leaching for example with acids, precipitation or solvent extraction are performed using the most common organic leaching agents (Innocenzi et al., 2014). The hydrometallurgical operations advantages are:

- Reproductively from small lab scale to larger ones that implies great control in processing recovery (Ghosh and Ray, 1991).
- Selectively dissolution of the inert metals to the ore leaving behind the higher fraction of impurities that implies simplicity in the process.

The disadvantages of this type of treatment are:

- Residual chemicals are left behind in the leaching creating hazardous pollution in the environment. (Hudson et al.. 1999)
- Some undesirable components may pass into solution complication the subsequent extraction and complex formation (Ca, Si). (Fulford et al., 1991)

Many parameters complicated to estimate are necessary to optimize the treatment:

- Physical attributes: leaching temperature, leaching time, agitation rate, pressure, particles of the untreated sample, liquid-solid ratio, amount of sample to treat, number of leaching stages, amount of leaching agent to involve.
- Chemical attributes: nature and grade of the sample, choice of the leaching agent, acidity of the leaching agent, corrosiveness of the leaching agent, percentage of impurities in the sample, pre-treatment before the leaching stages, dissolution rate of the REEs, solubility of the other element along with REEs.
- General attributes: type of sample treated, cost of the raw material (including the transport), percentage of recovery/extraction of the REEs, pre-treatments, cost of materials (leaching agents, mechanical agitation etc.). (Baral et al., 2014).

Several attributes affect the optimization of this kind of treatment and it can be useful to apply a Multiple Attributes Decision Making scheme (MADM) implemented with mathematical and graphical methods to analyze the different alternatives. (Baral et al., 2014).

In this thesis several tests are made with different leaching agent (acid/ base, organic/inorganic): H_2S0_4, HF, HNO_3, HCl, CH_3COOH, HNO_3+3HCL, NaOH.

4.1.2 Rotary Evaporator

The Rotary Evaporator is useful to remove solvents from solution. It is composed by the evaporation flask for the sample, a thermostatic bath to regulate the temperature by conduction, the vacuum system to reduce the pressure in the system and enhancing the rate of the process, the motorized mechanism for the rotation of the system, the condenser inclined, in this particular device, to knock the vapor developed in the sample flask and a second flask to collect the distilling solvent after it re-condenses.

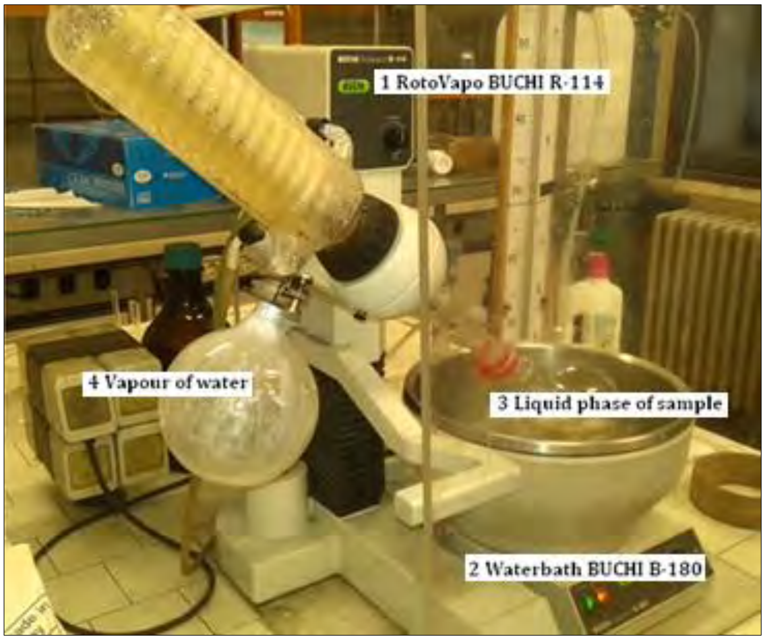


Image31: Detail Rotary evaporation device

4.1.3 ESEM analyses - Environmental scanning electron microscope

The scanning electron microscope (SEM) is a type of microscope that hits the sample with parallel beams of electrons to evaluate its composition. The electrons interact with the sample in 3 ways: some are reflected (elastic diffusion), others penetrate the surface of the samples, others are absorbed by the atoms of the sample producing electrically excited ions. These ions, returning to their fundamental states, emit secondary electrons, Auger electrons or photons at a high spectral X energy (fluorescence). Handling the emissions of photons is possible to extrapolate the morphology information (measure of the angle between the incidental beam of secondary electrons and the surface of the sample) and composition of the surface of the sample (measure of the atomic number of elements in the sample), finally is possible to create an image of the sample (measure of the electrons backscattered).

In the PC monitors two images appear: the first one is related to the diameter of the electron beam, smaller is the diameter higher the resolution will be; the second one is related to the energy of the electron beam, higher the energy deeper the beam will penetrate the sample surface and higher will be the volume of backscattered electrons, this image allows to distinguish the heavier elements (lighter) from the lighter element (darker).

In this work that ESEM model is used: model XL-30 (Philips). The difference between an ESEM and an ordinary SEM is in the absence of high vacuous in the sample chamber. The sample is maintained in low value of vacuous and it is not necessary to treat it (with gold layer) before the analysis, it is also possible to analyze material such as glass (or not electro-conductive), that usually becomes charged crashing the result.

The third goal of the ESEM analysis is to create a fluorescence spectrum, characterized by some intensity peaks related to energy (keV). Each element presents a characteristic spectrum with primary and secondary peaks. The spectrum allows qualitative analysis of the elements of the sample. The intensity of the peaks is linked to the abundance of the atoms of the particular specie in the sample volume. The area subtended under the peaks-curve is proportional to the concentration of the different species. Every manufacturer company gives the correction parameters end errors for these types of tools.

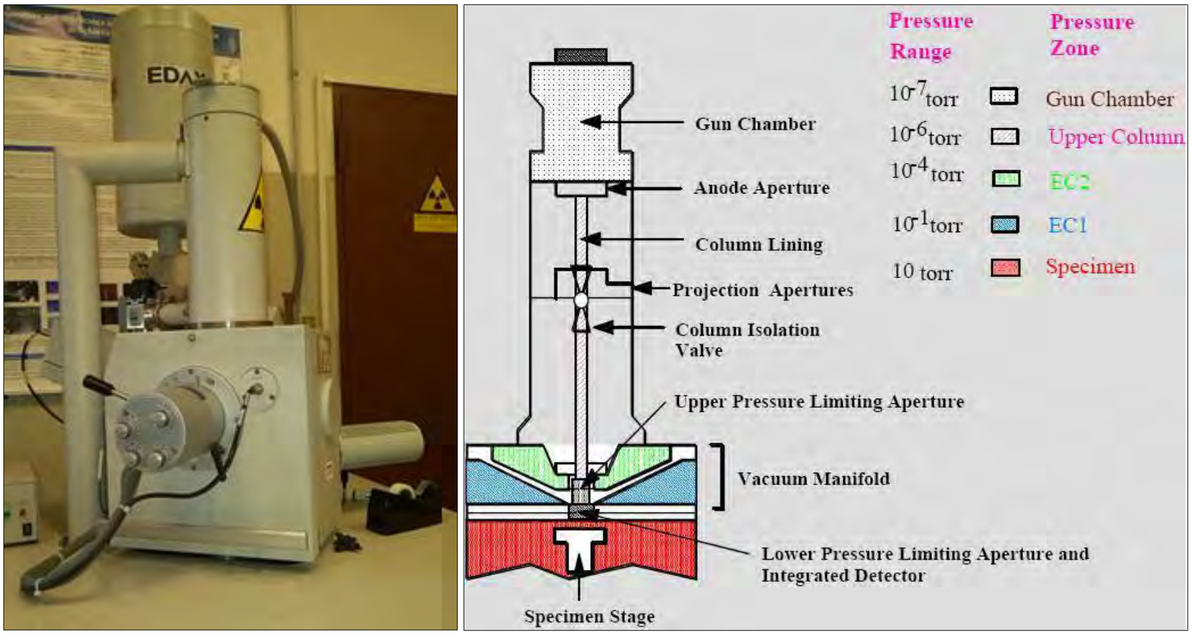
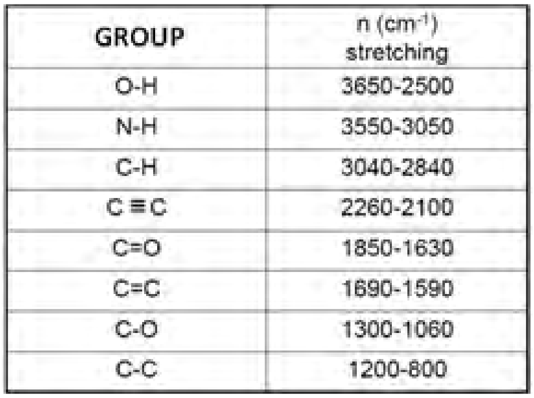


Image32: ESEM Environmental Scanning Electronic microscope. (http://www.unipd.it/cugas/esem.htm)

4.1.4 FT-IR (Fourier transform infrared spectrometer)

The FT-IR spectroscopy is useful to obtain a qualitative analysis about the characteristics of the functional groups, starting from their absorption properties. When a molecule is hit by an IR beam, of a certain wavelength, a variation in the level of vibration energy changes the length of the chemical bond (stretching) or it charges the 'bond angle' (bending). The specific device used in this work of thesis is: FT-IR PerkinElmer Spectrum100, the results are after adapted with OMNIC software.



GROUP	n (cm^{-1}) stretching
O-H	3650-2500
N-H	3550-3050
C-H	3040-2840
C≡C	2260-2100
C=O	1850-1630
C=C	1690-1590
C-O	1300-1060
C-C	1200-800

Image33: characteristic bands of the main functional groups

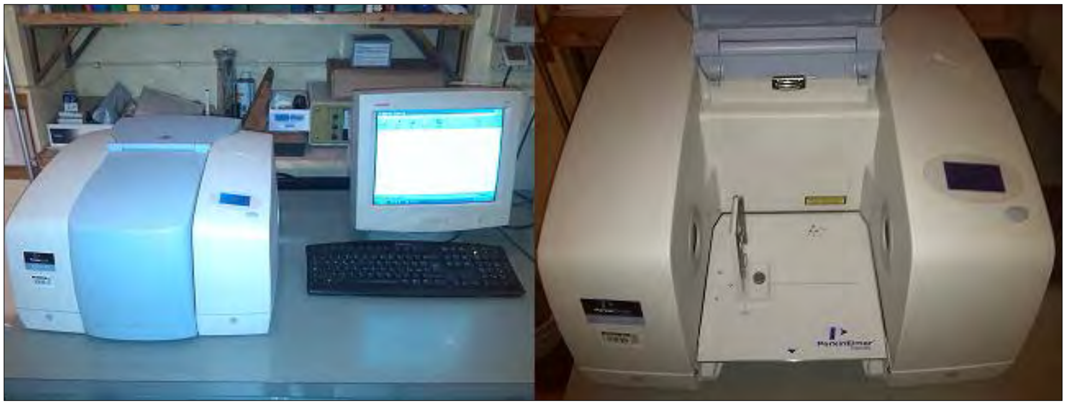


Image34: Devices for the FT-IR analysis: FT-IR PerkinElmer Spectrum100

Before the analysis is essential to build up a proper sample: it is necessary to create a pastille made of a higher amount of KBr (Potassium Bromide) and a little amount of Yttrium Oxalate (a ratio of about 1:50).

Image35: Instruments for the preparation of the pastille for the FT-IR analysis.

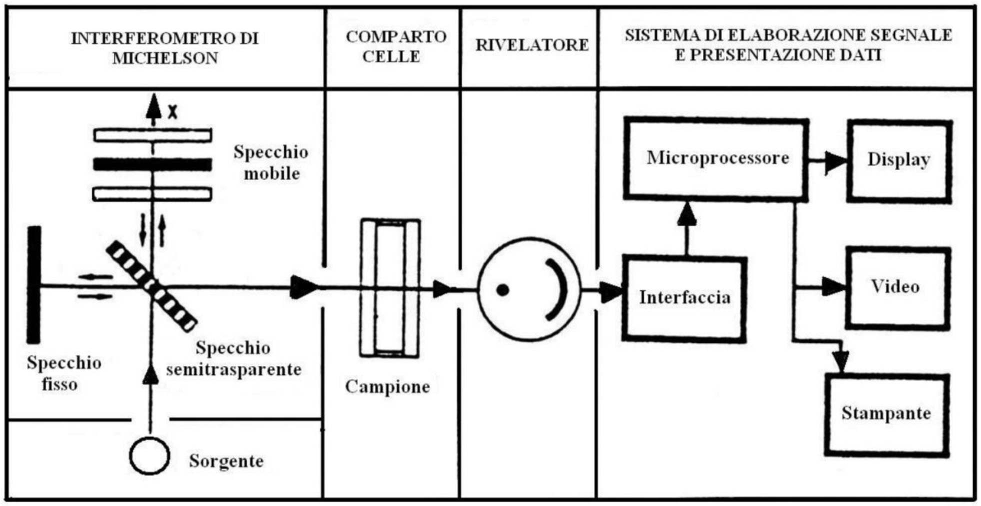
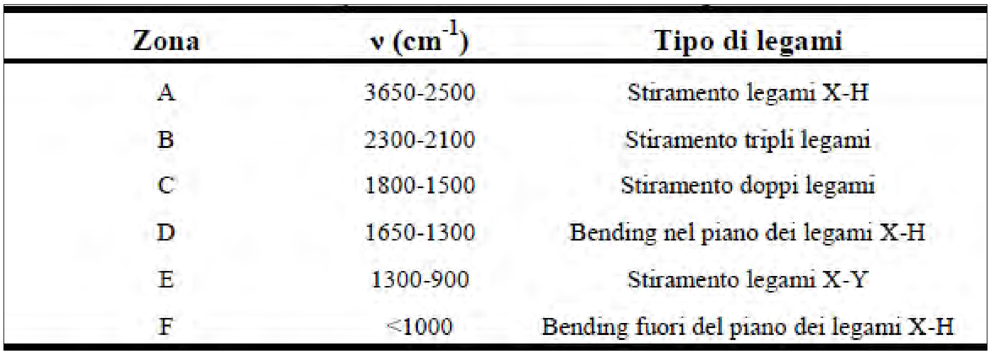


Image36: Functioning scheme of a FT-IR system



Zona	ν (cm^{-1})	Tipo di legami
A	3650-2500	Stiramento legami X-H
B	2300-2100	Stiramento tripli legami
C	1800-1500	Stiramento doppi legami
D	1650-1300	Bending nel piano dei legami X-H
E	1300-900	Stiramento legami X-Y
F	<1000	Bending fuori del piano dei legami X-H

Image37: FT-IR system, classification of zones of the spectrum

The most interesting zone of the FT-IR spectrum is the ones that stands between υ = 650-1300 cm^{-1}, this zone is called ‘’area of fingerprint’’. This area is the most interesting because allows the individualization of the single atoms by its vibration behavior in the molecular skeleton.

4.1.5 Microwave treatments

Microwave digestion operates at higher temperature and pressure by exposing the sample to very strong acid, to lowering the pH, in a closed vessel. In that way is possible to make faster the thermal decomposition of the sample and the solubility of it, so the microwave goal is to enhance the reaction kinetics.

The microwave oven used is the Ethos 1600 *Milestone*. It contains 10 vessels for acid digestion, the samples suggested are from easily to medium-difficult digestible (from soils, sludge, sediments, wastewater, food and feed, metals, alloys to coal, ashes, rocks, plastics, lubricants, pharmaceuticals and ceramics). Nine of the vessels are standard segments one of them is a reference segment to check temperature and pressure.

The vessel material is Teflon, resistant to acid, the volume is 100 m L, the maximum temperature and pressure sustainable are respectively 300°C and 100 Bar.

The chamber in which the vessel is put is mad on HTC (high-performance plastic) and it is schematized below:

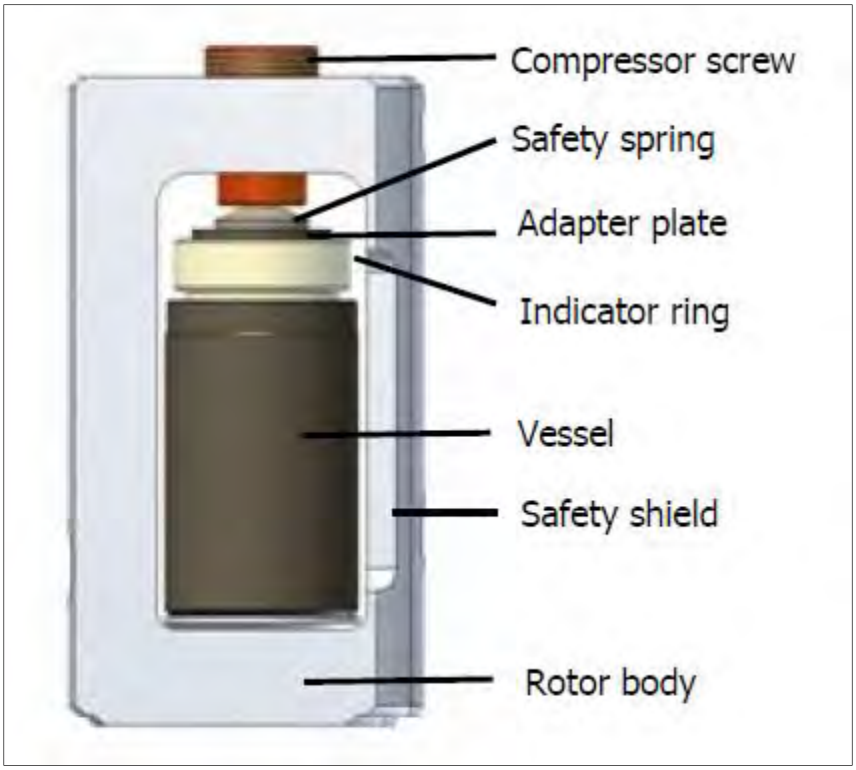


Image38: Microwave vessels

The instruments described must be regularly checked in their performance by looking at the variation of shape or the colors.

A torque wrench with a pre-imposed torque moment is used to tighten each vessel. All the vessels are introduced in the oven plate and over it is fixed the rotor top plate. After having setting also the reference, it is set the program of cooking and the procedure starts.

(SK-10 and SK-12 User Manual (Rev. 06-2009), Milestone Cookbook for acid digestion: update 1 January 1996).

4.1.6 Thermo-gravimetric analysis: TDGA

This analysis provides a technique in which the weight of a compound is measured during heating process under controlled boundary condition. The parameters involved in this test are: loss of weight of the sample, rising value of the temperature, time of process.

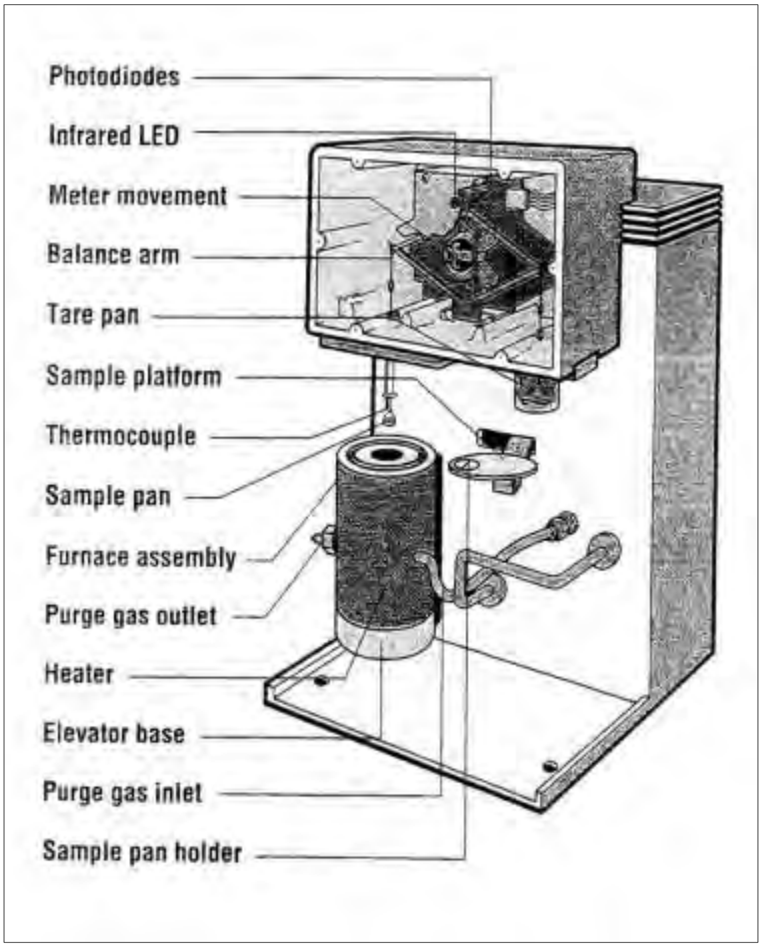


Image 39: TDGA instrument (www.polymertechnology.it)

4.2 Fluorescent lamps

They called fluorescent tube, due its celebrity to its high luminous efficiency that can reach the 15% against the 4% of the incandescent light bulb (Ronda et al., 1988, Nazarov and Noh, 2010, Rapaport and Miliez, 2006 and Ye et al., 2011).

In recent years LEDs have shown their capability if provide high energy saving lighting with a luminous efficacy of 50-80 lm/W, moreover they provide high quality of light with a color rendering index of 80-90 and a continuous spectrum. They have a long service life (up to 50,000 hours), they show good switching stability, fast start-up time period and good response to vibrations and shocks (Buchert M. et al. 2012)

It consists in a tube made of glass and filled with a noble gas, at low pressure, and Mercury in vacuum conditions. In the internal surface is applied a fluorescent material with a matrix composed primary of Calcium. In the extremis of the tube two electrodes are integrate to complete the structure. When the electrons contained in the tube start to move, the electrodes excited the Mercury atoms, by the absorbance of radiation that emitted UV radiation. The fluorescent material in the internal surface hit by the radiations emitted, in turn, visible light. The visible light has a lower wave length respect the UV radiation, for this reason part of the energy is lost as heat. The fluorescent material of the internal surface is made of a mixture of three phosphors with different short emission band and REEs. Five rare-earth phosphors are often present in fluorescent lamps: the red phosphor Y2O3:Eu3+ (YOX), the green phosphors LaPO4:Ce3+,Tb3+ (LAP), (Gd, Mg)B5O12:Ce3+,Tb3+ (CBT), (Ce, Tb)MgAl11O19 (CAT) and the blue phosphor BaMgAl10O17:Eu2+ (BAM) (Justel et al., 1998; Yu and Chen, 1995; Ronda, 1995).

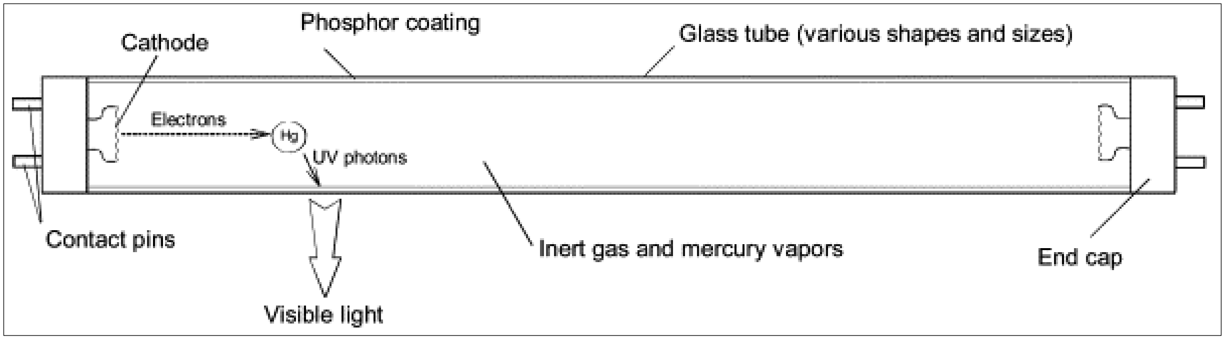


Image 40: Representation of a fluorescent lamp (Tunsu et al., 2012)

The percentage of rare earths in the fluorescent powders varies according to the type and year of manufacture, in general the concentration of RE oxides in the lamp phosphors can fluctuate from 27.9% and 10% of RE oxides (Binnemans et al., 2013, Innocenzi et al, 2014).

Table 6: Main phosphor in fluorescent lamps

Emission band (nm)	Color	Phosphor
613	Red	Eu:Y_2O_3
545	Green	Tb:(La, Ce)PO_4
450	Blue	Eu:$BaMgAl_{10}O_{17}$

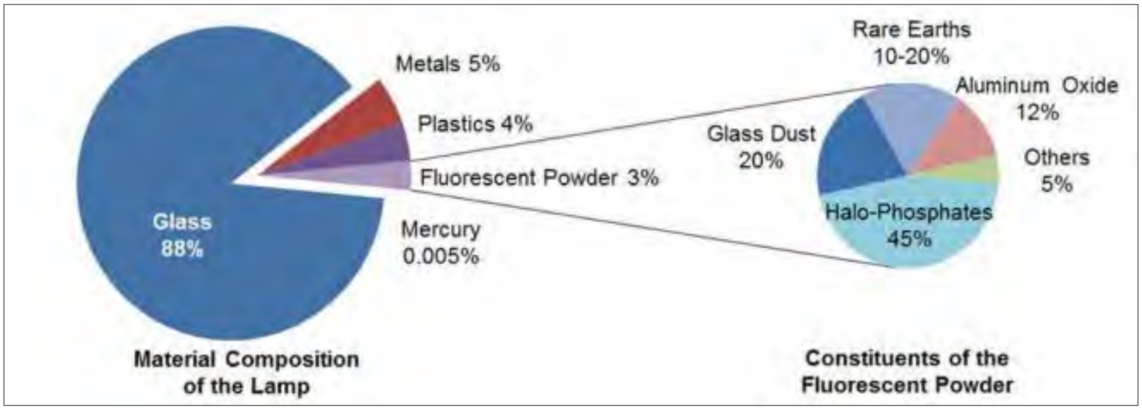


Image41: Composition of compact fluorescent lamps (Rhodia via von Grafenstein, 2013, (Zecha, g., 2014)

The composition of the power of lamps can be generally divided into two parts: a coarser one composed by Si (Silica), K (Potassium) and Na (Sodium) and a finer part, at which the REEs belong to, that does not exceed 7µm.

About recycle of the lamps three ways are the most proposed:

1. Direct re-use of lamp phosphor mixture in new lamps
2. Separation of lamp phosphor mixture into different phosphor compounds
3. Recovery of REEs content.

(Binnemansaand Jonesb, 2014).

Some studies about future performance and utilization of the lamps have been done: in China has been forecast a lighting demand increasing in 2020 will increase more than 70% over 2008. The annual growth rate of lighting demand will be about 4.6%, with a consequence of increasing waste production (Institute of Building Physics, China Academy of Building

Research). In 2011 about 4800 millions of fluorescent lamps were scraped (Wang and Zheng, 2010; Zhang 2012) and only in the domestic market the value of the REEs contained in the fluorescent waste was more than 1600 million dollars (China Rare earth market prices, 2011).

Moreover several researches works show possible hazardous consequences due to the REEs handle, as production or recycle. Mercury vapors and dust containing lead and yttrium but also leaching residues and acids are the main toxic effects and compounds that affect employers at different step processes. The mercury content is one issue why the fluorescent lamps are classified as hazardous elements in the European Waste Catalogue (EWC) (Belardi et al,. 2014). The analysis of different type of fluorescent lamps shows different concentration of mercury from 1.5 to 27 mg/lamp, knowing the EU threshold 5 mg/lamp (Dos Santos et al., 2000).

The lamps are processed to recycle glass, metal (filaments, supply electrodes, caps), plastics (caps, insulators), phosphor powder and mercury. Clean glass is used for the production of new lamps, or new glass products. Metal parts are sent to recycling facilities and plastic parts are burnt to gain energy (Binnemansa et al,. 2013).

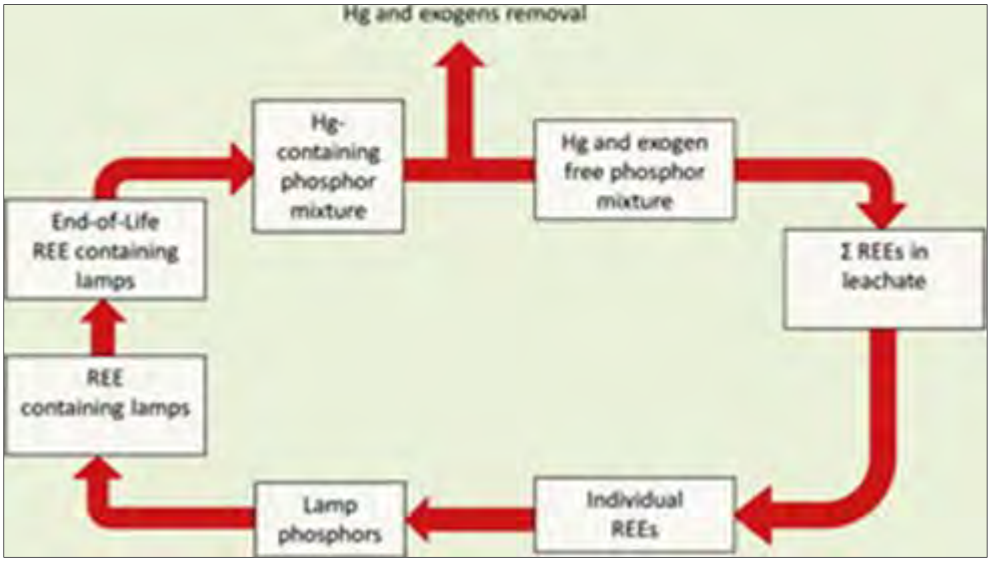
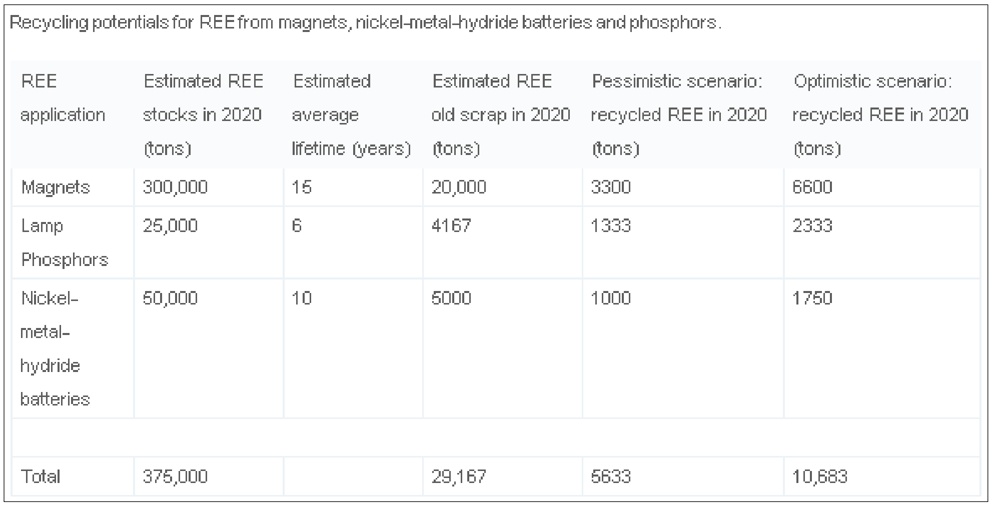


Image42: Simplified recycling flow sheet for REE lamp phosphors (Binnemansa, Jonesb, Blanpainb , Van Gervenc, Yangd, Waltone and Buchertf , 2013).



Recycling potentials for REE from magnets, nickel-metal-hydride batteries and phosphors.

REE application	Estimated REE stocks in 2020 (tons)	Estimated average lifetime (years)	Estimated REE old scrap in 2020 (tons)	Pessimistic scenario: recycled REE in 2020 (tons)	Optimistic scenario: recycled REE in 2020 (tons)
Magnets	300,000	15	20,000	3300	6600
Lamp Phosphors	25,000	6	4167	1333	2333
Nickel-metal-hydride batteries	50,000	10	5000	1000	1750
Total	375,000		29,167	5633	10,683

Image43: Comparison recycling potential of REEs in different WEEE (Binnemansa, Jonesb, Blanpainb , Van Gervenc, Yangd, Waltone and Buchertf , 2013).

5. EXPERIMENTS AND RESULTS

5.1 Starting material: characterization of powders from exhausted fluorescent lamps

A company interested in the recovery of REEs has furnished six types of lamps' powder: come 1M, 2M, 3M, 1D, 2D, e 3D. The powders represent the result of pre-treatment on different kind of exhausted fluorescent lamps. The samples are the result of previous waste treatment, concerning first the remove of plastic and metallic parts, then the pretreatment on mercury content. To identify the material faced it is decided to start with a characterization of the material furnished by the company.

5.1.1 ESEM analysis

The morphology of the samples is detected with an ESEM back-scattering. In this way there is a direct connection between the atomic number of the element and the color of the particles: heavier elements are darker. The analysis gives information about the composition and distribution of the elements in the sample and also the shape of the particles. The images given by the microscope are obtained with a zoom of 400x. The dimension of the furnished powder are around 5 and 50 μm, the bigger particles are made of Silicon (SiO_2), the smaller ones are instead heavier material with different compositions and shapes. It is possible to notice both aggregated around 1.5μm and broken crystals 3-10μm.

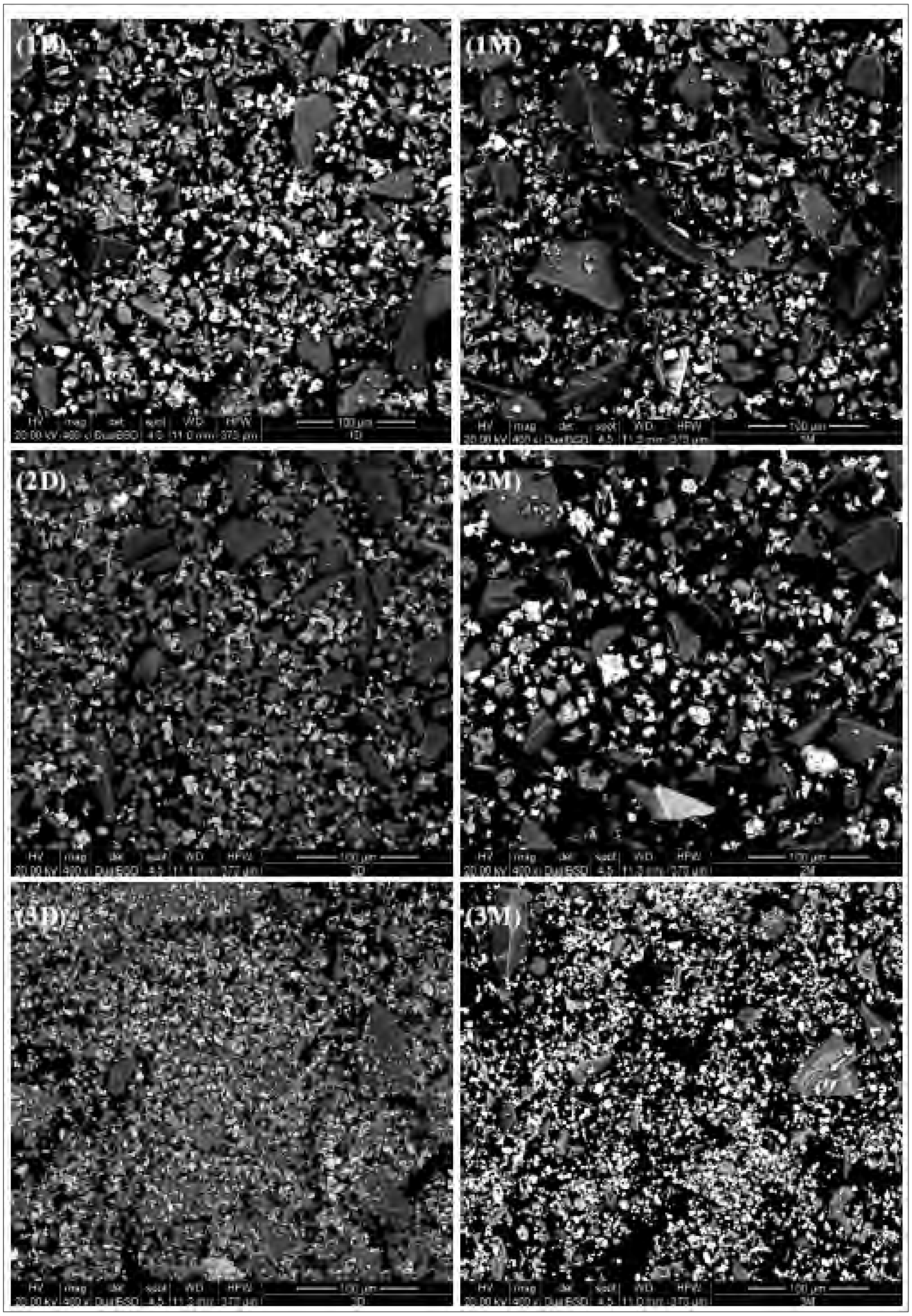
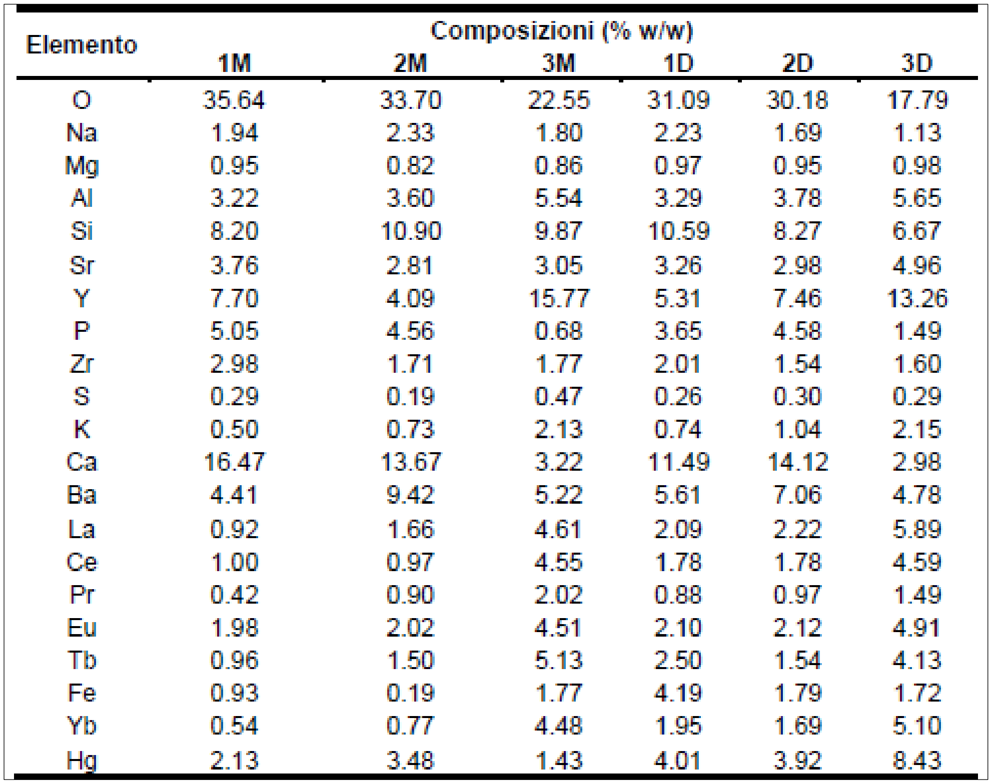


Image44: ESEM images 400x of the six powders

The table shows that in the samples 3 the concentration of REEs in particular yttrium and europium, the ones in which the company is more interested, are higher. The Silicon concentration is lower of about 40%, the y enhances of about 100%, moreover the Ca decreases of 80%. In next chapter it is shown that the silicon and the calcium make difficult the completely recovery of REEs. Between sample 3D and 3M the first shows higher percentage of mercury that is hazardous and considerable as an impurity for this process.



Elemento	Composizioni (% w/w)					
	1M	2M	3M	1D	2D	3D
O	35.64	33.70	22.55	31.09	30.18	17.79
Na	1.94	2.33	1.80	2.23	1.69	1.13
Mg	0.95	0.82	0.86	0.97	0.95	0.98
Al	3.22	3.60	5.54	3.29	3.78	5.65
Si	8.20	10.90	9.87	10.59	8.27	6.67
Sr	3.76	2.81	3.05	3.26	2.98	4.96
Y	7.70	4.09	15.77	5.31	7.46	13.26
P	5.05	4.56	0.68	3.65	4.58	1.49
Zr	2.98	1.71	1.77	2.01	1.54	1.60
S	0.29	0.19	0.47	0.26	0.30	0.29
K	0.50	0.73	2.13	0.74	1.04	2.15
Ca	16.47	13.67	3.22	11.49	14.12	2.98
Ba	4.41	9.42	5.22	5.61	7.06	4.78
La	0.92	1.66	4.61	2.09	2.22	5.89
Ce	1.00	0.97	4.55	1.78	1.78	4.59
Pr	0.42	0.90	2.02	0.88	0.97	1.49
Eu	1.98	2.02	4.51	2.10	2.12	4.91
Tb	0.96	1.50	5.13	2.50	1.54	4.13
Fe	0.93	0.19	1.77	4.19	1.79	1.72
Yb	0.54	0.77	4.48	1.95	1.69	5.10
Hg	2.13	3.48	1.43	4.01	3.92	8.43

Image45: Composition of the six powder % w/w

5.1.2 XRD analysis

Analysis on diffraction x are made on two of the six powder sample: 1M and 3M because their very different composition. The results are manipulated with the software “Match!” (Crystal Impact)

Each spectrum is compared with a standard spectrum find in literature.

The spectrum of 1M sample appears very complex with a higher number of peaks both at high and lower frequency. The peaks corresponding to Y_2O_3:Eu and $Ca_8Tb_2(PO_4)_6O_2$ are clearly visible.

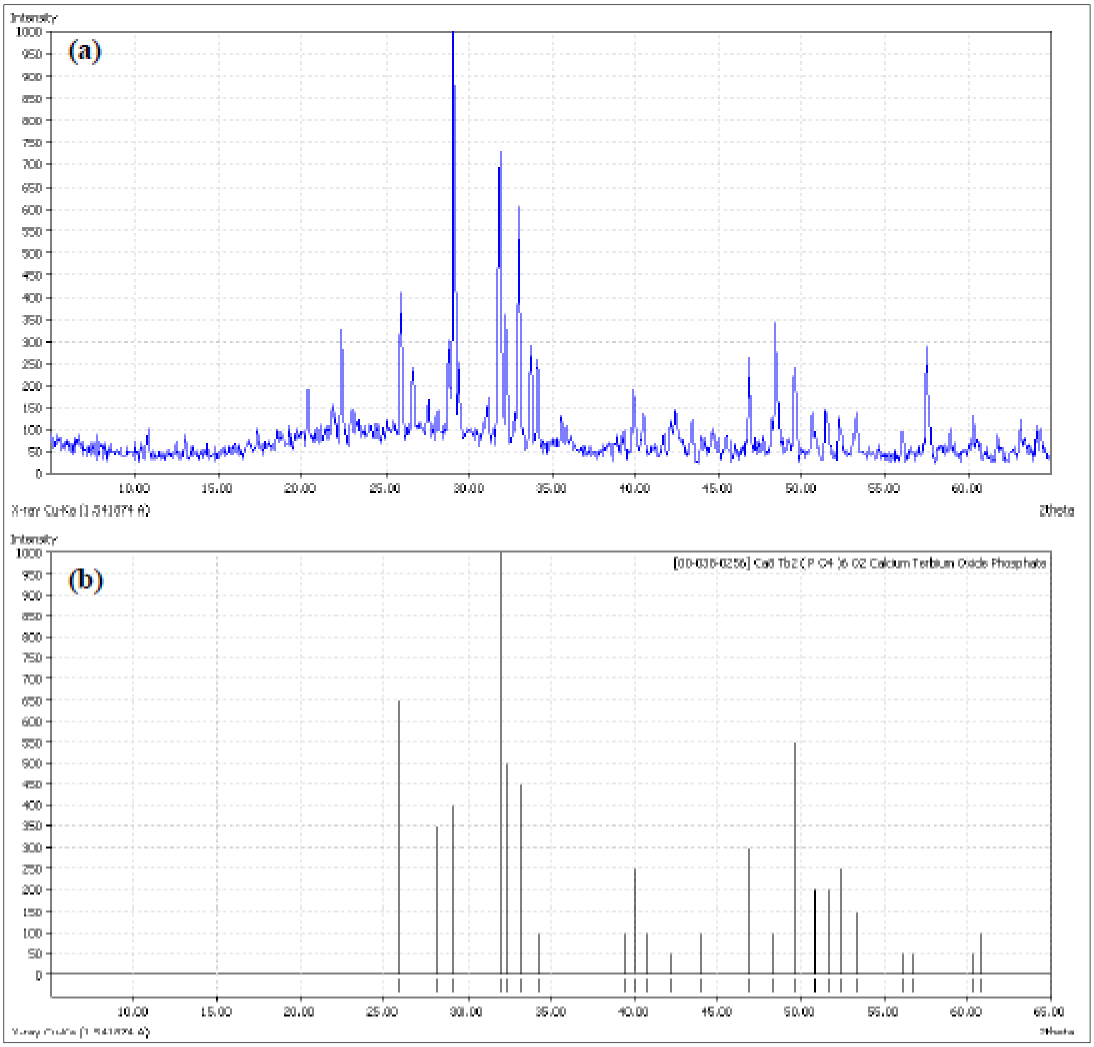


Image46: XRD spectrum 3M (a) in comparison with Y2O3:Eu (b)

The spectrum of the sample 3M is related to the one of the Y2O3:Eu: they appear similar, the lower peaks present in the 3M spectrum are not clearly identifiable.

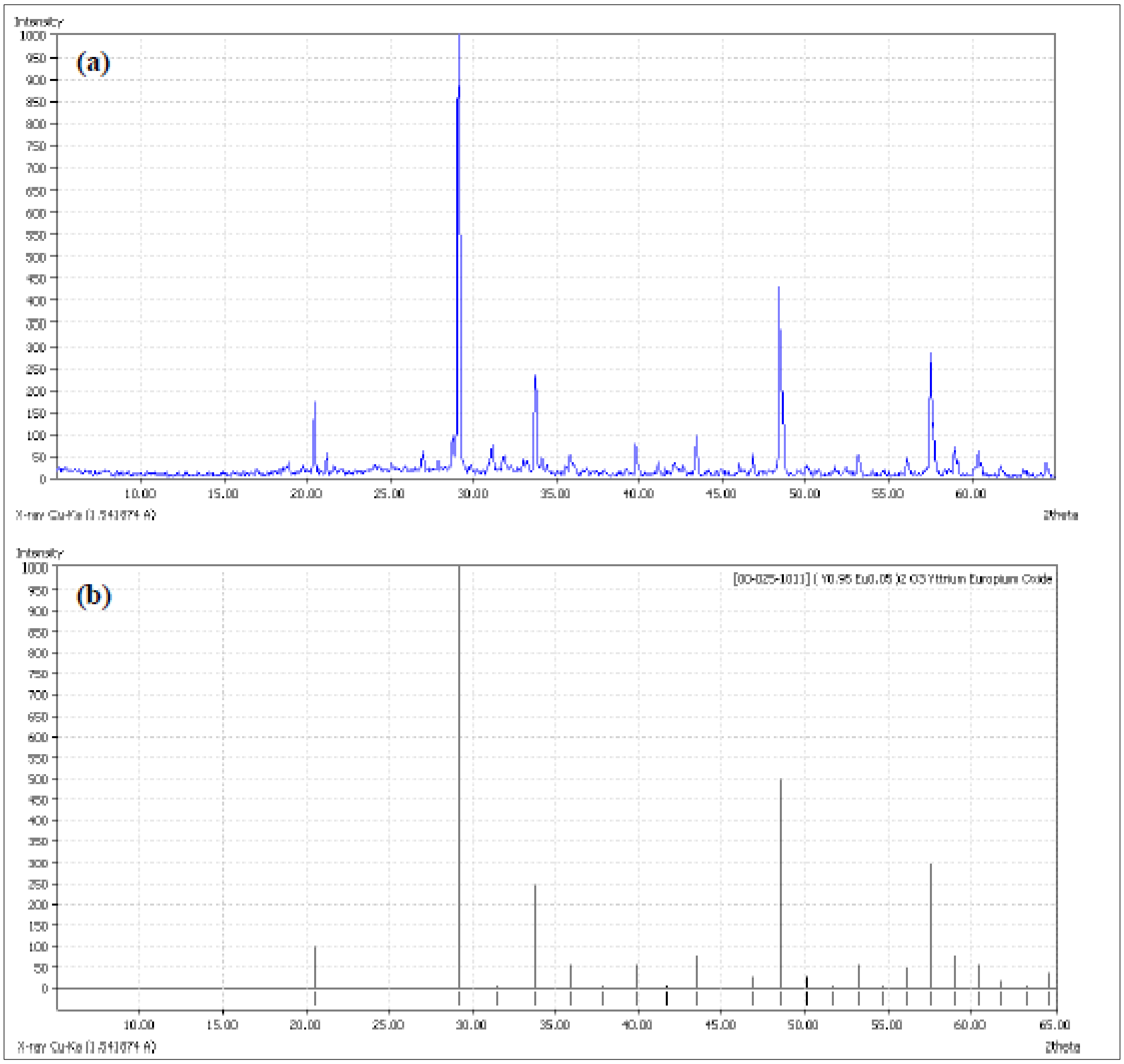


Image47: XRD spectrum of 1M (a) related to the ones of Ca8Tb2(PO4)6O2 (b)

5.1.3 FT-IR analysis

The analysis as said before is supported on a KBr pellet. The spectra of the different powder are presented below. 3D sample shows a slightly difference with a high absorbance in the area below 1000 cm-1, the other spectra appear similar.

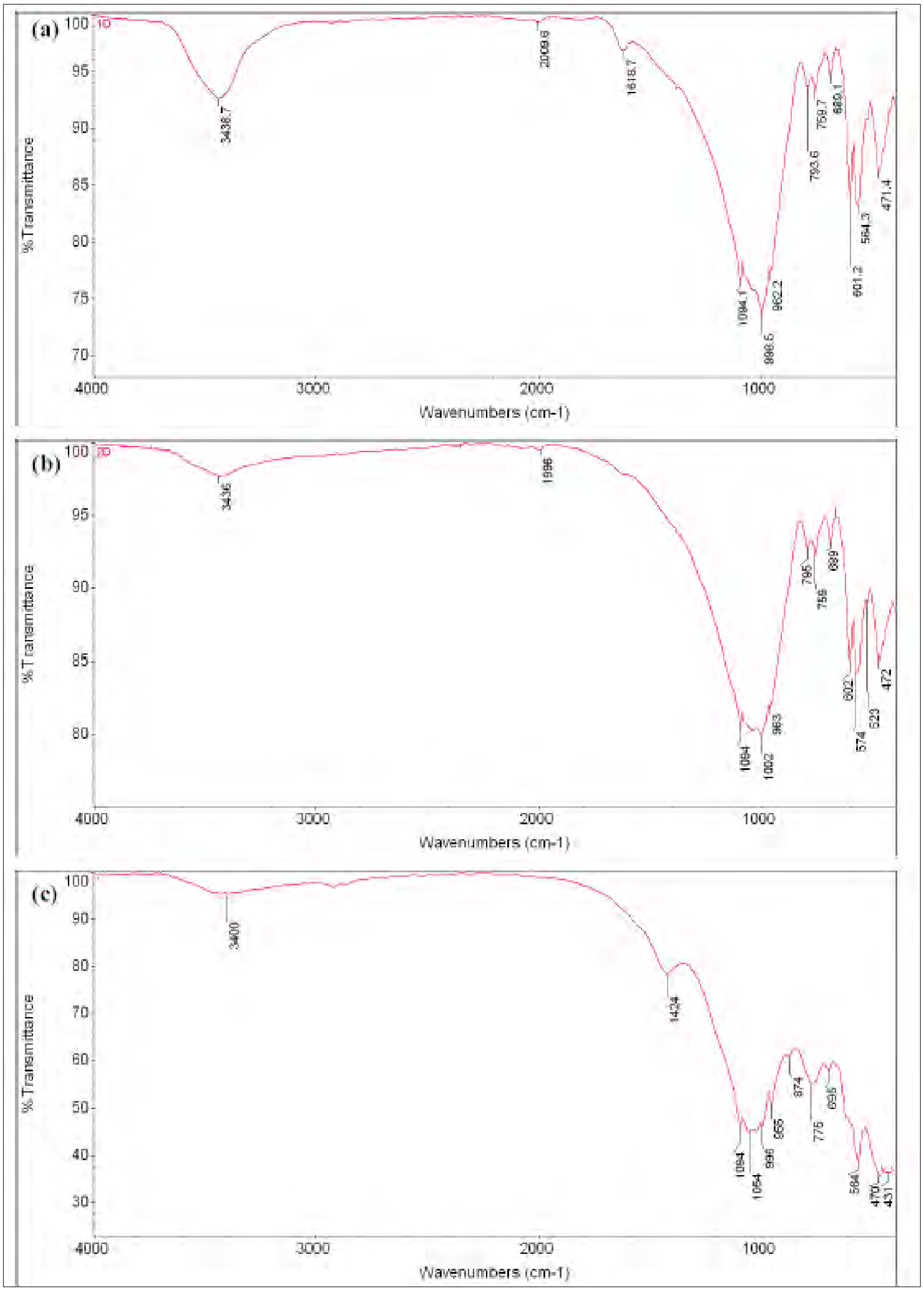


Image48: FT-IR spectra of 1D 2D 3D samples

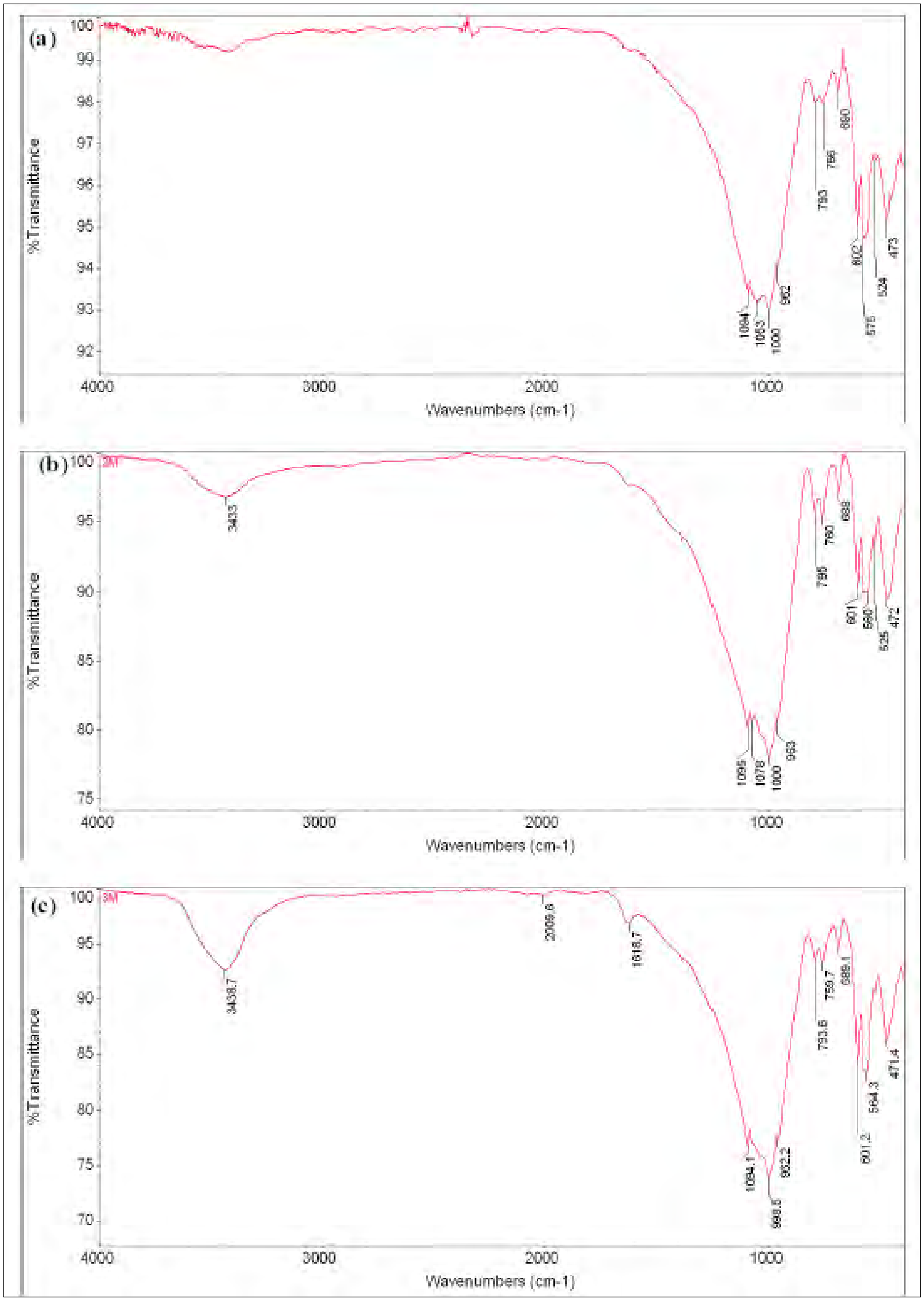
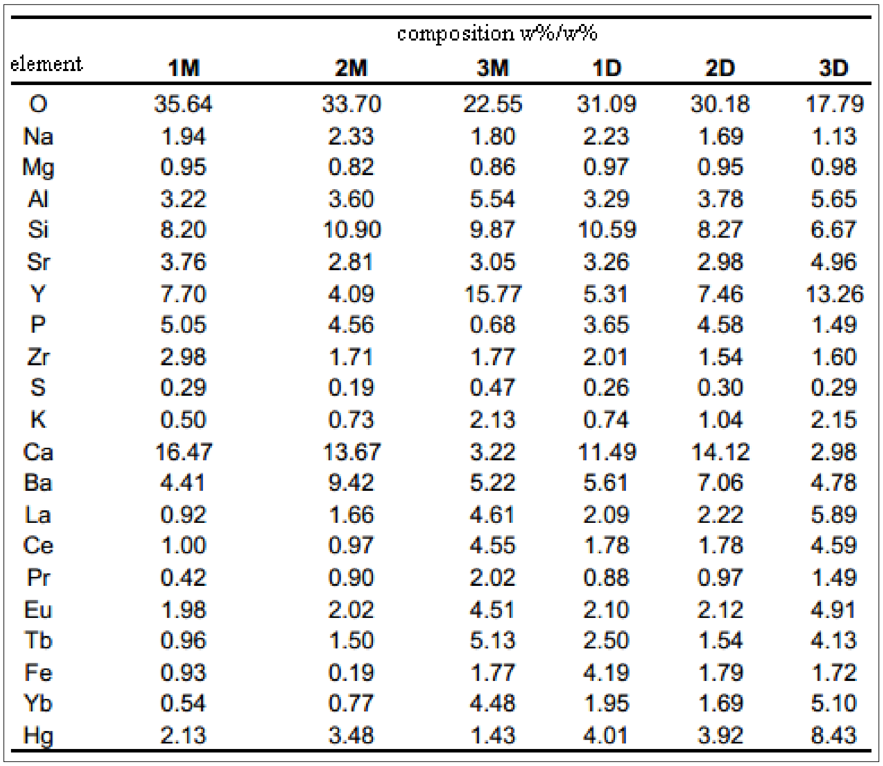


Image49: FT-IR spectra of 1M 2M 3M samples

5.2 Treatment on 3M sample

The sample 3M is selected between the six lamp powders with different origins (morphology and chemical composition) called 1D, 2D, 3D , 1M, 2M and 3M, the samples is chosen from the other ones furnished for two main reasons:

1. The samples 3 show a higher concentration of REEs respect the samples 1 and 2.
2. The sample 3M shows a half concentration of mercury (Hg) respect the 3D sample.

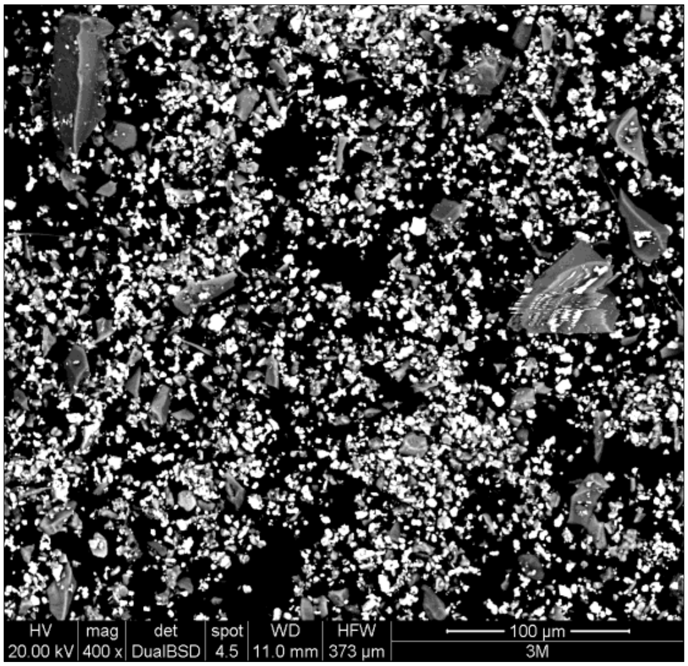


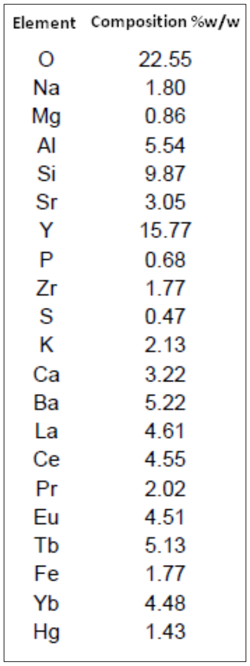
	composition w%/w%					
element	**1M**	**2M**	**3M**	**1D**	**2D**	**3D**
O	35.64	33.70	22.55	31.09	30.18	17.79
Na	1.94	2.33	1.80	2.23	1.69	1.13
Mg	0.95	0.82	0.86	0.97	0.95	0.98
Al	3.22	3.60	5.54	3.29	3.78	5.65
Si	8.20	10.90	9.87	10.59	8.27	6.67
Sr	3.76	2.81	3.05	3.26	2.98	4.96
Y	7.70	4.09	15.77	5.31	7.46	13.26
P	5.05	4.56	0.68	3.65	4.58	1.49
Zr	2.98	1.71	1.77	2.01	1.54	1.60
S	0.29	0.19	0.47	0.26	0.30	0.29
K	0.50	0.73	2.13	0.74	1.04	2.15
Ca	16.47	13.67	3.22	11.49	14.12	2.98
Ba	4.41	9.42	5.22	5.61	7.06	4.78
La	0.92	1.66	4.61	2.09	2.22	5.89
Ce	1.00	0.97	4.55	1.78	1.78	4.59
Pr	0.42	0.90	2.02	0.88	0.97	1.49
Eu	1.98	2.02	4.51	2.10	2.12	4.91
Tb	0.96	1.50	5.13	2.50	1.54	4.13
Fe	0.93	0.19	1.77	4.19	1.79	1.72
Yb	0.54	0.77	4.48	1.95	1.69	5.10
Hg	2.13	3.48	1.43	4.01	3.92	8.43

Image 50: weight percentage elements for each sample power.

Different types of analysis are made to investigate the initial sample given by the company: ESEM, XRD and FTIR.

ESEM images:

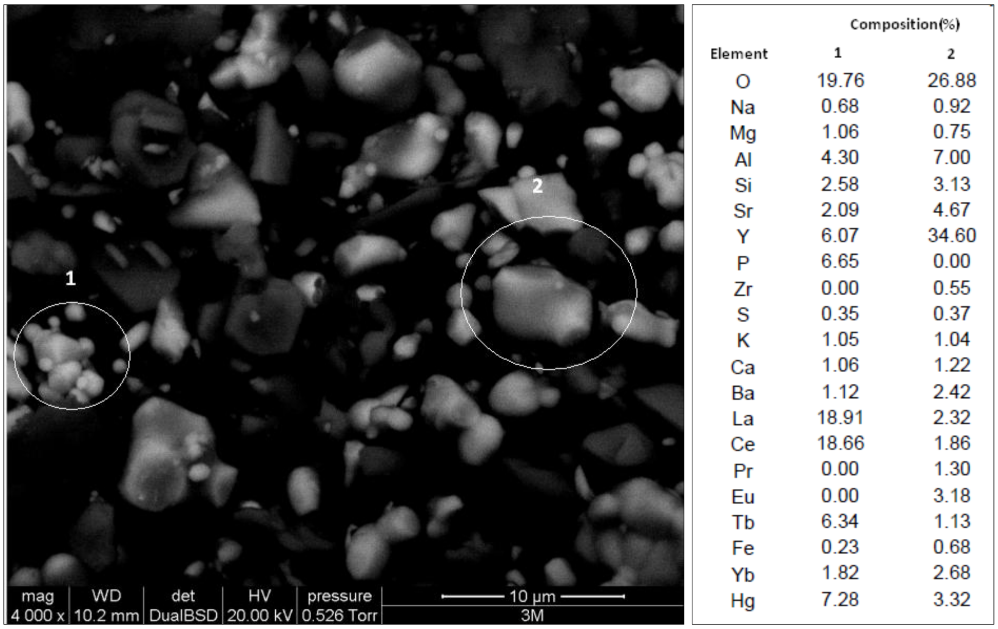




Element	Composition %w/w
O	22.55
Na	1.80
Mg	0.86
Al	5.54
Si	9.87
Sr	3.05
Y	15.77
P	0.68
Zr	1.77
S	0.47
K	2.13
Ca	3.22
Ba	5.22
La	4.61
Ce	4.55
Pr	2.02
Eu	4.51
Tb	5.13
Fe	1.77
Yb	4.48
Hg	1.43

Image51: 3M sample 400x image from ESEM and composition

The image shows different shapes and 2 main groups are identify: the first (1) presents a same quantity of Ce e La about 20%, moreover Y, Tb e P 6% and Al 4% are presented; the bigger particles (2) are mainly formed by Y 35%, Al 7% e Eu 3%.



Element	Composition(%) 1	2
O	19.76	26.88
Na	0.68	0.92
Mg	1.06	0.75
Al	4.30	7.00
Si	2.58	3.13
Sr	2.09	4.67
Y	6.07	34.60
P	6.65	0.00
Zr	0.00	0.55
S	0.35	0.37
K	1.05	1.04
Ca	1.06	1.22
Ba	1.12	2.42
La	18.91	2.32
Ce	18.66	1.86
Pr	0.00	1.30
Eu	0.00	3.18
Tb	6.34	1.13
Fe	0.23	0.68
Yb	1.82	2.68
Hg	7.28	3.32

Image52: ESEM zoom 4000x sample 3M and composition of (1) and (2)

XRD: x-Rays analysis is made on the initial sample and the spectrum is adjusted with software 'Match!' (Crystal Impact) the purpose is to focus the attention on the main chemicals present.

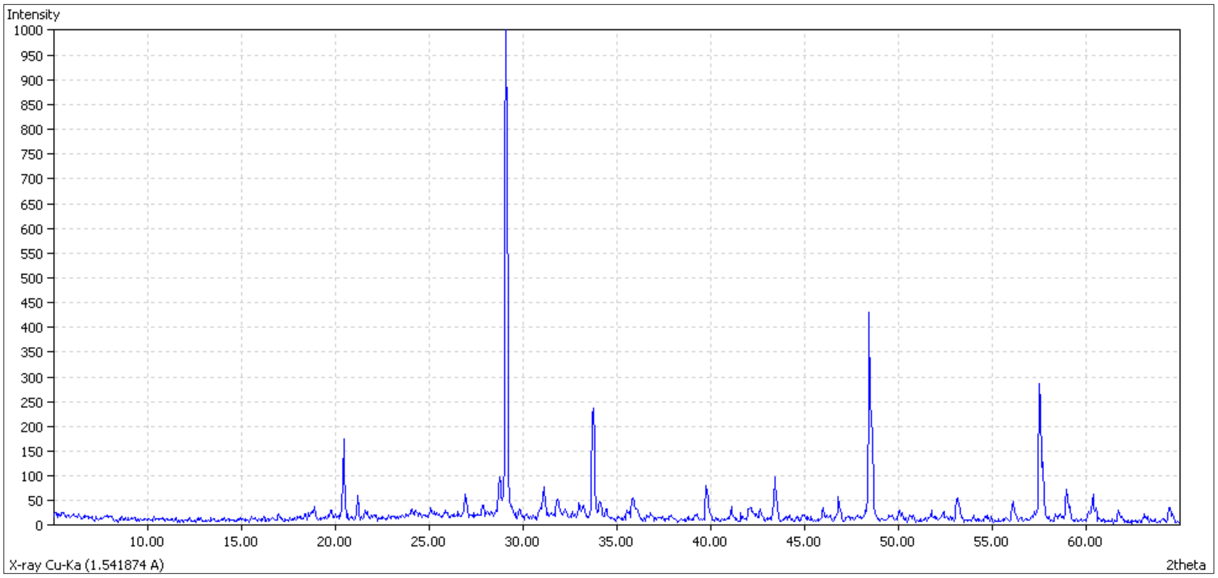


Image53: XRD spectrum of sample 3M

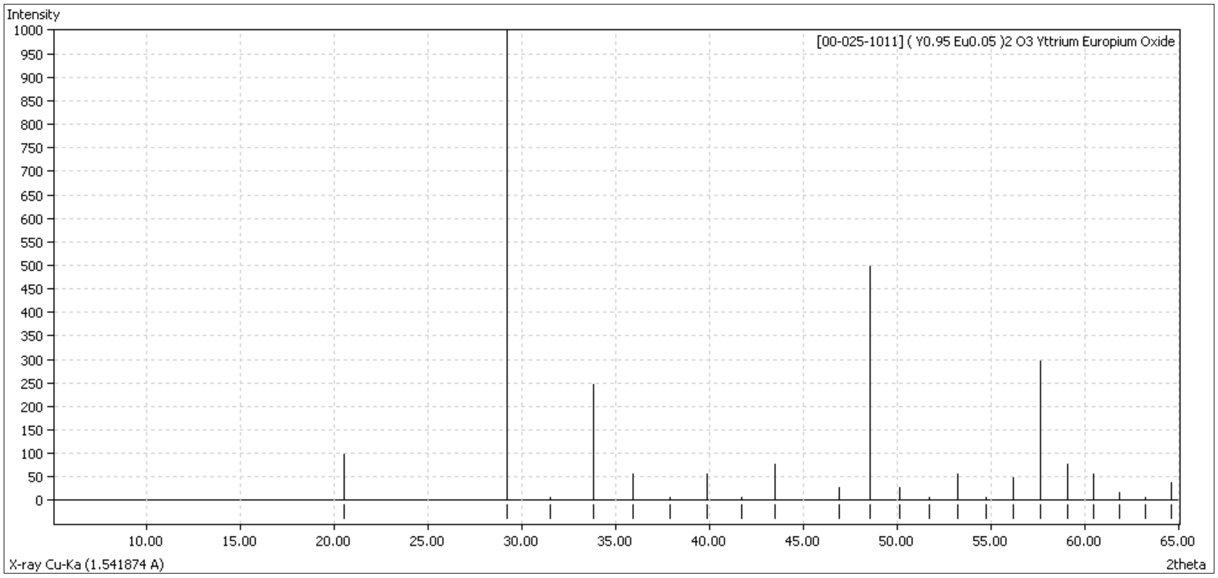


Image54: Reference spectrum of Y2O3: Eu

The images show the characteristic peaks of 3M sample and of Y2O3: Eu. Lower peak are not analyzed because are not identifiable.

FT-IR: this analysis is made on little pastille made of KBr (Potassium Bromide) created with a particular device described later. An infrared spectrum obtained is put in comparison with a reference:

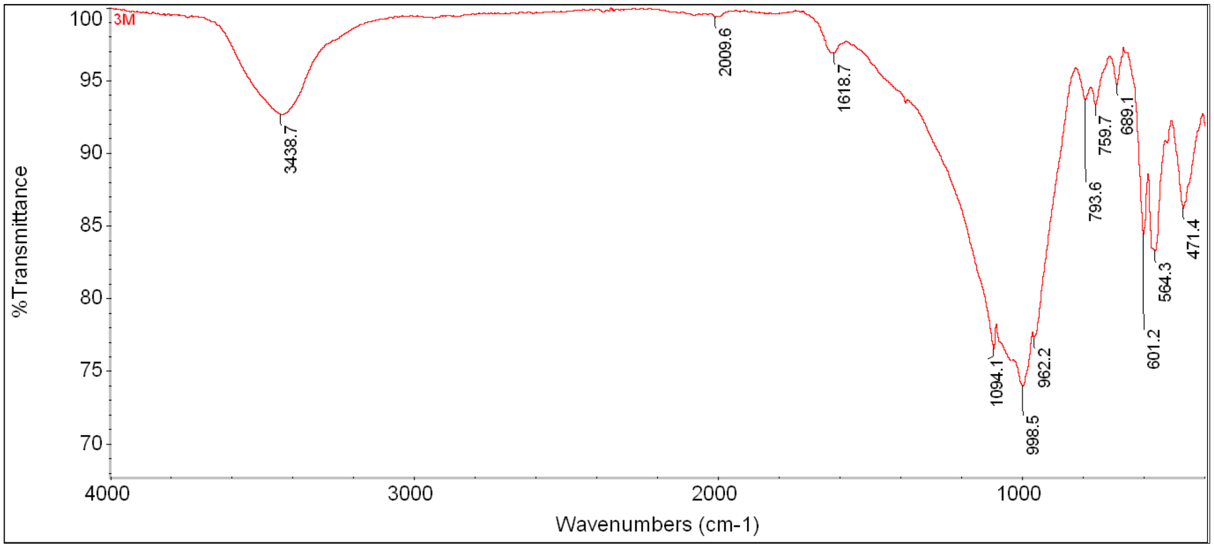


Image55: FT-IR spectrum for 3M sample

5.3 Sieving procedure

Sieving treatment of the sample 3M is performed to decrease the silica content.

The powder, hereafter called 3M, is sieved with a mesh of 20 µm (*Filtra, N°50316/1*) with the target of primary rough separation of the silicon from the finer REEs fraction. The process of sieving is made with de-ionized water, to avoid influences of charges between elements and impurities; in particular the potential energy (gravity) helps the smaller particles of the sample to pass through the micro-mesh.

Image56: Filtra, N°50316/1.

Image57: particular of the sieve Filtra N° 50316/1.

After this first physical treatment two fractions are obtained: the first part that passes through the sieve is supposed to contain the higher percentage of REEs, it is diluted in a high quantity of water (3-4 liters); the second ones, having higher particles' diameter, is kept from the sieve, at a first sight it is similar to grey coarse mud.

The no-passed fraction is put inside an oven to about 60°C degrees, and dried, sand-similar product results. It is hypnotized that this part contains a high percentage of silicon.

Image58:Detail of the part held by the sieve.

Image59:Detail of the part settled in the bucket.

The part passed throw the sieve is divided in mud-settled fraction and turbid-solution with clearly some dissolved elements thanks to a pipette.

The diluted part is spin-dried (AWEL centrifugation MF 20) in falcons of 35 ml (48g) with a speed of 10000 rotations/min for 5 minutes. In this way the sample presents two more fractions: a yellow dirty liquid and a finer settled in the bottom of the container.

The settled part of the bucket is collected and put inside the oven at 60°C degrees; the result is a fine gray powder.

Image60:Detail of the fraction passes through the sieve (1 liquid phase after the centrifugation, 2 settled phases after the centrifugation, 3 starting material).

Image61: Detail of the equipment for centrifugation.

5.3.1 Rotary evaporation of the liquid phase

The liquid yellow phase is now handled to extract the dissolved part. The operation is vaporization in void condition of the sample heated in a warm-bath. The void condition is maintained with a pressure of about 72cm of Hg column , the temperature is about 40-50°C, to avoid the backwash of the liquid by the pump, the quantity of sample is about 300ml. The total of liquid is 7 liters.

The result is water in one side of the instrument and dry deposit of material in the flask, this second fraction in put inside the oven at 60°C.

The final results are the samples that will be analyzed with the ESEM:

1. Fraction held by the sieve, coarser L2 (expected rich of Si)
2. Fraction passed through L1 (very fine and expected rich of REEs)
3. Deposit from the liquid phase L3

Image62: Result of the phase1, from left to right: fraction passed and settled, fraction held, liquid fraction.

5.3.2 ESEM Analysis

For simplicity the results of the ESEM analysis are divided in steps:

a. *Sample passes through the sieves L1:* comparison with no sieved sample 3M, comparison between the particles contained in the sample itself.

b. *Sample L1, L2, L3:* comparison between the three results

a. The hereafter fraction called L1 is the part of 3M sample that is passed through the sieve; it is put in the centrifugation and finally dried in the oven at 100°C until all the water is evaporated.

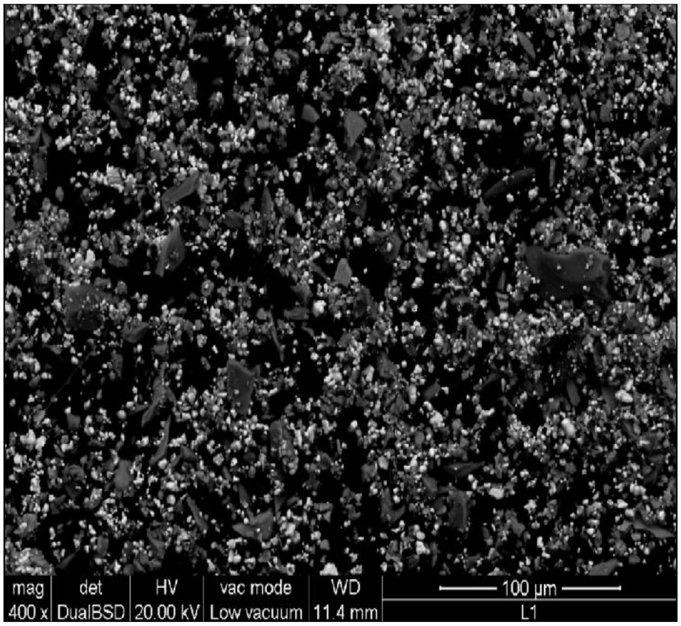


Image63: L1 ESEM zoom 400x.

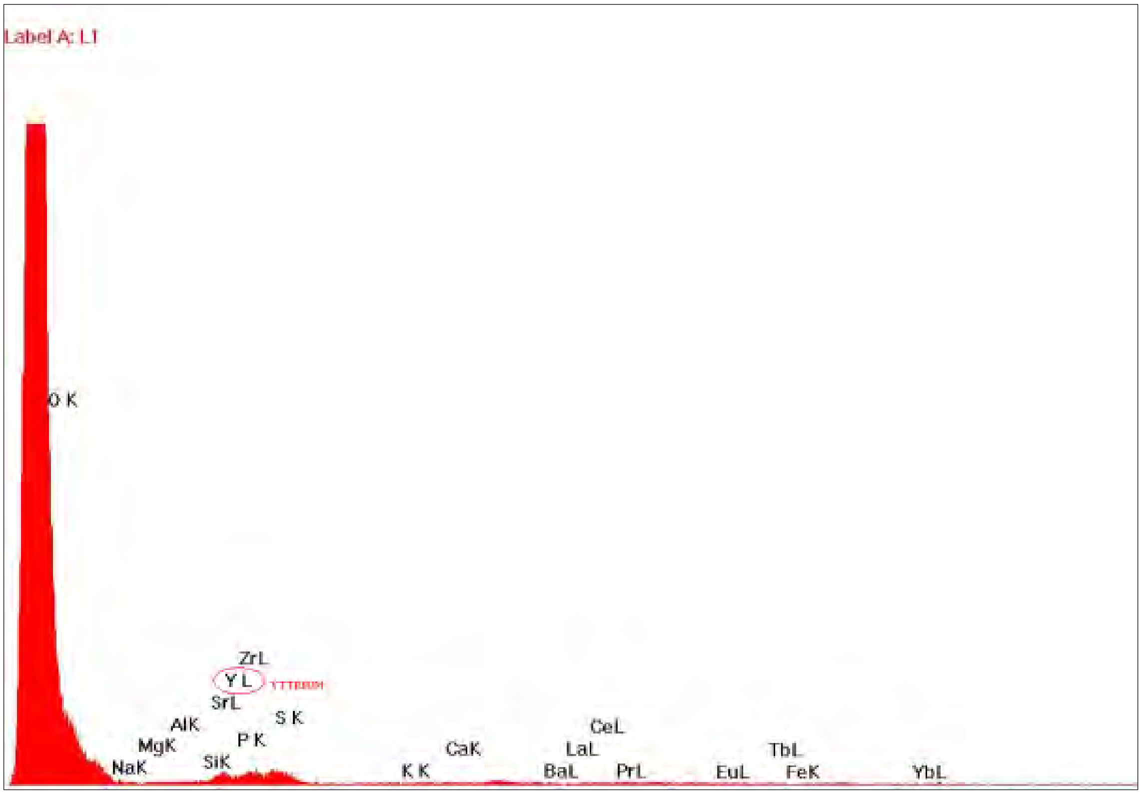
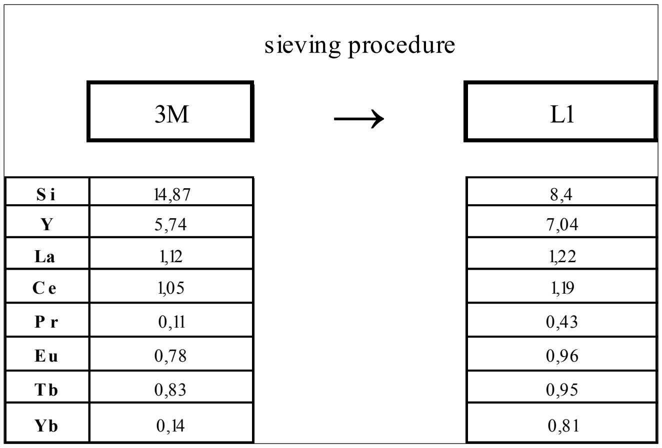


Image64: L1 ESEM fluorescence analysis

A.1 Comparison 3M vs L1

Comparison between atomic percentage of the sample not sieved 3M and the finer fraction of the sample sieved L1 with a mesh of 20 µm (Filtra, N°50316/1).



	3M	L1
Si	14,87	8,4
Y	5,74	7,04
La	1,12	1,22
Ce	1,05	1,19
Pr	0,11	0,43
Eu	0,78	0,96
Tb	0,83	0,95
Yb	0,14	0,81

Image 65: Sieving procedure scheme

Table 7: 3M-L1 ESEM atomic percentage

	Atomic percentage %	
elements	3M	L1
O	52,16	54,45
Na	2,42	2,42
Mg	0,86	2,05
Al	7,61	9,08
Si	14,87	8,4
Sr	1,89	1,85
Y	5,74	7,04
P	1,65	1,7
Zr	0,38	0,42
K	2,61	1,48
Ca	3,08	2,45
Ba	1,16	1,01
La	1,12	1,22
Ce	1,05	1,19
Pr	0,11	0,43
Eu	0,78	0,96
Tb	0,83	0,95
Fe	0,57	0,84
Yb	0,14	0,81
Hg	0,53	0,72

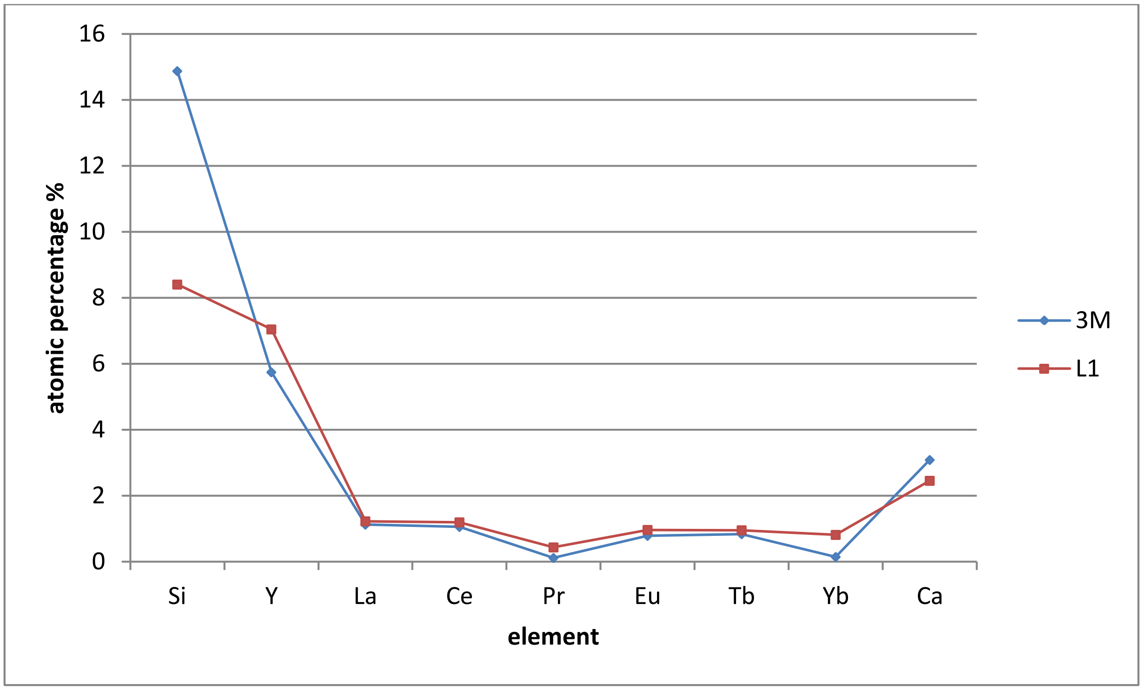


Image 66: 3M-L1 comparison

- The relative percentage of *silicon* decreases
- The relative percentage of *REEs* increases in particular for praseodymium and ytterbium

The result of this analysis shows how, in the finer part of the sample sieved L1, silicon's relative content decreases with pre-treatment with the sieving procedure, the REEs are more concentrated.

This analysis is useful to understand the fraction of silicon removed increasing the concentration of REEs and thus the efficiency of the following extraction procedures.

A advantage is also the decreasing of the calcium concentration necessary because this element, as also the metallic ions, disturbs in the procedure of complex formation for the settling of yttrium by competing in the formation of oxalate. In this regard is underlined the necessity of the use of de-ionized water during the sieving procedure for two main reasons:

1. The de-ionized water helps the finer particles to pass through the sieving mesh

2. The washing process of the powder with water helps to remove a fraction of the metal ions contained in the powder, in particular soluble salts of the alkaline metals that annoying the next reactions of complex formation.

A.2 Comparison of fraction of L1: crystal, cr, white and small white particles

Comparison between the particles contained in the finer fraction of the sample L1 sieved with a mesh of 20 µm (Filtra, N°50316/1): Cristal, particle, small particle and cr

The morphology of the sample L1 is detected by evaluating separately the different particles.

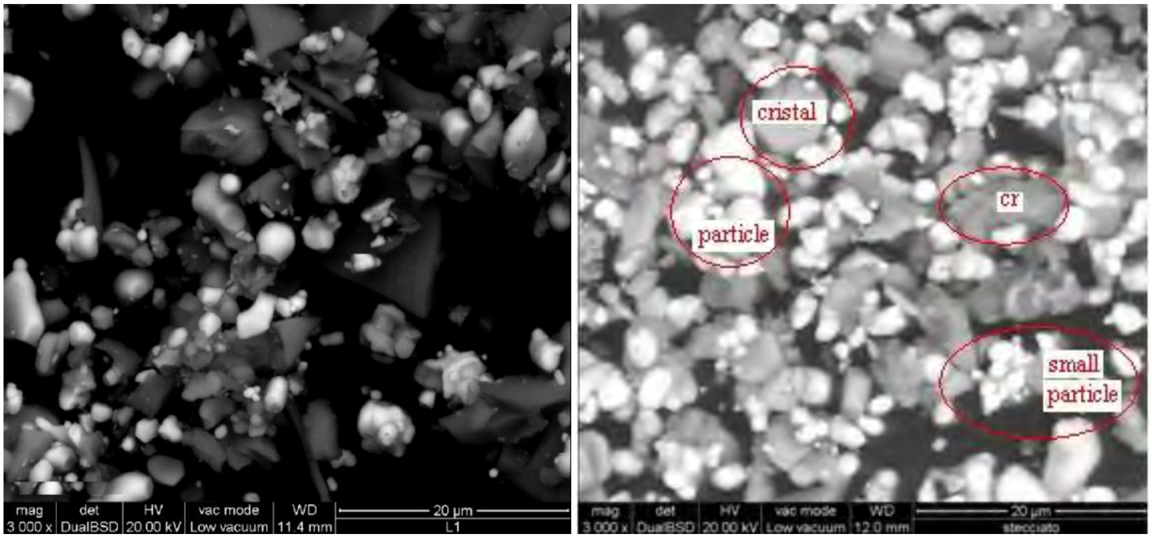


Image67: L1 ESEM zoom 3000x.

Is possible to investigate deeper the nature of the sample by zooming the attention on the singular elements: crystals (dimensions estimated: 6µm), small white particles(dimensions estimated: 2µm), white particles (dimensions estimated: 3µm) and cr (dimensions estimated: 10µm)

1. Cristal:

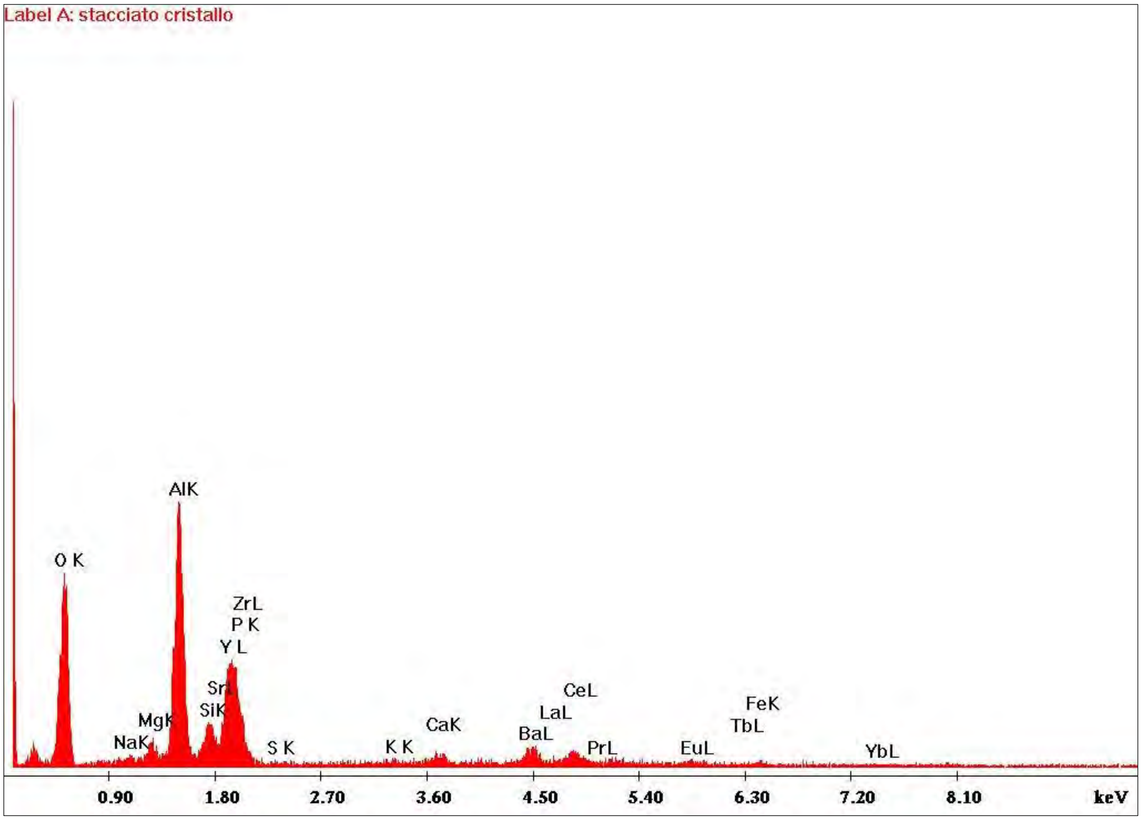


Image68: L1-crystal. ESEM fluorescence analysis.

2. White particle:

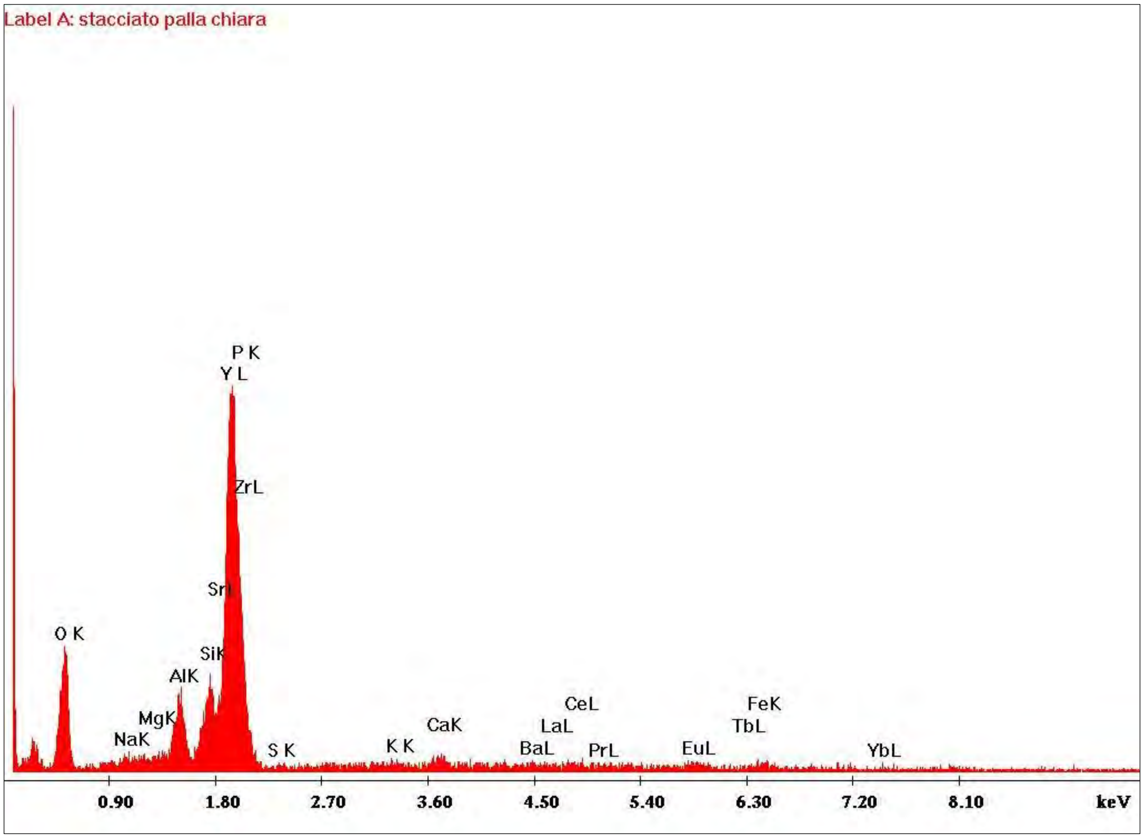


Image69: L1-white particle ESEM fluorescence analysis.

3. Smaller white particle:

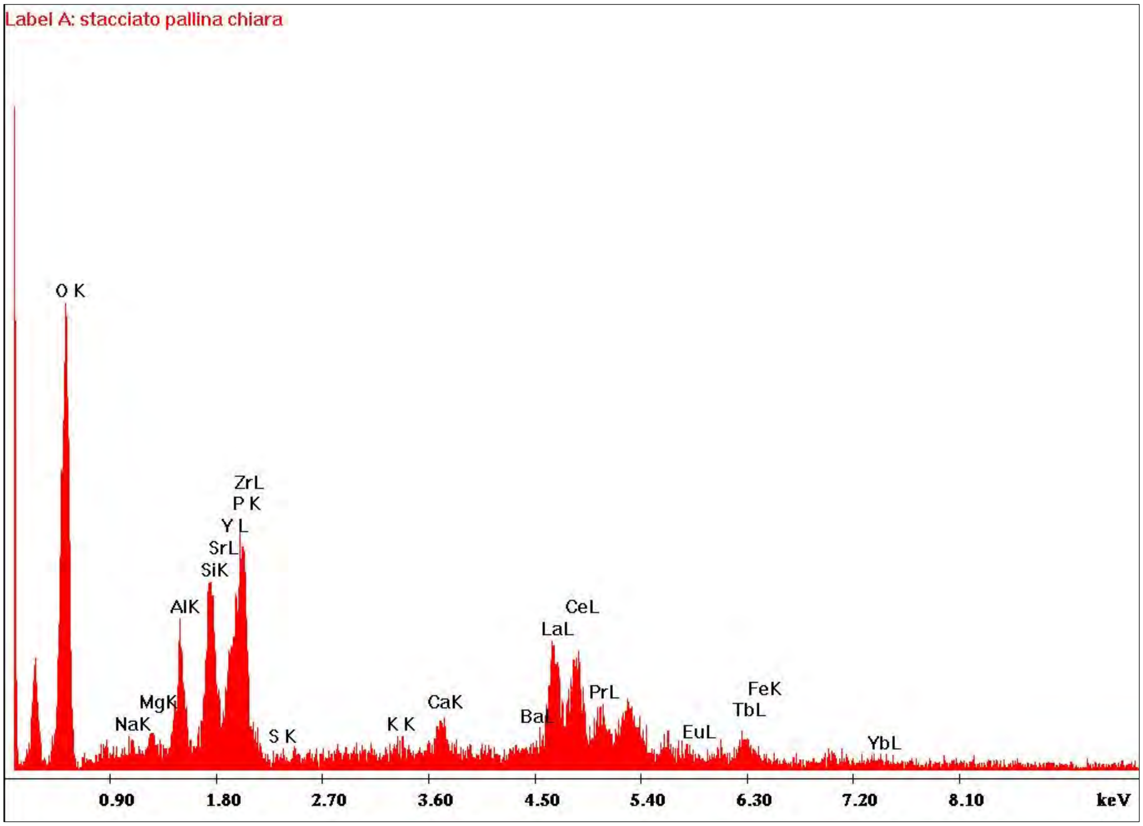


Image70: L1-small white particle ESEM fluorescence analysis.

4. Cr

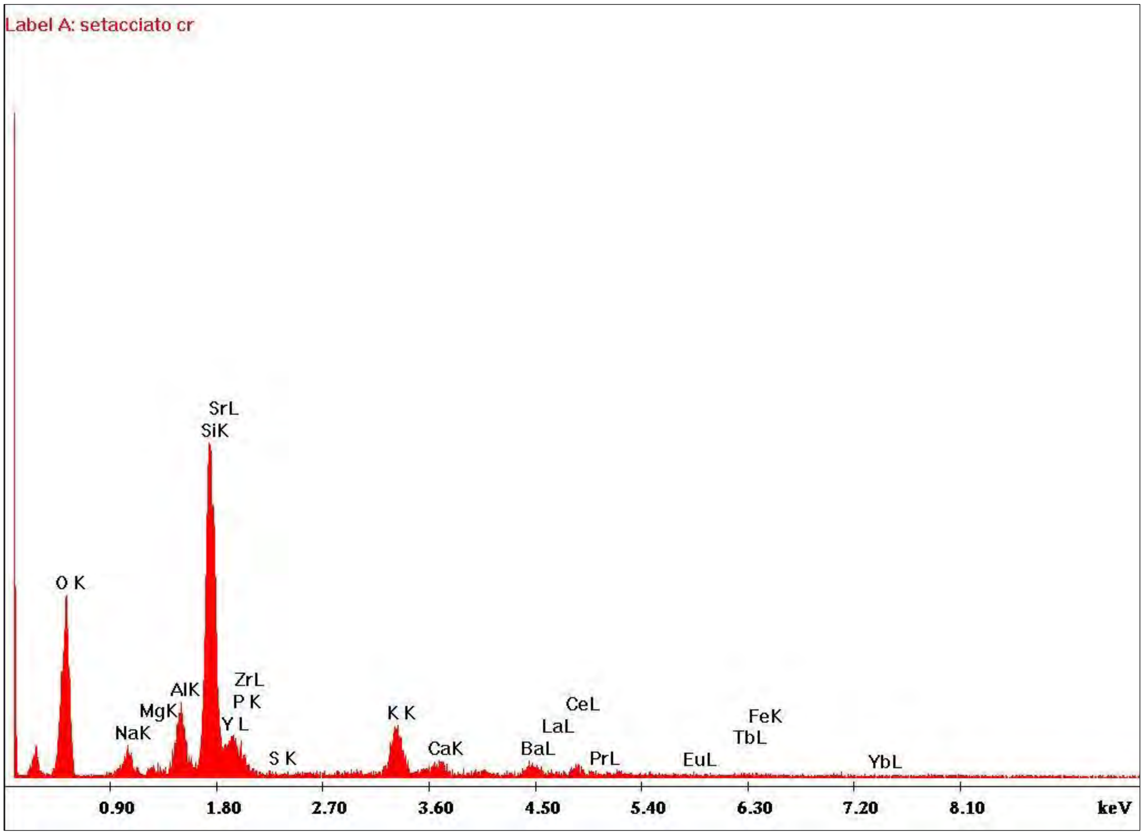
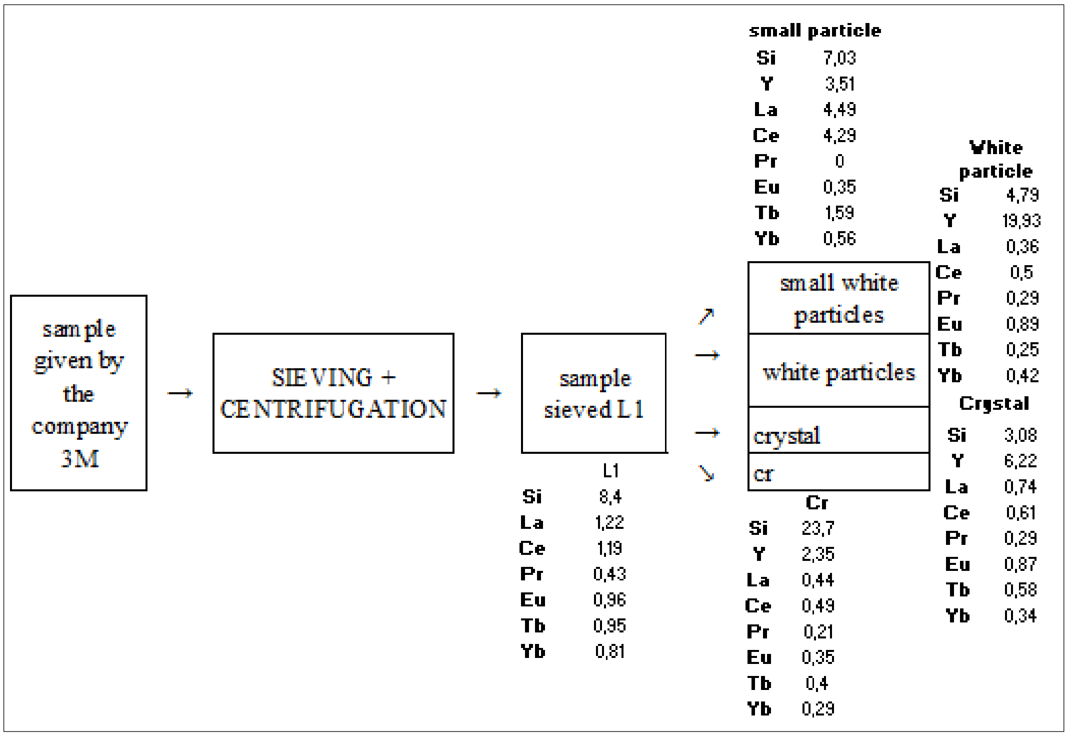


Image71: L1-cr ESEM fluorescence analysis.



	L1
Si	8,4
La	1,22
Ce	1,19
Pr	0,43
Eu	0,96
Tb	0,95
Yb	0,81

	small particle
Si	7,03
Y	3,51
La	4,49
Ce	4,29
Pr	0
Eu	0,35
Tb	1,59
Yb	0,56

	Cr
Si	23,7
Y	2,35
La	0,44
Ce	0,49
Pr	0,21
Eu	0,35
Tb	0,4
Yb	0,29

	Vhite particle
Si	4,79
Y	19,93
La	0,36
Ce	0,5
Pr	0,29
Eu	0,89
Tb	0,25
Yb	0,42

	Crystal
Si	3,08
Y	6,22
La	0,74
Ce	0,61
Pr	0,29
Eu	0,87
Tb	0,58
Yb	0,34

Image 72: Sieving procedure and analysis on L1 particles scheme

Table 8: 3M-L1 particles ESEM atomic percentage

	Atomic percentage at%					
elements	3M	L1	Crystal	white particle	small particle	cr
O	52,2	54,45	56,84	56,98	57,15	54,23
Na	2,42	2,42	1,41	1,92	1,75	3,3
Mg	0,86	2,05	2,6	1,39	2,05	0,94
Al	7,61	9,08	19,14	5,5	5,17	4,89
Si	14,9	8,4	3,08	4,79	7,03	23,7
Sr	1,89	1,85	1,15	2,38	1,02	0,76
Y	5,74	7,04	6,22	19,93	3,51	2,35
P	1,65	1,7	0,94	0	6,30	0
Zr	0,38	0,42	0,11	0,37	0,71	0,51
K	2,61	1,48	0,61	0,65	0,58	4,04
Ca	3,08	2,45	1,15	1,1	1,37	1,07
Ba	1,16	1,01	1,85	0,36	0,50	1,16
La	1,12	1,22	0,74	0,36	4,49	0,44
Ce	1,05	1,19	0,61	0,5	4,29	0,49
Pr	0,11	0,43	0,29	0,29	0,00	0,21
Eu	0,78	0,96	0,87	0,89	0,35	0,35
Tb	0,83	0,95	0,58	0,25	1,59	0,4
Fe	0,57	0,84	0,52	0,76	0,36	0,33
Yb	0,14	0,81	0,34	0,42	0,56	0,29
Hg	0,53	0,72	0,47	0,76	0,76	0,4

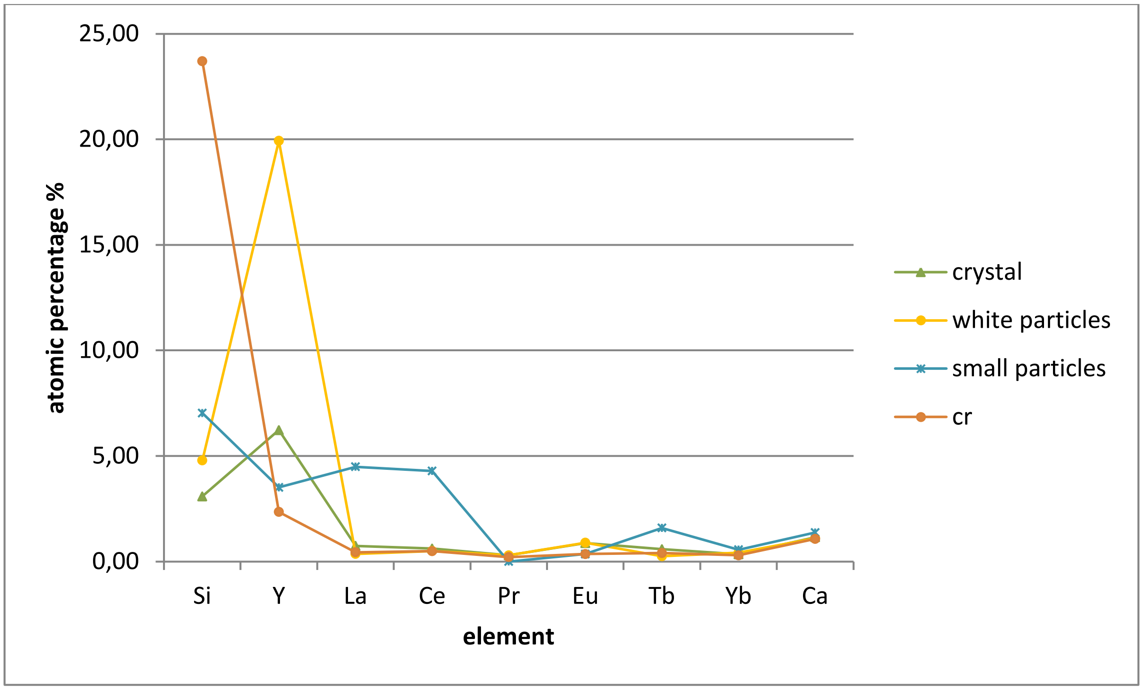


Image 73: L1 particles comparison

The efficiency is calculate using sample L1 as reference

- The *silicon* is almost contained in the particle called cr
- The *REEs*:
    - *Yttrium* is almost contained in the white particle
    - *Europium* is contained in the crystal and white particle
    - *Lanthanum* is contained in the small particle
    - *Cerium* follows lanthanum behavior
    - *Praseodymium* is equally contained in the crystal and the white particle as europium
    - *Terbium* is contained mostly in the small particle
    - *Ytterbium* follows terbium behavior
- *Calcium i*s equally distributed in the particle with a little peak in the small particle

From the ESEM image: the lighter fraction is the heavier (molecular weight) and thus richer of REEs (REEs can have an atomic weight equal to seven time the silicon ones). The darker fraction is richer of lower atomic weight elements such as silicon or other metals as barium, magnesium and sodium.

The small white particles are mainly composed by lanthanum, cerium and terbium phosphors; the white particles with higher dimension are mainly molecules with yttrium and europium. The particles called cr have higher dimension and lamellar structure, they develop in a preferential direction and contain high percentage of silicon but also other metals such as barium and potassium. The prismatic particles have dark color, they are called crystals, and contain metal oxides made of aluminum, barium and magnesium, they also contain a certain percentage of yttrium and europium.

From this analysis is possible to understand, in a qualitative way, how REEs are distributed inside the finer part of the sieved sample, more over is also understandable which type of molecules they create (oxides or phosphors).

B. Comparison between fraction of the sieving procedure (L1, L2 and L3)

Comparison between the fractions passed through the sieve (L1), the fraction hold by the sieve (L2) the liquid fraction (L3).

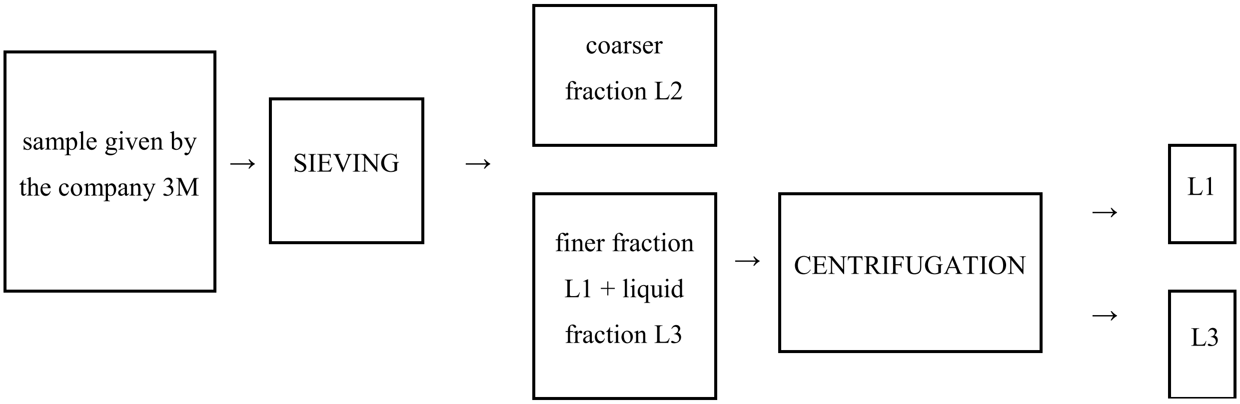


Image 74:scheme of procedure discussion 2

The fraction called *L1* is the ones that has passed through the sieving, then with a particles' dimension lower of 20µm; this fraction is more deeply analyzed in the following discussions, it is the more precious fraction of the original sample because it contains the higher percentage of REEs.

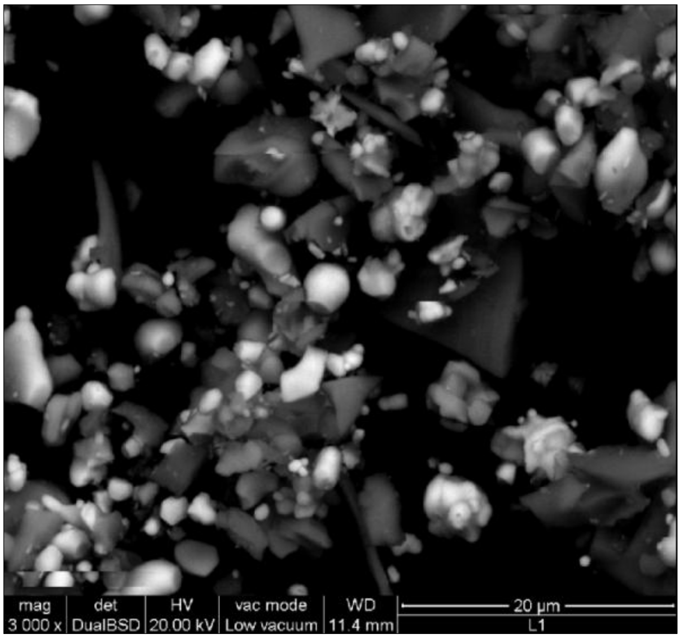


Image 75: L1 ESEM zoom 3000x

The fraction called *L2* is the part hold by the sieving, a coarser part of the original sample. From the ESEM analysis is understandable that is composed mainly of silicon oxides: dark flakes (lamellar structures) with low atomic weight.

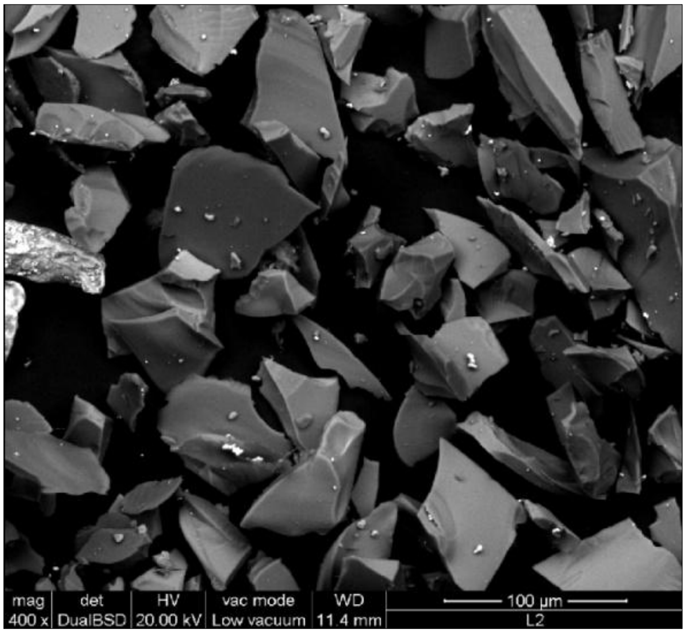


Image 76: ESEM image L2

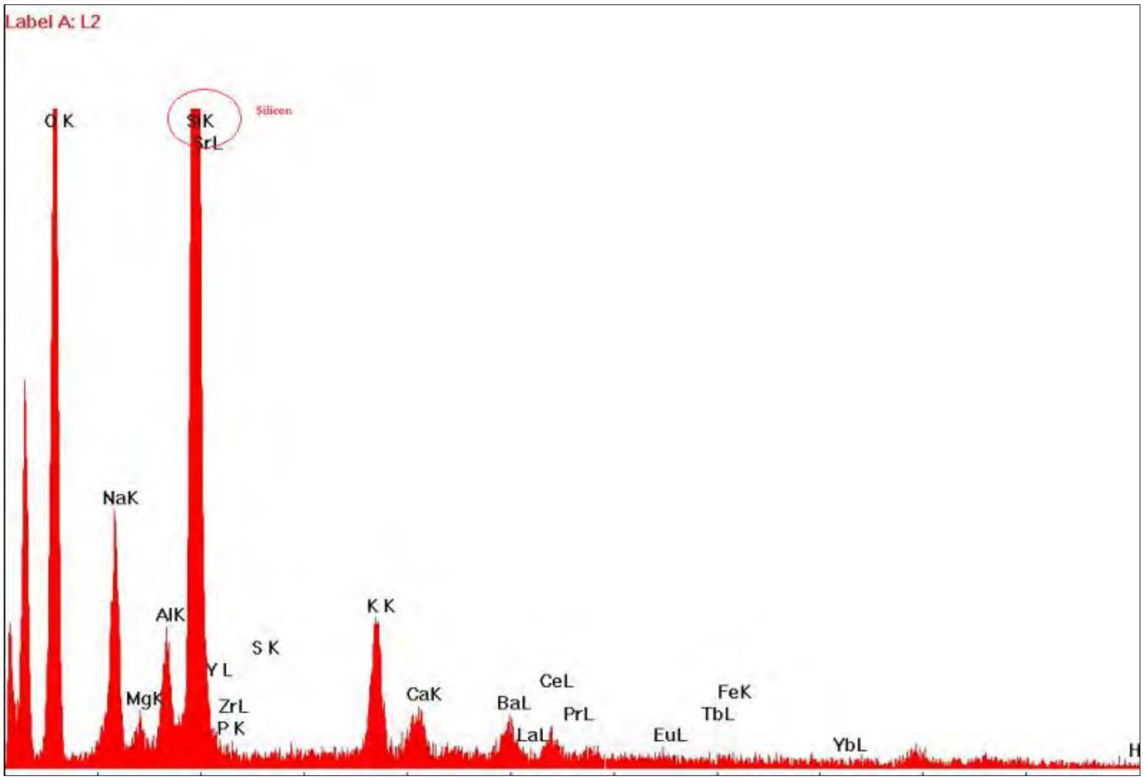


Image77: ESEM fluorescence analysis for sample L2.

The fraction called *L3* is mainly constituted of a liquid phase collected from the pass passed through the sieve. This fraction is treated with the rotary evaporator, it shows a total different nature: it mainly contains carbon and oxygen; its morphologic aspect shows porous characteristics.

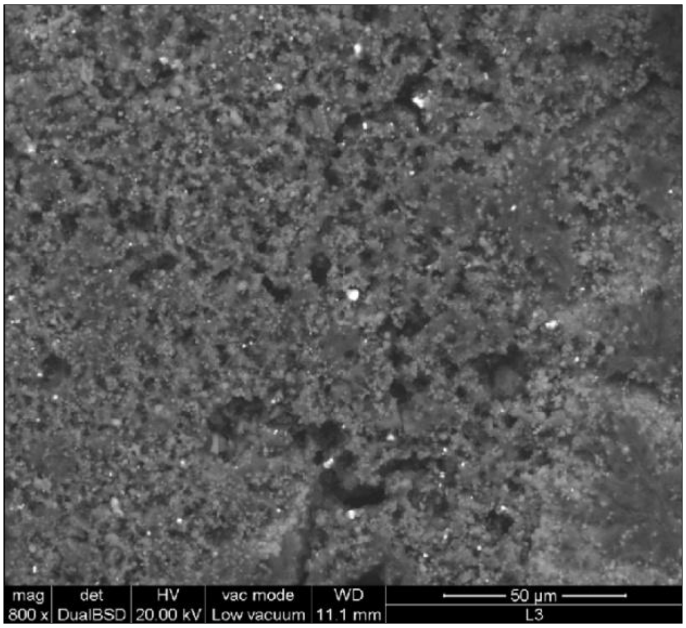


Image 78: ESEM image L3

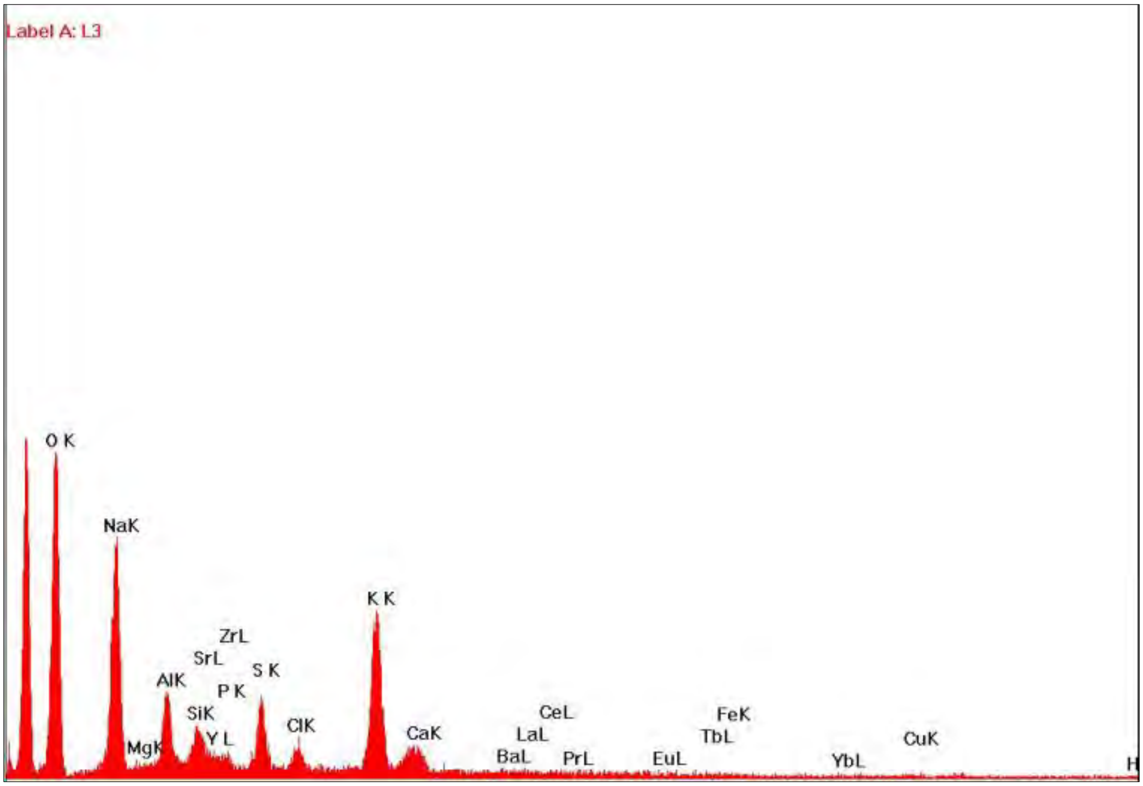


Image79: ESEM fluorescence analysis for sample L3.

Table 9: L1 L2 L3 ESEM atomic percentages

Atomic percentage at%				
elements	3m	L1	L2	L3
O	52,16	54,45	57,36	32,88
Na	2,42	2,42	7,43	6,21
Mg	0,86	2,05	0,55	0,10
Al	7,61	9,08	2,06	1,15
Si	14,87	8,40	25,38	0,47
Sr	1,89	1,85	0,77	0,20
Y	5,74	7,04	0,03	0,06
P	1,65	1,70	0,00	0,15
Zr	0,38	0,42	0,00	0,00
K	2,61	1,48	2,96	2,37
Ca	3,08	2,45	0,99	0,31
Ba	1,16	1,01	0,96	0,02
La	1,12	1,22	0,14	0,02
Ce	1,05	1,19	0,20	0,00
Pr	0,11	0,43	0,08	0,01
Eu	0,78	0,96	0,26	0,03
Tb	0,83	0,95	0,18	0,04
Fe	0,57	0,84	0,18	0,04
Yb	0,14	0,81	0,12	0,00
Hg	0,53	0,72	0,33	0,17

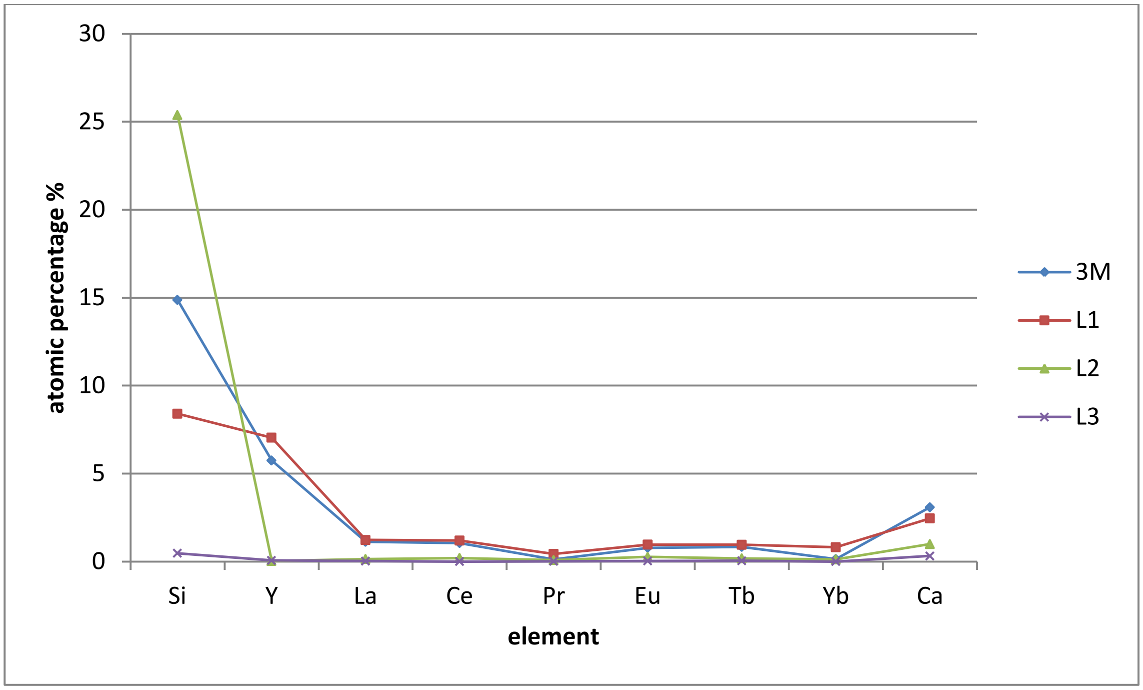


Image 80: L1 L2 L3 comparison

from the previous analysis is shown that a treatment of sieving before the handle of the powders should improve the efficiency of the following steps by lowering the silicon-REEs ratio. Moreover the analysis of the residues improves the awareness that a fraction of REEs is lost in low amount in the residues of the sieving process.

5.4 Extraction process

5.4.1 Preliminary results of extractions on not-sieved sample

Especially for the recovery of the yttrium and europium the extraction with sulfuric acid is the more suitable as literature shows (De Michelis et al. 2011). Moreover sulfuric acid make calcium settle, this element is a competitor in the following experiment of complex formation. With the previous assumption experiments are primary test with sulfuric acid with the goals to set a list of the better conditions at which perform the process. Both concentrated and diluted sulfuric acid are used, moreover test are executed to gain better conditions in terms of solid-liquid ratio, temperature, reaction time period and stirred-system velocity.

Other acid are still tested to check the possible selectivity of the extraction on other REEs.

General instruments and methods of analysis:

Dilution of solutions with purified water 0,6µS/cm

Stirred process: magnetic stirred (Ika) and Teflon anchor (500-700 RPM), room temperature (20-25°C)

Filter separation liquid-leaching phases: WhatMan 595, 15cm with addition of water in case of acid solutions

Exsiccation process or centrifugation process

ESEM analysis

5.4.1.1 Sulfuric acid

Sulfuric acid 96% concentrated

Reaction time period: 24h

Temperature: 20°C

Sample: 4g of sample 3M, solid-liquid ratio = 0,2 g/ml

Results: the residues has a reduction in yttrium content to 90%; europium, terbium and ytterbium have a extraction efficiency of about 50%; cerium, lanthanum and praseodymium the result is lower than 30%.

Sulfuric acid 2M diluted

- **Solid ratio influence**

Acid: H_2SO_4 20ml, 2M

Reaction time period: 30h

Temperature: 20°C

Sample: 4g of sample 3M

Solid-liquid ratio range: 0,01 – 0,25 g/ml

Results: yttrium is extracted in constant rate of about 90%, on contrary the other rare elements have a limit value of 0,2g/ml.

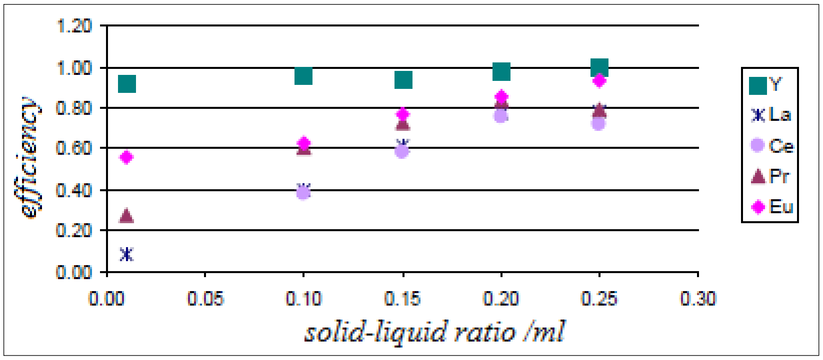


Image81: Solid-liquid ratio influence on efficiency

- **Temperature variation**

Acid: H_2SO_4 20ml, 2M

Reaction time period: 6h

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20 - 80°C

Results: yttrium is extracted in constant rate of about 90%, except at 60°C where is shown a slightly decrease; at the same temperature the other REEs show higher decrease. It seems convenient to operate at 20°C (room temperature).

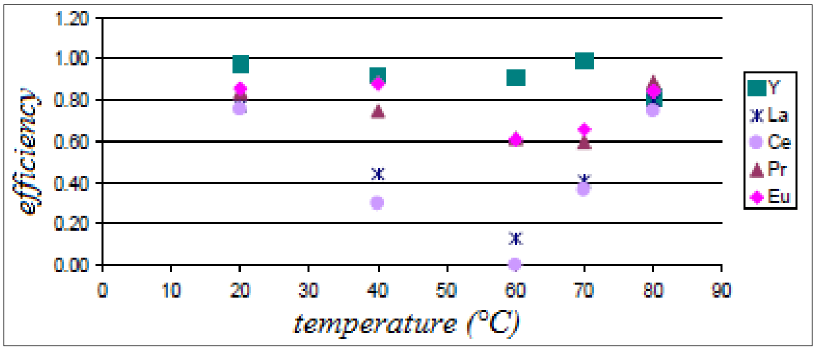


Image82: Temperature influence on efficiency

- **Reaction time period**

Acid: H_2SO_4 20ml, 2M

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20°C

Reaction time period range: 6h-55h

Results: yttrium is extracted in constant rate of about 90%, the other REEs show higher decrease to longer reaction time period. It seems reasonable to fix the reaction time period of 24h.

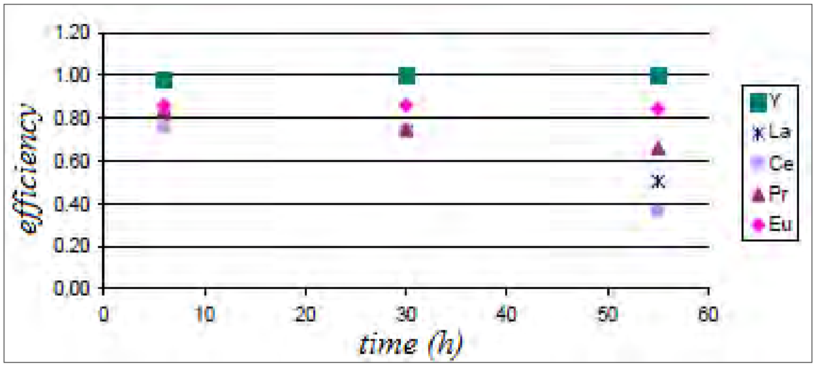


Image83: Reaction time period influence on efficiency

- **Stirred-system velocity**

Acid: H_2SO_4 20ml, 2M

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20°C

Reaction time period: 30h

Stirred velocity option: ON (700 RPM) - OFF

Results: yttrium is extracted with an efficiency of 90% with stirred device process and 80% without stirred device. It seems useful to employ the stirred device.

From the previous tests a list of the best conditions to extract yttrium is set up:

Acid: H_2SO_4 20ml, 2M

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature: 20°C

Reaction time period: 24h

Stirred velocity: ON (700 RPM)

Results: yttrium has a efficiency on recovery of about 90%, for europium, terbium and ytterbium the efficiency fluctuate between 50-60%, for cerium, lanthanum and praseodymium the efficiency is lower than 30%.

5.4.1.2 Other acid extractions

Double extraction

The sample handle in final *optimum* condition, but a concentration of 96%, is subject to a second extraction one with *sulfuric acid* the second with *phosphoric acid:*

Acid: H_2SO_4 20ml, 2M or H_3PO_4 20ml, 2M

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20°C

Reaction time period: 24h

Stirred velocity: ON (700 RPM)

Results: a second extraction has not a meaningful influence on efficiency.

Phosphoric acid 85% concentrated

Acid: H_3PO_4 20ml, 85%

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20°C

Reaction time period: 24h

Stirred velocity: ON (700 RPM)

Results: phosphoric acid extracts about 90% of yttrium, 80% of europium, terbium and lanthanum, 70% of cerium and less than 30% of praseodymium. Phosphoric acid seems not to be convenient to extract REEs with lower concentration (2M), moreover it has the disadvantage of extracting with high efficiency (80%) calcium.

Hydrofluoric acid 40%

Acid: HF 20ml, 40%

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20°C

Reaction time period: 24h

Stirred velocity: ON (700 RPM)

Exothermic reaction

Results: to investigate the efficiency another method should be used because hydrofluoric acid tends to dissolve completely silicon. A morphologic examination of the residue sample has been done with the ESEM microscope and it seems that this acid does not show high efficiency in extraction of REEs.

As literature already provides to show the more suitable acid for extraction of REEs is sulfuric acid, although other acids tested do not show interesting behavior.

5.4.2 Extraction process on sieved sample

As found in literature (De Michelis, 2011) sulfuric acid perform the better extraction especially for yttrium. Next chapter presents test with sulfuric acid on sieved sample for a comparison with the not sieved sample extraction performed in the previous analysis. Moreover other tests are executed to understand if other REEs should be extracted with other acids, mixture of acid or sequence of acid. In particular are performed the experiment using this list of acids/mixture of acids/sequence of acids:

--single acid

-H_2SO_4 extraction

-HF extraction

-HNO_3 extraction

-HCl extraction

-CH_3COOH extraction

--mixture of acids

-mixture HCl+HNO_3 extraction (Aqua Regis)

--sequence of acids

-sequence HF extraction performed twice

-sequence HF extraction and double extraction with CH_3COOH

5.4.2.1 Single extraction

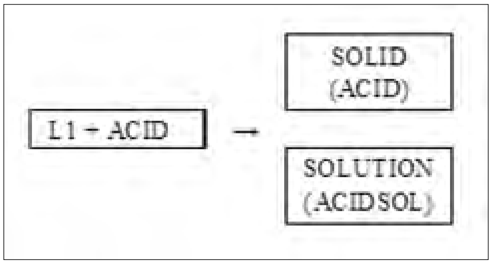


Image 84: Single extraction acid scheme

5.4.2.1.1 Sulfuric acid extraction

Four grams of sample L1 are diluted in 20ml of H2SO4 (with a concentration 2 mol/l), with a solid liquid ratio of 0,2 g/ml. From the commercial sulfuric acid 96% (concentrated) is prepared the 2 molar concentration of the acid in a bottle of 920ml of sulfuric acid. The solution is put on a magnetic stirred to mix up.

Image85: Start step of extraction.

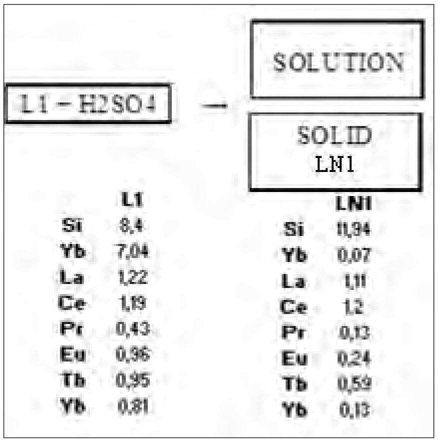
Image86: Final step of extraction.

After a week the sample is filtered in another flask adding de-ionized water and let dried.

Image87: Filtration second step of extraction

After the sample dries, in a period of a week, the result of procedure are: a solution (from now on called S1) and a solid sample on the paper filter (from now on called LN1). The solid fraction is analyzed with the ESEM. The liquid phase, passed through the filter, is handled with a procedure explained in the next pages.

ESEM Analysis



	L1
Si	8,4
Yb	7,04
La	1,22
Ce	1,19
Pr	0,43
Eu	0,36
Tb	0,95
Yb	0,81

	LN1
Si	11,94
Yb	0,07
La	1,11
Ce	1,2
Pr	0,13
Eu	0,24
Tb	0,59
Yb	0,13

Image 88: H2SO4 extraction scheme

The solid fraction of the sample LN1 is analyzed with the ESEM.

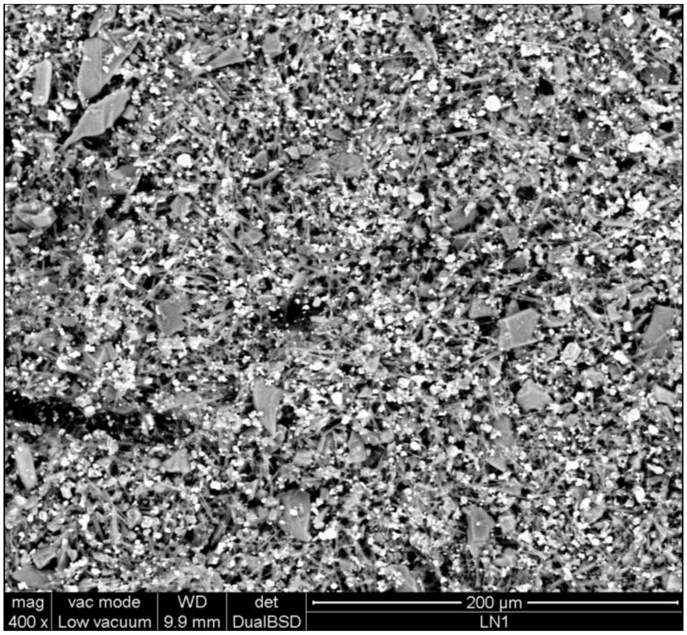


Image89: LN1 ESEM zoom 400x

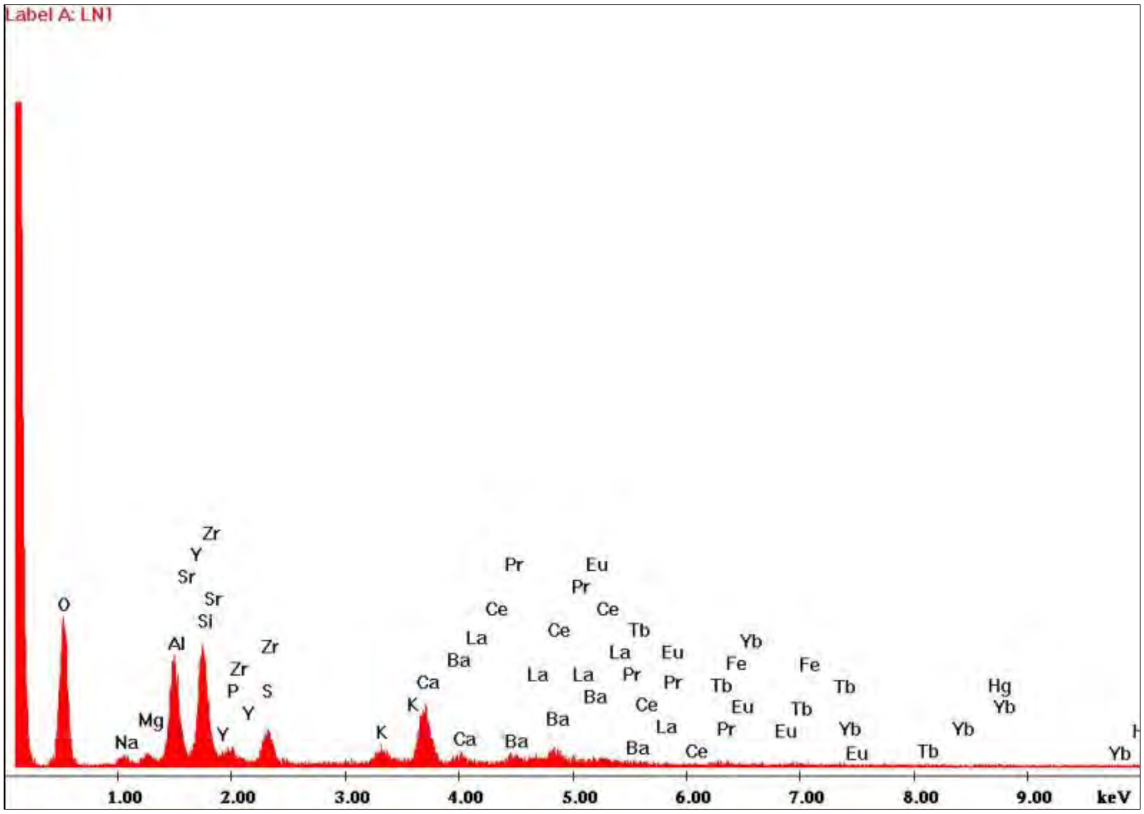


Image90: LN1 ESEM fluorescence analysis

Table 10: H2SO4 extraction ESEM atomic percentage

Atomic percentage at.%		
elements	L1	LN1
O	54,45	56,85
Na	2,42	1,78
Mg	2,05	1,16
Al	9,08	11,88
Si	8,4	11,94
Sr	1,85	1,53
Y	7,04	0,07
P	1,7	1,37
Zr	0,42	0,21
K	1,48	1,32
Ca	2,45	3,99
Ba	1,01	1,08
La	1,22	1,11
Ce	1,19	1,2
Pr	0,43	0,13
Eu	0,96	0,24
Tb	0,95	0,59
Fe	0,84	0,49
Yb	0,81	0,13
Hg	0,72	0,13

- *Silicon* :does not change considerably in percentage, as expected it is not extracted by the sulfuric acid, it remains in the solid fraction on the filter after the filtration step.
- *REEs*: in particular yttrium, europium and ytterbium have low percentage in the solid fraction that means they are recovered in the solution (well extracted by the sulfuric acid).

From these analysis is understandable, as literature highlights, how the sulfuric acid is capable to extract the mayor part of the REEs in particular yttrium and europium. Moreover the percentage of silicon is high in the solid fraction (settled in the balloon and collected after the filtration step), that makes easier the following step of complex formation (of the yttrium oxalate).

Table 11: H2SO4 extraction ESEM weight percentage sample sieved and not sieved

		weight percentage w/w%		
elements	3m	L1	LN1	LN1 not sieved
O	52,16	23,7	28,99	27,48
Na	2,42	1,51	1,09	2,09
Mg	0,86	1,35	0,96	0,71
Al	7,61	6,67	10,09	7,93
Si	14,87	6,42	10,03	13,63
Sr	1,89	4,42	2,18	3,14
Y	5,74	17,03	2,14	2,03
P	1,65	1,43	0,64	0,92
Zr	0,38	1,04	1,12	0,4
K	2,61	1,57	1.85	2,9
Ca	3,08	2,68	6,88	4,66
Ba	1,16	3,77	5,33	5,52
La	1,12	4,62	4,55	4,45
Ce	1,05	4,54	6,19	6,73
Pr	0,11	1,63	1,3	2,54
Eu	0,78	3,98	1,49	2,73
Tb	0,83	4,13	3,44	3,34
Fe	0,57	1,28	0,87	0,57
Yb	0,14	3,82	1,49	3,07
Hg	0,53	3,95	6,11	0

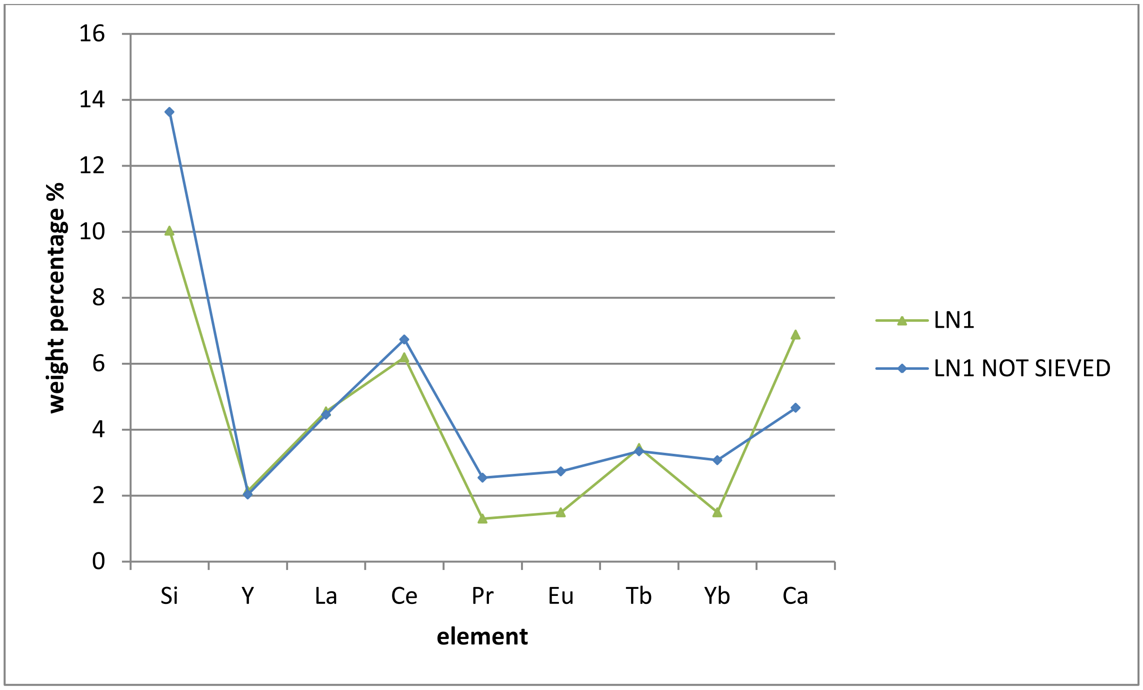


Image 91: H2SO4 extraction comparison sample sieved and not sieved

About the comparison between extraction procedure with sieving process (LN1) and the ones without (LN1 not sieved) is remarkable the results about:

- Decrease of silicon content in LN1
- Increase of yttrium content in LN1

Sulfuric acid is the acid more suitable to perform a extraction especially for yttrium and europium, by adding the sieving procedure the content of silicon in the starting sample is lower, that enhance the efficiency of the extraction. By analyzing the residues of the extractions performed with sulfuric acid on the sample sieved and not sieved can be noticed that higher content of REEs is left in solution for the sample sieved. Last affirmation means higher extraction efficiency when a sieved treatment is performed before the extraction. From the comparison also calcium seems to be better removed when sieving treatment are applied.

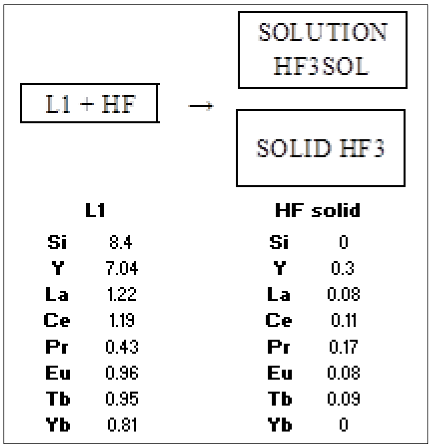
5.4.2.1.2 Hydrofluoric acid

The solvent used to perform the extraction procedure is Hydrofluoric acid. The purpose is to melt the silicon particles with a strong acid. The sample (L1) weights 4g and put in a flask with 50ml of HF for 24 hours is left react and filtered. In this reactions is important to remember the exothermic behavior: ice cubes are added in the crystallized to prevent the boiling of the HF. The stirrer device does not heat the sample and the speed is about 500 rpm. The results are a solid part HF3 and a liquid part HF3SOL.

Image92: Two HF extraction with ice for the exothermic property of the reactions.

ESEM Analysis

COMPOSITION: the sample 3M is sieved and 4g of it is put in a solution of 50mL of HF (40%). The solution is left reacting for 24h in a crystallizer with some ice cubes because the reaction is exothermic, and then dried. The solid fraction weighted 2.4830g and directly analyzed with ESEM, the solution is dried with Rotary Evaporator.



L1		HF solid	
Si	8.4	**Si**	0
Y	7.04	**Y**	0.3
La	1.22	**La**	0.08
Ce	1.19	**Ce**	0.11
Pr	0.43	**Pr**	0.17
Eu	0.96	**Eu**	0.08
Tb	0.95	**Tb**	0.09
Yb	0.81	**Yb**	0

Image 93: HF extraction procedure

Solid part: HF3

Image94: HF3 sample.

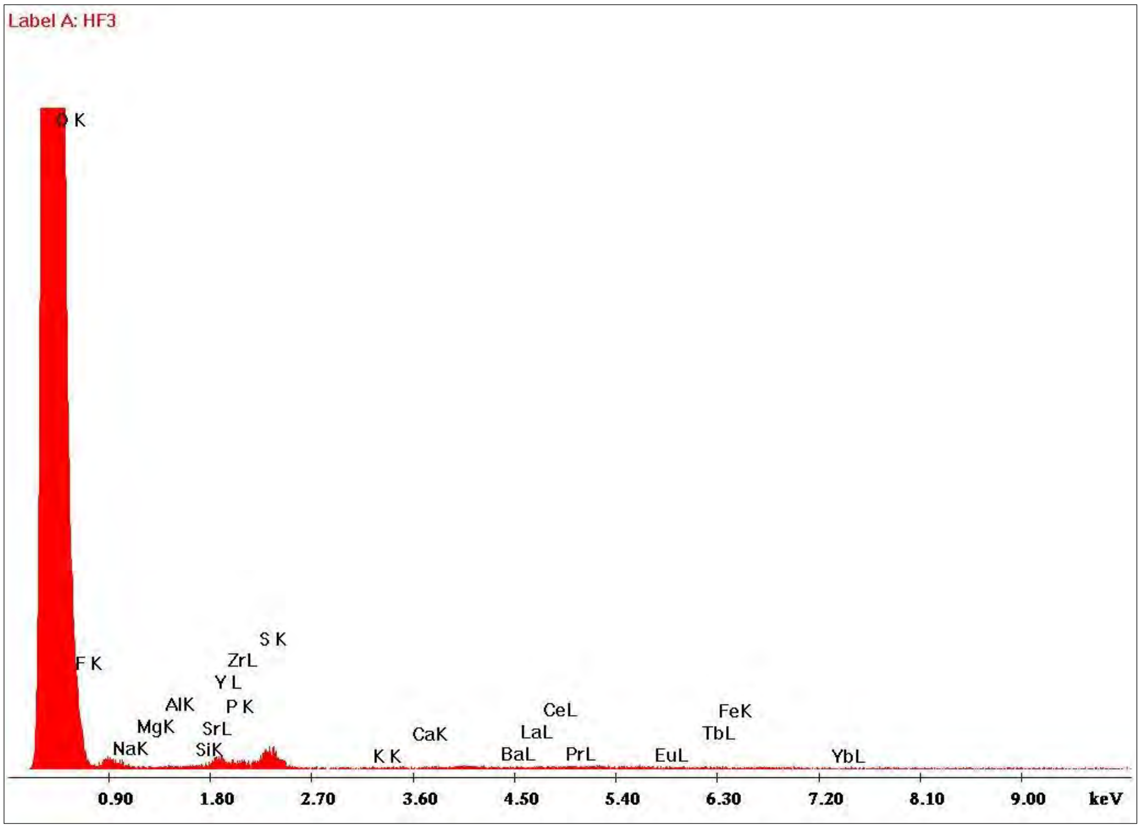


Image95: HF3 ESEM fluorescence analysis.

Liquid fraction treated in the Rotary evaporator: HF3SOL

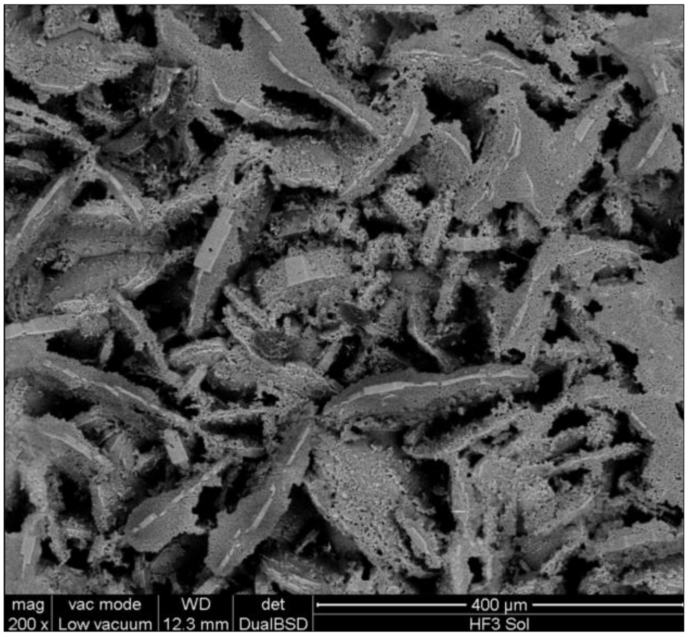


Image 96: HF_3SOL ESEM zoom 200x.

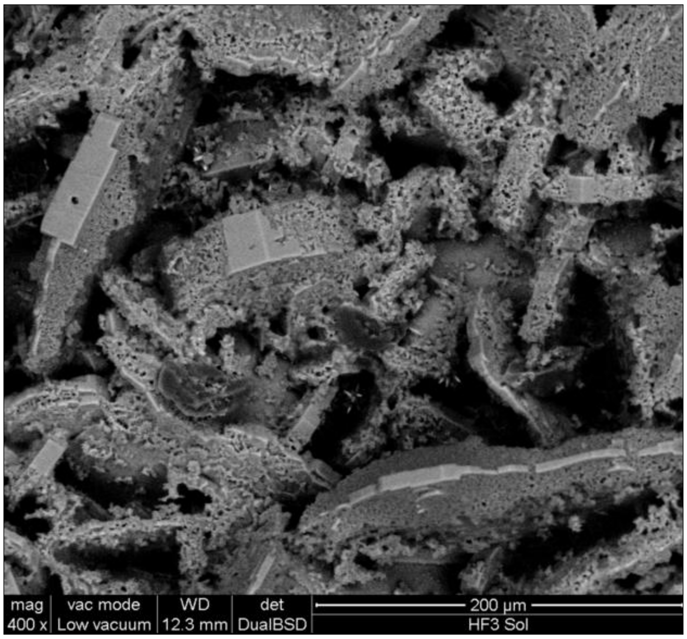


Image 97: HF$_3$SOL ESEM zoom 400x.

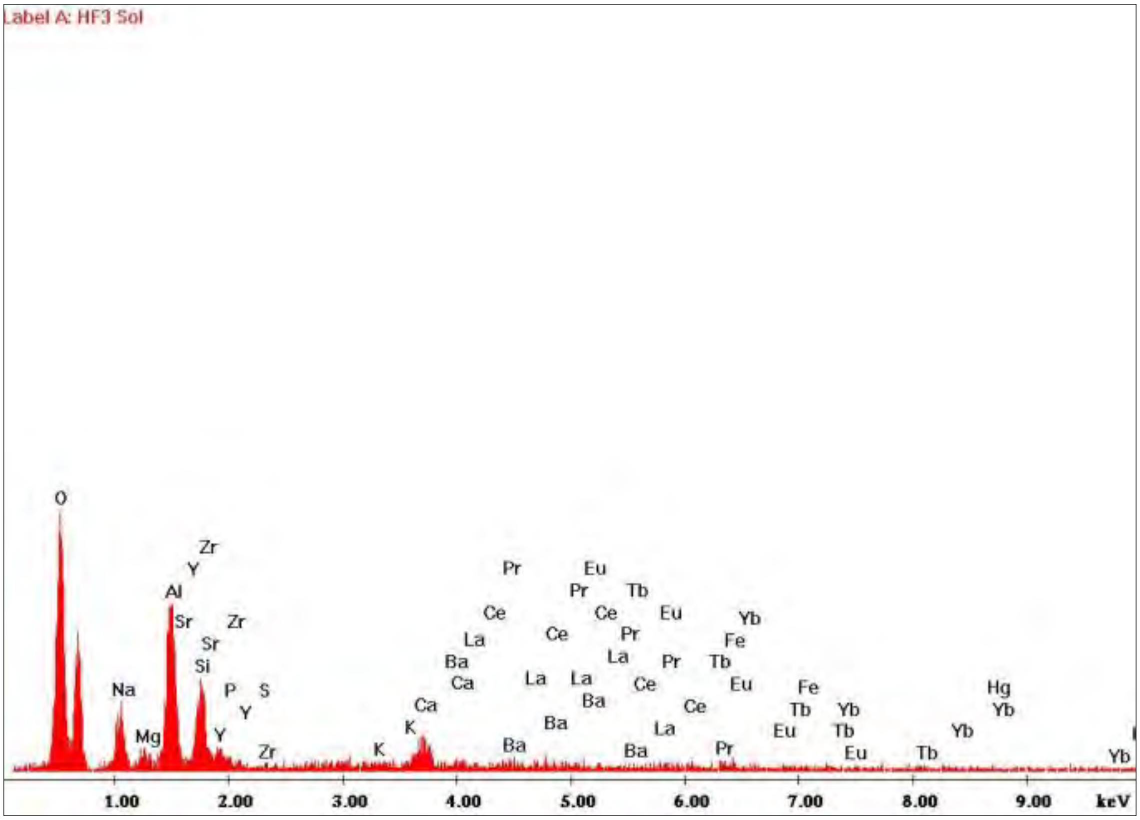


Image 98: HF$_3$SOL ESEM fluorescence analysis.

Table 12: Hydrofluoric extraction ESEM atomic percentage

Atomic percentage at.%			
elements	L1	HF solid	HF solution
O	54.45	82.89	62.92
F	/	13.58	/
Na	2.42	0.85	7.04
Mg	2.05	0	1.01
Al	9.08	0	14.19
Si	8.4	0	6.53
Sr	1.85	0.26	0.53
Y	7.04	0.3	0.86
P	1.7	0	0
Zr	0.42	0.17	0
K	1.48	0.04	0.26
Ca	2.45	0.08	2.2
Ba	1.01	0.06	0.44
La	1.22	0.08	0.33
Ce	1.19	0.11	0.2
Pr	0.43	0.17	0.35
Eu	0.96	0.08	0.58
Tb	0.95	0.09	0.56
Fe	0.84	0.06	0.72
Yb	0.81	0	0.58
Hg	0.72	0	0.69

Hydrofluoric acid extraction is performed because it has the power to dissolve the silicon, no silicon appear in the solid residue. In the residue of the extraction percentages of REEs still appeared. Even if HF used in a single extraction on the sieved powder samples does not show interesting result in the next paragraph the solid residue is handled both with a second HF extraction and a CH_3COOH *double extraction to test the ability of recover the REEs-residues in the solid fraction.*

5.4.2.1.3 Nitric acid

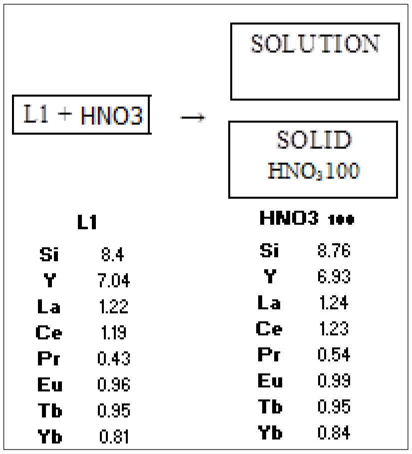
L1 sample is added to a solution of HNO_3 (1M) in this ratio: 30g of L1/500mLof HNO_3. The solution is put on a stirred with 500 RPM as velocity and no heat. The extraction is carried for 24 hours and then filtered. The solid fraction is called $HNO_3$100.

Image 99: HNO_3 extraction.

The experiment is performed also with a solid/liquid ratio of 30%: 30g of L1 and 100mL of HNO3. Both solutions are filtered with a result of a solid part ($HNO_3$100 and $HNO_3$500) directly detected with ESEM, and solutions phases left dried under the fume hood ($HNO_3$100SOL, $HNO_3$500SOL).

ESEM Analysis

The result of the ESEM analysis for the first experiment:



	L1	HNO3 100
Si	8.4	8.76
Y	7.04	6.93
La	1.22	1.24
Ce	1.19	1.23
Pr	0.43	0.54
Eu	0.96	0.99
Tb	0.95	0.95
Yb	0.81	0.84

Image 100: HNO3 extraction procedure scheme.

Solid: $HNO_3$100

The solid $HNO_3$100 is weighted: 28.22g and analyzed with ESEM.

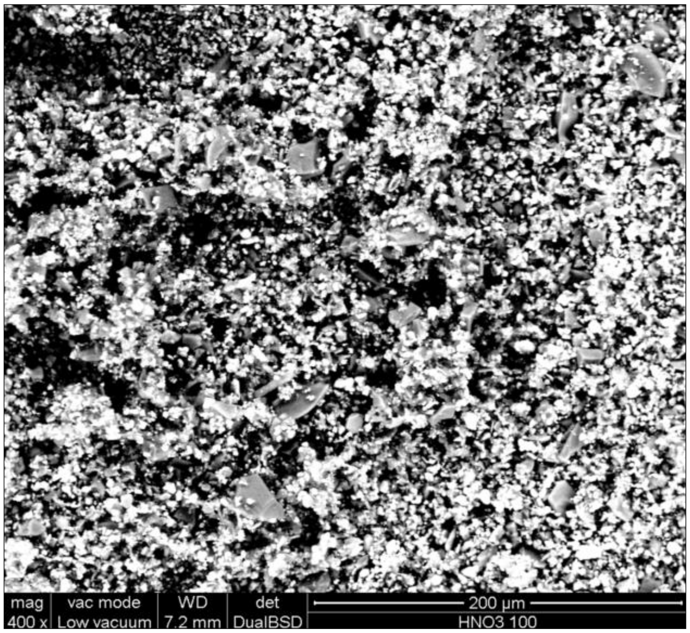


Image 101: $HNO_3$100 ESEM zoom 400x.

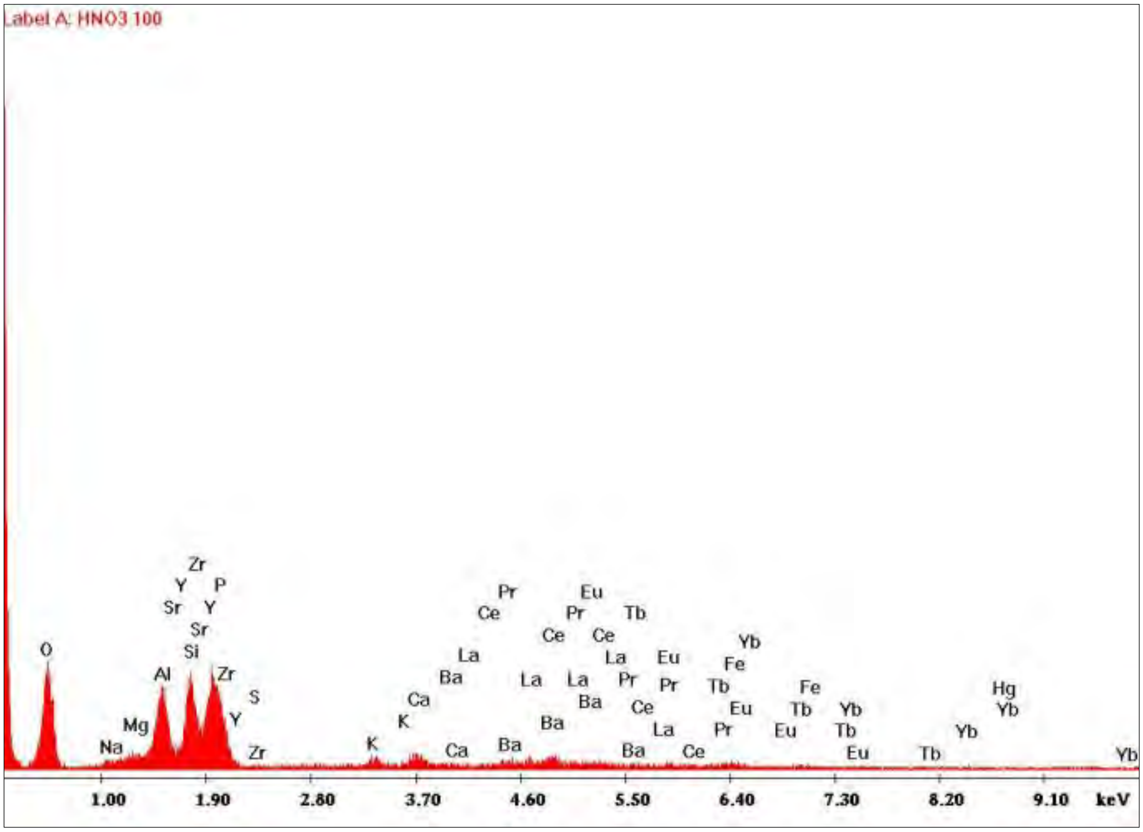
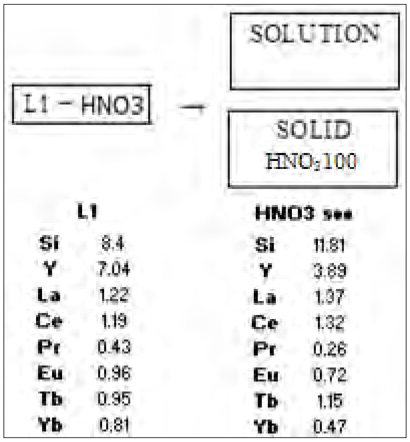


Image 102: $HNO_3$100 ESEM fluorescence analysis.

The result of the ESEM analysis for the second experiment:



L1		HNO3 500	
Si	8.4	Si	11.81
Y	7.04	Y	3.89
La	1.22	La	1.37
Ce	1.19	Ce	1.32
Pr	0.43	Pr	0.26
Eu	0.96	Eu	0,72
Tb	0.95	Tb	1.15
Yb	0,81	Yb	0.47

Image 103: HNO_3 extraction procedure scheme

Solid: $HNO_3$500

The solid $HNO_3$500 is weighted: 17.74g and analyzed with ESEM.

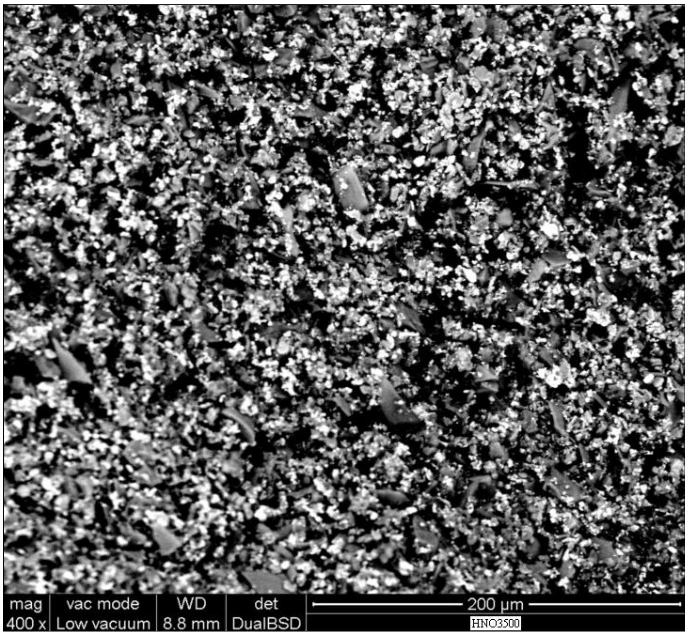


Image 104: $HNO_3$500 ESEM zoom 400x.

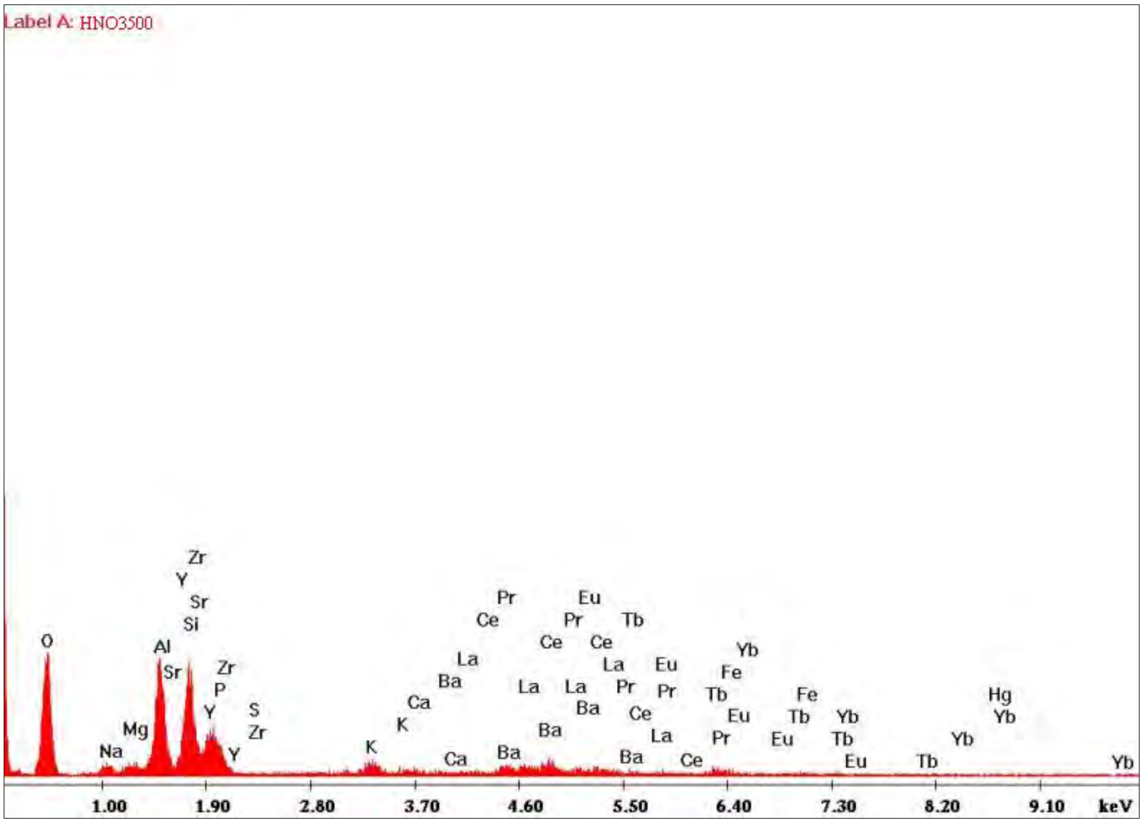


Image 105: HNO_3500 ESEM fluorescence analysis.

Table 13: $HNO_3$100 and $HNO_3$500 ESEM atomic percentage

Atomic percentage at%			
elements	**L1**	**HNO_3 100 solid**	**$HNO_3$500 solid**
O	54.45	50.94	52.35
Na	2.42	1.79	2.23
Mg	2.05	2.34	1.88
Al	9.08	10.22	14.75
Si	8.4	8.76	11.81
Sr	1.85	3.03	1.59
Y	7.04	6.93	3.89
P	1.7	3.28	1.11
Zr	0.42	1.16	0.38
K	1.48	1.35	1.61
Ca	2.45	1.64	0.67
Ba	1.01	1.17	1.28
La	1.22	1.24	1.37
Ce	1.19	1.23	1.32
Pr	0.43	0.54	0.26
Eu	0.96	0.99	0.72
Tb	0.95	0.95	1.15
Fe	0.84	1.06	0.8
Yb	0.81	0.84	0.47
Hg	0.72	0	0

$HNO_3$100: solid liquid ration s/l = 0.3

- *Silicon*: not extracted
- *REEs:* not extracted
- *Calcium*: extracted

$HNO_3$500: s/l = 0.06

Despite the different concentration the result does not change respect the previous experiment in term of selectivity in the extraction, except a higher extraction of yttrium and a lower concentration of calcium in the solution for the more concentrated acid that should be investigated deeply.

5.4.2.1.4 Acetic acid

A test of extraction with Acetic acid is tried. 1 gram of the sample just sieved L1 is put in a flask with 10mL of Acetic acid, for a solid/liquid ratio of 1/10 g/mL. The flask is disposed on a magnetic stirrer with a speed of about 500 RPM, the room temperature is chosen and the solution is left react and after 24 hours it is filtered. Then in filtered and weighted 0.9790 g.

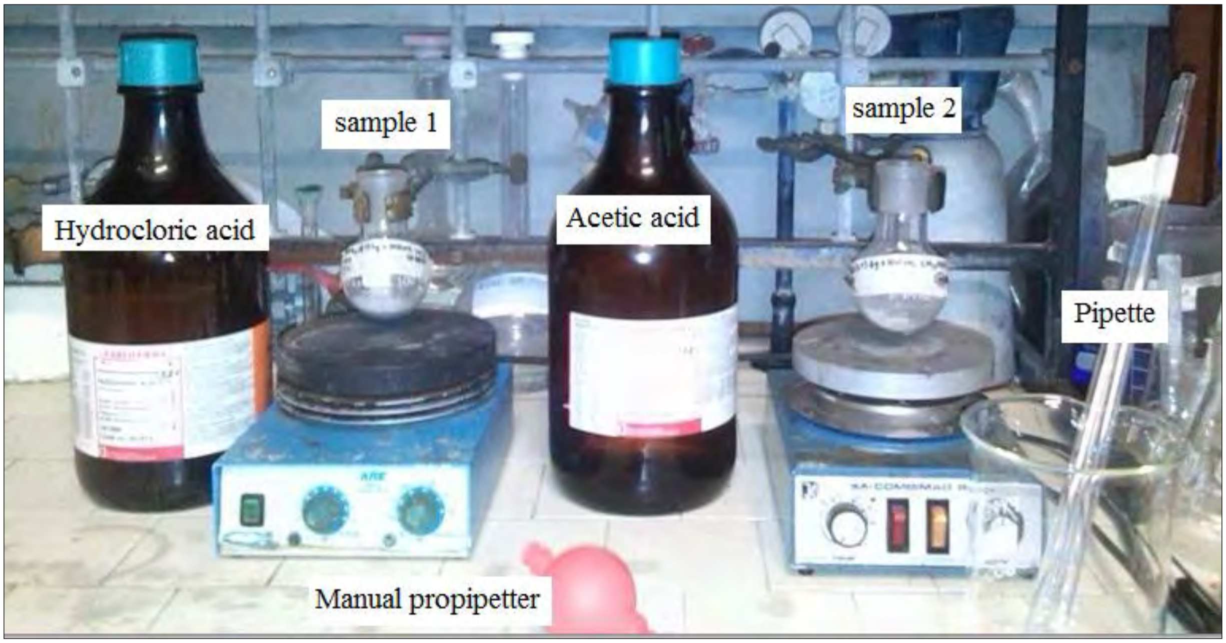
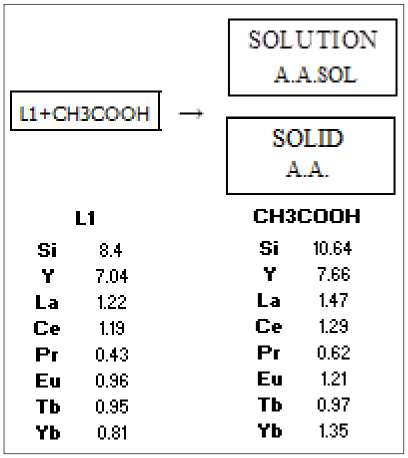


Image 106: Preparation of the double experiment with Acetic acid and Hydrochloric acid: instruments and materials.

ESEM Analysis



	L1		CH3COOH
Si	8.4	Si	10.64
Y	7.04	Y	7.66
La	1.22	La	1.47
Ce	1.19	Ce	1.29
Pr	0.43	Pr	0.62
Eu	0.96	Eu	1.21
Tb	0.95	Tb	0.97
Yb	0.81	Yb	1.35

Image 107: Acetic acid extraction procedure scheme

Solid A.A. filtrated after the CH_3COOH extraction

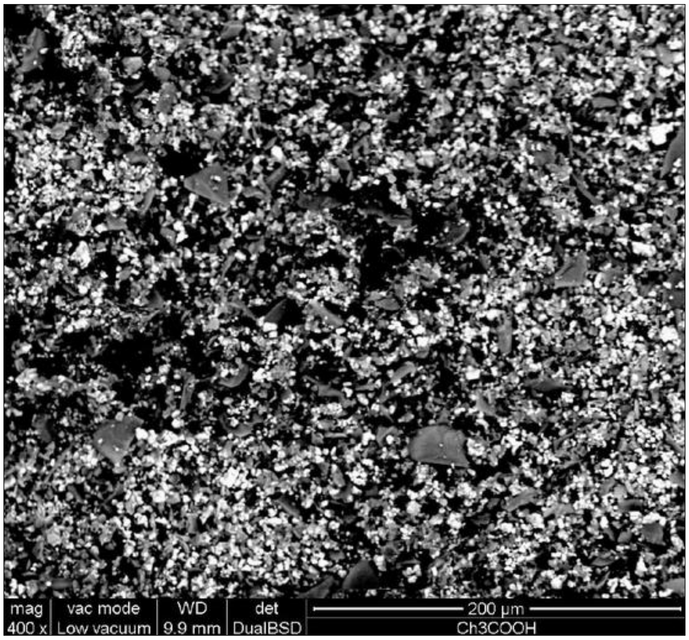


Image 108: A.A. solid filtrated after the CH_3COOH extraction ESEM zoom 400x.

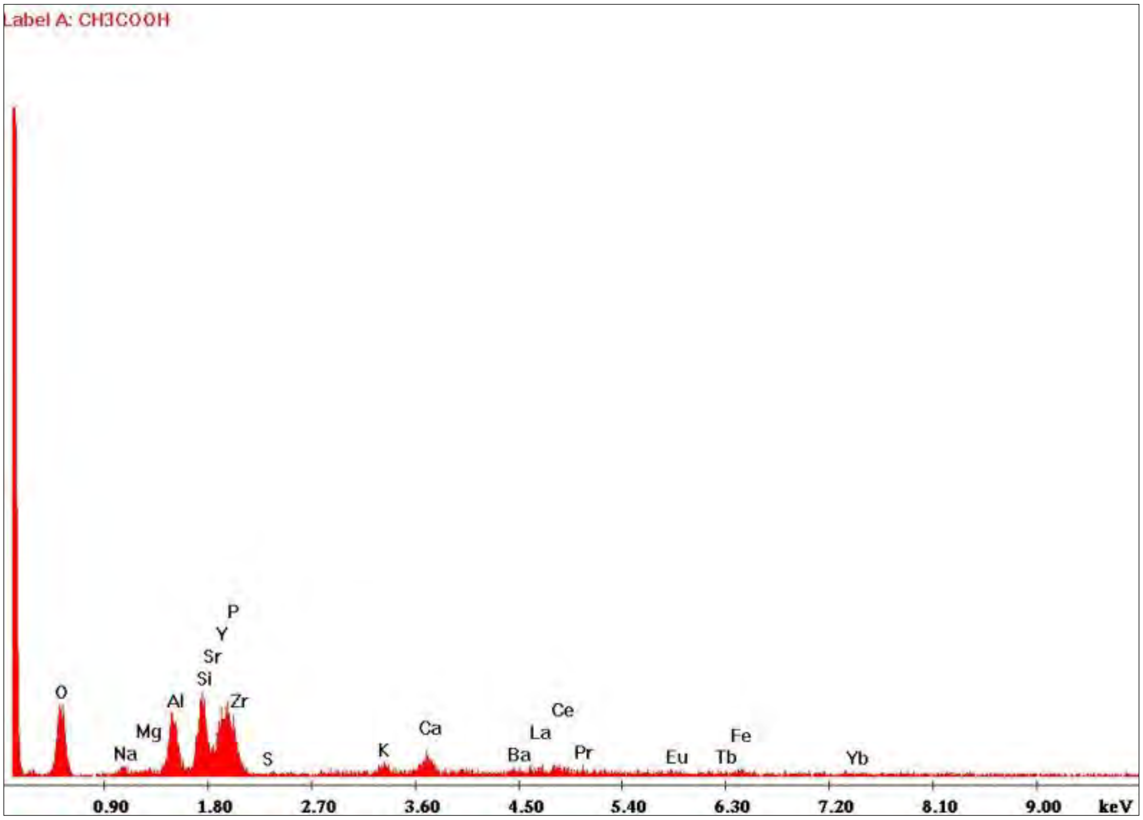


Image 109: A.A. solid filtrated after the CH_3COOH extraction ESEM fluorescence analysis.

From the ESEM image is possible to distinguish both darker and lighter fraction, the first is mainly formed by silica and alumina, the second ones is rich in yttrium. No other lanthanides high concentration can be appreciated.

Solution: A.A.SOL

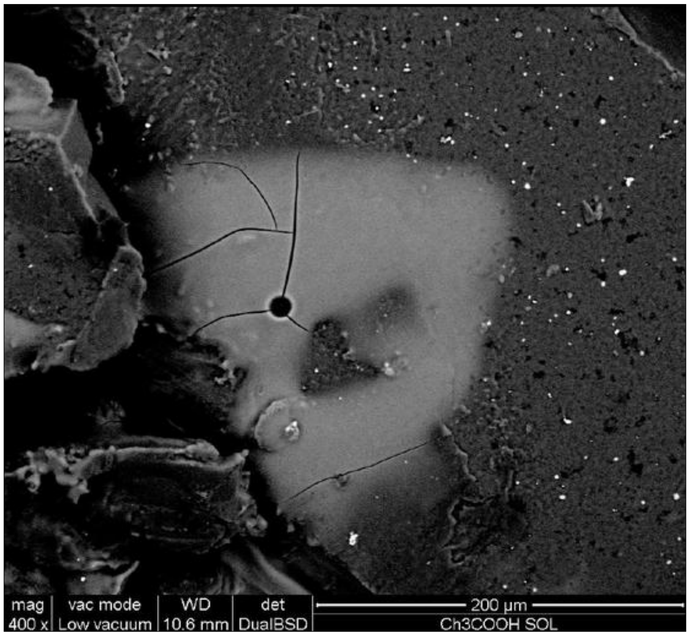


Image 110: A.A.SOL solution dried from the CH_3COOH extraction ESEM zoom 400x.

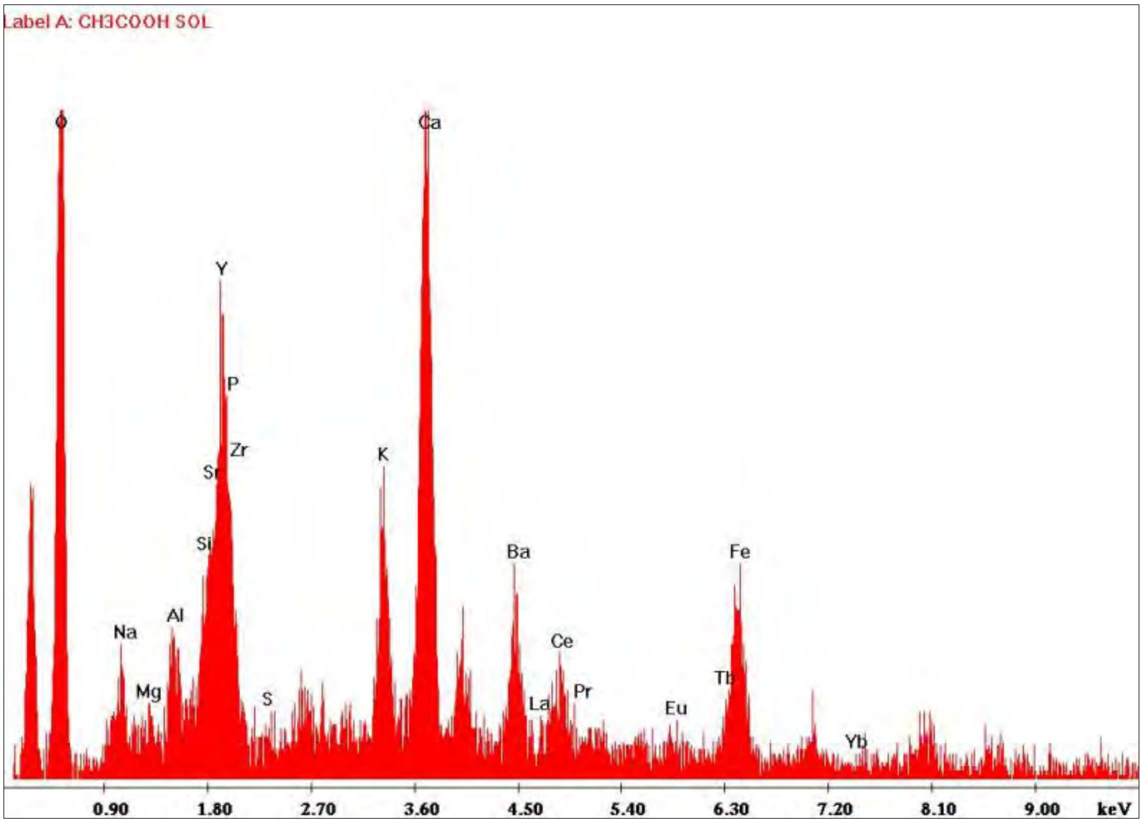


Image 111: A.A.SOL solution dried from the CH_3COOH extraction ESEM fluorescence analysis.

The hole in the middle of the ESEM image is an air bobble that appears because of the sample is not perfectly dried. In that sample is possible to appreciate a higher darker composition but there are also little fraction of lighter particles (heavier in atomic weight). The heaviest element is the yttrium, but calcium, potassium and barium are also present.

Table 14: A.A. and A.A.SOL ESEM atomic percentage.

elements	L1	CH_3COOH solid	CH_3COOH solution
O	54.45	48.03	65.86
Na	2.42	2.31	3.08
Mg	2.05	1.37	0.2
Al	9.08	10.03	1.53
Si	8.4	10.64	0.71
Sr	1.85	1.67	1.76
Y	7.04	7.66	4.18
P	1.7	2.45	0.14
Zr	0.42	0.82	0
S	0.53	0.48	0
K	1.48	1.8	3.44
Ca	2.45	2.9	10.63
Ba	1.01	1.24	2.43
La	1.22	1.47	0.2
Ce	1.19	1.29	0.35
Pr	0.43	0.62	0
Eu	0.96	1.21	0.24
Tb	0.95	0.97	0
Fe	0.84	1.15	4.93
Yb	0.81	1.35	0
Hg	0.72	0.54	0.33

CH_3COOH: acetic acid is a weak acid, there is low dangerous level respect the other acid used, moreover also the environmental pollution is lower.

- *Silicon*: not extracted
- *REEs:* not extracted
- *Calcium*: extracted

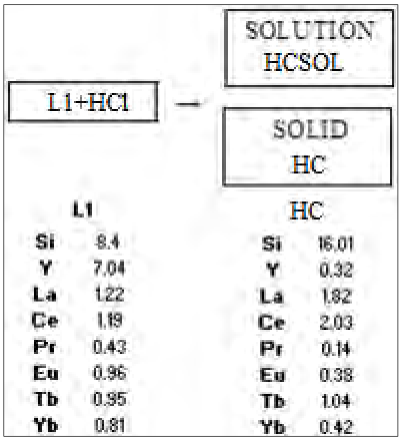
Even though no relevant results are achieved is interesting how the solution of this experiment is poor of yttrium, lanthanum, cerium and europium: can be useful to test a washing procedure with this acid in other solid sample rich in lanthanides content.

5.4.2.1.5 Hydrochloric acid

A test of extraction with Hydrochloric acid is made. 1 gram of the sample just sieved, named L1, is put in a flask with 10mL of Hydrochloric acid, for a solid/liquid ratio of 1:10. The flask is disposed on a magnetic stirrer with a speed of about 500 RPM, the room temperature is chosen and the solution is left reacting 24 hours. Then the solution is filtered and the solid is weighted 2132 g. The solution is left dried at room temperature and some eye-visible crystals settled, they are analyzed at the ESEM .

Image 112: Preparation of experiment with and HR-200 digital analytical balance.

ESEM Analysis



	L1		HC
Si	8.4	Si	16.01
Y	7.04	Y	0.32
La	1.22	La	1.82
Ce	1.19	Ce	2.03
Pr	0.43	Pr	0.14
Eu	0.96	Eu	0.38
Tb	0.95	Tb	1.04
Yb	0.81	Yb	0.42

Image 113: HCl extraction procedure scheme

Solid HC (0.2132 g)

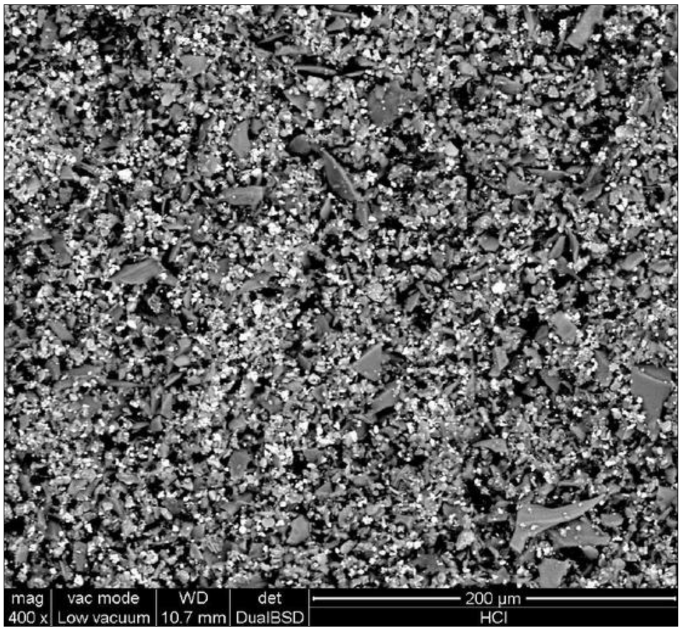


Image 114: HC solid fraction of HCl extraction ESEM zoom 400x.

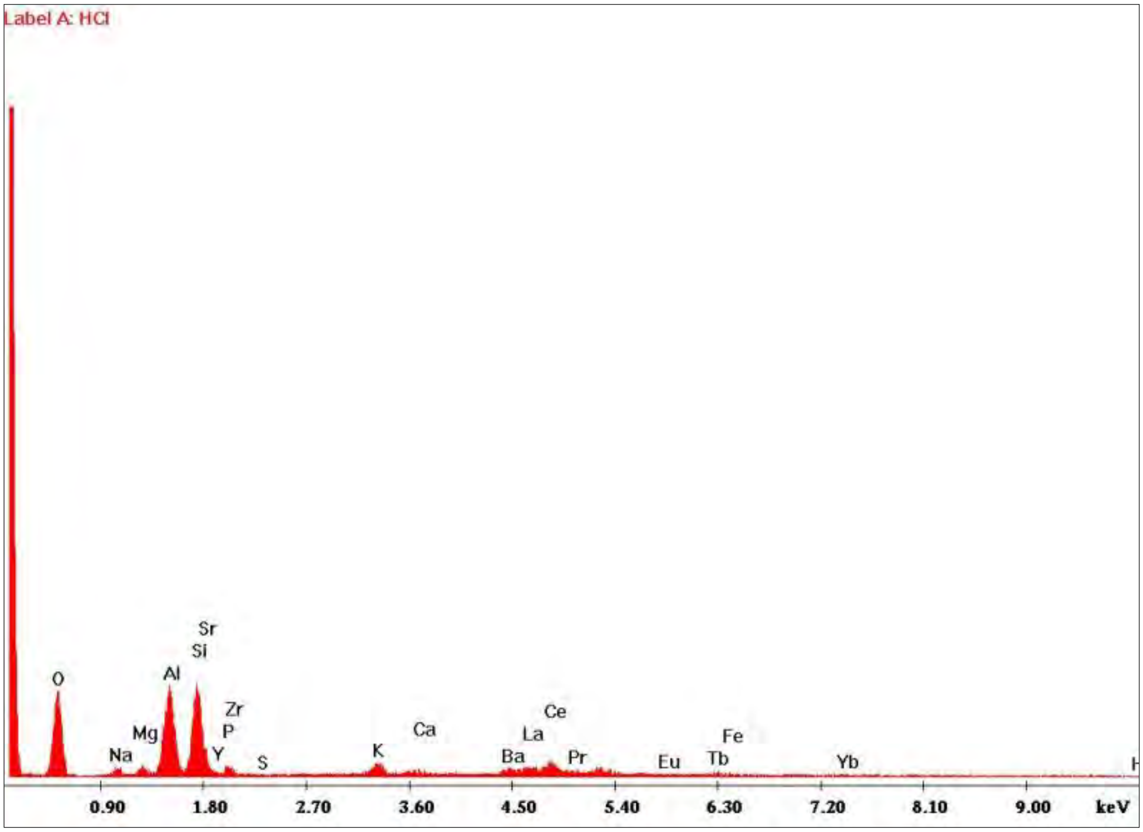


Image 115: HC solid fraction of HCL extraction ESEM fluorescence analysis.

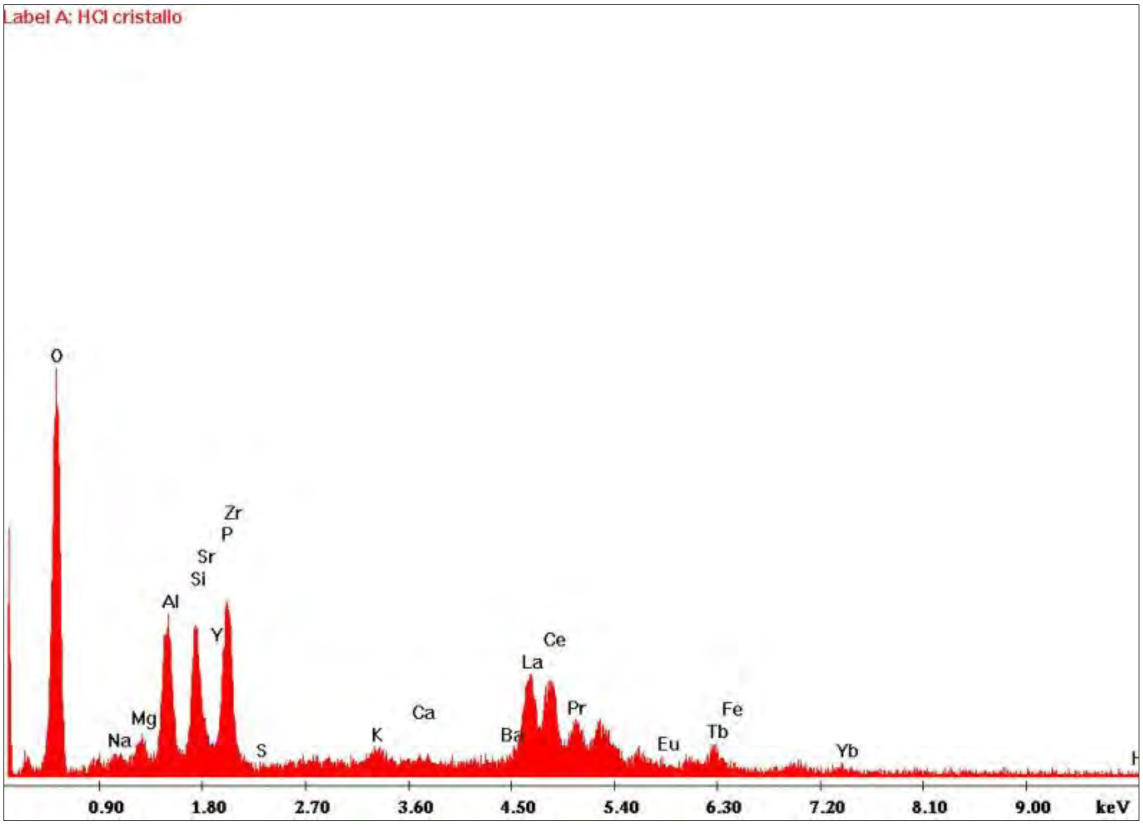


Image 116: HCl crystal ESEM fluorescence analysis.

Table 15: HC solid fraction of the HCl extraction ESEM atomic percentage

elements	L1	HCl solid
O	54.45	48.03
Na	2.42	2.41
Mg	2.05	2.04
Al	9.08	17.2
Si	8.4	16.01
Sr	1.85	0.94
Y	7.04	0.32
P	1.7	1.65
Zr	0.42	0.18
S	0.53	0.34
K	1.48	1.82
Ca	2.45	0.68
Ba	1.01	1.24
La	1.22	1.82
Ce	1.19	2.03
Pr	0.43	0.14
Eu	0.96	0.38
Tb	0.95	1.04
Fe	0.84	0.36
Yb	0.81	0.42
Hg	0.72	0.94

HCl: Hydrochloric acid is a strong acid.

- *Silicon:* not extracted
- *REEs:* in general are extracted and remain in solution, the percentage of recovery over 50% are calculated for yttrium, europium, praseodymium and ytterbium.
- *Calcium*: extracted

The result of this experiment shows as a washing procedure with HCl can be positive for a selective recovery of europium and yttrium respect other lanthanides.

5.4.2.2 Mixture of acids extraction

5.4.2.2.1 Aqua Regis

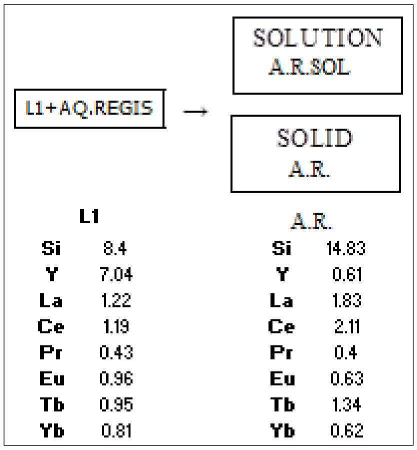
A test of extraction with Aqua Regis is tried. Firstly the mixture of acid is prepared: in a bottle are mixed 90mL of Hydrochloric acid and 30mL of Nitric acid. The solution is left reacting: the color passes from a light yellow tint to a red ones.

Image 117: The changing in color in the Aqua Regis reaction.

1 gram of the sample just sieved, named L1, is put in a flask with 10mL of Aqua Regis, for a solid/liquid ratio of 1/10. The flask is disposed on a magnetic stirrer with a speed of about 500 RPM, the room temperature is chosen and the solution is left react for 24 hours and it is filtered. The solid fraction is weighted 0.3169 g.

Image 118: Aqua Regis extraction.

ESEM Analysis



	L1		A.R.
Si	8.4	**Si**	14.83
Y	7.04	**Y**	0.61
La	1.22	**La**	1.83
Ce	1.19	**Ce**	2.11
Pr	0.43	**Pr**	0.4
Eu	0.96	**Eu**	0.63
Tb	0.95	**Tb**	1.34
Yb	0.81	**Yb**	0.62

Image 119: Aqua Regis extraction procedure scheme

Solid fraction of the Aqua Regis extraction A.R.

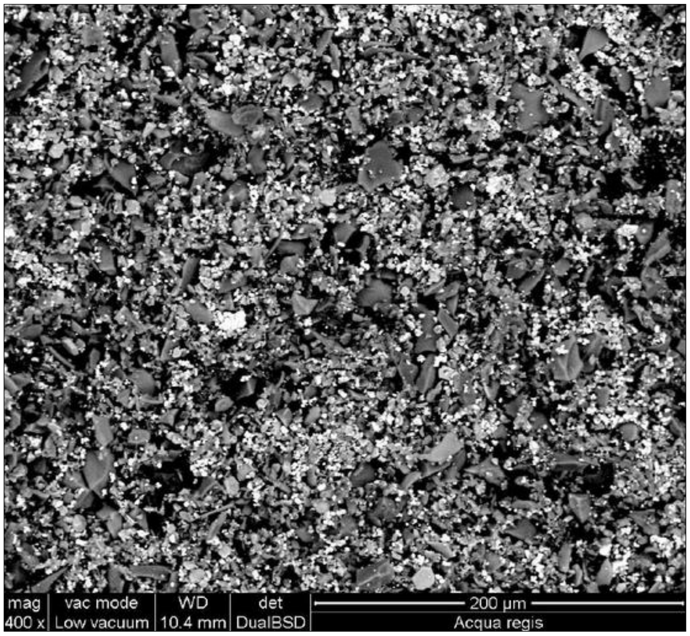


Image 120: A.R. solid fraction of the extraction with Aqua Regis ESEM zoom 400x.

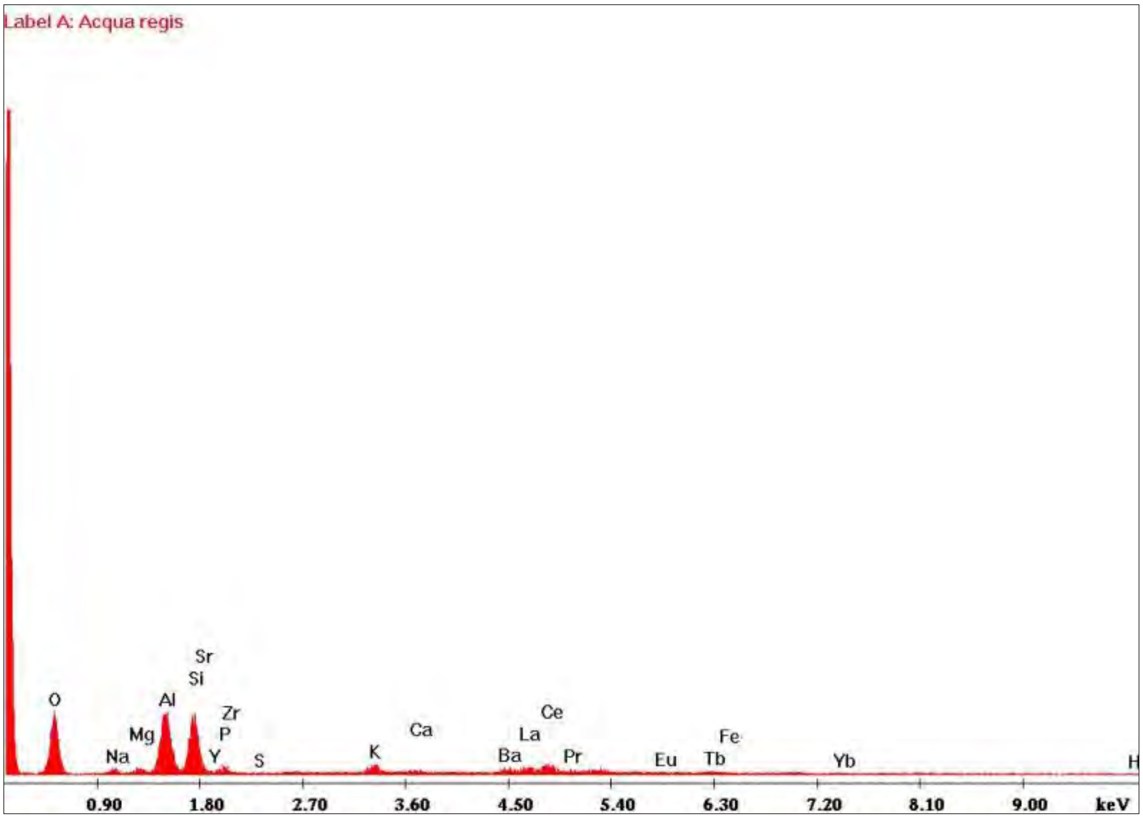


Image 121: A.R. solid fraction of the extraction with Aqua Regis ESEM fluorescence analysis.

Table 16: Aqua Regis extraction solid fraction ESEM atomic percentage

element	L1	A.R. solid
O	54.45	47.58
Na	2.42	2.23
Mg	2.05	1.97
Al	9.08	17.4
Si	8.4	14.83
Sr	1.85	0.77
Y	7.04	0.61
P	1.7	1.06
Zr	0.42	0.44
S	0.53	0.37
K	1.48	2.08
Ca	2.45	0.93
Ba	1.01	1.57
La	1.22	1.83
Ce	1.19	2.11
Pr	0.43	0.4
Eu	0.96	0.63
Tb	0.95	1.34
Fe	0.84	0.45
Yb	0.81	0.62
Hg	0.72	0.79

AQ. REGIS: it is a mixture of acid 3 part of hydrochloric acid and one of nitric acid.

- *Silicon* not extracted
- *REEs:* in general are extracted and remain in solution, the percentage of recovery over 50% are calculated for yttrium, europium, praseodymium and ytterbium.
- *Calcium:* extracted

From analysis of the result is hypnotized that the advantages of this reaction are due to the presence of hydrochloric acid.

5.4.2.3 Sequence of acids extraction

5.4.2.3.1 Sulfuric extraction + Hydrofluoric extraction

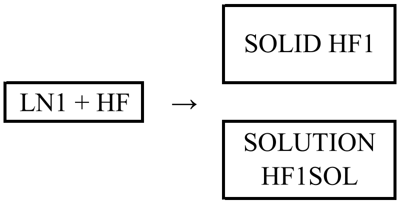


Image 122: Sulfuric + hydrofluoric extraction procedure

The sample filtrated from the H_2SO_4 performed reaction (LN1) weights 2.3560g. Two fractions are prepared: the first 1.1876g of LN1, the second 1.1684g of LN1, both are put in a flask and filled with 50mL of HF 40% (concentrated, maximum concentration allowed to prevent toxicological dangerous effects). Both the solutions are placed on a magnetic stirrer (no heat, 500 rpm of speed) inserted inside a crystallizer filled with ice and water because the reaction in exothermic. The first solution is make react for one week, the second ones for 24 hours. After the filtration the results of the first test are named HF1 and HF1SOL, for the second ones HF2 and HF2SOL. The HF1 and HF2 can directly be detected with ESEM; instead the solutions HF1SOL and HF2SOL must be dried.

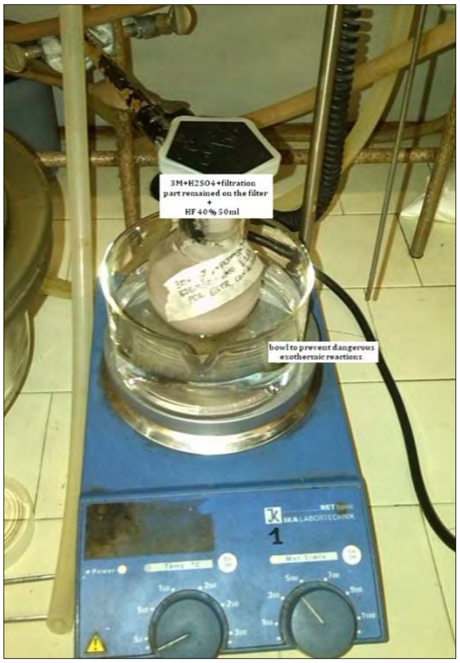


Image 123: Extraction procedure on LN1 with the addition of Hydrofluoric acid.

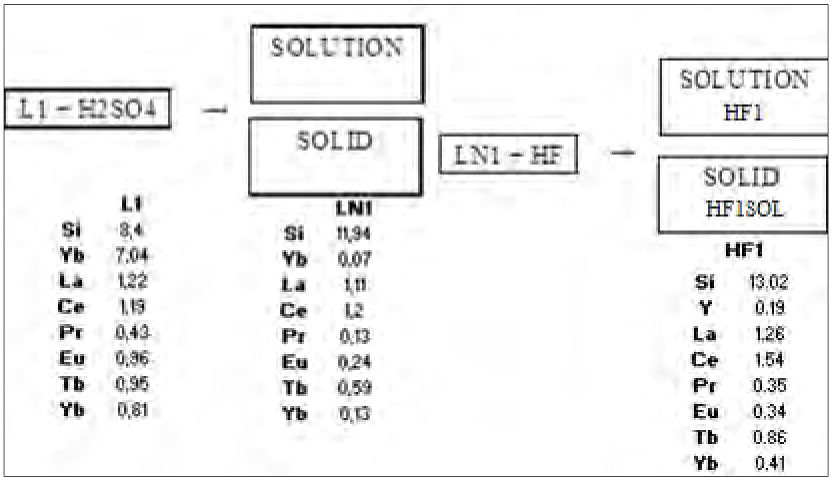
ESEM Analysis

a. The result of the ESEM analysis for the sample HF1:

COMPOSITION: the sample 3M is sieved and put in a solution of H2SO4. The solution is filtered and the solid fraction is put in solution with 50mL of HF (40%). The solution is left reacting for one week in a crystallizer with some ice cubes because the reaction is exothermic., then filtered. The solid fraction weighted 1.9663g.

Solid: HF1

Image124: HF1 sample.



	L1
Si	8,4
Yb	7,04
La	1,22
Ce	1,19
Pr	0,43
Eu	0,96
Tb	0,95
Yb	0,81

	LN1
Si	11,94
Yb	0,07
La	1,11
Ce	1,2
Pr	0,13
Eu	0,24
Tb	0,59
Yb	0,13

	HF1
Si	13.02
Y	0.19
La	1.26
Ce	1.54
Pr	0.35
Eu	0.34
Tb	0.86
Yb	0.41

Image 125: H_2SO_4+HF extraction procedure scheme

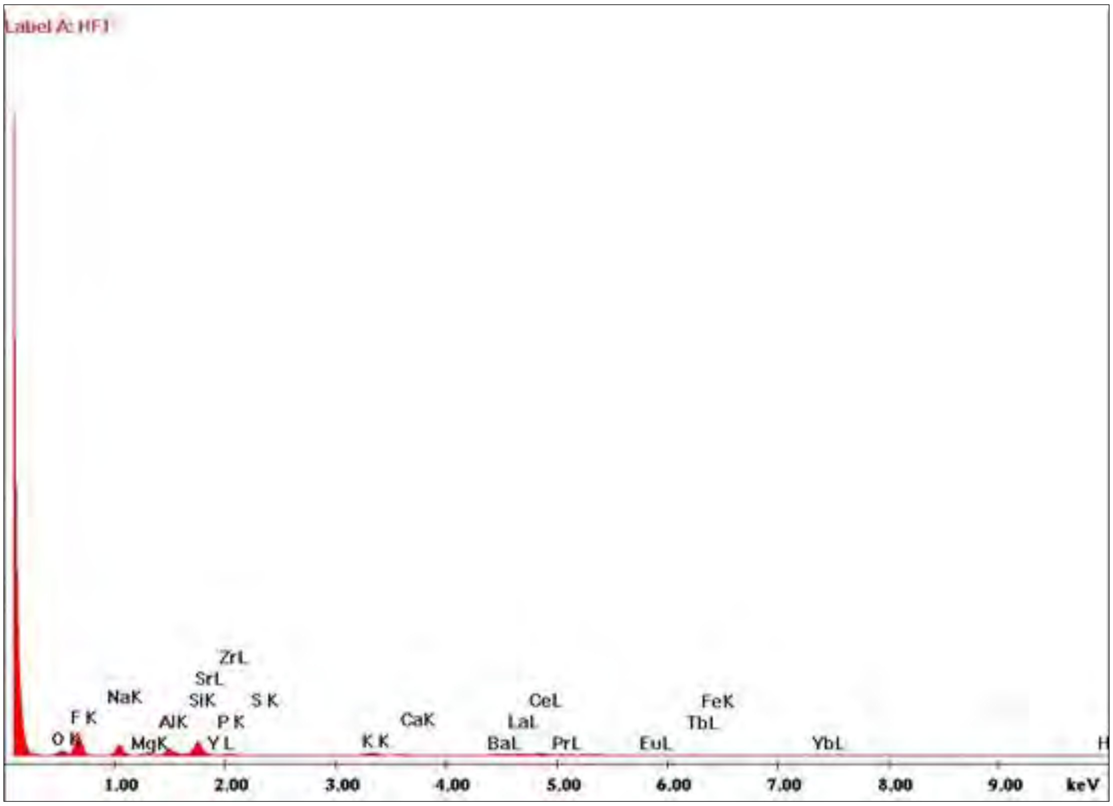


Image126: HF1 ESEM fluorescence analysis.

Solution: HF1SOL

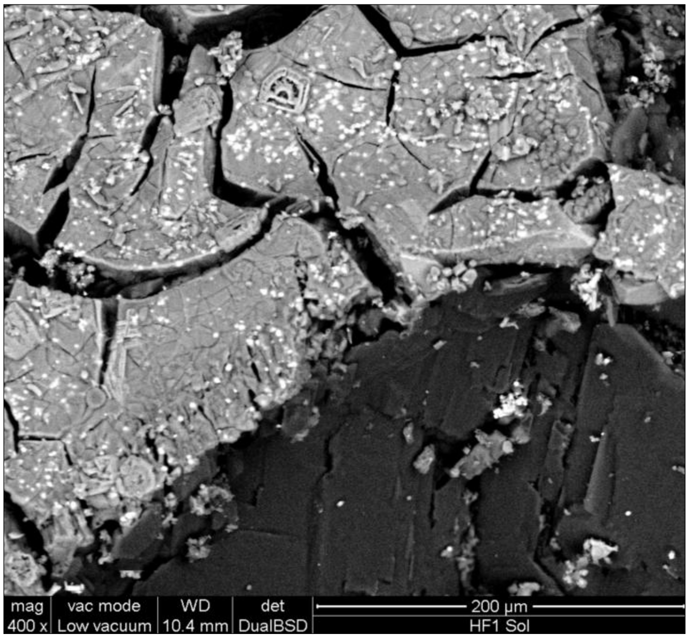


Image127: HF1SOL ESEM zoom 400x.

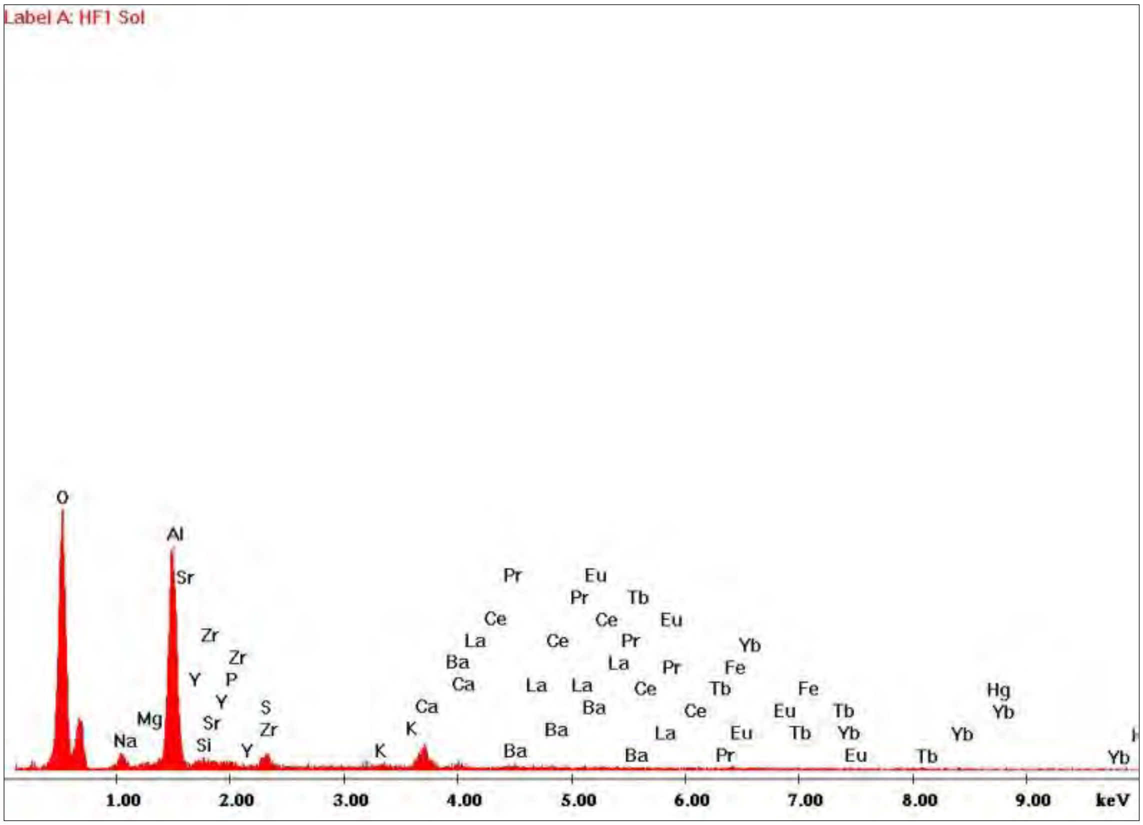


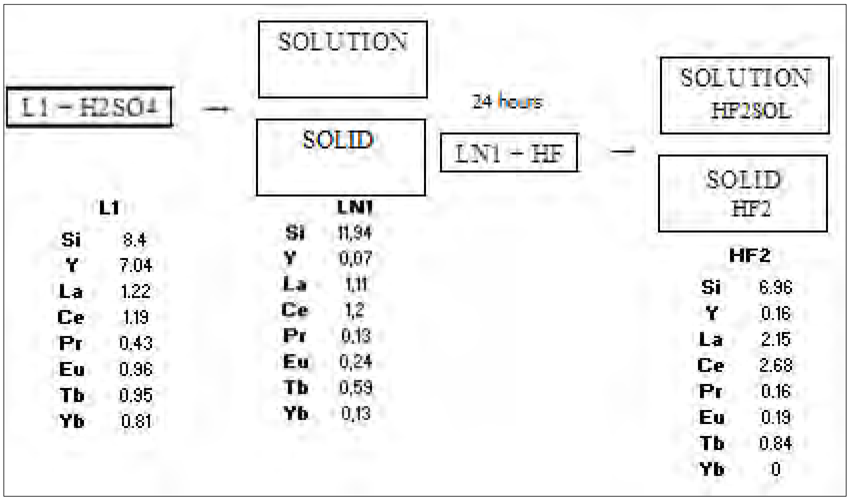
Image128: HF1SOL ESEM fluorescence analysis.

b. The result of the ESEM analysis for the first filtration of the sample HF2:

COMPOSITION: the sample 3M is sieved and put in a solution of H_2SO_4. The solution is filtered and the solid fraction is put in solution with 50mL of HF (40%). The solution is left reacting for only 24h in a crystallizer with some ice cubes because the reaction is exothermic. The solid fraction weighted 1.2474g and it is analyzed directly with ESEM, the solution is left drying under the fume hood.

Solid: HF2

Image 129: HF2 sample



L1	
Si	8.4
Y	7.04
La	1.22
Ce	1.19
Pr	0.43
Eu	0.96
Tb	0.95
Yb	0.81

LN1	
Si	11,94
Y	0,07
La	1,11
Ce	1,2
Pr	0,13
Eu	0,24
Tb	0,59
Yb	0,13

HF2	
Si	6.96
Y	0.16
La	2.15
Ce	2.68
Pr	0.16
Eu	0.19
Tb	0.84
Yb	0

Image 130: H2SO4+HF 24 hours extraction procedure scheme

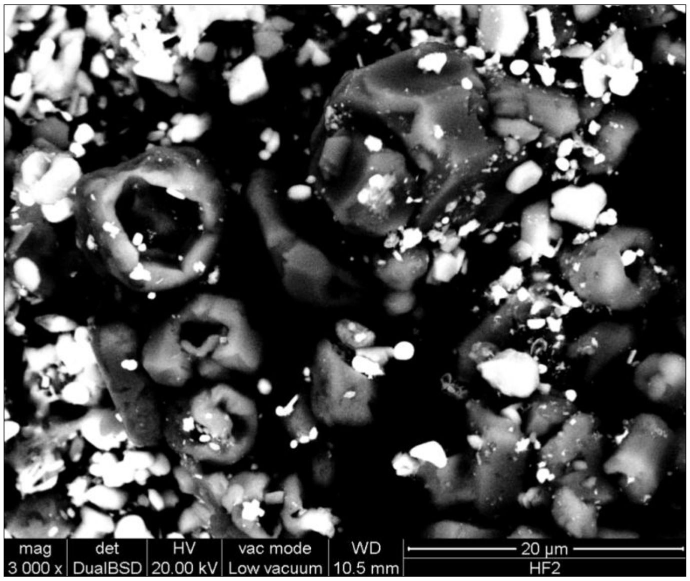


Image131: HF2 ESEM zoom 400x.

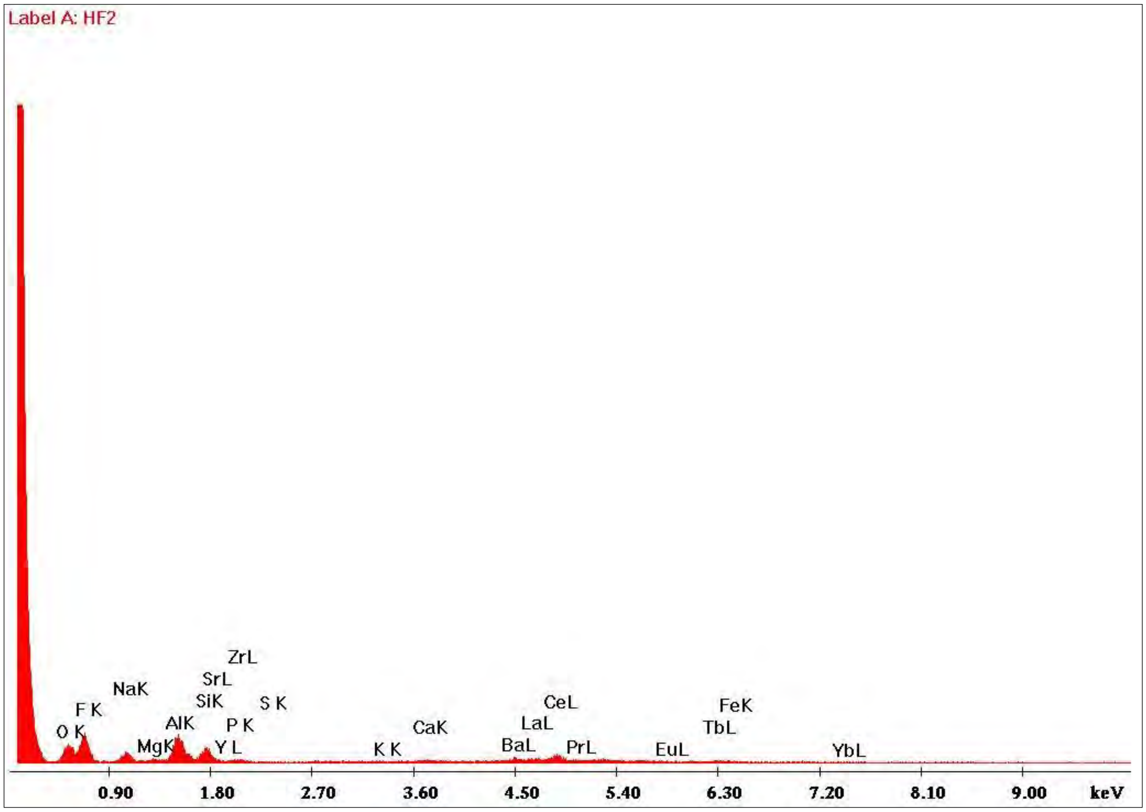


Image132: HF2 ESEM fluorescence analysis.

Solution: HF2SOL

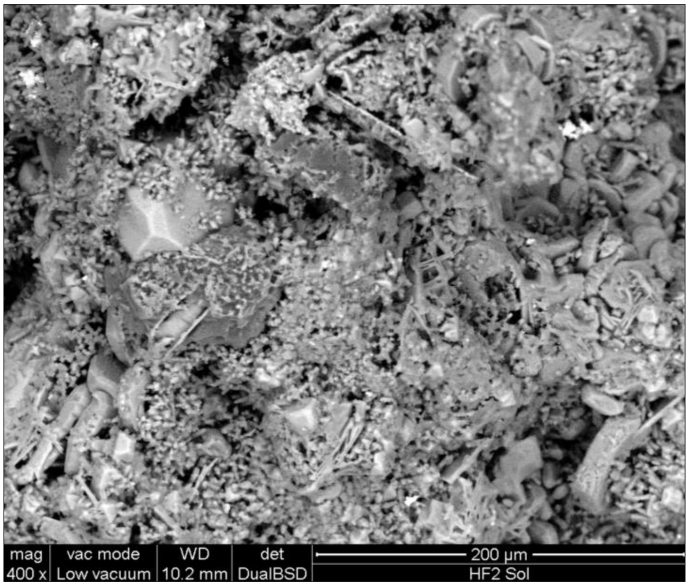


Image133: HF2SOL ESEM zoom 400x.

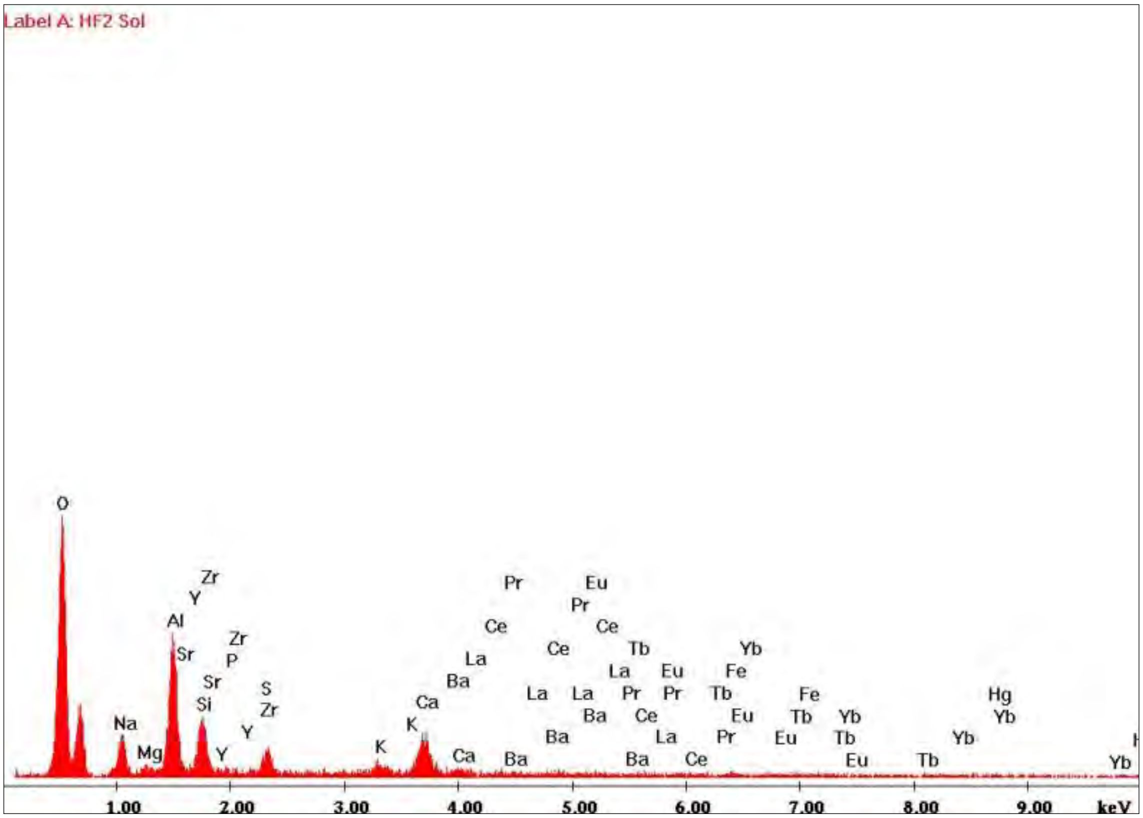


Image134: HF2SOL ESEM fluorescence analysis.

Table 17: HF1 HF2 ESEM atomic percentage

elements	L1	LN1	HF1	HF1 sol	HF2	HF2 sol
O	54.45	55.88	15.98	70.55	26.03	69.63
F	/	/	34.57	/	26.81	/
Na	2.42	1.46	16.22	2.25	9.66	5.37
Mg	2.05	1.21	1.49	0.43	2.58	0.7
Al	9.08	11.53	6.96	20.89	13.64	11.05
Si	8.4	11.01	13.02	0.39	6.96	4.43
Sr	1.85	0.77	0.94	0.23	2.04	0.22
Y	7.04	0.74	0.19	0.11	0.16	0.31
P	1.7	0.63	0.67	0.38	0.96	0.07
Zr	0.42	0.38	0.55	0	0.91	0.1
S	0.53	3.12	0.37	0.91	0.36	1.74
K	1.48	1.46	1.82	0.17	0.23	0.94
Ca	2.45	5.3	0.23	1.83	1.14	3.1
Ba	1.01	1.2	1.11	0.31	1.89	0.23
La	1.22	1.01	1.26	0.11	2.15	0.13
Ce	1.19	1.36	1.54	0.1	2.68	0.23
Pr	0.43	0.28	0.35	0.12	0.16	0.19
Eu	0.96	0.3	0.34	0.11	0.19	0.22
Tb	0.95	0.67	0.86	0.08	0.84	0
Fe	0.84	0.48	0.48	0.39	0.62	0.44
Yb	0.81	0.27	0.41	0.24	0	0.22
Hg	0.72	0.94	0.67	0.41	0	0.67

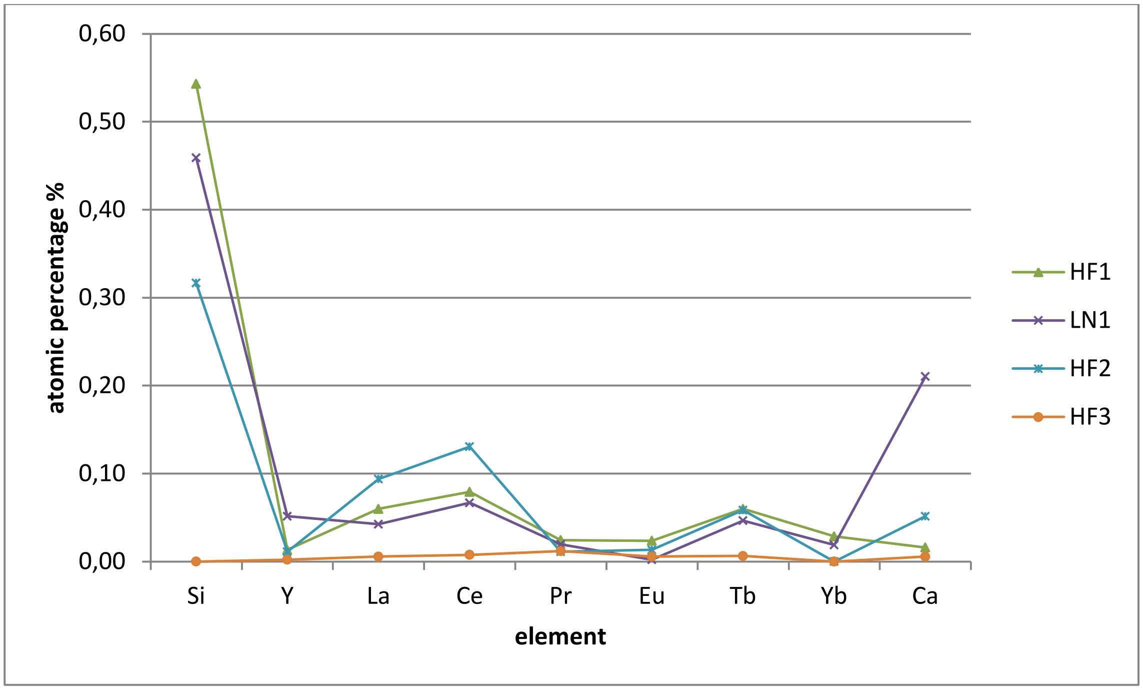


Image 135: Results comparison with hydrofluoric acid

HF1 VS HF1 SOL: terbium, praseodymium, cerium and lanthanum are not extracted, there is a slight selection of yttrium and europium in the extraction. The relevant fraction is not extracted.

HF2 VS HF2 SOL: as the previous experiment result

HF1 VS HF2: this two experiments has a different reaction time: 24 hours or a week. No relevant differences are noticed. The experiment is performed on the solid fraction of the sulfuric acid reaction because from the ESEM analysis small white particles are noticed in the sample (residues of H2SO4 extraction). The experiment gives no satisfaction.

No interesting result is achieved by changing the time reaction in the sulfuric plus hydrofluoric extractions. Respect a single sulfuric extraction a sequence does not shows advantages in the remove of silicon and calcium, neither in the percentage of REEs left in solution.

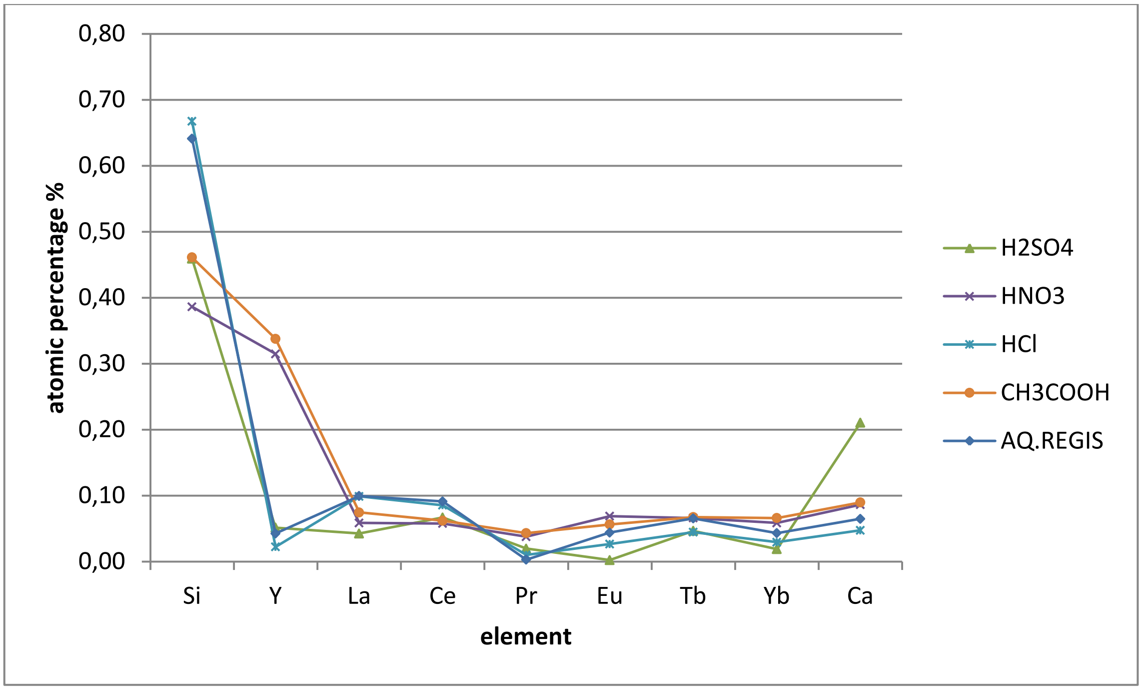
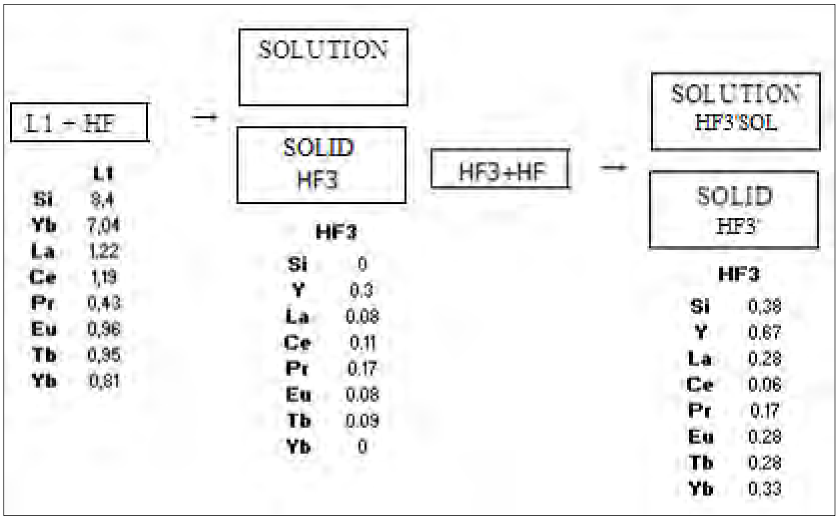


Image 136: Summary acid extractions comparison

5.4.2.3.2 Double hydrofluoric extraction

1g of the solid sample HF3 is selected and 25m L of HF (>40%) are added. The solution is putted on the stirrer with a anchor with a medium velocity. The flask is put inside a decanter full of ice, because it is known that this type of reaction is usually exothermic. After 24 hours it is filtered and two phases result: HF3',as solid readily analyzable (1.0387 g), and HF3'SOL, as solution put drying under the fume hood.

ESEM Analysis



	L1
Si	8,4
Yb	7,04
La	1,22
Ce	1,19
Pr	0,43
Eu	0,96
Tb	0,95
Yb	0,81

	HF3
Si	0
Y	0.3
La	0.08
Ce	0.11
Pr	0.17
Eu	0.08
Tb	0.09
Yb	0

	HF3
Si	0,38
Y	0.67
La	0.28
Ce	0.06
Pr	0.17
Eu	0.28
Tb	0.28
Yb	0.33

Image 137: HF+HF extraction procedure scheme

Solid: HF3’

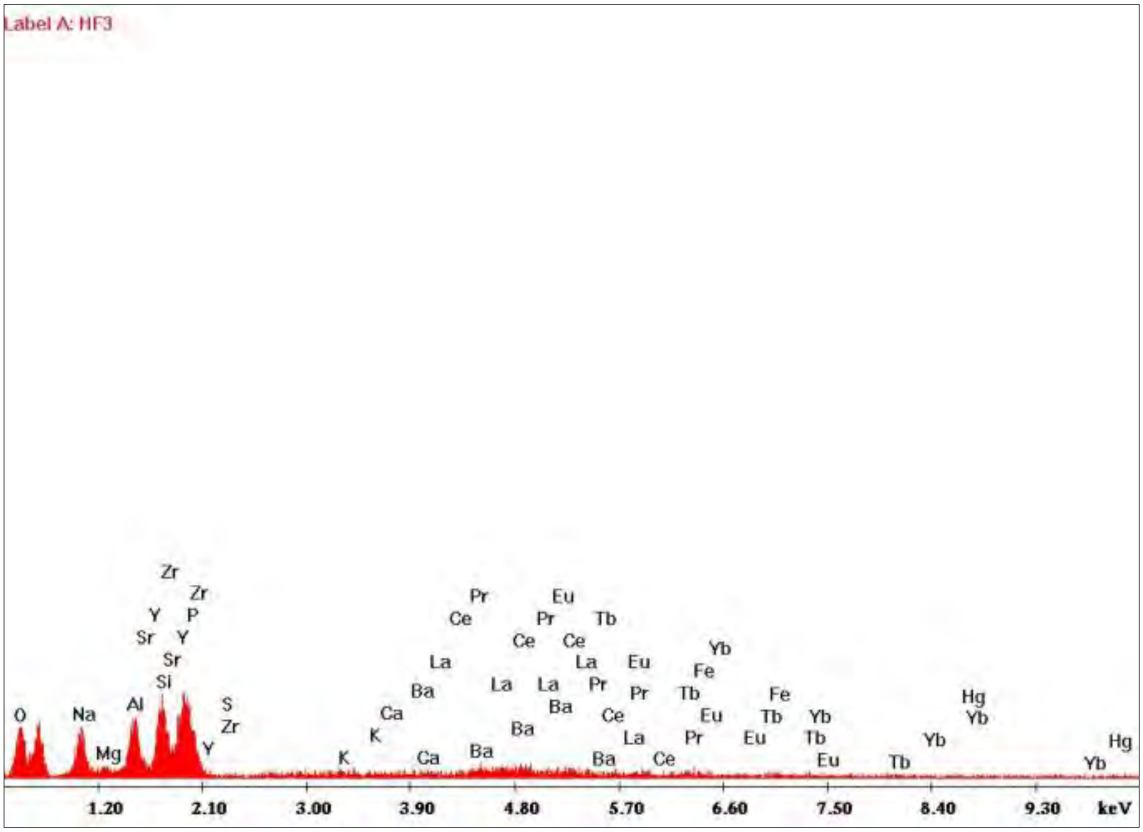


Image138: HF3' ESEM fluorescence analysis.

Solution: HF3’SOL

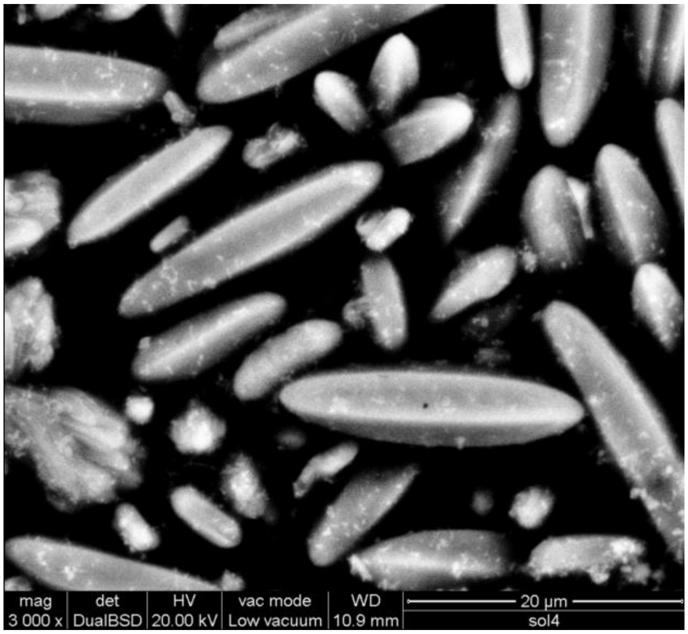


Image139: HF3’SOL ESEM zoom 3000x.

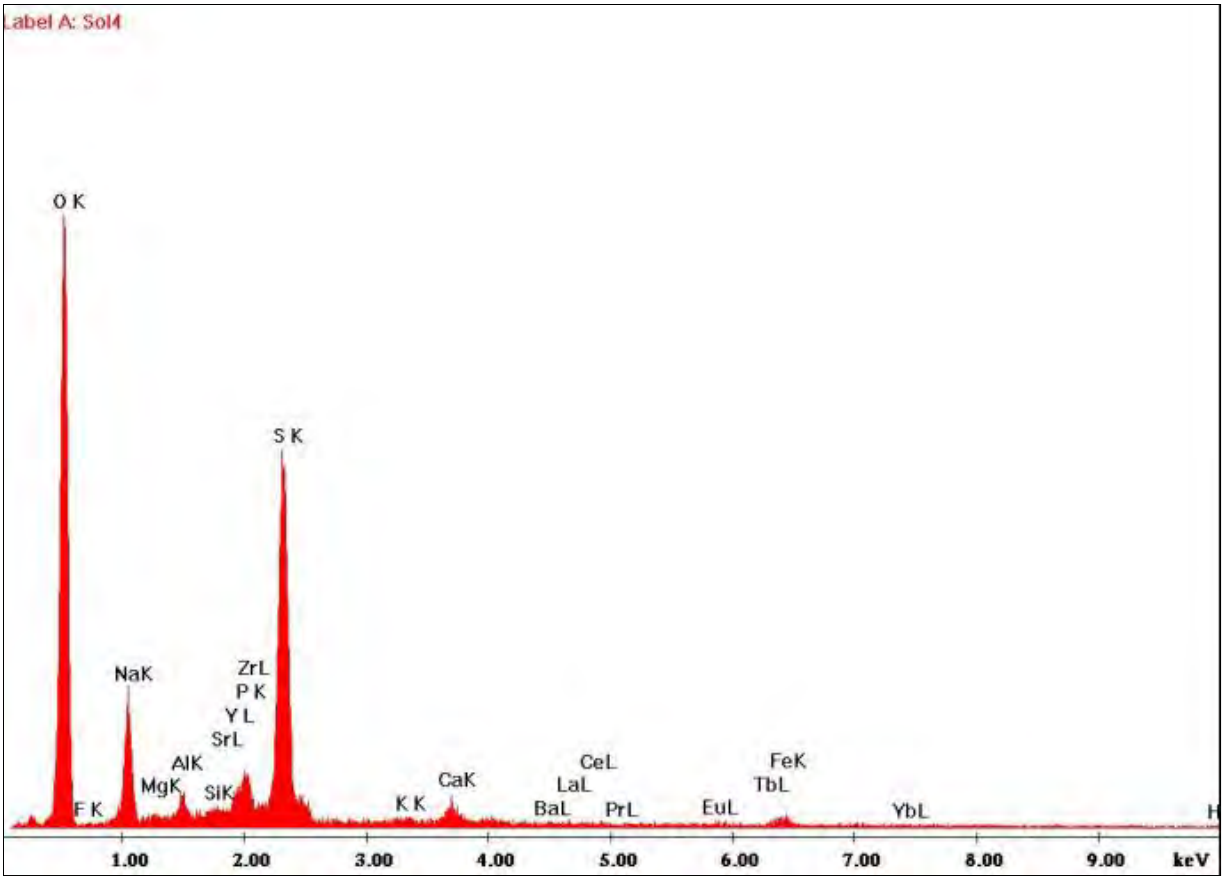


Image140: HF3'SOL ESEM fluorescence analysis.

Table 18: Double HF extraction atomic percentage

elements	L1	HF solid	HF solution	HF3' solid	HF3' solution
O	54.45	82.89	62.92	63.43	34.6
F	/	13.58	/	8.15	/
Na	2.42	0.85	7.04	0.18	1.44
Mg	2.05	0	1.01	0.66	2.52
Al	9.08	0	14.19	22.13	10.83
Si	8.4	0	6.53	0.38	11.12
Sr	1.85	0.26	0.53	0.25	2.12
Y	7.04	0.3	0.86	0.67	9.85
P	1.7	0	0	0.07	1.85
Zr	0.42	0.17	0	0	0.55
K	1.48	0.04	0.26	0.37	1.2
Ca	2.45	0.08	2.2	0.8	0.89
Ba	1.01	0.06	0.44	0.5	1.86
La	1.22	0.08	0.33	0.28	1.99
Ce	1.19	0.11	0.2	0.06	1.44
Pr	0.43	0.17	0.35	0.17	0.58
Eu	0.96	0.08	0.58	0.28	1.48
Tb	0.95	0.09	0.56	0.28	1.79
Fe	0.84	0.06	0.72	0.43	1
Yb	0.81	0	0.58	0.33	1.23
Hg	0.72	0	0.69	0.49	1.08

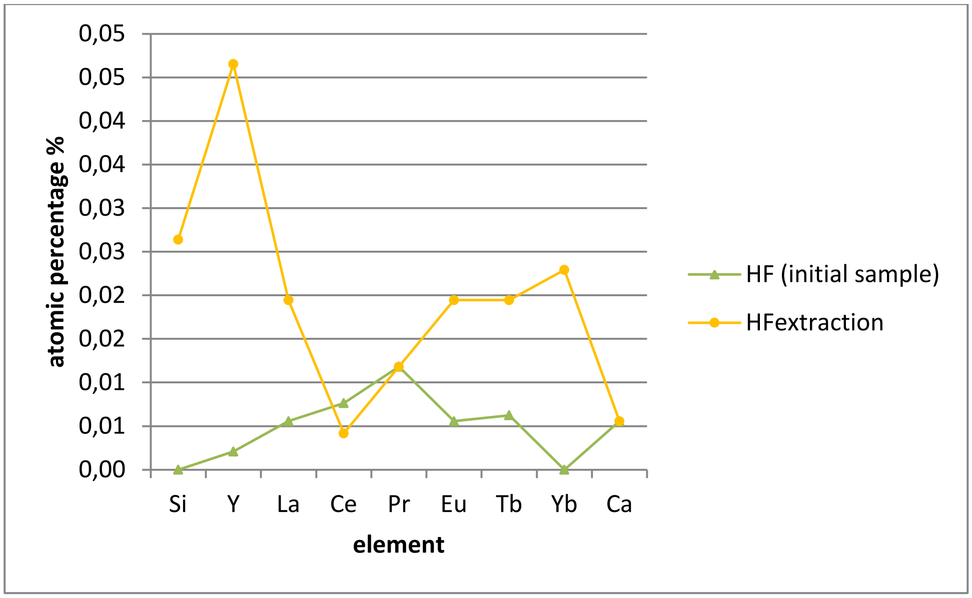


Image 141: Results extraction sequence.

HF3': low percentage of silicon in the solid fraction.

From the previous analysis should be useful to handle the solid residue. A new experiment is setup on the residue by a double extraction with CH3COOH with the purpose to perform a selective extraction of REEs

5.4.2.3.3 Hydrofluoric extraction + double Acetic acid extraction

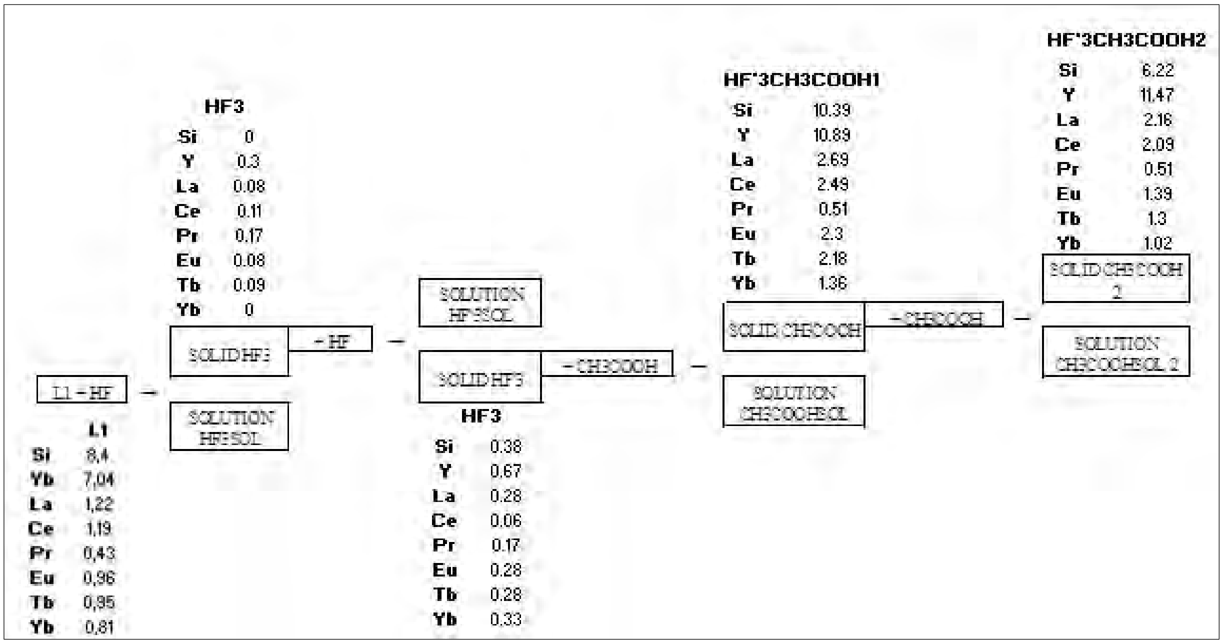


Image 142: Hydrofluoric + double acetic acid extraction scheme

Other extraction is tested on the solid sample that comes from the double hydrofluoric extraction of the previous phase . The solid fraction called previously HF’3 is mixed with 18 mL of CH_3COOH in a quantity of 0.9 g. the time of reaction is 24 hours, the temperature is the room ones and the test is performed on a stirrer with a velocity of about 500-700 rpm. The results are a solid HCH1 (0,551 g) and a HCHSOL1 solution fraction after the performed filtration.

Image 143: Extraction from the solid HF'3 with CH_3COOH.

ESEM HCH1 solid fraction of CH_3COOH extraction on HF3'

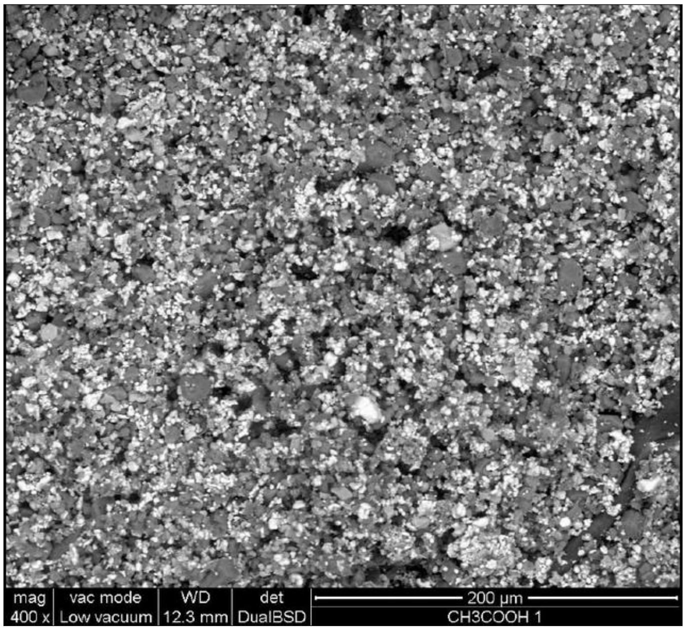


Image 144: HCH1 solid fraction of CH_3COOH extraction ESEM zoom 400x.

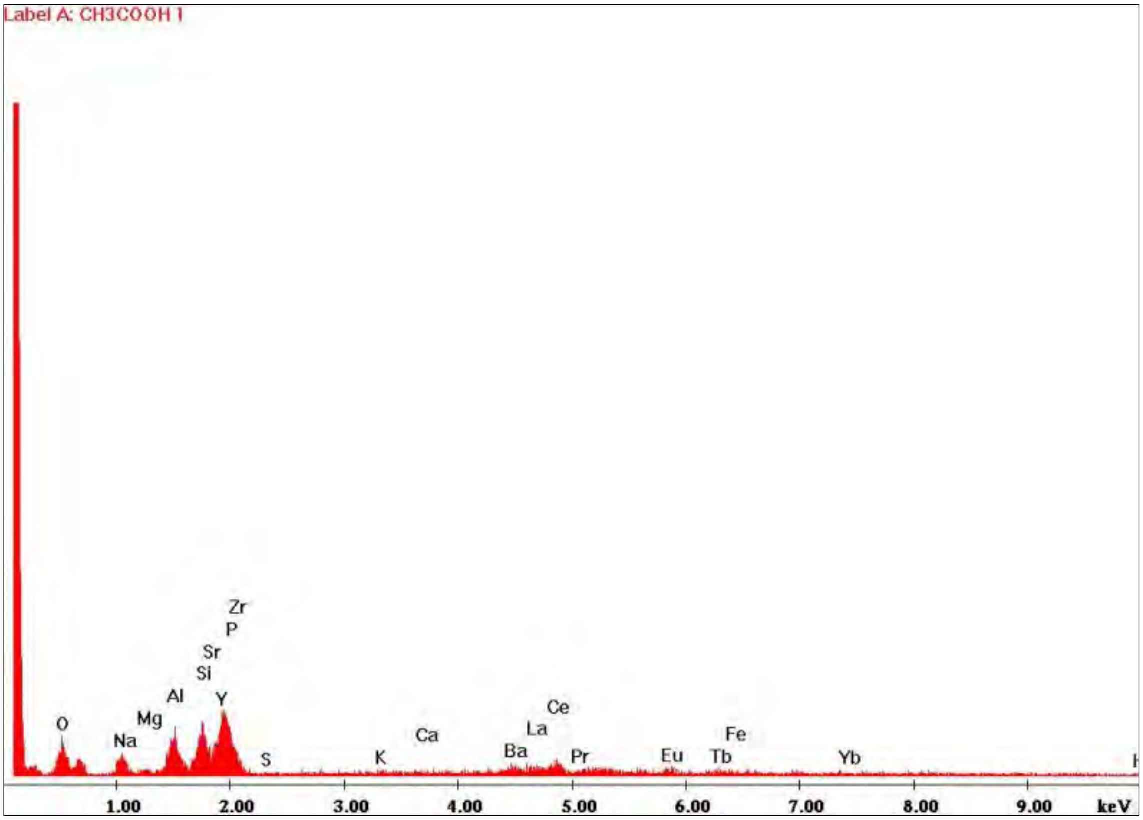


Image 145: HCH1 solid fraction of CH_3COOH extraction ESEM fluorescence analysis.

ESEM HCH2 solid fraction of CH_3COOH extraction on HCH1

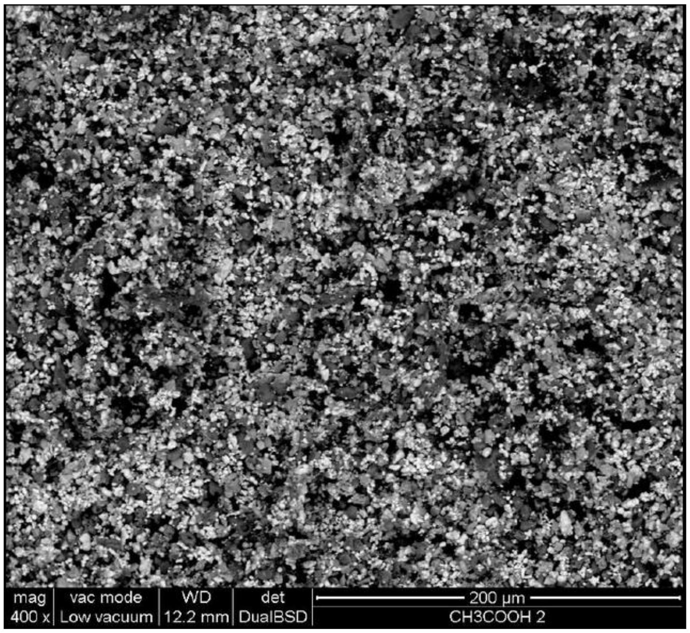


Image 146: : HCH2 solid fraction of CH3COOH extraction on HCH1 ESEM zoom 400x.

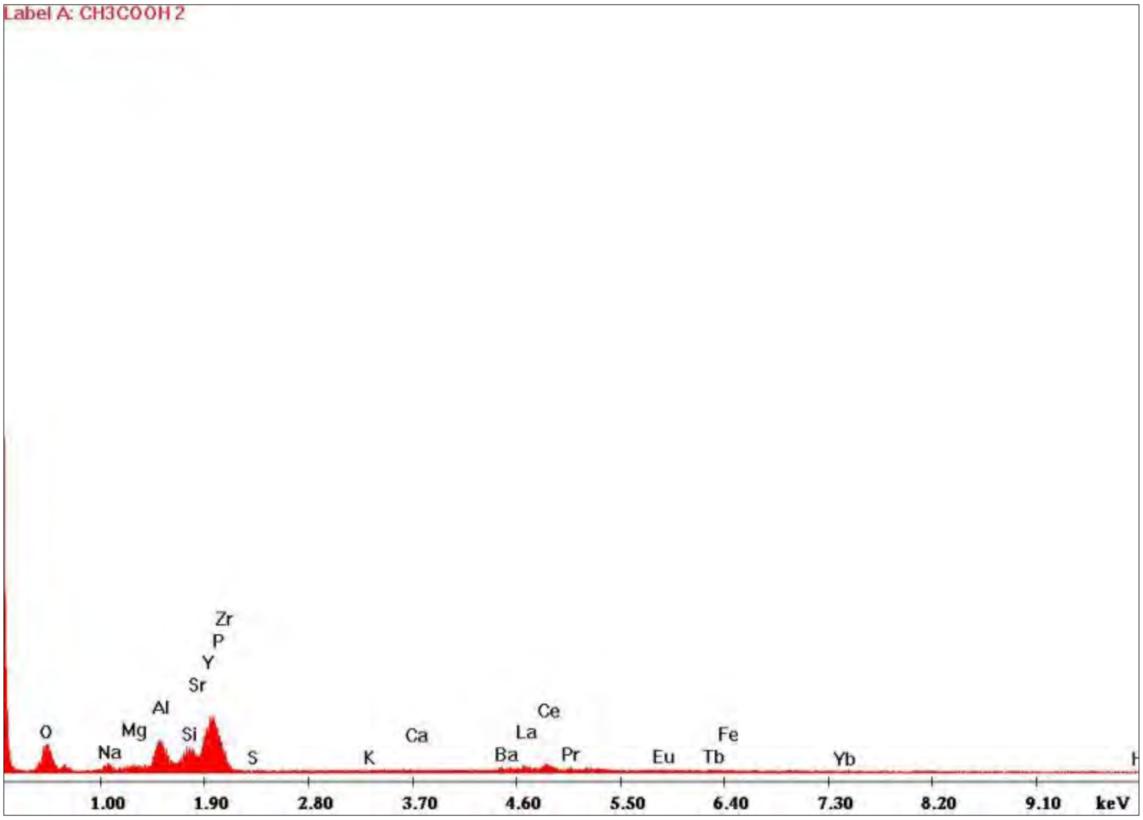


Image 147: HCH2 solid fraction of CH3COOH extraction on HCH1 ESEM fluorescence analysis.

Table 19 Hydrofluoric + double acetic acid extraction ESEM atomic percentage

elements	L1	HF'3CH3COOH1 solid	HF'3CH3COOH2 solid
O	54.45	31.39	40.28
Na	2.42	7.88	4.28
Mg	2.05	2.24	3.07
Al	9.08	11.54	11.72
Si	8.4	10.39	6.22
Sr	1.85	2.7	3.04
Y	7.04	10.89	11.47
P	1.7	3.11	5.38
Zr	0.42	0.54	0.95
K	1.48	1.14	0.91
Ca	2.45	1.14	0.89
Ba	1.01	2.4	1.65
La	1.22	2.69	2.16
Ce	1.19	2.49	2.09
Pr	0.43	0.51	0.51
Eu	0.96	2.3	1.39
Tb	0.95	2.18	1.3
Fe	0.84	1.05	0.92
Yb	0.81	1.36	1.02
Hg	0.72	1.19	0

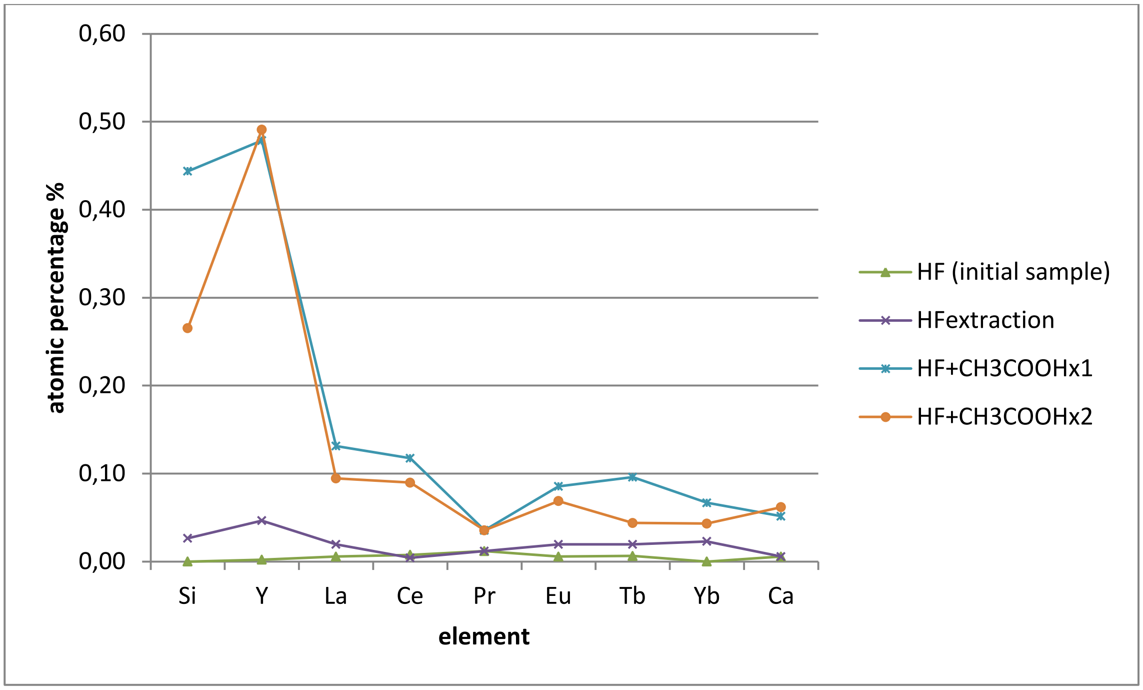


Image 148: Results extraction sequence

- *Silicon*: decrease the concentration in the solid fraction
- *REEs:* increase the concentration in the solid fraction
- *Calcium:* decrease the concentration in the solid fraction

The solid fraction filtered from the solution appears rich of REEs especially the concentration of lanthanum, cerium and terbium enhances of 50%. It is reasonable to consider further test on the solid fraction obtained in order to perform selective extraction for the lanthanides over mentioned.

5.4.3 Summary of selected results of the extraction processes

Table 20: Summary of extraction process where yes means compound extracted, no means compound not settled

Extraction process	Y	Eu	Ce	Yb	Pr	Tb	Si	Ca
Single acid extraction								
H_2SO_4	yes	yes		yes	yes		no	no
HF	yes	yes	yes	yes	yes	yes	yes	yes
HNO_3 (30g/500mL)	yes	no	no	no	no	no	no	yes
HNO_3 (30g/100mL)	no	no	no	no	no	no	no	no
CH_3COOH	no	no	no	no	no	no	no	no
HCl	yes	no	no	yes	yes	no	no	yes
Mixture of acids								
Aqua Regis	yes	no	yes	no	no	no	no	yes
Sequence of acids								
H_2SO_4 + HF	no	no	no	no	no	no	no	yes
HF + HF	no	no	no	no	no	no	no	no
HF + HF + CH_3COOH+ CH_3COOH	no	yes	no	no	no	yes	no	no

5.5 Complex formation process

Yttrium seems to be the most suitable rare earth element to be extracted and results moreover the more abundant in the samples, for these reasons the attention is focuses mainly on this element. It is now necessary to analyze the complex formation of yttrium, in particular to find out the better complex agent to let the element precipitate and be collected. Other studies (Cotton 1972 and Hart 1987) show the compounds that REEs are more likely form:

- Binary compound
- Hydroxides
- Hydrated salt
- Halogen complexes
- Bounds with Oxygen
- Bounds with Nitrogen
- Bounds with Phosphorous

The nature of the precipitated compound depends moreover on the pH of the solution because of the presence of other ions interferences. The presence of calcium ions annoying the precipitation of yttrium oxalate.

A preliminary study is made on the behavior of Y^{3+} and CA^{2+} in solution in presence of oxalic acid, using the software PITMAP (in collaboration with Prof. Di Marco of the Department of chemical science) the diagram of Y^{3+} species distribution are obtained varying the pH value and with an initial concentration of 10^{-2}M in presence of acid oxalate.

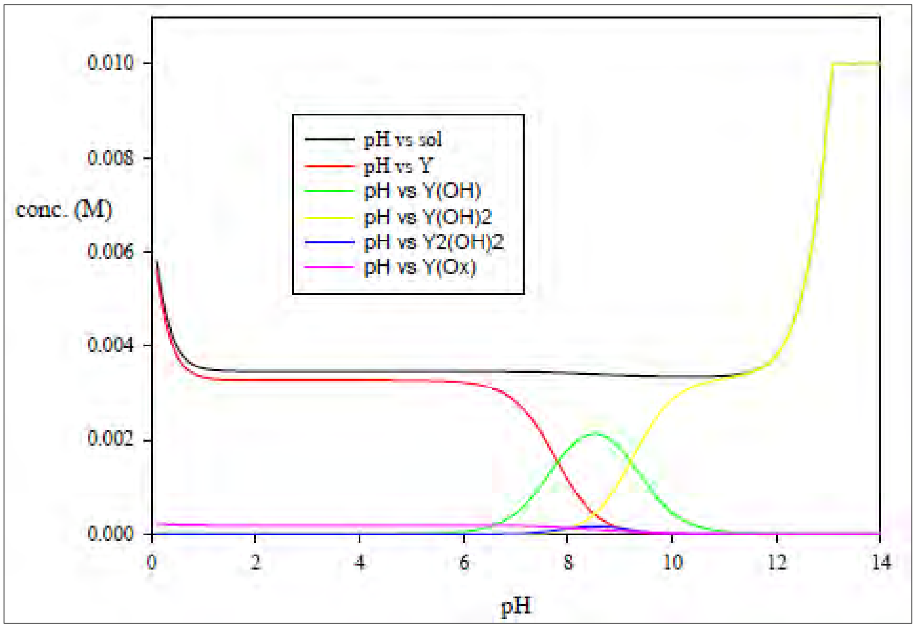


Image 149: Y^{3+} species distribution.

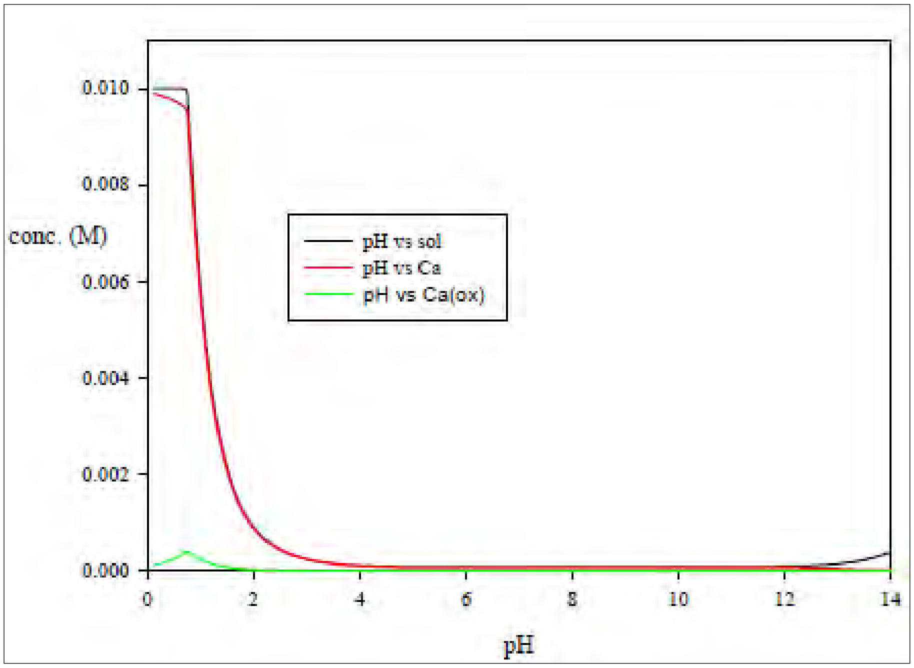


Image 150: Ca^{2+} species distribution.

In case of presence of oxalic acid. at almost all pH values a low soluble salt settles, at pH values higher than 2 no more Ca^{2+} appears in solution.

The study on the pH behavior shows the most suitable values to reach a fractional precipitation of calcium (Ca^{2+}) and the yttrium (Y^{3+}):

- In pure water with a pH range of 7- 12 the Y^{3+} precipitates as hydroxide, the Ca^{2+} remains in solution,
- In water with an addition of Oxalic acid with a pH value lower than 1 Y^{3+} precipitates partially, the Ca^{2+} remains in solution,
- In water with an addition of Oxalic acid with a pH value between 4 - 6 Y^{3+} partially, the Ca^{2+} precipitate completely,

The pH value is thus a definite parameter for the efficiency of the precipitation on Y3+ in presence of oxalic acid different techniques to change pH value are tested on sample 3M because it contains the lower concentration of calcium.

This result does not take in consideration that in the sample analyzed there is the presence of another ion that can annoy the settling of the yttrium (sulfate or phosphate). Different precipitation experiments are carried out and schematized below.

5.5.1 Preliminary results of complex formation on not-sieved sample

The experiment is performed in Pyrex balloons on the solution coming from the extraction processes. On the solution an excess of 40% of the total quantity of yttrium estimated is added. The complex agents used are three carboxylic compound as crystalline solid with purity 99%: Oxalic acid (Merk), Maleic acid (M.A. Sigma-Aldrich) Ethylenediaminetetric acetic acid (EDTA tetra-sodium, Carlo-Erba).

The solution is left reacting for 4 hours on a stirrer (700RPM), after that the pH is increased in two different ways: with a solution of NaOH (Sigma-Aldrich) 6M or with NH3 at 25%. When settling material appears the pH is measured with Litmus test (Macherey-Nagel) and filtered. The solid fraction is dried and analyzed with ESEM.

Precipitation of Y^{3+} from H_2SO_4 with oxalic acid and NH_3

Acid: H_2SO_4 20ml, 2M

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20°C

Reaction time period: 24h

Before starting the experiment a first filtration has been done, the solid residues is mainly formed by CaSO4

After a week the procedure to enhance pH is performed, on the solution fraction, with NH3, and the O.A has been added:

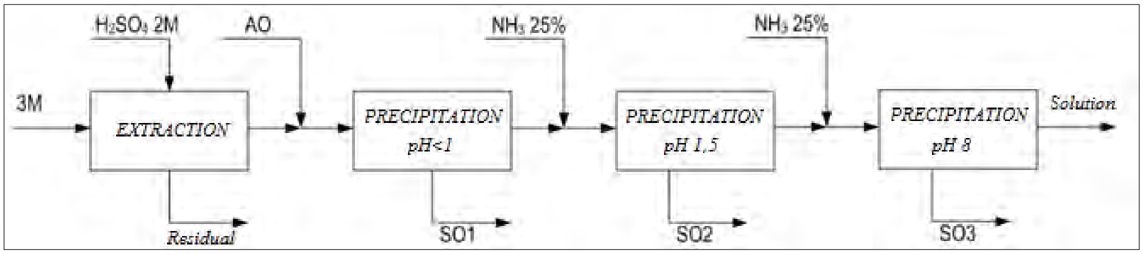


Image151: Scheme of procedure of precipitation with oxalic acid. and NH3.

Results: the analysis is made with FT-IR device, three steps are performed (SO1, SO2, and SO3). All the 3 spectrum are compared with the typical yttrium oxalate given by literature: SO1 is the only results seems to have 3 of the 4 characteristic peaks (3390, 1639, 1321, 800 cm^{-1}) of the spectrum, moreover the other peaks belong to the other salts precipitated in the solution.

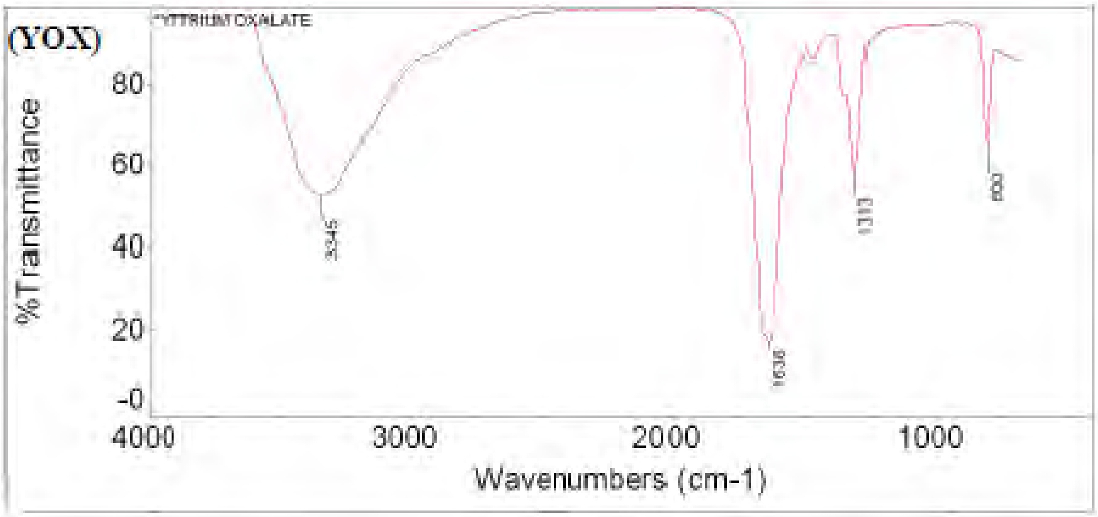


Image152: FT-IR literature yttrium oxalate.

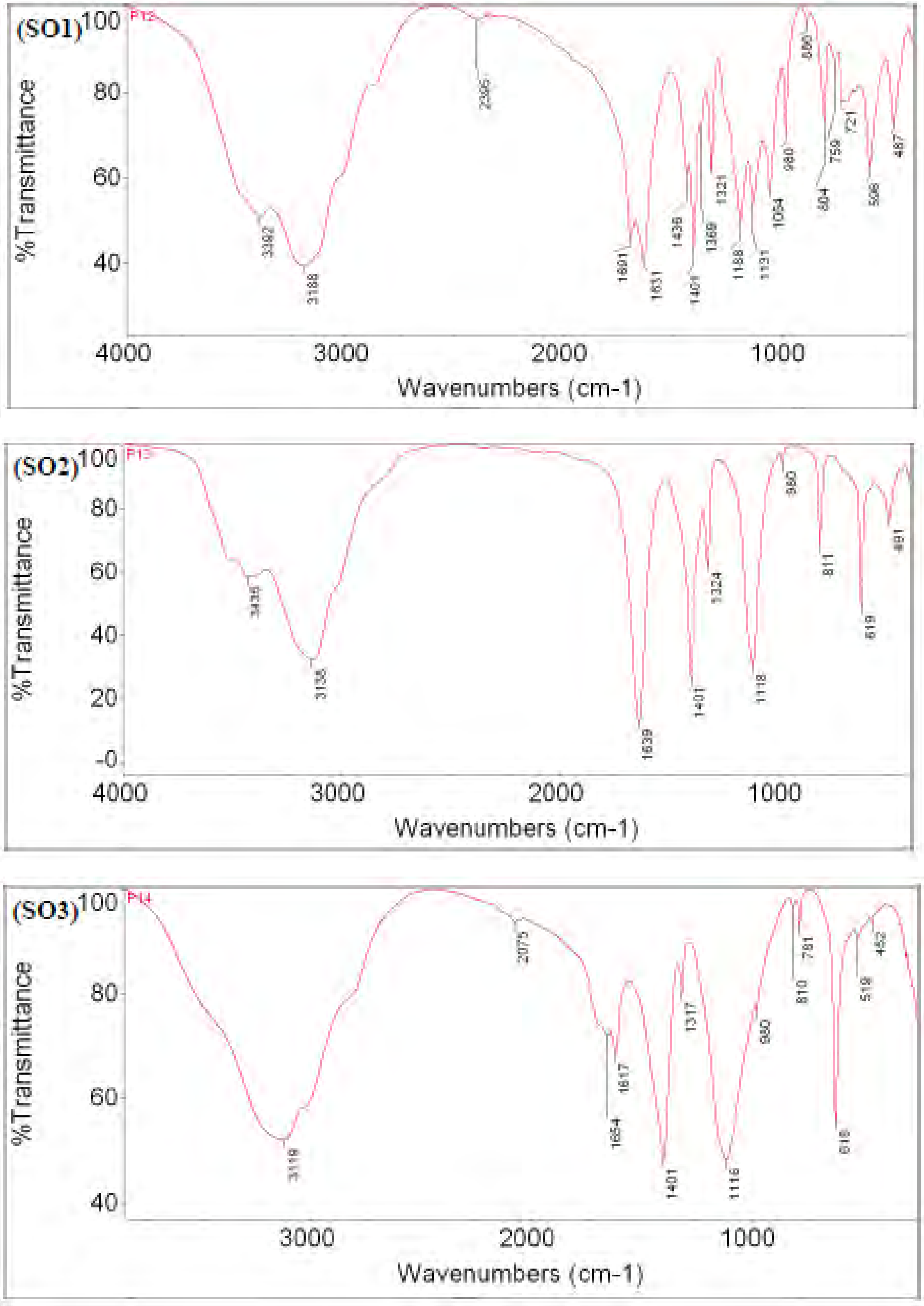


Image153: FT-IR sample SO1 SO2 SO3.

Precipitation of Y_{3+} from H_2SO_4 with oxalic acid and NaOH

Acid: H_2SO_4 20ml, 2M

Sample: 4g of sample 3M

Solid-liquid ratio: 0,2 g/ml

Temperature range: 20°C

Reaction time period: 24h

pH enhanced at 1.5 and 8, with NaOH:

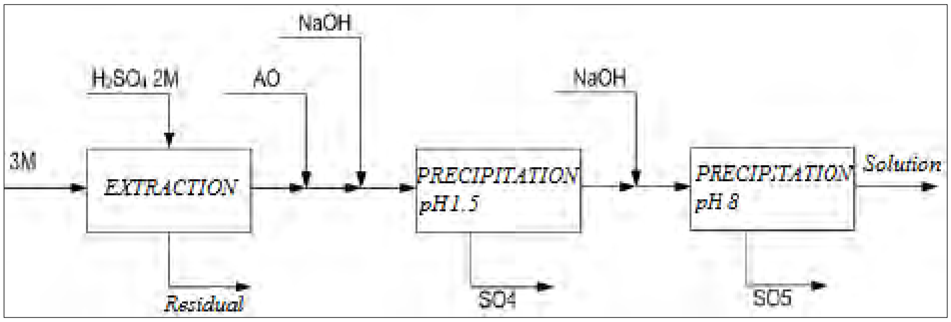


Image154: Scheme of procedure of precipitation with oxalic acid. and NaOH.

Results: two steps are performed (SO4 SO5), the first one shows better fitting with the literature spectrum of yttrium oxalate, moreover by comparing these results with the previous one is clear the absence of a lot of other pecks because in this experiment there are not ammonia salt that can precipitate. SO5 is mainly formed by S and Na because the mayor peaks are the sulfate ones: 1100 and 618 cm^{-1}

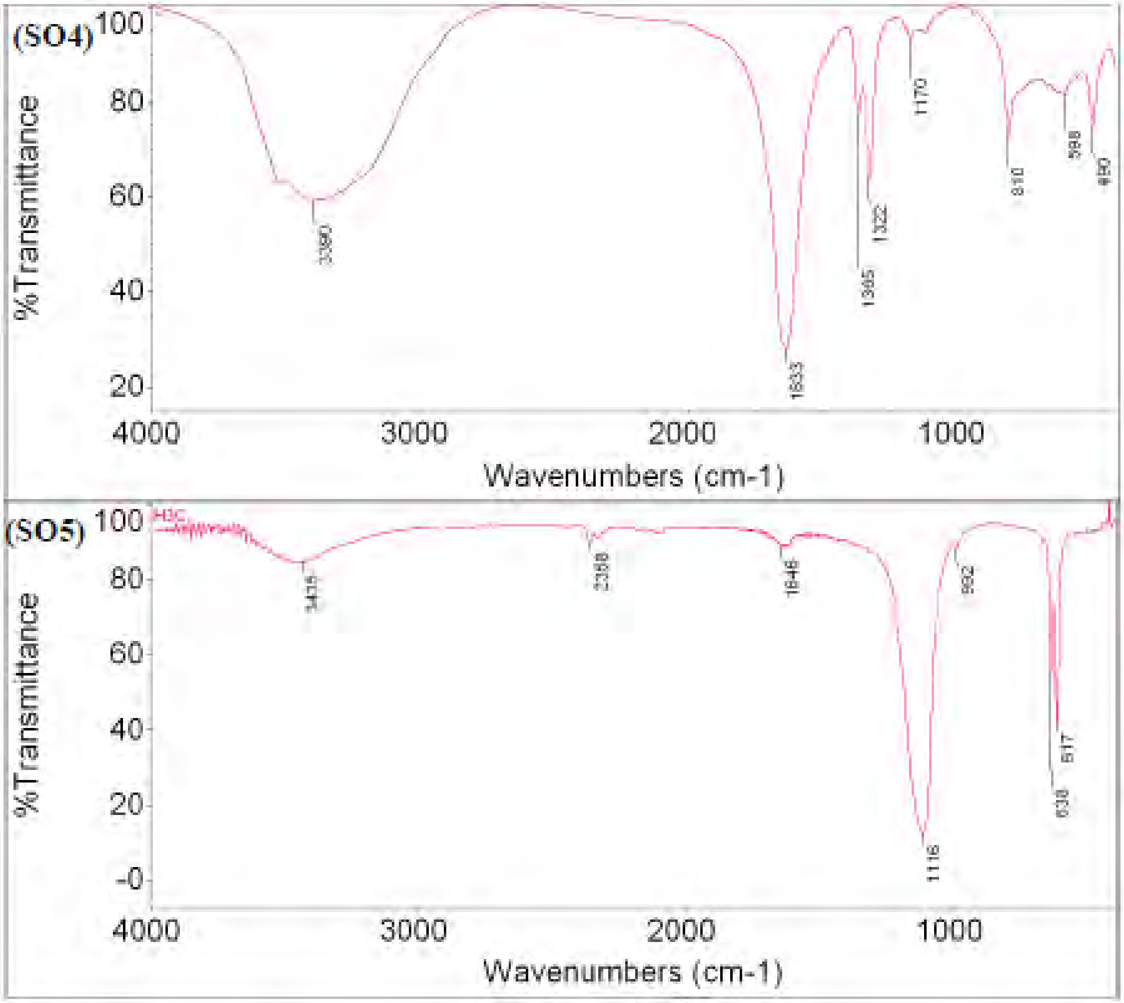


Image155: FT-IR sample SO4 SO5.

Precipitation of Y^{3+} from H_3PO_4 with oxalic acid AND NH_3

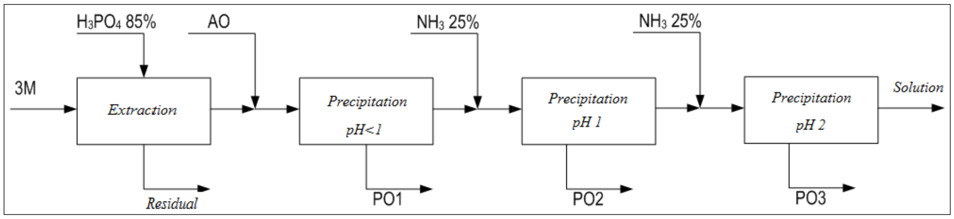


Image156: Scheme of procedure of precipitation with oxalic acid and NH_3.

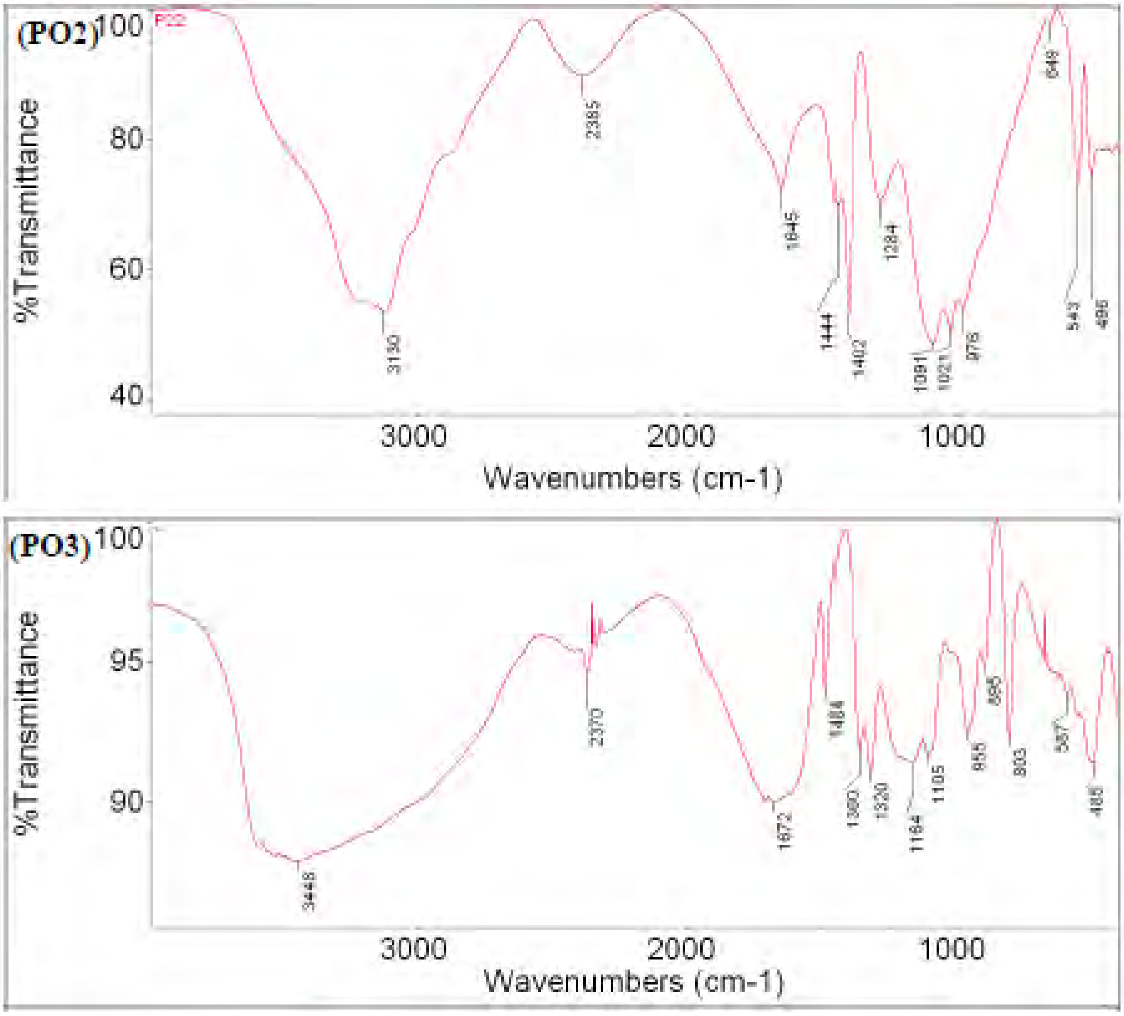


Image157: FT-IR sample PO2 PO3.

Precipitation of Y^{3+} from H_3PO_4 with EDTA and NH_3

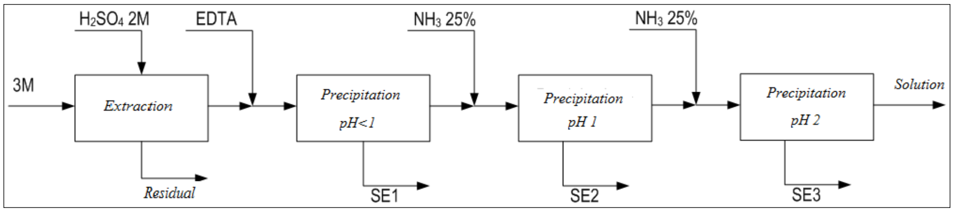


Image 158: Scheme of procedure of precipitation with EDTA and NH3

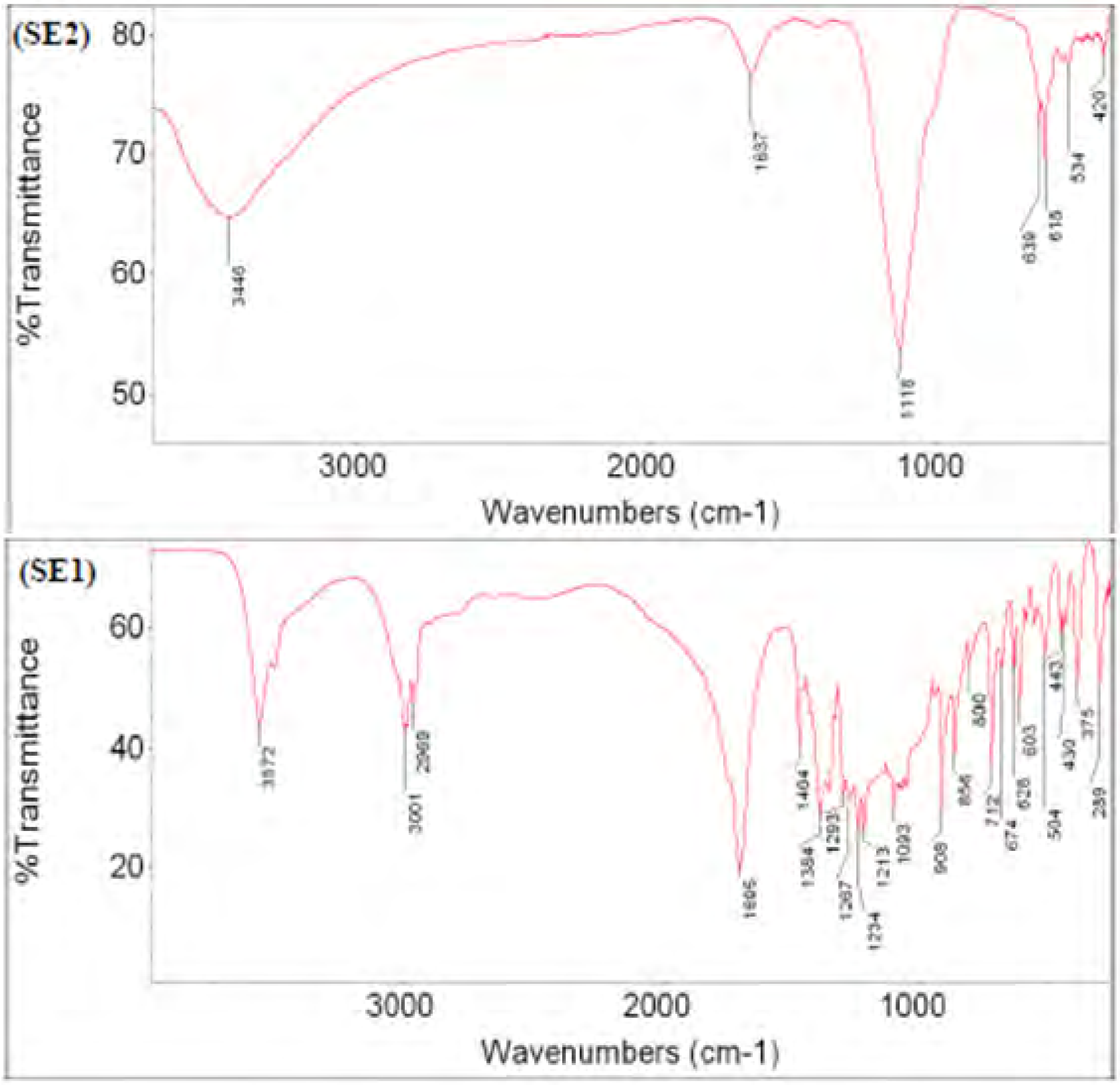


Image 159: FT-IR sample SE1 SE2

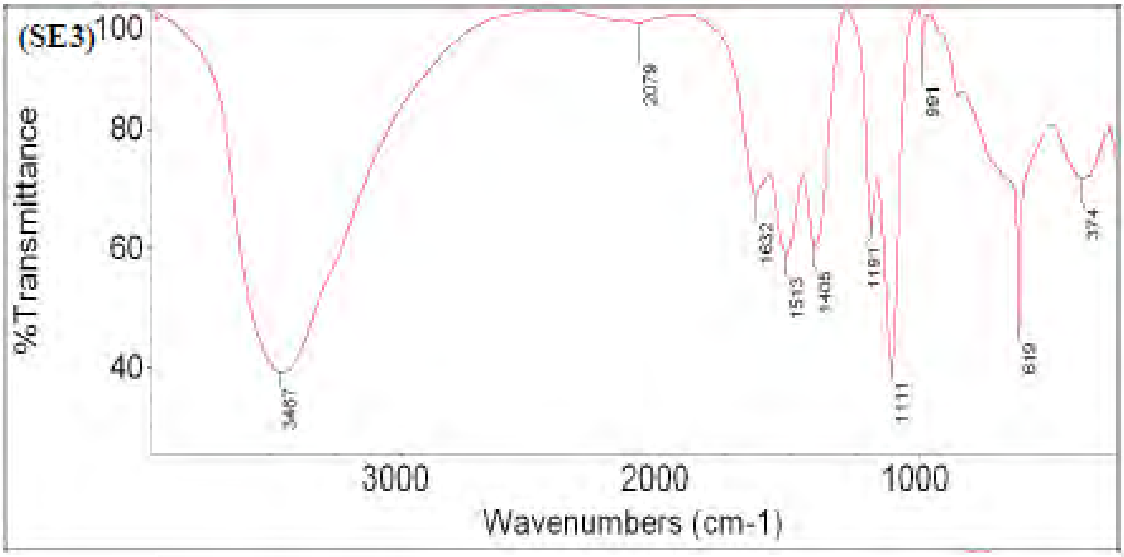


Image160:FT-IR sample SE3.

Precipitation of Y^{3+} from H_2SO_4 with M.A. and NH_3

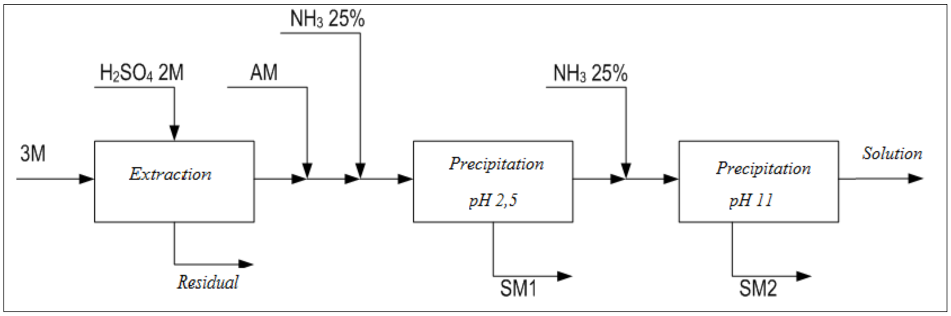


Image161: Scheme of procedure of precipitation with malic acid(M.A.) and NH_3.

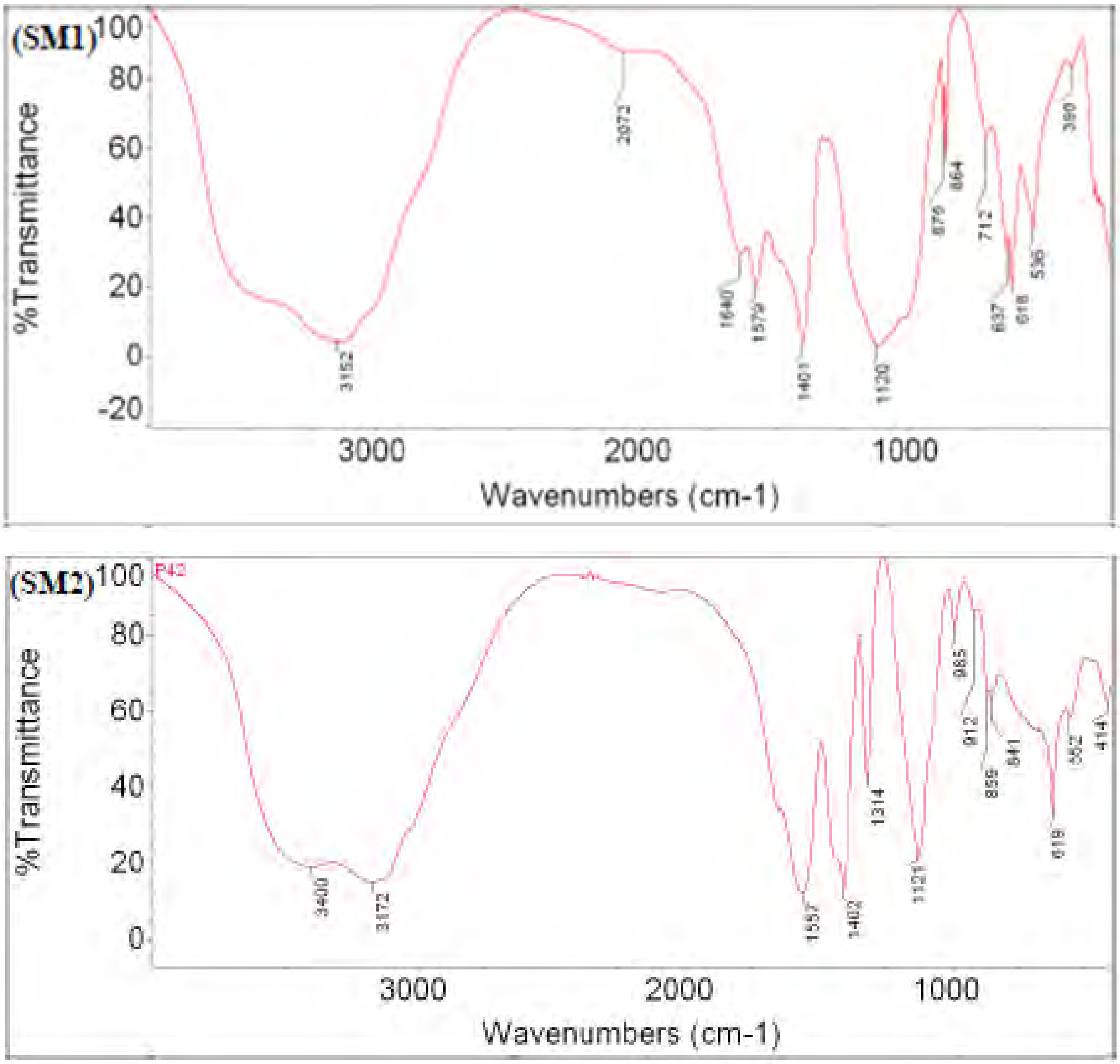


Image162: FT-IR sample SM1 SM2.

5.5.2 Complex formation on sieved sample treated with H_2SO_4

From the previous analysis are determined the main parameters to consider in a reaction of complex formation: complex agent and pH value. The precipitation of the REEs sulfate can be obtained by reaction with acid oxalate the solubility of the sulfates suggests two different categories: low soluble salts Ce, La and Eu and high ones Y. The literature suggests a pH of procedure in a range of 1-3.

The variation of the pH is carried out by adding NaOH, the purpose, after has measured the pH of the solution, is to enhance it till 1.5.

Before the complex formation reaction:

A. Preparation of 50ml of NaOH with a molar concentration of 6M (PM 40 g/mol). To prevent the exothermic reaction is necessary to work inside a cold water cylinder.

Image163: Instrument, chemicals and procedure of NaOH preparation.

B. Preparation of1L of Oxalic acid (hereafter shorten as O.A.) is prepared 0.2M (17.5g/(90g/mol))

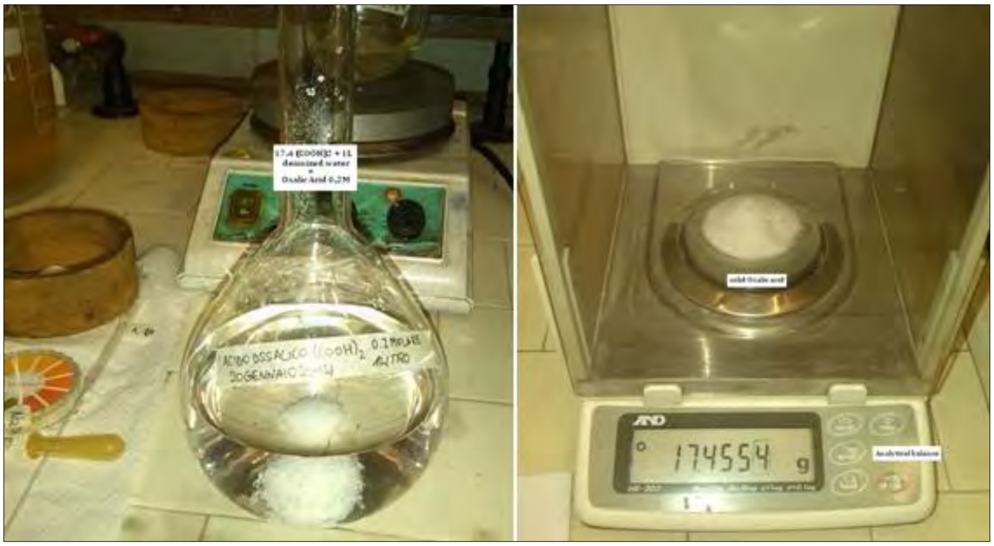
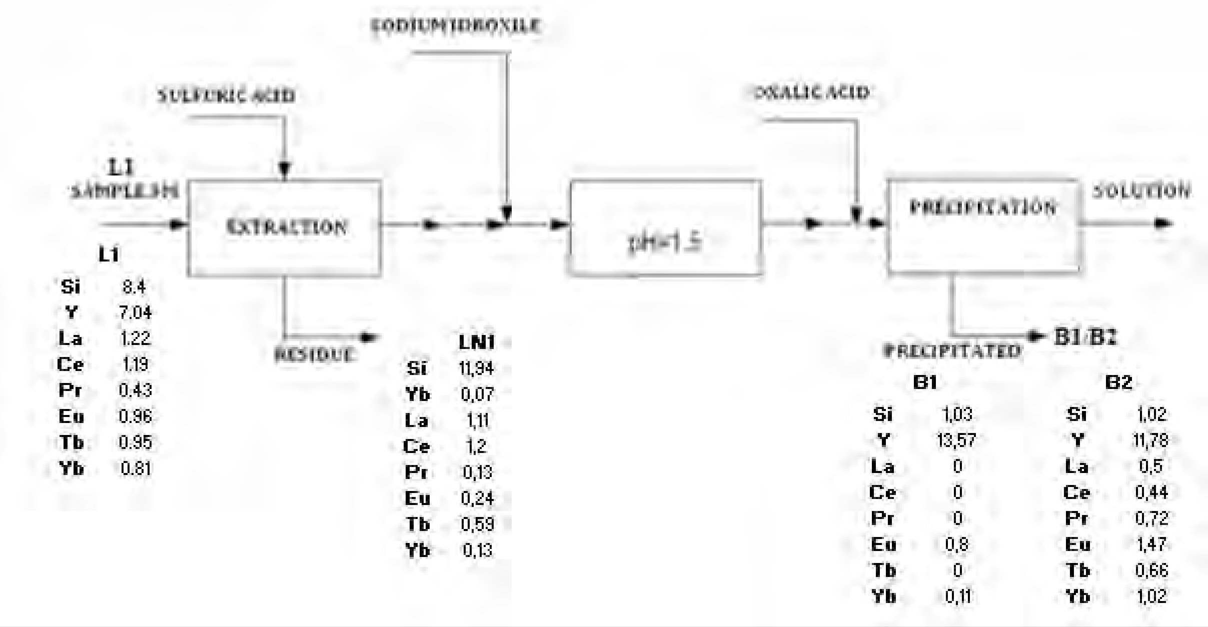


Image164: Instrument and chemicals of O.A. preparation.

C. Scheme of extraction and precipitation (Sieved sample + Sulfuric acid + O.A. + NaOH)



L1	
Si	8.4
Y	7.04
La	1.22
Ce	1.19
Pr	0.43
Eu	0.96
Tb	0.95
Yb	0.81

LN1	
Si	11,94
Yb	0,07
La	1,11
Ce	1,2
Pr	0,13
Eu	0,24
Tb	0,59
Yb	0,13

B1		B2	
Si	1,03	Si	1,02
Y	13,57	Y	11,78
La	0	La	0,5
Ce	0	Ce	0,44
Pr	0	Pr	0,72
Eu	0,8	Eu	1,47
Tb	0	Tb	0,66
Yb	0,11	Yb	1,02

Image165: Schematic procedure of precipitation of Yttrium.

It is measured the pH of the solution S1, it results about 0.5. The pH is increased at about 1.5, by adding 6 times 1ml of NaOH (6M) with a Pasteur pipette.

Image166: PH enhance with NaOH, paper test.

After having checked the pH value of about 1.5, 50mL of Oxalic Acid (COOH2) is added with a concentration of 0.2 moles per liter. The (500mL) flask is shaking for about 30 minutes. To verify that all the dissolved element is precipitated more O.A. is added little by little (helped with a Pasteur pipette). During the adding is noticed that if some dissolved element is left in solution an opalescent effect appears, that means that it is needed more O.A. This procedure lasts till no more opalescent effect appears. 5 Pascal pipettes other 15mL of O.A. are added to the solution. After 45 minutes the situation is checked in terms of pH and content of dissolved element.

Image167: Opalescent effect by adding more O.A. to the solution.

Totally 60mL and 18 Pasteur pipettes of O.A. are added to the flask with S1. After one hour the solution is filtered by helping with de-ionized water. A second filtration is performed on the solution.

Image168: Filtration of the solution (3M+H_2SO_4+NaOH+O.A.).

The results of this test are: a solution fraction (named hereafter S2) and a double solid fraction (called hereafter B1 and B2) because a double filtration is performed.

The liquid fraction is treated by using Rotary evaporation device.

The solid fractions are collected and weighted: 3.4563g (B1), 0.362g (B2). These two solid samples are prepared for an ESEM and an IR analysis.

ESEM Analysis

The result of the ESEM analysis for the first filtration of the sample B1:

COMPOSITION: the sample 3M is sieved and put in a solution of H2SO4, NaOH is added to enhance the pH level to 1.5; Oxalic Acid is added to precipitate the dissolved fraction. Finally the sample is filtrated twice. The solid fraction B1 of the first filtration is weighted:3.4563g.

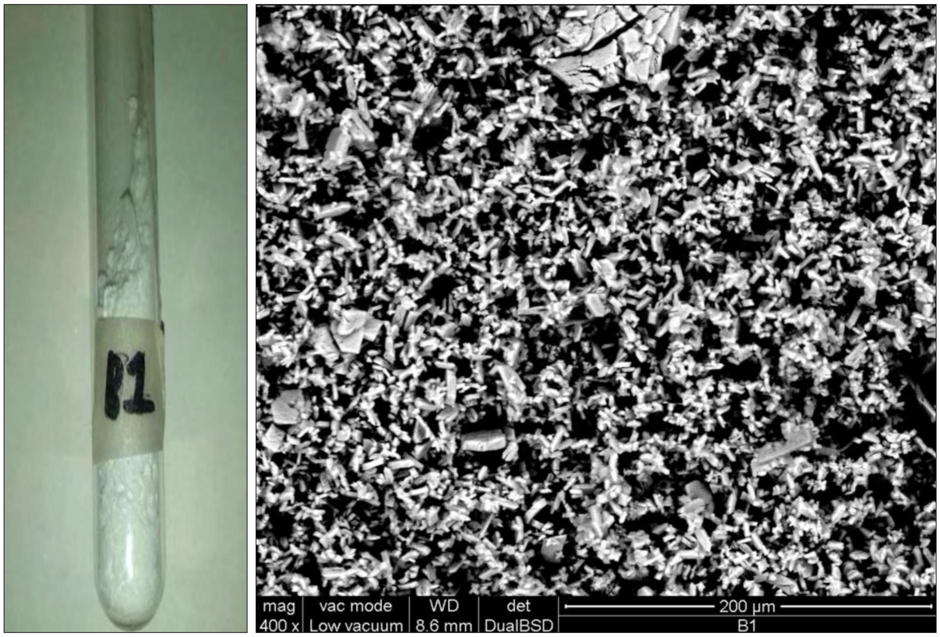


Image169: B1 ESEM zoom 400x.

From the ESEM analysis is evident the content of yttrium oxide, around 2 keV. Unfortunately due to the presence of other lanthanides with high atomic weight the signal is disturbed between the peaks with higher energy (>4 keV).

The result of the ESEM analysis for the second filtration of the sample B2:

COMPOSITION: the sample 3M is sieved and put in a solution of H2SO4, NaOH is added to enhance the pH level to 1.5, Oxalic Acid added. Finally the sample is filtrated twice. The solid fraction of the second filtration weighted 0.362g.

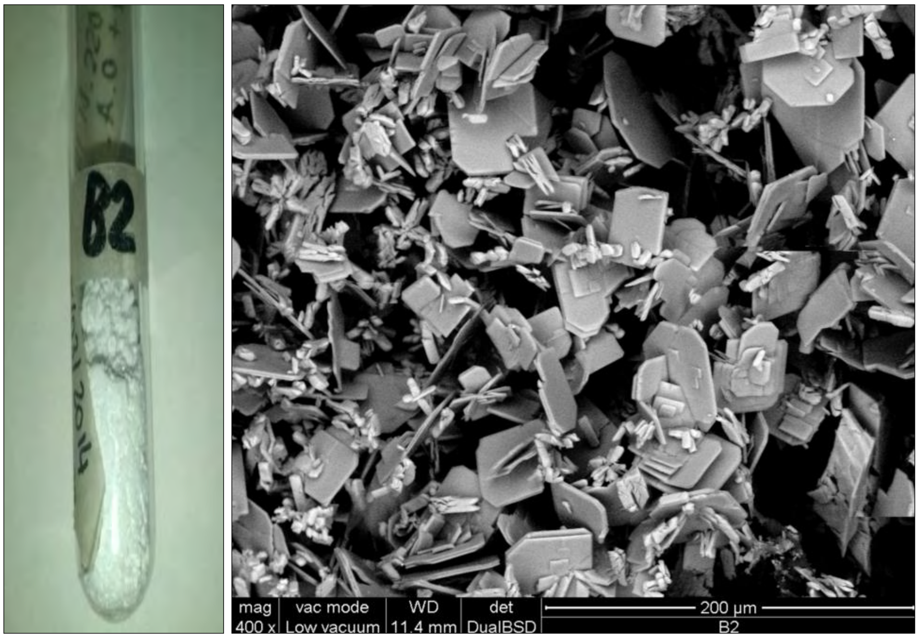


Image170: B2 ESEM zoom 400x.

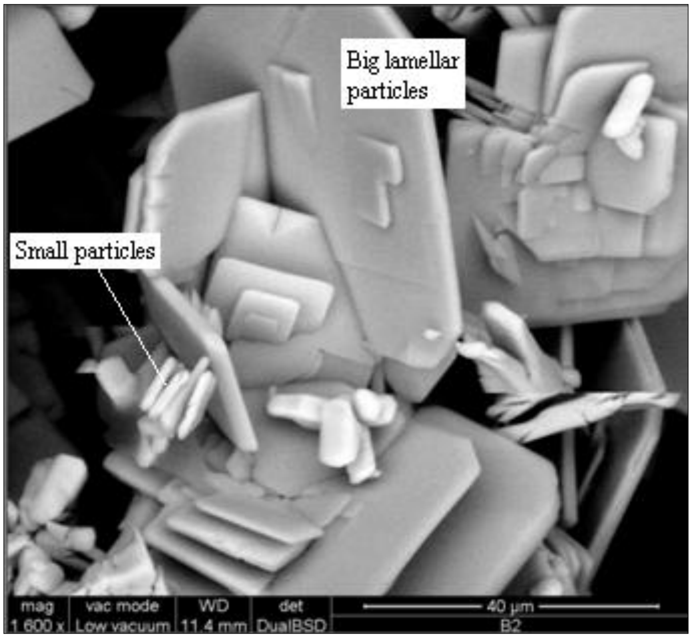


Image171: B2 ESEM zoom 1600x.

Table 21: B1 and B2 ESEM atomic percentage

elements	B1 at%	B2 at%
O	81,54	71,39
Na	0,36	4,14
Mg	0,13	0,49
Al	0,14	0,65
Si	1,03	1,02
Sr	1,3	1,33
Y	13,57	11,78
P	0	0
Zr	0	0,24
S	0	0,18
K	0	0,6
Ca	0,5	0,57
Ba	0,1	0,54
La	0	0,5
Ce	0	0,44
Pr	0	0,72
Eu	0,8	1,47
Tb	0	0,66
Fe	0	0,72
Yb	0,11	1,02
Hg	0,43	1,55

Table 22: B1 and sample not sieved ESEM atomic percentage

weight percentage w/w%		
elements	B1	sample not sieved
O	44,54	30,81
Na	0,28	0,76
Mg	0,11	0,49
Al	0,13	0,33
Si	0,98	1,29
Sr	3,89	3,2
Y	41,20	33,36
P	0	0
Zr	0	0
K	0	0,51
Ca	0,68	0,78
Ba	0,47	2,08
La	0	1,89
Ce	0	2,52
Pr	0	2,7
Eu	4,17	6,83
Tb	0	3,74
Fe	0	0,97
Yb	0,63	3,77
Hg	2,91	0

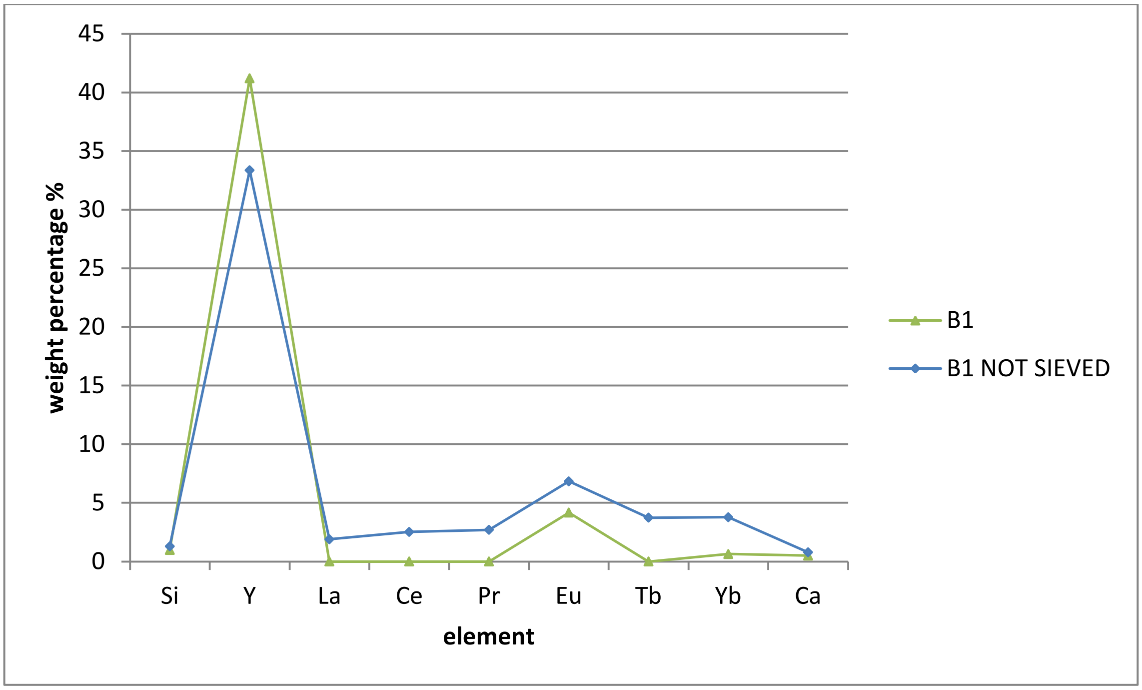


Image 172: Results comparison B1 with sieving procedure or not.

FT-IR Analysis

The FT.IR analysis is performed on the dried sample: yttrium oxalate B1, it is after compared with the spectrum of the previous experiment without the pre-treatment of sieving procedure and also compared with the spectrum found in literature. It is created a proper sample to perform the analysis: a disc made of a higher amount of KBr (Potassium Bromide) and a little amount of Yttrium Oxalate (a ratio of about 1:50).

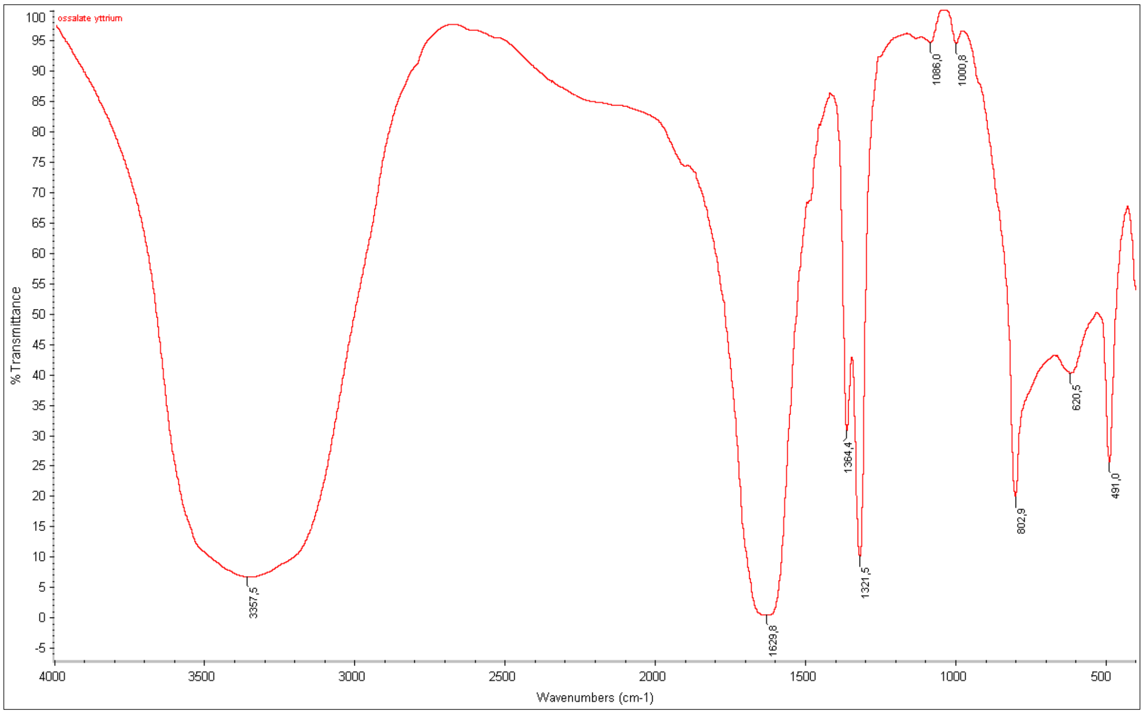


Image 173: B1 FT-IR spectrum

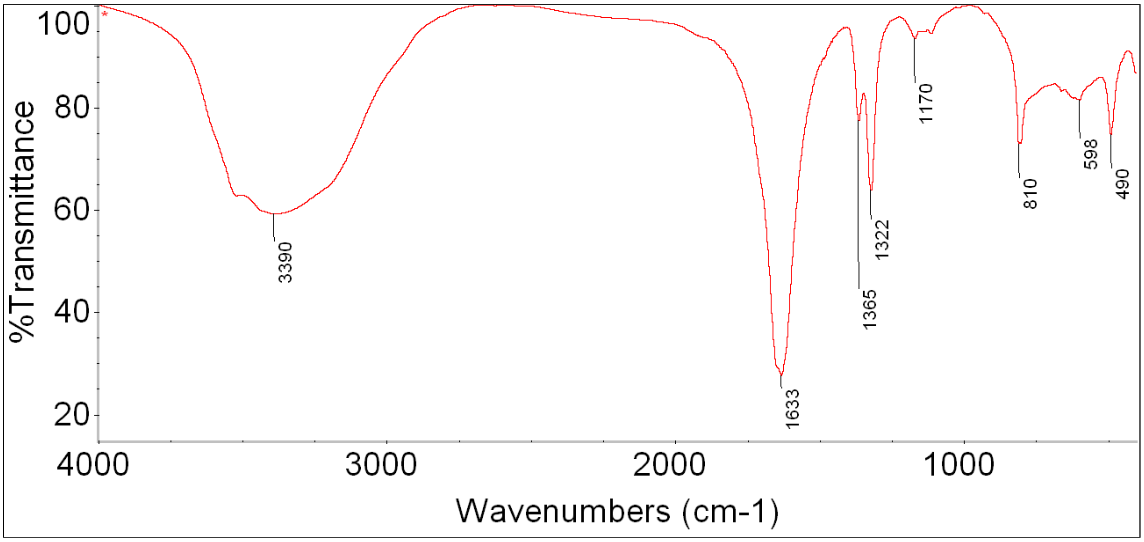


Image 174: Yttrium oxalate gain without sieving procedure FT-IR spectrum

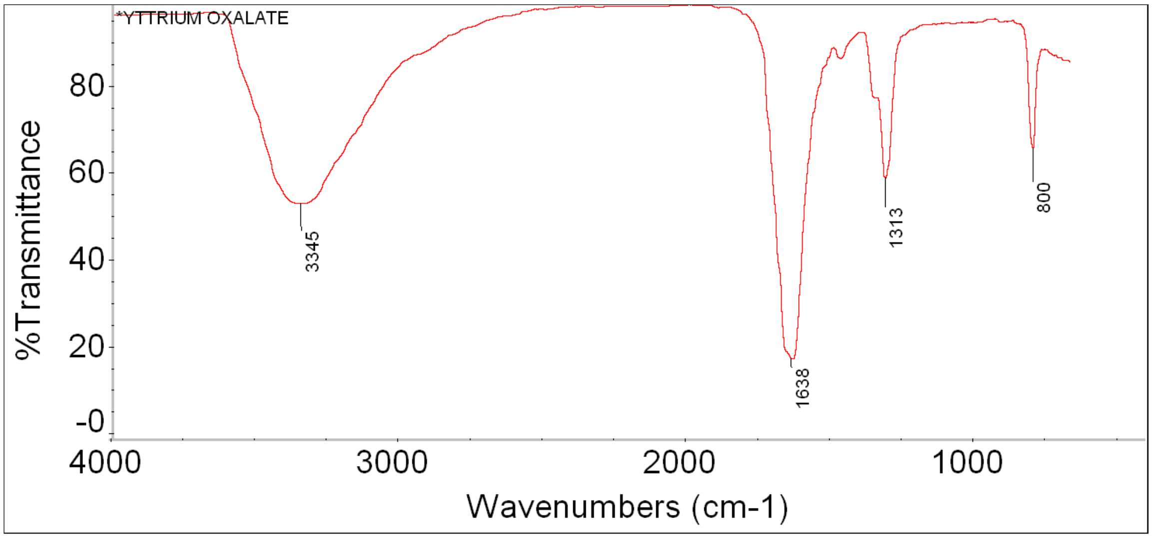


Image 175:YOX literature spectrum

The solid obtain contains a higher percentage of yttrium respect the sample treated without sieved treatment. The FT-IR analysis shows that the spectrum of the sample obtained from the experiment and the literature result are comparable so they contain the same species

5.6 Preparation of yttrium oxide

A thermal treatment on the sample obtained in the previous experiment of complex formation is performed with the purpose of convert organic complex of REEs to oxides

In an industrial process system the thermal imply high costs for production and high quantity of energy so it is necessary to detect the more efficiency temperature in term of benefits and costs. A thermos-gravimetric analysis to describe on the behavior of the yttrium compound is performed. The sample is put in a mitten and the temperature is rises of 10°C from 0°C to 1000°C and kept constant for 25 minutes.

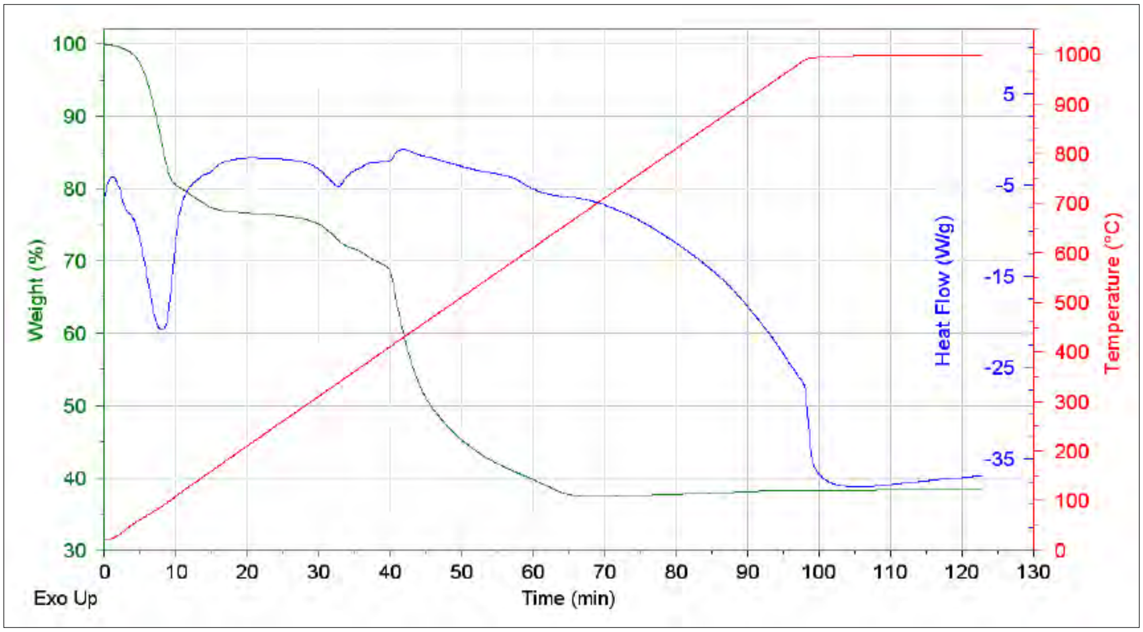


Image 176: Thermo-gravimetric analysis.

The image shows a loss of weight of about 20% between 20 and 100°C, at 89°C a endothermic process appears in relation to the evaporation of the water of hydration. Above 90°C the decomposition of oxalate starts till 675°C with different rates. After 675°C when the sample has lost 45% of the initial weight, there is a slightly increase of weight and an important absorption of heat indicator of a endothermic conversion of the crystalline phase. Finally the FT-IR analysis is also performed to show the presence of yttrium oxide.

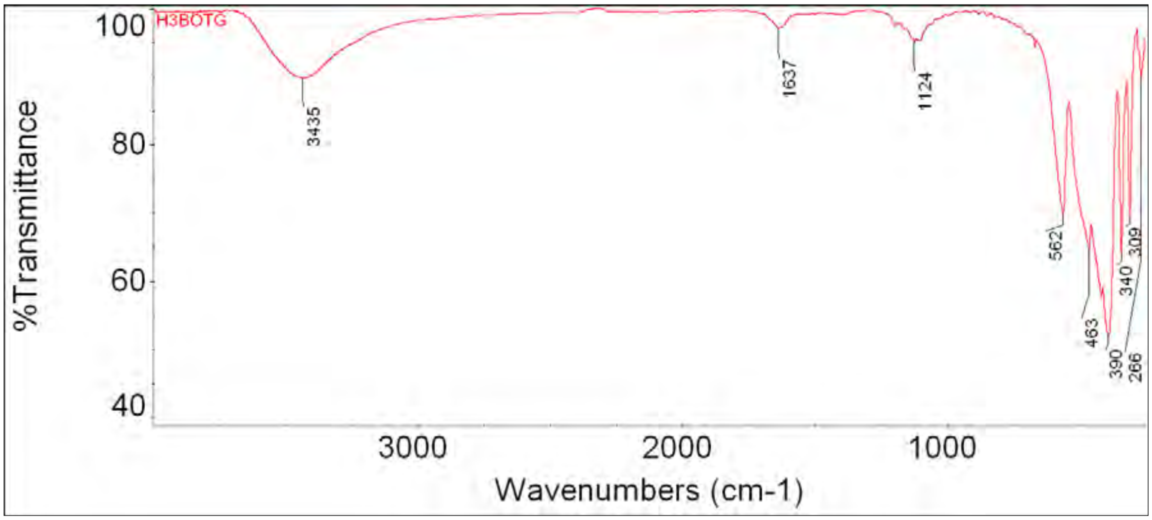


Image 177: FT-IR Y oxides after the thermo-gravimetric analysis.

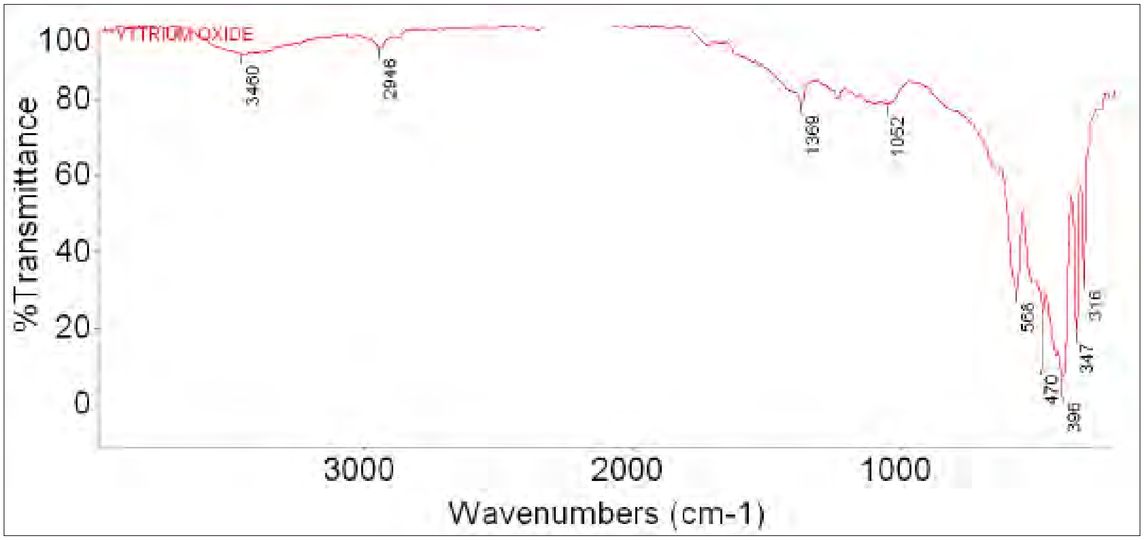


Image 178: Y oxide FT.IR spectrum from literature.

By the comparison between the yttrium oxalate spectrum and the yttrium oxide ones is clear that the structure of the compounds are radically changed: the absorption peaks characteristic for the yttrium oxalate passes from 1639, 1321 and 804 cm^{-1}, to the peaks of the oxides of 565, 470, 395 and 310 cm^{-1}, also the literature reference is reported as comparison.

An XRD analysis is also performed for the yttrium oxide and it is compared to the Y2O3:found in literature.

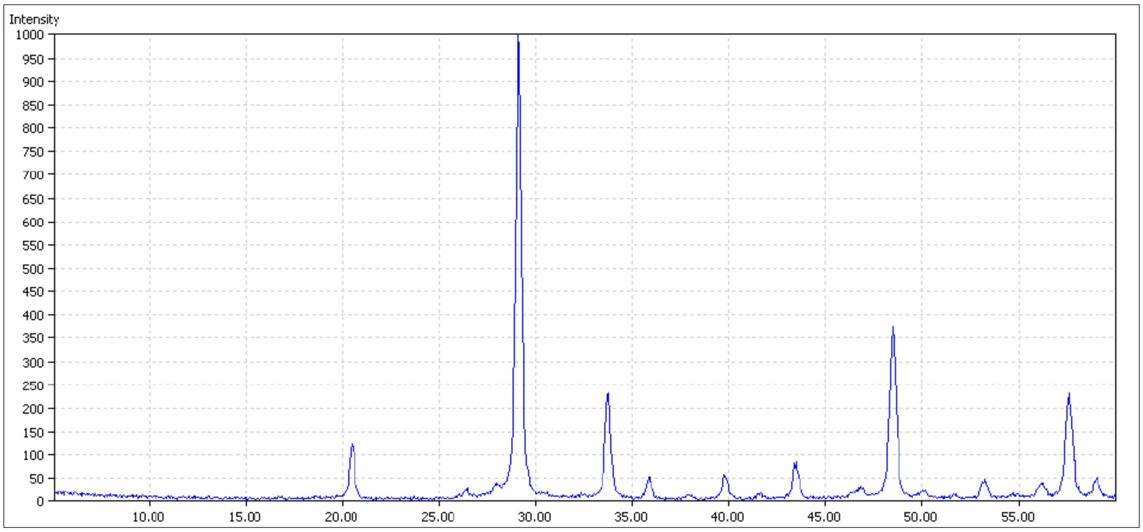


Image 179: XRD Y oxide after thermal treatment.

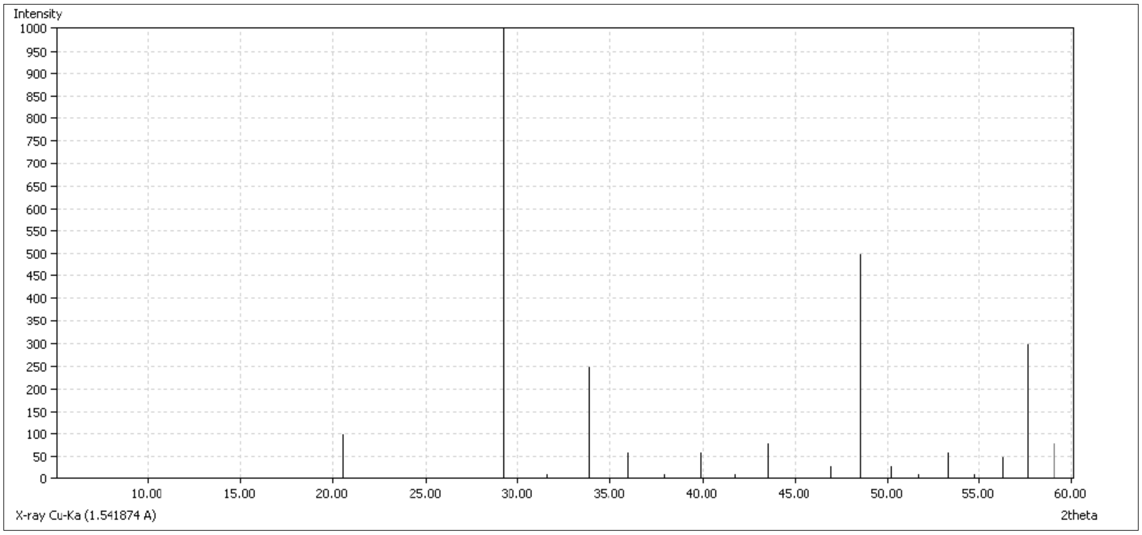


Image 180: XRD the Y2O3 of literature.

The spectrum found correspondence that confirms the presence of yttrium and europium.

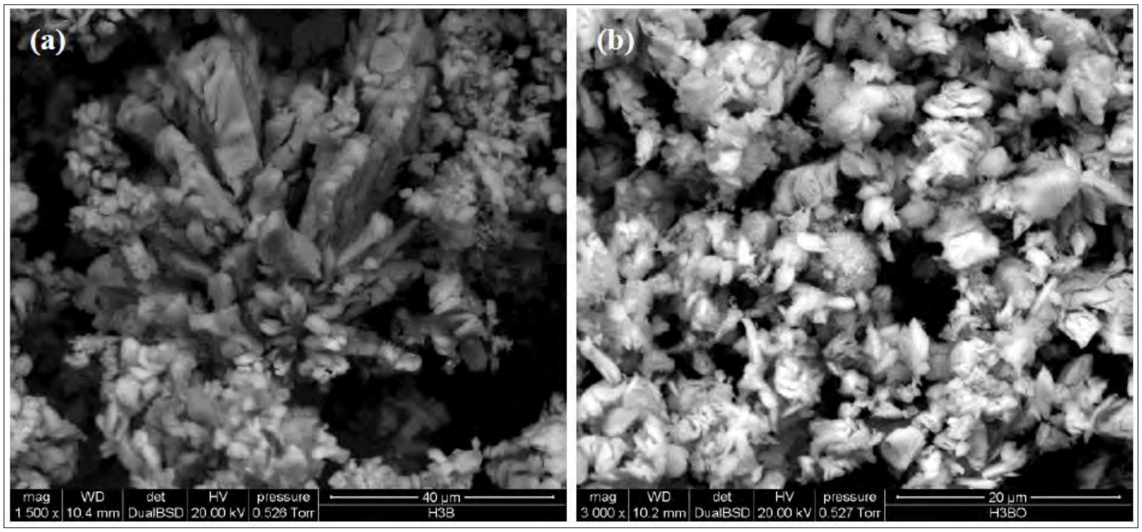


Image 181: ESEM image Y oxalate (a) and Y oxide (b).

The images of ESEM show that the morphology of the two samples are similar: both contain single and aggregated crystals of different dimensions, in the yttrium oxide the particles are nearly 4 time smaller than in the oxalate (from 1 a 5 µm in the oxide).

It is possible to conclude that a complete formation of the yttrium oxide is achieved at 675°C with a recover of the 99%. However more studies are recommended to improve the treatment in particular to make it suitable for the industrial processes. About other REEs other techniques should be implemented for example Microwave treatments.

5.7 Microwave treatment

Microwave treatment is performed on sample to test new techniques to recover in a selective way the REEs. The main parameters of a microwave process are: temperature and pressure, solid liquid ratio and power of the microwave. The programs to set the experiments are found in the manual: Cook-Book.

Microwave extractions

The microwave tests are carried out following program of the manual CooK-Book. In particular 5 samples are prepared:

a. 2 samples with respectively 0.1059 g and 0.1036g of sample L1+ 4mL H_2S0_4 (96%) + 250mg NH_4Cl, below them are unified and called MWA

b. 2 samples with 0.1049 g and0.1008g of sample L1 + 2mL HNO_3 (65%) + 200mg NH_4Cl, below them are unified and called MWC

c. 1 sample with 0.5006g of sample L1 +3mL HCl (37%) + 3mL HNO_3 (65%) + 2mL HF (40%), below it is called MWB

Image182: Experiment set.

The program set on the microwave is:

name of experiment	sample	compounds added	phase n°	time (minutes)	power (watt)	solid	solution
MWA	L1	$H_2SO_4 + NH_4Cl$	1	5	250	MWAs	MWASOL
			2	5	400		
			3	5	600		
			4	5	250		
MWC	L1	$HNO_3 + NH_4Cl$	1	5	250	MWCs	MWCSOL
			2	5	400		
			3	5	600		
			4	5	250		
MWB	L1	$HCl + HNO_3 + HF$	1	5	250	MWBs	MWBSOL
			2	5	400		
			3	5	600		
			4	5	250		

Image183: Microwave treatment program.

After the microwave digestion process the solutions are left to cooling down for a day inside the machinery, then filtered diluting them with de-ionized water to prevent the dissolution of the paper filters.

Image184: Filtration step.

The solutions are named MWASOL, MWBSOL AND MWCSOL. For the high concentration of acids they are difficult to make evaporate under the fume hood at room temperature. The samples are left dry for about 5 month. The solution MWBSOL dried is detected with ESEM. The solution MWASOL and MWCSOL are instead samples for complex formation process explained in the next paragraphs.

Image185: Heating of solution to dry.

ESEM Analysis

After the filtration all the solid fractions remained on the filter are sampled. The MWA and MWC amounts of solid are negligible instead for the experiment MWB the amount of solid collected is 0.44g. The samples are analyzed with ESEM.

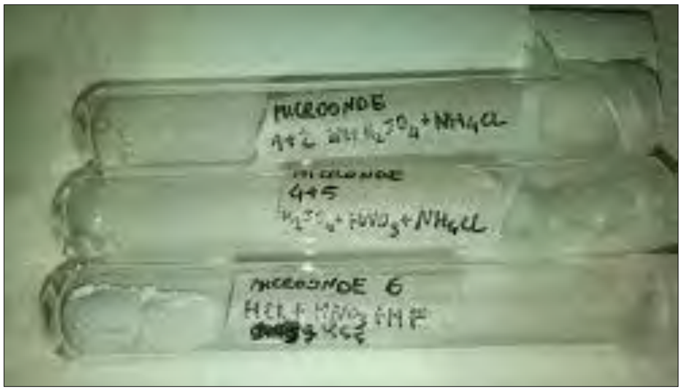
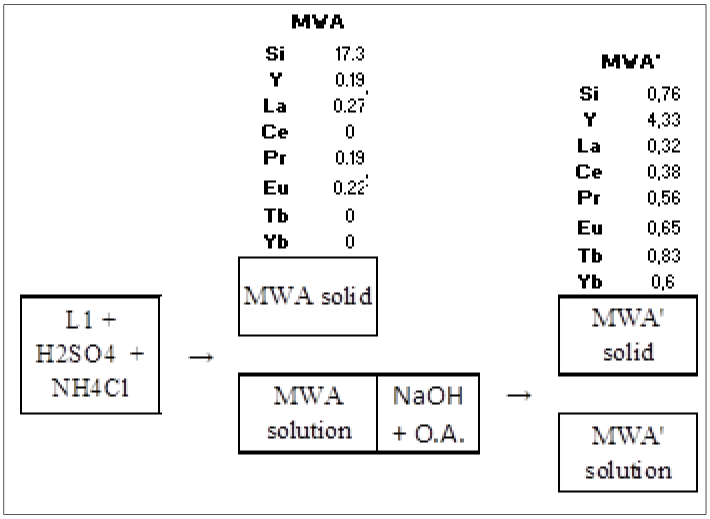


Image 186: solid samples.

5.7.1 MWA microwave treatment



MVA	
Si	17.3
Y	0.19
La	0.27
Ce	0
Pr	0.19
Eu	0.22
Tb	0
Yb	0

MVA'	
Si	0,76
Y	4,33
La	0,32
Ce	0,38
Pr	0,56
Eu	0,65
Tb	0,83
Yb	0,6

Image 187: MWA microwave treatment process scheme

Solid: MWAs

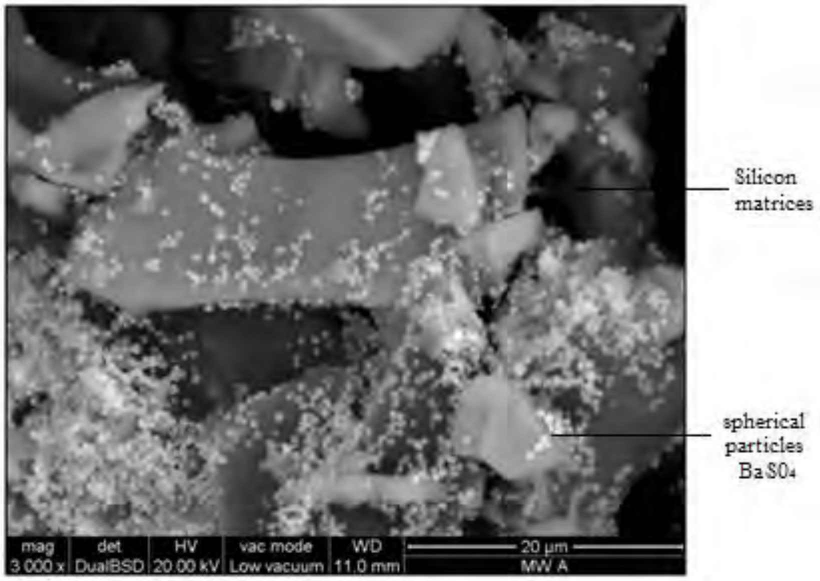


Image 188: MWAs ESEM zoom 3000x.

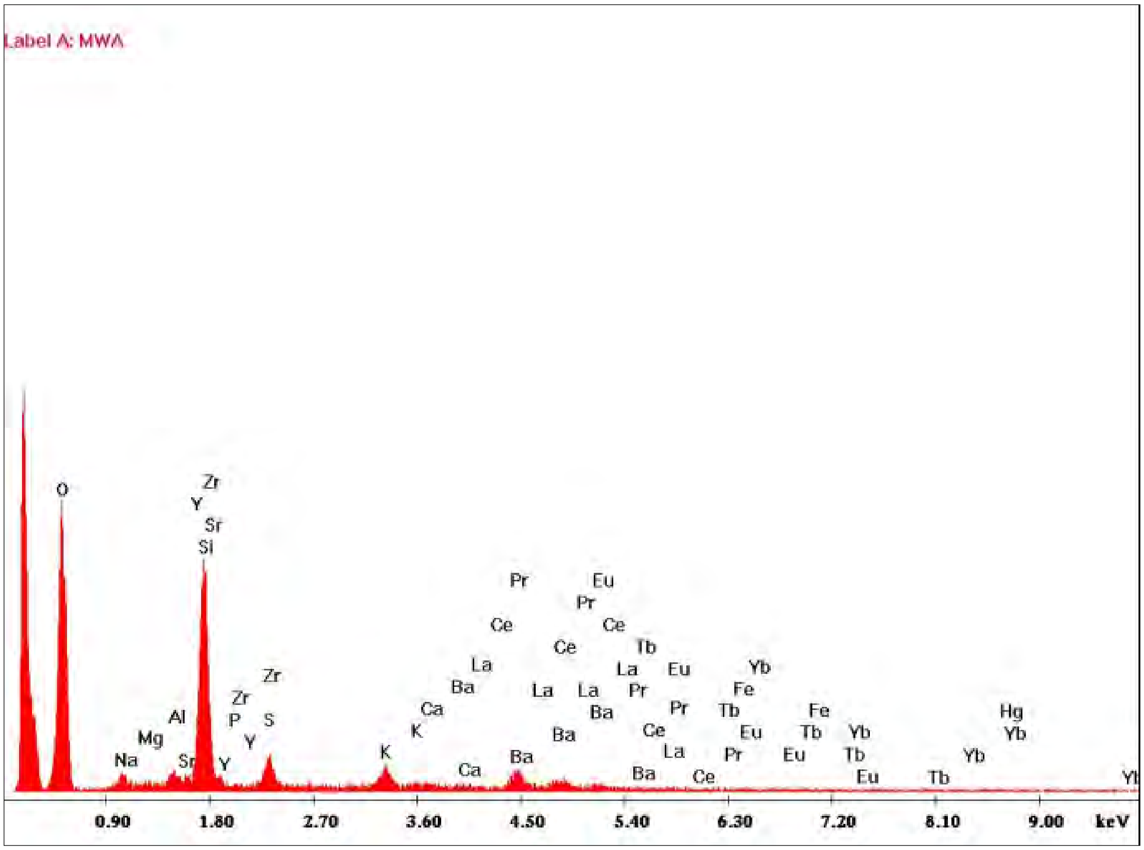


Image 189: MWA ESEM fluorescence analysis.

Table 23: : MWAs solid and MWA crystal ESEM atomic percentage

elements	L1	MWA solid	MWA crystal
O	54.45	71.42	67.78
Na	2.42	1.76	0.31
Mg	2.05	0.16	0.26
Al	9.08	1.2	0.84
Si	8.4	17.3	4.30
Sr	1.85	0.37	0.95
Y	7.04	0.19	6.62
P	1.7	0	0.00
Zr	0.42	0.07	0.08
K	1.48	1.63	0.67
Ca	2.45	0.42	1.85
Ba	1.01	1.9	0.69
La	1.22	0.27	0.85
Ce	1.19	0	1.01

Pr	0.43	0.19	0.29
Eu	0.96	0.22	1.01
Tb	0.95	0	0.80
Fe	0.84	0.2	0.16
Yb	0.81	0	0.50
Hg	0.72	0.3	0.57

- *Silicon*: not extracted
- *REEs:* extracted
- *Calcium:* extracted

The extraction shows good results despite the presence of calcium in the final solution, disadvantage for the next step the complex formation.

From the 400x zoom image of ESEM solid sample is characterized in three fractions: a darker ones is composed by silicon, the lighter crystals are mainly formed of carbon, probably they are pieces of the filter paper, finally the really small light particles are made of barium fluoride ($BaSO_4$) and other elements such as sulfur and silicon.

MWA crystals

The solution MWASOL presents in the bottom of the cylinder some solid crystals visible to naked eye, they are analysed separately.

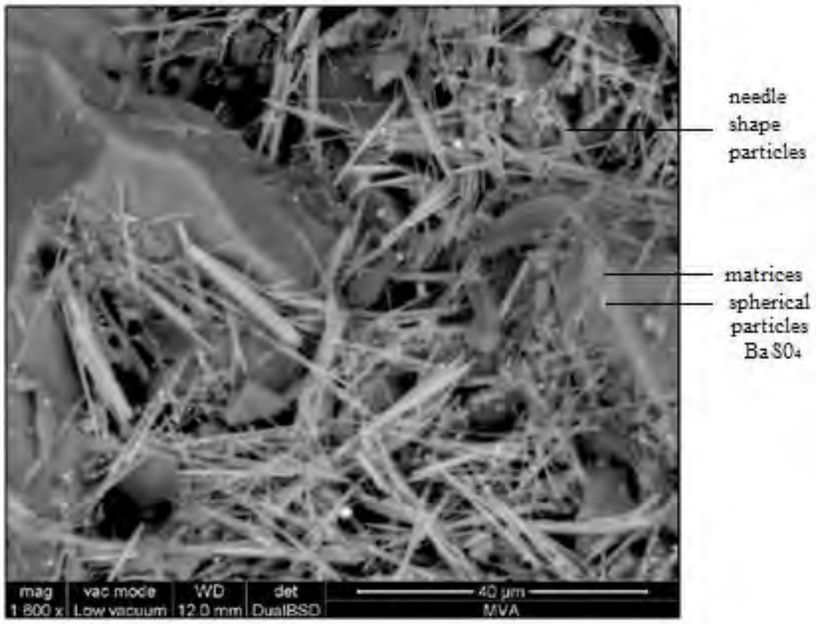


Image 190: MWA crystal ESEM zoom 1600x.

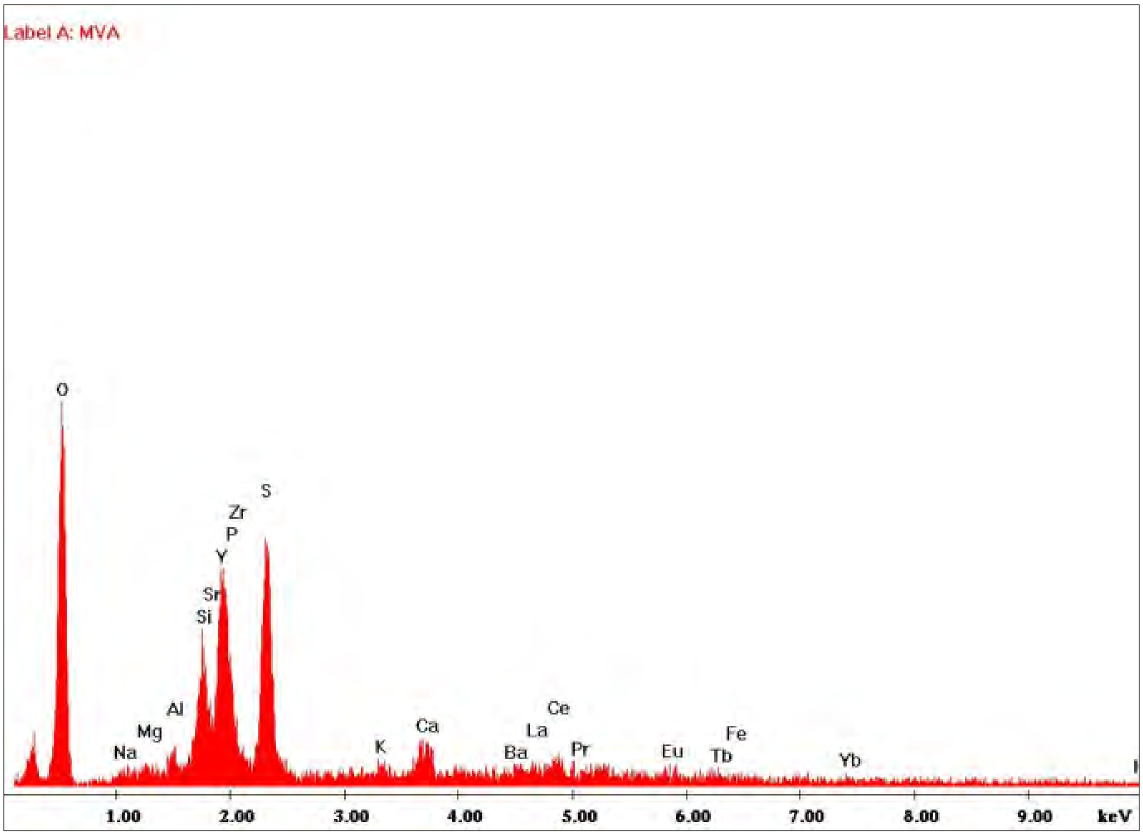
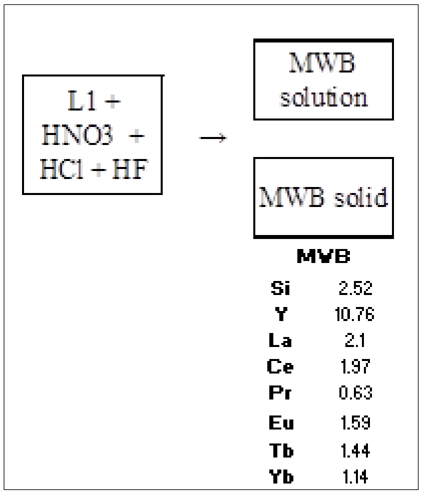


Image 191: MWA-CRYSTALS fluorescence ESEM analysis.

The sample is divided into two parts: matrices made of yttrium and sulfur and little white particles heavier (atomic weight), they are aggregations of lanthanum and cerium, aggregation of calcium and cerium or lanthanum, no yttrium appears.

The morphology of the sample shows molecules similar to needles.

5.7.2 MWB microwave treatment



	MWB
Si	2.52
Y	10.76
La	2.1
Ce	1.97
Pr	0.63
Eu	1.59
Tb	1.44
Yb	1.14

Image 192: MWB microwave treatment process scheme

Solid: MWBs (weight 0,44 g)

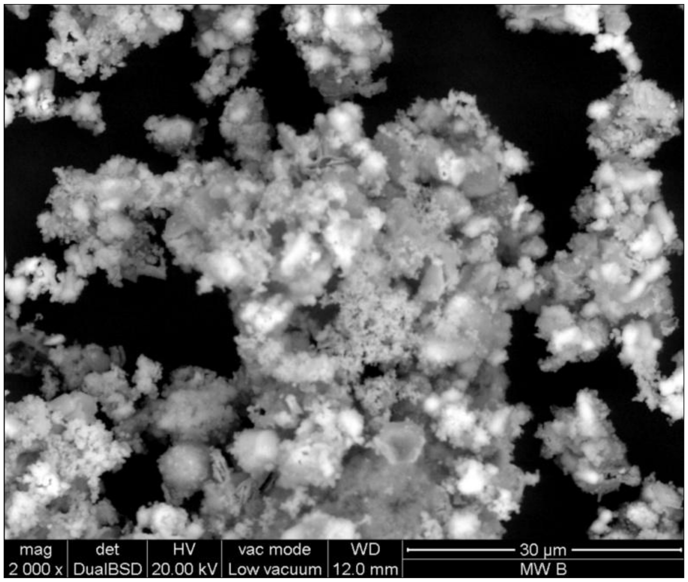


Image 193: MWBs ESEM zoom 2000x.

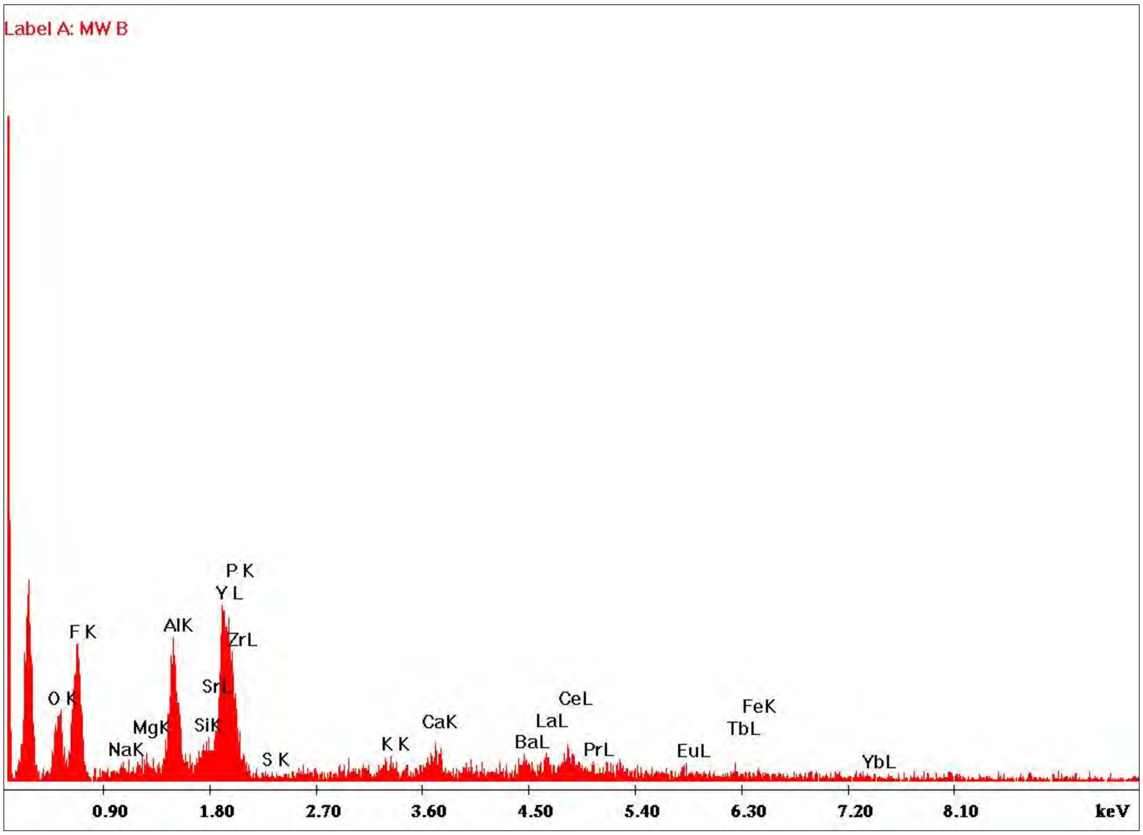


Image 194: MWBs ESEM fluorescence analysis.

Solution: MWBSOL (weight 0.3914 g)

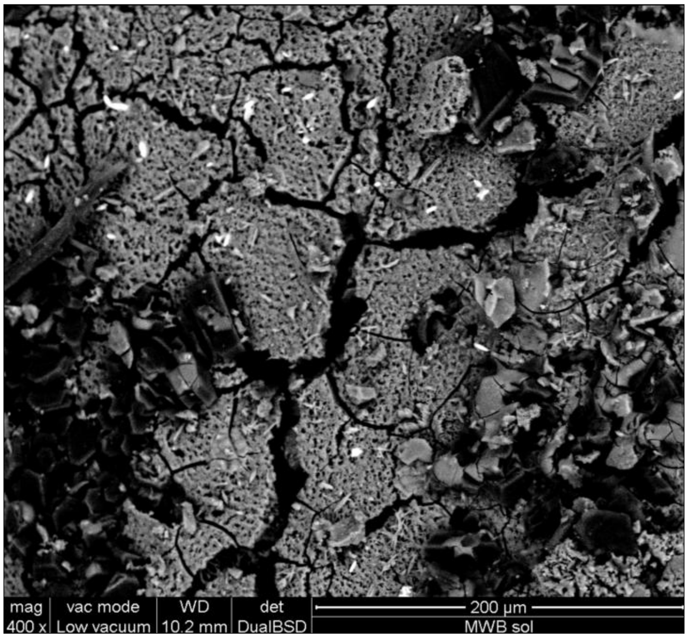


Image 195: MWBSOL ESEM zoom 400x.

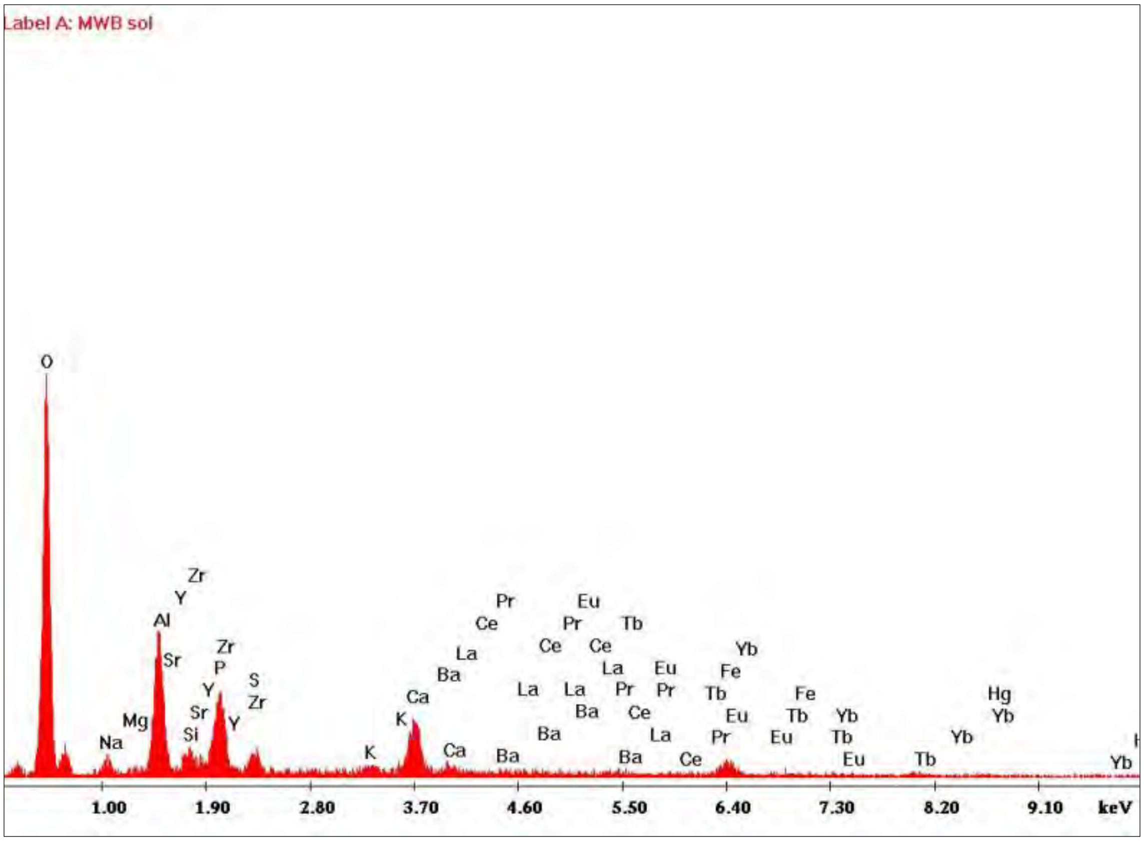


Image 196: MWBSOL ESEM fluorescence analysis

Table 24: MWBs and MWB crystal ESEM atomic percentage

elements	L1	MWB solid	MWB solution
O	54.45	24.07	74.91
F	/	25.7	/
Na	2.42	2.4	1.83
Mg	2.05	2.59	0.39
Al	9.08	11.69	8.62
Si	8.4	2.52	1.05
Sr	1.85	1.86	0.23
Y	7.04	10.76	0.57
P	1.7	0.29	3.87
Zr	0.42	0.22	0.29
K	1.48	1.85	0.39
Ca	2.45	2.65	3.26
Ba	1.01	2.07	0.24
La	1.22	2.1	0.16
Ce	1.19	1.97	0.1
Pr	0.43	0.63	0.05
Eu	0.96	1.59	0.24
Tb	0.95	1.44	0.27
Fe	0.84	0.86	1.64
Yb	0.81	1.14	0.43
Hg	0.72	0.92	0.4

- *Silicon*: extracted
- *REEs:* extracted are not extracted except ytterbium
- *Calcium:* extracted

The extraction shows good results in terms of extraction of ytterbium but bad results in terms of presence of silicon and calcium in solution. From the ESEM image is shown that the presence of HF dissolves silicon in the solid fraction.

5.7.3 MWC microwave treatment

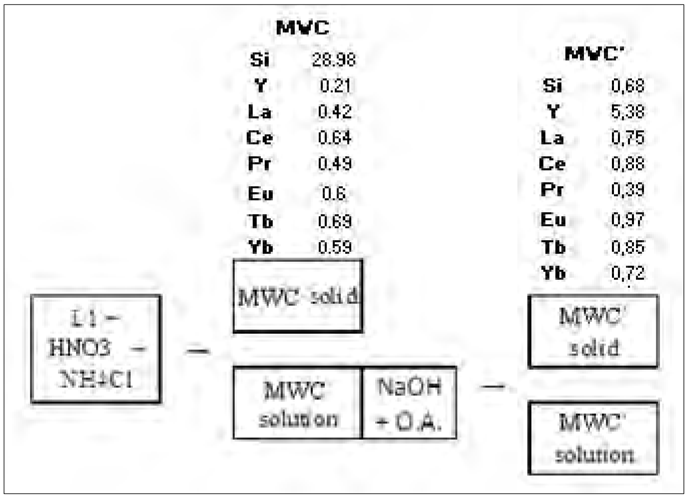


Image 197: MWC microwave treatment process scheme.

Solid: MWCs

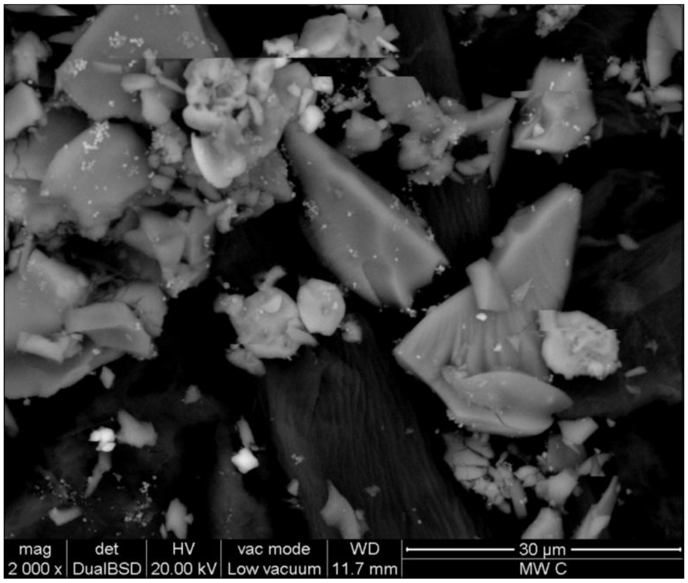


Image 198: MWCs ESEM sample.

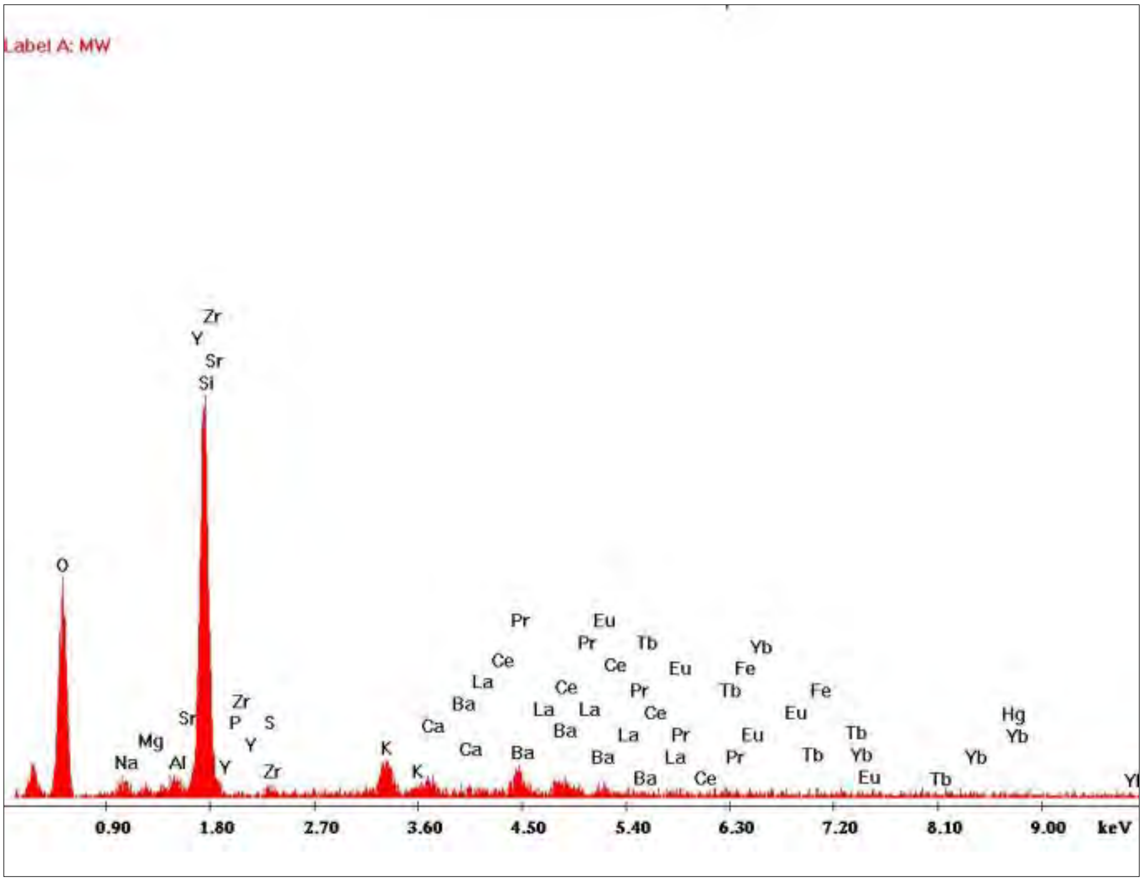


Image 199: MWCs ESEM analysis.

Table 25: MWCs and MWC crystal ESEM atomic percentage

elements	L1	MWC solid	MWC crystal
O	54.45	54.53	77.16
Na	2.42	1.97	0.12
Mg	2.05	0.69	0
Al	9.08	1.53	0.17
Si	8.4	28.98	0.39
Sr	1.85	0.49	0.51
Y	7.04	0.21	4.7
P	1.7	0	0
Zr	0.42	0.26	0.36
S	0.53	0.71	12.46
K	1.48	2.82	0.19
Ca	2.45	1.21	0.4
Ba	1.01	2.28	0.21
La	1.22	0.42	0.47
Ce	1.19	0.64	0.47
Pr	0.43	0.49	0.1
Eu	0.96	0.6	0.49
Tb	0.95	0.69	0.38
Fe	0.84	0.49	0.3
Yb	0.81	0.59	0.35
Hg	0.72	0.4	0.77

- *Silicon*: not extracted
- *REEs:* extracted
- *Calcium:* extracted

The silicon is not extracted due to the presence of hydrochloric acid. Yttrium is well extracted and moreover in comparison with the experiment MWA the solution shows a lower percentage of calcium. The result implies an advantage to face the step of complex formation of the solution MWCSOL.

From the analysis with ESEM the sample appears as a mixture of silicon, barium, calcium, potassium, the lighter particles are sulfur of barium.

MWC crystal

The solution is left concentrate by the evaporation of water (heated at 50°C on a stirrer with possibility to set the temperature), some eyes visible crystal settled.

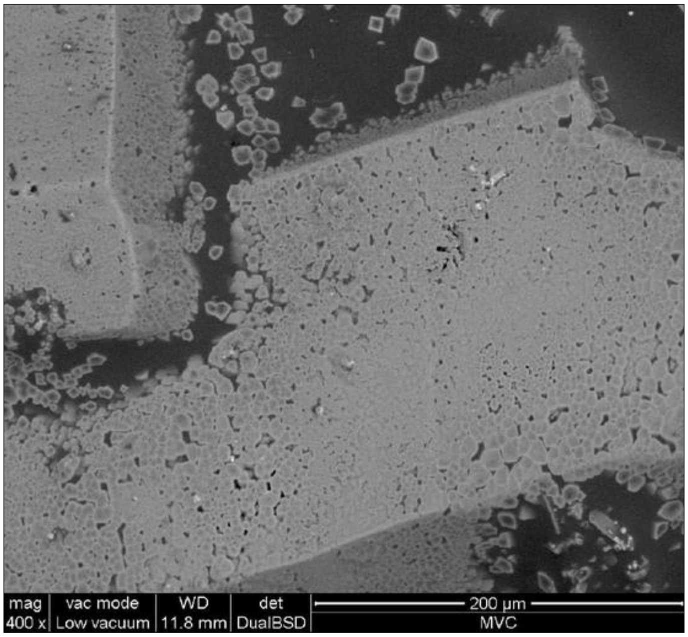


Image 200: MWC crystal ESEM sample

Analyses from ESEM shows that the sample can be characterized by three fraction: crystal with higher dimensions (as agglomeration of smaller particles) are rich in sulfur and yttrium, a paste-matrices similar to gel is composed by oxygen and sulfur, finally smaller particles are made of yttrium sulfate (yttrium and sulfur)

Microwave extraction shows interesting result in the experiment called MWA and MWC, no interesting information for this thesis are achieved in the process called MWB. With these assumptions a reaction of complex formation is performed on the sample MWASOL and MWCSOL solutions.

Under this condition REEs are not significantly extracted, more experiment should be performed.

5.7.4 Complex formation

It is tested a complex formation procedure on the solutions that come from the microwave extractions performed in the previous chapters Both the solutions called respectively MWASOL and MWCSOL are let dry for about 2 months at room temperature, and for a period of 1 day heated with a temperature of 50°C, the results are two very concentrated samples. The solutions present very different aspects: MWASOL is darker respect MWCSOL, moreover in the bottom of both the cylinders some settled particles are found.

The solution is filtered, the solid part is analyzed with at the ESEM, and the pH of the solution is checked with pH test strips: for both the sample the value is around 0.5.

Image 201: Filtration of the MWASOL and MWCSOL.

Image 202: Comparison between respectively MWASOL and MWCSOL.

Image 203: Heating treatment of the two solutions MWASOL and MWCSOL.

The samples are putted in two 100 m L balloons and on a stirrer, in room temperature and with a velocity of about 500-700 rpm.

The first step is to measure and enhance the pH of both the liquids: as in the previous phase the pH is enhanced by adding NaOH with a concentration of 6mol/L.

For the solution MWA 35 (52 mL) Pasteur pipettes of NaOH are added,

For the solution MWC 20 (30 mL) Pasteur pipettes are added.

The purpose is to have a pH around 1 and 1.5.

After the increase of the pH the oxalic acid is used as complex agent.

5mL of oxalic acid. are added to the solution with intervals per each milliliter of about 20 minutes. To evaluate if the oxalic acid added is enough 3 Pasteur pipettes (4.5 mL) are added to the flasks looking if opalescent effects appear in the liquid phase: the opalescence is the effect of the formation of oxides in the liquid.

ESEM Analysis solid fraction of complex formation on the solution of the MWA treatment with microwave: MWA2

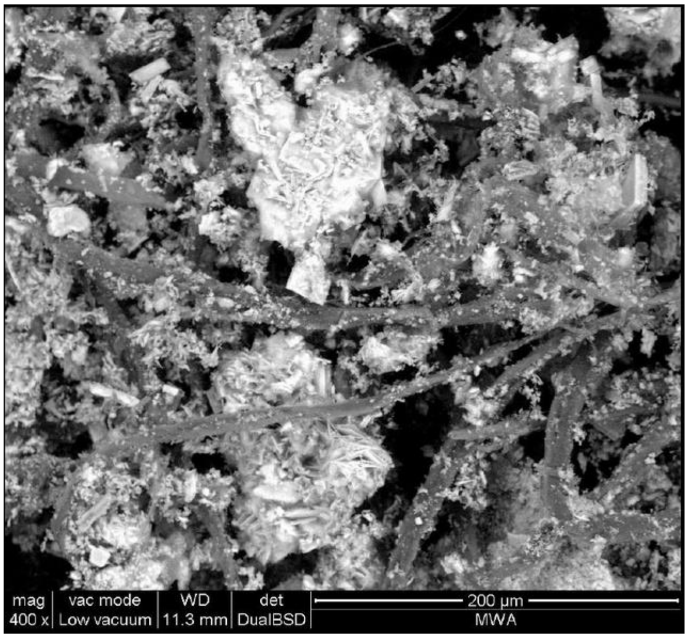


Image 204: MWA2 ESEM zoom 400x.

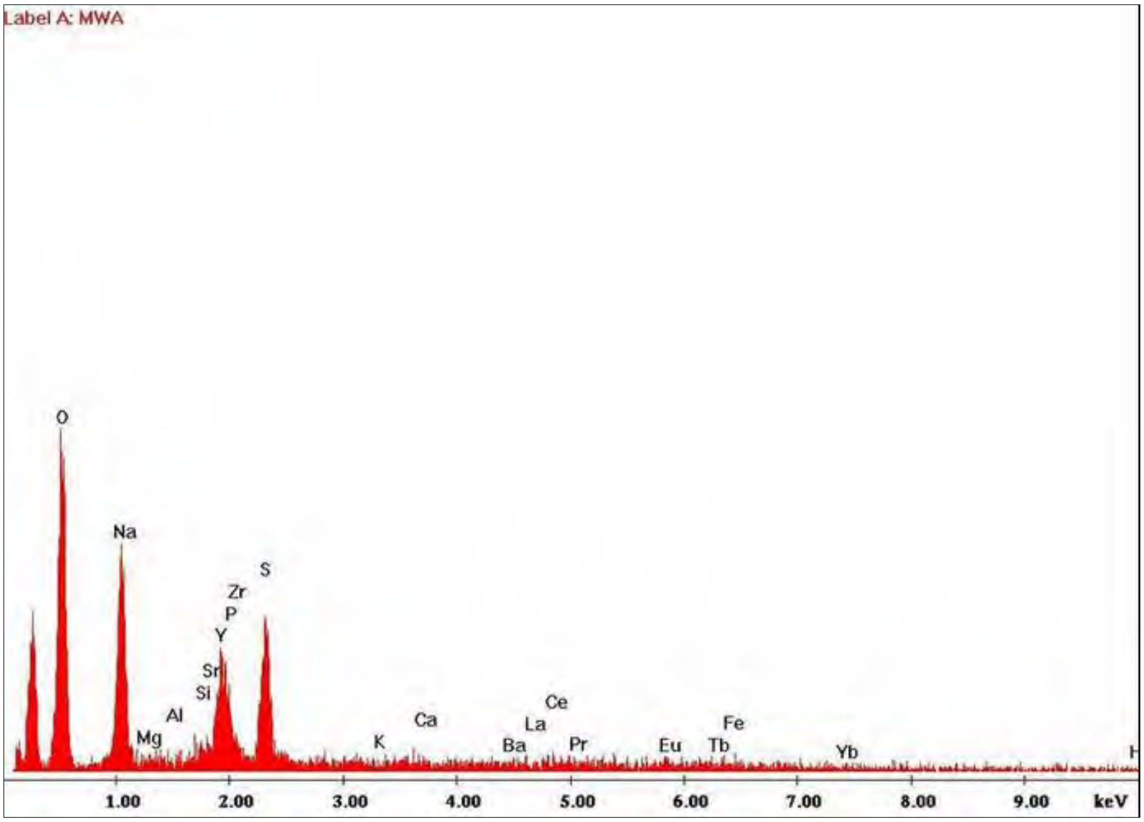


Image 205: MWA2 ESEM fluorescence analysis.

ESEM Analysis solid fraction of complex formation on the solution of the MWC treatment with microwave: MWC2

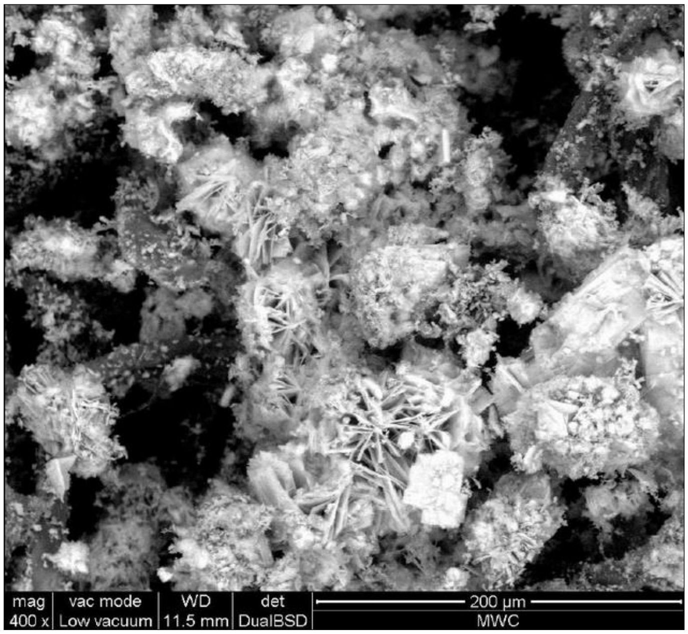


Image 206: MWC2 ESEM zoom 400x.

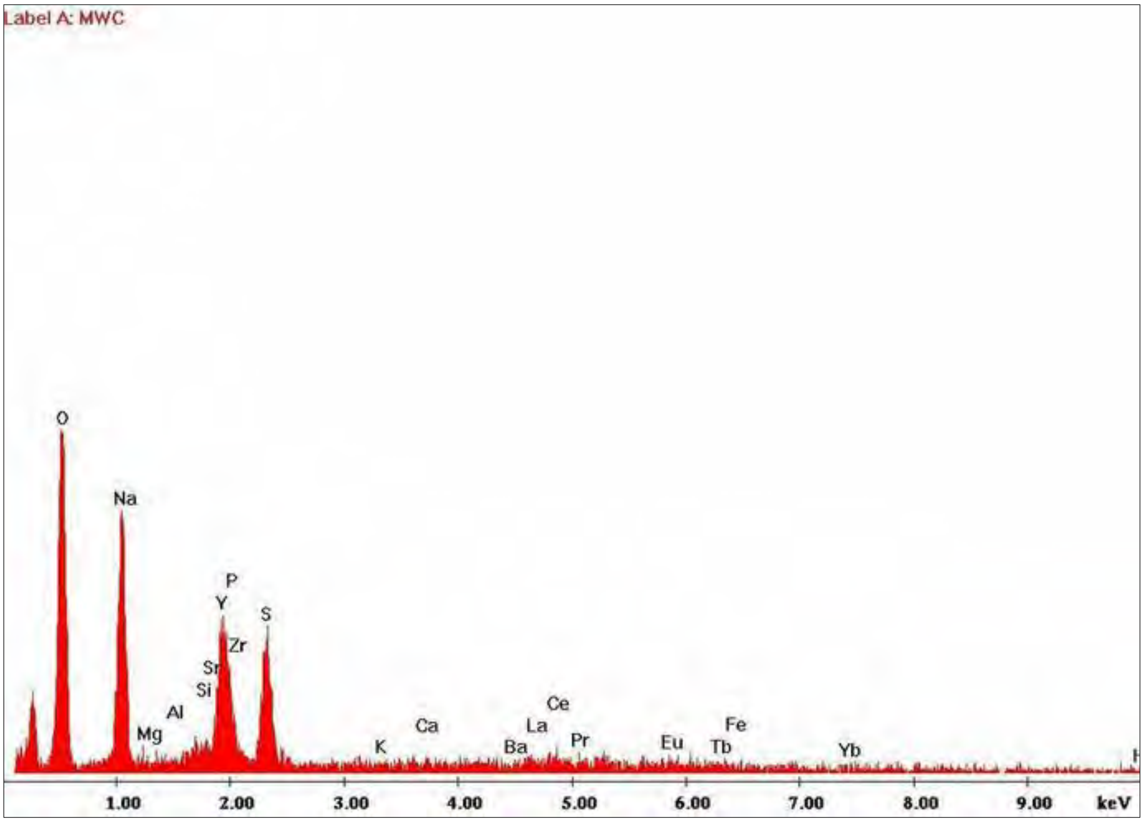


Image 207: MWC2 ESEM fluorescence analysis.

Table 26: MWA2 and MWC2 ESEM atomic percentage

Atomic percentage		
elements	MWA'	MWC'
O	62,49	60,5
Na	17,75	18,94
Mg	0,71	0,44
Al	0,42	0,25
Si	0,76	0,68
Sr	0,63	0,57
Y	4,33	5,38
P	0	0
Zr	0,23	0,1
S	7,17	6,21
K	0,14	0,38
Ca	0,34	0,38
Ba	0,37	0,39
La	0,32	0,75
Ce	0,38	0,88
Pr	0,56	0,39
Eu	0,65	0,97
Tb	0,83	0,85
Fe	0,66	0,42
Yb	0,6	0,72
Hg	0,65	0,81

In the results obtained high percentage of REEs is observed, for time reasons no further analysis have been done to characterize the species present in the solid fraction obtained.

From the complex formation process performed on the extraction treatment with microwave further research on conditions should be performed.

6. CONCLUSIONS AND CONSIDERATIONS

The research activity was devoted to the recovery of REEs from powders obtained by exhaust fluorescent lamps. The powders have been obtained by the lamps after a preliminary separation of metal parts, a milling with subsequent separation of thin and coarse parts. The thin part was thermally treated in order to reduce Hg content and used by us as received (after a check that radioactive elements were not present).

The whole treatment can be summarized as follows:

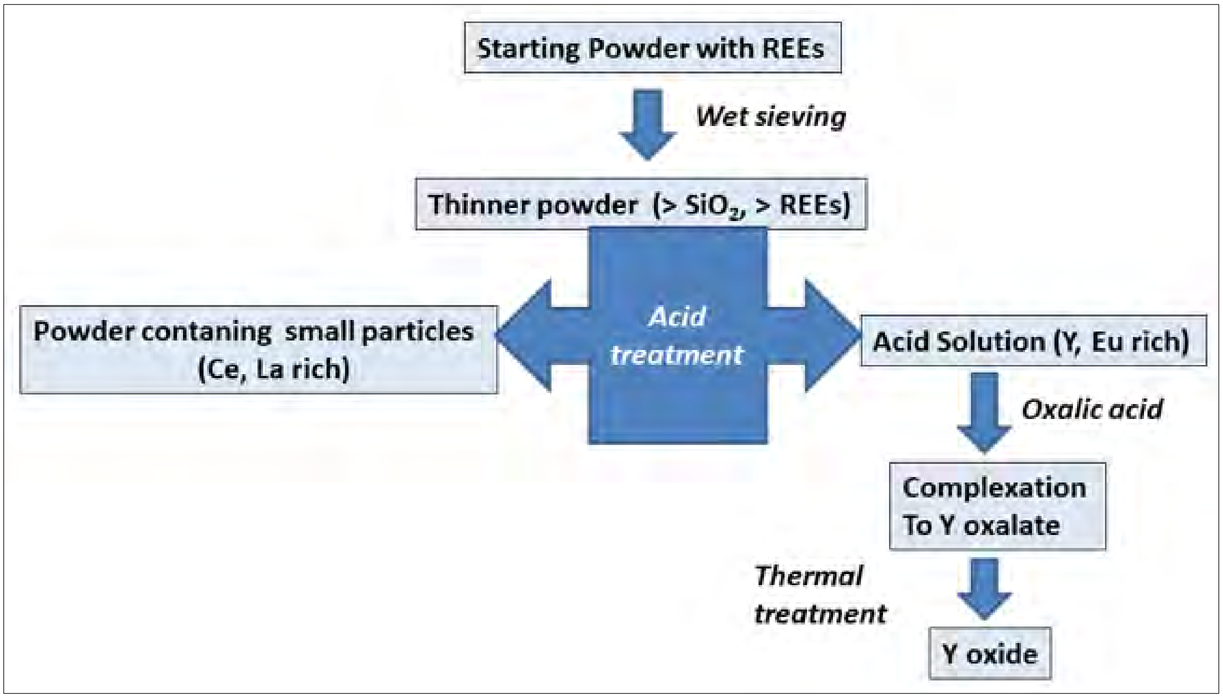


Image 208: summary of the treatment performed in the thesis work

A key aspect for the efficiency of the final recovery is connected with the concentration of the REEs in the sample treated and the absence of interfering elements.

For that reason an additional mechanical sieving pre-treatment (20 µm mesh) was added to the standard procedures found in literature in order to maximize the content of REEs in the initial sample. The primary separation between coarser silica and finer REEs particles is thus performed on the initial powders shows good advantages because silicon content decreased of almost 57% (atomic percentage) and consequently the REEs atomic percentage increases in particular for yttrium, europium, praseodymium and ytterbium.

ESEM analysis of the sieved sample was useful to recognize the composition of the different particles and how REEs are distributed in these particles.

Also the analysis of the coarser fraction was made to verify that the percentage of precious material lost in the pre-treatment procedure was extremely low.

The sieving process (20 micron) required the use of water (de-ionized water) in order to avoid the formation of static electric charges on the particles: thus the treatment resulted very useful non only to eliminate the larger fragments of silica, but also to dissolve soluble salts (at least partially) such as calcium, sodium and potassium which could interfere in the following steps.

As for extraction process different extraction procedures were tested with the target to verify the acid, sequence of acids, mix of acids or bases that better perform the recovery of REEs as a group-compounds but also separately one by one.

For the particular case of the yttrium the best extraction obtained provided: sulfuric acid, room temperature, s/l ratio equals to 2 mg/l, room temperature for 24 hrs. One of the advantages of H_2SO_4 extraction was the settling of calcium that was only partially dissolved due to the formation of not soluble $CaSO_4$, thus enhancing the efficiency and selectivity of the next step of complexation.

The sieving procedure increased the efficiency of the extraction process by decreasing the silicon content and enhancing the yttrium ones. By analyzing the solid filtered fraction from the sulfuric acid reaction it was noticed the presence of small white particles (by ESEM analysis) indicating that some REEs were not dissolved, in particular cerium and lanthanum. On the contrary yttrium was almost extracted by dissolution in the liquid phase. This observation indicated that further extraction procedures were necessary in order to achieve the extraction of other REEs (the problem is well known in the literature: the small REEs rich particles derive from the fluorescent lamps preparation). Thus experiments on the solid fraction containing mainly cerium and lanthanum with HF or NaOH and thermal treatments or by using microwave reactors have been carried out.

Interesting preliminary results were obtained with HF and CH_3COOH which appeared to be suitable to give a selective separation of the REEs .

On contrary experiments with nitric acid and aqua Regis did not show relevant results.
As for extraction processes carried out with a sequence of acids: double HF extraction showed high percentage of silicon in the solution highlighting the advantageous decision of obtain the solid fraction rich in REEs suitable for subsequent treatments. In particular the treatment with HCl showed the extraction of yttrium, praseodymium, europium and ytterbium with a relevant reduction of dimension of small particles in the solid fraction. These preliminary results are very intriguing, even if they deserve further research work.

About microwave experiments interesting results are achieved for the selective recovery of REEs but further researches are essential to improve the processes.

As for complex formation process the main parameters are: pH value and type of complex agent. The pH value must be increased: different bases have been studied, NaOH revealed to be the best.
Also different complexation agents have been used: oxalic acid showed to be the best. The principal issue of this step is the presence of calcium that appears as competitor for the formation of yttrium oxalate. So far the best conditions achieved were: pH value 1-1.5 reached with addiction of NaOH and acid oxalate as complexation agent. Yttrium oxalate in high yield was obtained (more than 90% with respect the content in the starting powder).

Yttrium oxalate must be converted into the corresponding oxide. Thus a thermo-gravimetric study has been carried out in order to optimize the temperature for the conversion process: 675°C appears to be the suitable temperature for the conversion of yttrium oxalate into yttrium oxide with a no-toxic residue production of CO_2 from oxalate.

As for the purity of yttrium oxide it was not possible to gain the result because of the absence of the *standard* but references found in the literature about FT-IR and XRD spectra appear comparable to those obtained for the products obtained in the experiments here reported.

Further tests will be performed to achieve better results in particular in relation to the industrial feasibility (efficiency) and environmental sustainability (production of waste) of the whole process.

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