Sustainable processes development for recycling of fluorescent phosphorous powders – rare earths and mercury separation

A literature report

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Abbreviations

AAS	atomic absorption spectrometry
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
CFLs	compact fluorescent lamps
CVAAS	cold vapor atomic absorption spectrometry
CVAFS	cold vapor atomic fluorescence spectrometry
GLC-ECD	gas-liquid chromatography-electron capture detection
HPLC	high performance liquid chromatography
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-OES	inductively coupled plasma-optical emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
NAA	neutron activation analysis
NEMA	National Electrical Manufacturers Association
OSHA	Occupational Safety and Health Administration
REEs	rare earth elements
REMs	rare earth metals
RBS	Rutherford backscattering spectroscopy
SEM/EDS	scanning electron microscopy-energy dispersive spectroscopy
TBP	tri-n-butyl phosphate
TDAAS	thermo-desorption atomic absorption spectrometry
US	United States of America
UV	ultraviolet
VIS	visible
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence

1. Introduction

The advantages compared to incandescent bulbs, marketing campaigns and environmental concerns have led to an increase in the number of fluorescent lamps used all over the world. Lower energy consumption (about 75% less energy consumed to produce the same light output as an incandescent bulb) and longer life expectancy (about 10 times) [1], as well as the decisions made by some governments to phase out incandescent lighting, have greatly contributed to the rising use of fluorescent lamps. Although the cost of such lamps is higher (3 to 10 times more than comparable standard bulbs) [1], the advantages mentioned above are expected to compensate for this.

When fluorescent lamps reach their end of life, they are usually discarded as waste products. However, because all fluorescent lamps contain mercury [2, 3], they are classified as hazardous waste. Before disposing, treatment in order to reduce the toxicity of the waste below the allowed limits is required.

Recycling is one of the solutions to the large quantities of waste generated every year. While it allows decontamination of fluorescent lamps waste (mercury removal), it can also lead to the recovery of valuable materials. Glass and aluminum end caps can be recycled into production cycles. Also, recovery of the contained rare earth metals (REMs), key components of these lamps, is receiving more and more attention. Considering the availability and supply risk of certain raw materials [4], fluorescent lamps are viewed as potential urban mining resources for the recovery of REMs and other elements [5].

So far in the world hundreds of millions of fluorescent lamps are sold and disposed every year [6-8]. Viewed as a whole, these products contain tons of phosphorus powder which contains, among others, high amounts of mercury and a large quantity of REMs. Developing an industrial process which, in a sustainable way, removes mercury from the phosphorus powders and individually recovers the contained REMs is of great importance.

The purpose of this report is a survey of the literature in order to find the latest achievements in waste recycling. The focus will be the methods that can be applied for the efficient recovery of mercury and REMs from phosphorus powders, in the hope of determining a viable and profitable procedure that can be scaled up to an industrial process.

1.1. The importance of recycling fluorescent lamps

Two aspects are of great importance when it comes to recycling of fluorescent lamps: mercury and REMs content.

Experimental data has shown that many fluorescent lamps contain high concentrations of mercury, failing the toxicity characteristics when they are disposed [2]. One of the problems that fluorescent lamps waste recycling poses is mercury contamination. Without special treatment it is always a possibility that recycled components such as glass and metal caps will be contaminated with hazardous mercury. Also, although it’s not difficult to separate the phosphorus powder from the other components, the material will be contaminated as well. In order to recover the REMs contained in the phosphorus powder, mercury must first be removed. An efficient method for this is thermal treatment. However, this will not remove all mercury that is absorbed on the powder’s particles, due to strong interactions. The phosphors can be dissolved in acids to bring all mercury and REMs into solution. From here, mercury can be removed using different methods. Sometimes, in the absence of an efficient process that separates REMs from the phosphors, the powder is usually landfilled or stored.

Obtaining access to certain raw materials is becoming a challenge for many countries all over the world. According to a recent European Commission report [4], 14 raw materials are considered critical for the EU, the highest on scale being the REMs (Figure 1).

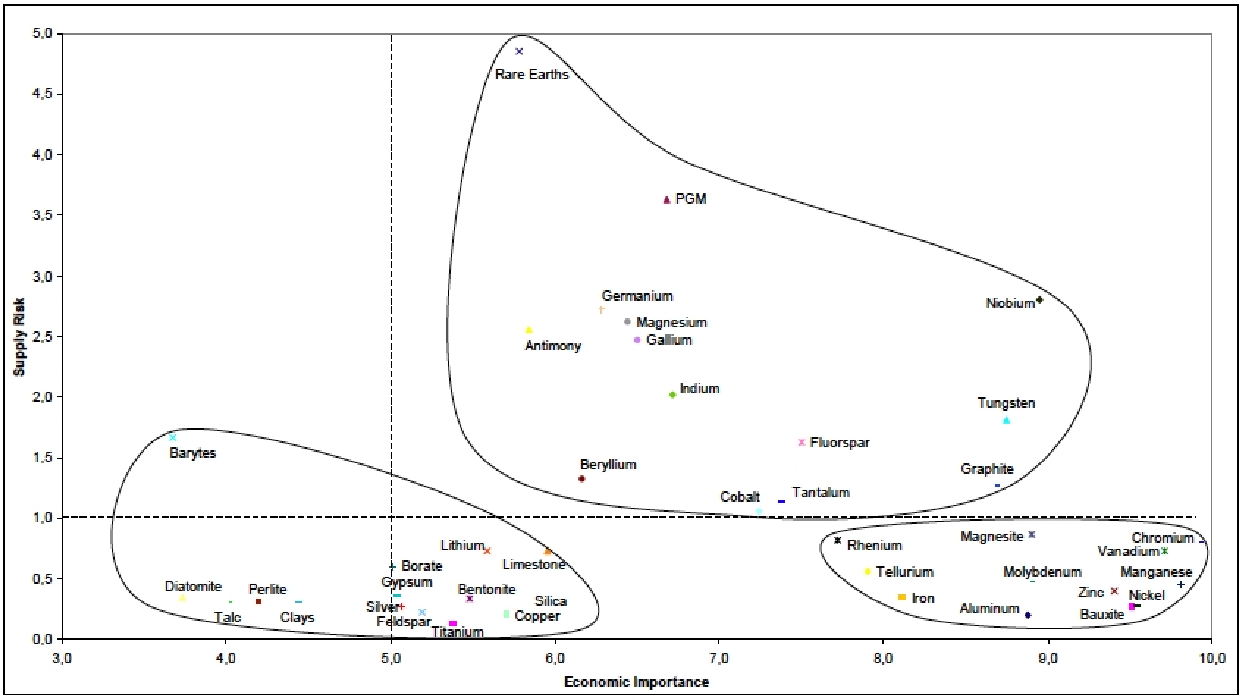

Figure 1: Important raw materials for the EU [4]

REMs prices, especially for those used in the manufacturing of phosphorus powders experienced very big variations during the last years. Today approximately 97% of all REMs are produced in China. Because of demand growth and the country’s policy to limit exports, REMs suffered significant price increases. According to Rhodia, the prices of yttrium, terbium and europium have increased roughly 45%, 420% and 53%, respectively, from 2000 to 2009 [10]. Additionally, in June 2006, a 10% tariff on REMs has been established. For key phosphors, the tariff in 2009 was 25%. Thus, recycling of REMs from spent fluorescent lamps is of great importance and putting the basis of a suitable industrial process for recovering REEs is critical. Such a process would provide an independent source of these elements and negate Chinese export quotas and price increases.

To sum up, several reasons stand behind the efforts to develop an efficient process for recycling of fluorescent lamps:

- environmental benefits: prevent the spreading of toxic chemicals (mercury and its compounds) in the environment; reduction of landfill areas and clean landscapes;
- material supply: materials can be recycled back into production cycles; increasing the availability of certain compounds (REMs);
- taking care of natural resources: reducing exploitation and conserving natural deposits;
- economic reasons: reducing the costs of raw materials, processing costs, logistic costs.

2. Fluorescent lamps – construction and composition, principles of operation

In the present, two types of lamps are mainly used in lighting: mercury-containing ones (fluorescent lamps), and lamps without mercury (incandescent lamps and halogen/dichroic lamps) [8].

Fluorescent lamps are gas discharge lamps that use mercury vapors to produce light. The typical construction of a straight tube fluorescent lamp is presented in Figure 2. The lamp comprises of a glass tube, filled with an inert gas. The inside of the tube is coated with a thin layer of phosphorus powder. Mercury is added in the manufacturing process into elemental form, and it plays a vital role: conversion of electrical energy into radiant energy. UV photons are emitted from the interaction of mercury atoms with the electrons emitted by the cathode. The inner coating layer of the lamp absorbs the UV energy causing the phosphors to fluoresce and emit visible light [11]. The composition of the phosphorus powder is responsible for the light's color and intensity [10, 12].

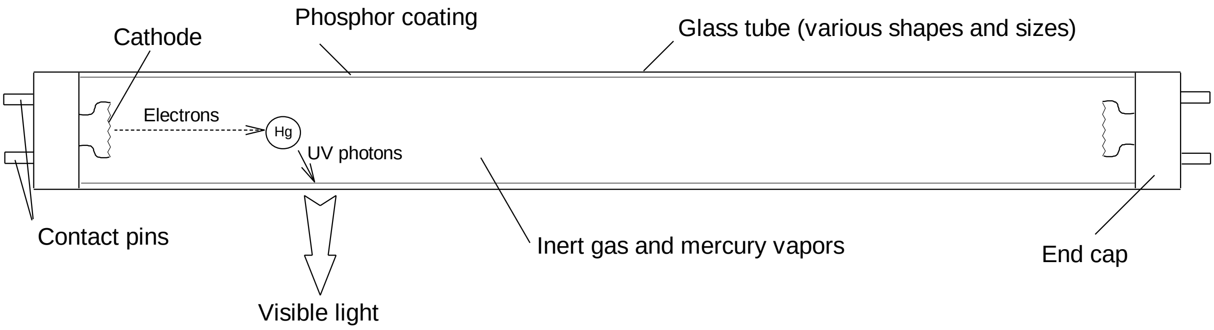

Figure 2: Schematic representation and operation principle of a fluorescent lamp

Fluorescent lamps are available in different forms and sizes. The tube can be straight, bent or coiled into different shapes [1]. All lamps are identified by a code that contains information regarding shape, dimensions and operation characteristics. Aesthetic and architectural reasons, as well as the need to provide large amounts of light in small areas, have led to the miniaturization of fluorescent lamps. Compact fluorescent lamps (CFLs) are a great example, with continuous rising use in residential sectors.

The operating life of a fluorescent lamp varies and it is based on the annual hours of use. If a lamp is operated between 4000 and 5000 hours each year, and has a typical life of 20000 hours, the life span is between four and six years [13].

3. Mercury recycling from industrial wastes

Mercury is a highly toxic element, being included in the priority list of 129 hazardous substances by the US Environmental Protection Agency [9]. It's persistence in the environment and bioaccumulation ability in living organisms requires special measures to be taken into consideration when disposing of mercury containing waste.

Despite its toxicity, several of its physical and chemical properties make mercury an essential material in many industrial products [9], especially fluorescent lamps.

3.1. Mercury in fluorescent lamps

All fluorescent lamps contain mercury. The quantity varies based on the type of lamp, manufacturer and the year of fabrication [2, 8, 13]. Taking into account environmental concerns and human safety, important progress has been made over the years to reduce the amount of mercury used in the lighting industry [2]. According to the National Electrical Manufacturers Association (NEMA) [11], the quantity of mercury used in the manufacture of fluorescent lamps decreased significantly, from 57 tons in 1984 to 6 tons in 2006. At that time, the mercury contained in a four-foot linear fluorescent lamp (the most common fluorescent lamp type) was about 8 mg. The survey says that, although the average mercury content in lamps declined from 48.2 mg in 1985 to 8.3 milligrams in 2001 (Figure 3), it is unlikely that an energy efficient mercury-free fluorescent lamp will be commercially available in the near future. In the absence of a substitute with the same efficient properties, a fluorescent lamp without mercury would consume approximately 3 times more energy than a mercury-containing lamp to produce the same light output.

The European Community established the limits for mercury in fluorescent lamps through the Directive 2002/95/EC. According to this document, mercury in CFLs must not exceed 5 mg per lamp. For general purposes straight fluorescent lamps the limits are 10 mg for halophosphate ones, 5 mg for triphosphate lamps with normal lifetime and 8 mg for those with long lifetime [14]. However, high mercury content lamps are still used. Recent analyses of mercury content in different types of compact fluorescent lamps revealed mercury quantities per lamp ranging from 1.6 to 27 mg, six samples out of 15 tested (40%) being above the allowed limit [15].

If mercury is introduced in insufficient quantities, premature failure of the lamp will occur, a phenomenon known as mercury starvation. A four feet, 40 W, fluorescent lamp with 20000 hours operating life needs about 10 mg of mercury [3]. Sometimes mercury is introduced in the manufacturing process in higher amounts than required, in order to ensure the stated lifetime of the lamp.

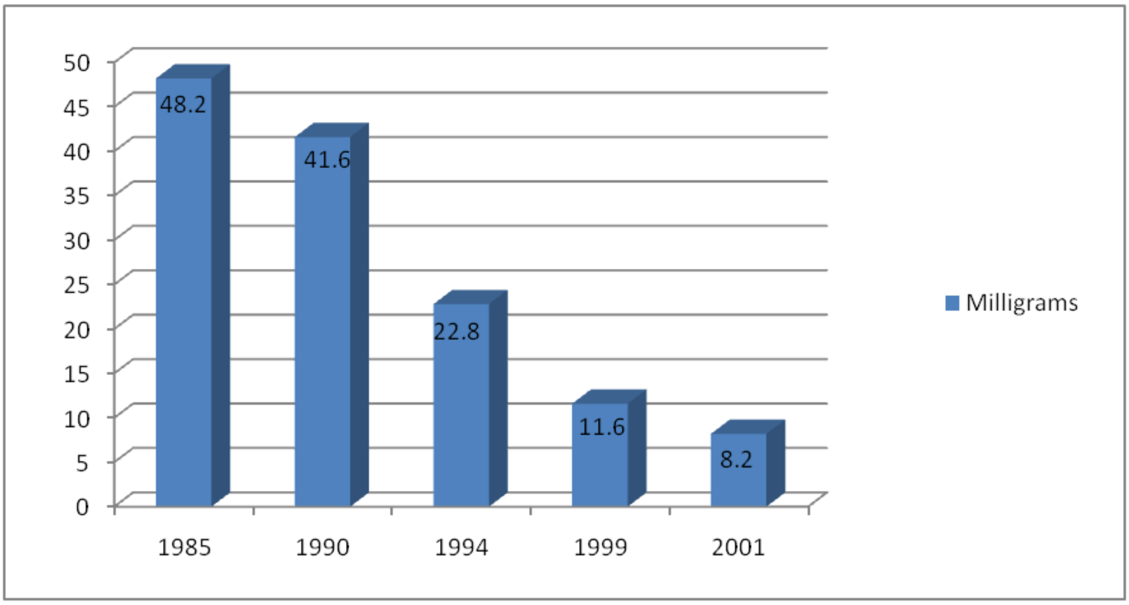

Figure 3: Mercury contained in Four-Foot Fluorescent Lamps – Industry Average [11]

3.2. Mercury interactions in fluorescent lamps

Investigations regarding the chemical reactions taking place in fluorescent lamps have been conducted, with focus on the interactions between mercury and various lamp components. Analytical results have shown that, throughout the lamps life, mercury is mainly adsorbed into the phosphorus powder and, in small quantities, into the glass and other components (end caps, electrodes etc.) [3, 16-18].

Studies regarding the interaction between mercury and various fluorescent lamp components (glass, conductive tin oxide, electrode, and its volatile emitter) have been conducted. Electron spectroscopy for chemical analysis (ESCA) and sputtered neutral mass spectrometry (SNMS) have been used in the investigations [17]. Four types of lamps were used, a center and an end portion being studied for each lamp. Lamp ends specific components such as coils and emitters were also studied. Both uncoated and phosphor coated lamps were used. Results revealed for the central part of the lamps strong interactions of mercury with sodium in the glass and, at the lamp ends, with volatile emitter materials. In the central part of uncoated lamps mercury was much more easily desorbed compared to phosphor coated lamps, suggesting stronger interactions for the latter.

Mercury-glass interactions in fluorescent lamps have been studied using X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS), scanning electron microscopy (SEM) and thermally stimulated evolution [16]. Investigations revealed that the amount of mercury that interacts with the glass is time dependent and it is inversely proportional to the phosphor weight. Local mercury concentration is clumpy and inversely proportional with sodium concentration in the glass. Very low interaction has been observed when the samples were physically shielded from the plasma by quartz.

Two of these observation were also made by Thaler *et al.* [18] who states that two parameters determine the amount of bound mercury on glass: the time of operation and the phosphor weight. An empirical model describing how much mercury is bound in the glass, as a function of these parameters was proposed:

$$M=A\cdot t+B\cdot[1-C\cdot W]\cdot t^{1/2}$$

In the equation M is the amount of bound mercury (µg/cm^2), W the phosphor weight (mg/cm^2), and t the time the operating time of the lamp (h). A, B and C are empirically determined fitting parameters, with the following values: $5.24\cdot10^{-5}$ µg/cm^2/h, 0.045 µg/cm^2/h$^{1/2}$ and 0.20 cm^2/µg respectively.

The mercury content in glass and phosphorus powders from new and spent fluorescent lamps was investigated by Raposo *et al.* [3]. After cleaning the lamps, they were carefully imploded under a hood and the phosphorus powder was collected by scraping. Phosphorus powder and glass samples were dissolved in nitric acid and the contained mercury was investigated using cold vapor atomic absorption spectrometry (CVAAS). The results showed that the main contribution to the hazardous aspect of spent fluorescent lamps waste belongs to the phosphorus powder matrix. Mercury concentrations in the powder of spent lamps were found to be, in some cases, 40 times higher compared to new lamps, reaching 13300±1300 µg/g. Very small concentrations were found in the glass of new lamps (about 18 µg/g) while, in the case of spent lamps, mercury concentrations reached 4300±1300 µg/g.

Recent research [19] shows that more than 85% (average value of 204.16±23.0 ppb) of the mercury introduced in compact fluorescent lamps binds to the phosphorus powder and more than 13% (average value of 18.74±2.0 ppb) diffuses through the glass.

Partitioning of mercury in fluorescent lamps has been examined by Jang *et al.* [2] and similar conclusions were drawn. Different types of spent and new fluorescent lamps were used in the experiments. The results showed that the quantity of mercury which interacts with certain components varies from one lamp to another (Table 1). More than 94% of total mercury interacts with the phosphorus powder coating and glass. Higher quantities of elemental mercury are present in the vapor phase of new lamps. In contrast, for spent lamps, mercury is found in higher quantities in the phosphorus powder and end-caps.

Table 1: Partitioning percentages of mercury for different components of fluorescent lamps [2]

Components	Spent T8 lamps (%)	Spent T12 lamps (%)	New T12 lamps (%)
End caps	2.07	0.50	0.09
Loose phosphor powders obtained during breaking and washing steps	2.86	5.34	2.72
Vapor phase	Not detected	0.04	0.17
Phosphor powders remained on the glass and glass matrices	95.08	94.12	97.02

Investigations with Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS), low-energy ion scattering, and thermal desorption mass spectroscopy revealed that the interactions between mercury and glass are greatly reduced if the glass is covered with a thin oxide film [20]. Three different oxides were investigated: cerium dioxide, tungsten (VI) oxide and yttrium oxide, each leading to different mercury concentration profiles in the films. Higher concentrations of mercury were registered close to the discharging side of the coating. Mercury interactions with the glass were reduced by about two orders of magnitude, mercury being bound mainly in the oxide films.

The interaction between mercury and the phosphorus powder matrix was studied using thermo-desorption atomic absorption spectrometry (TDAAS) [3]. This technique revealed the presence of both metallic (Hg^0) and ionic (Hg^{1+} and Hg^{2+}) mercury species. A predominance of Hg^0 and Hg^{1+} over Hg^{2+} was observed, although there were exceptions. The authors state that ionic species, compared to metallic mercury, can form compounds more soluble, and thus have a greater impact on the environment. This is due to much easier transportation, oxidation and methylation processes.

3.3. Mercury release from fluorescent lamps

Releases of mercury in the environment are correlated with the processing and disposal methods of spent fluorescent lamps. Direct landfilling is not a good option, leading to contamination of the air around the dumping site, especially if the lamps are crushed on site. Soil and groundwater are also affected by leaching of mercury species from the waste. One big concern is the possibility of conversion into extremely toxic species such as methyl mercury. Incineration of fluorescent lamps waste also poses problems if it is performed in the absence of air pollution control systems that capture generated mercury vapors [21]. Collection of spent fluorescent lamps and decontamination/recycling is the best options when taking into account those stated above.

Studies regarding leaching of mercury from fluorescent lamps in the environment have been performed [6, 22]. Anodic Stripping Voltammetry (ASV) was used to determine mercury content in CFLs and in the soil of a disposal site in India [22]. Analysis reported mercury concentrations up to 0.1175 mg/g in the lamps and 0.0149 mg/g in the soil. Laboratory investigations with artificially spiked spent fluorescent lamps were used to confirm the leaching of mercury in the soil.

It was reported that between 17 and 40% of the mercury in fluorescent lamps is released in the atmosphere during a two week period after breaking [6]. During the first 8 hours, about one third of the mercury release occurs. High temperatures affect the process, leading to increased percentages.

It was stated that the ionic species of mercury present in fluorescent lamps can form compounds more soluble than metallic mercury, thus having a greater impact on the environment. This is due to a much easier transportation via the aqueous phase, oxidation and methylation processes [3].

3.4. Mercury separation and determination

During the last years, environmental (pollution prevention) and economic (material supply) concerns have focused the attention on developing more efficient methods for removal of mercury from industrial waste.

According to [23], determination of mercury involves generally six steps:

- sample collection;
- sample pretreatment/preservation/storage;
- liberation of mercury from its matrix;
- extraction/clean-up/pre-concentration;
- separation of mercury species of interest;
- quantification.

3.4.1. Instrumental methods for mercury determination

Various instrumental methods are available for quantifying mercury: CVAAS, cold vapor atomic fluorescence spectrometry (CVAFS), inductively-coupled plasma-mass spectrometry (ICP-MS), inductively-coupled plasma-optical emission spectrometry (ICP-OES), electrochemical methods, and neutron activation analyses (NAA).

Some of the most frequently used methods for determination of mercury and their relative detection limits are presented in Table 2 [23].

Table 2: Frequently used methods for quantification of mercury and their relative detection limits [23]

Method		Detection limits
Colorimetric methods		0.01 - 0.1 µg/g
AAS	Graphite furnace (GF AAS) Cold vapour (CV AAS)	1 ng/g 0.01 - 1 ng/g
AFS	Cold vapour (CV AFS)	0.001 - 0.01 ng/g
NAA	Instrumental (INAA) Radiochemical (RNAA)	1 - 10 ng/g 0.01 - 1 ng/g
GC	Electron capture detector Atomic emission detector Mass spectrometer CV AAS/AFS	0.01 - 0.05 ng/g 0.05 ng/g 0.01 ng/g 0.01 - 0.05 ng/g
HPLC	UV CV AAS CV AFS Electrochemical detectors	0.1 ng/mL 0.5 ng/mL 0.08 ng/mL 0.1 - 1 ng/mL
ICP MS		0.01 ng/mL
ICP AES		2 ng mL
Photo-acoustic spectroscopy		0.05 ng
X ray fluorescence		5 ng/g - 1ng/g
Gold-film analyzer		0.05 µg/g

3.4.1.1. Cold vapor atomic absorption spectrometry

CVAAS is one of the most popular methods to quantify total mercury content in various types of samples. A reducing agent (tin chloride or sodium borohydride) is added to the sample in order to reduce mercury to its elemental form. Mercury vapors liberated from the sample are usually pre-concentrated on a gold surface then thermally desorbed into an inert gas stream which carries them into the cell of an atomic absorption spectrometer (AAS). The absorption is measured at 253.7 nm. Compared to many other techniques, the method is easy to perform, rapid, selective, and accurate [23]. However, spectral interferences can occur, most often caused by volatile materials which absorb at 253.7 nm. Proper selection of the pH and reducing agent can minimize or completely remove some of the interferences.

3.4.1.2. Cold vapor atomic fluorescence spectrometry

CVAFS can be used with great results for measuring trace amounts of volatile metals such as mercury. Compared to AAS, the method achieves much better sensitivities (less than 1 pg) and linearity over a wider concentration range [23]. An UV light source (253.7 nm) is used to excite mercury atoms. The absorbed energy is re-radiated by the mercury atoms and detected by a photomultiplier or UV photodiode.

A pre-concentration step can be performed (absorption on a gold surface, followed by thermal desorption) in order to increase the sensitivity of the method.

3.4.1.3. Inductively coupled plasma-mass spectrometry

ICP-MS is one of the most powerful techniques for metal determinations in aqueous phases because of its high sensitivity, large dynamic linear range, multi-element capability and possibility to perform isotopic measurements [24].

Memory effects, which are one of the major problems for the effective use of this method, are greatly reduced by introducing mercury as gaseous species into the plasma [23]. Isotopic speciation can offer valuable information about transformations of mercury species in environment and biological systems.

3.4.1.4. Neutron activation analysis

The method it is highly precise and sensitive and has the advantage that it does not destroy the sample, analyses being performed directly, without any pre-treatment. However, due to its high cost, safety requirements, the need for a nuclear reactor and special apparatus, this method is not used frequently [23].

One of the advantages is the possibility to analyze a large variety of samples: liquids, solids, gas, suspensions etc.

3.4.1.5. Atomic emission spectrometry

Photons emitted during the transition of mercury atoms from an excited state to a lower energy state are measured, the intensity of the emission being correlated with the concentration.

Several types of plasma sources (direct current, inductively coupled, and microwave induced) have been used for the determination of mercury [23, 25] and, although these methods are very sensitive compared to AAS and AFS, they are much more expensive and complex for routine analyses.

3.4.1.6. Photo-acoustic spectroscopy

For mercury determination, a pre-concentration step on a gold trap is performed; after thermal release, the sound produced from fluorescent quenching when the sample vapor is irradiated with a modulated mercury vapor lamp is measured. The detection limit is 0.05 ng [23]. Trace levels of mercury in air and snow have been successfully detected with this method [26, 27].

3.4.1.7. X-ray fluorescence

Compared to other methods, X-ray fluorescence (XRF) has some advantages: minimal sample preparation, fast and non-destructive analysis and it is indifferent to the chemical or physical state of the analyte. However, AAS and NAA offer better sensitivities. For direct XRF sample measurements, detection limits in the µg range can be achieved. A pre-concentration of mercury can improve the sensitivity [23].

3.4.1.8. Electrochemical methods

ASV is used as a method of quantifying mercury in solutions. One of the advantages, apart from the lower cost of instrumentation, is the possibility of separating mercury(I) and mercury(II) in aqueous solutions. However, because of the low sensitivities, these methods have become less popular and have been replaced by the others described above [23].

3.4.2. Determination of organic mercury

Gas-liquid chromatography with electron capture detection (GLC-ECD) is used for selective analysis of organomercury compounds [28]. The analytical procedure involves the extraction of methylmercury in the samples with an organic solvent followed by back-extraction into a cysteine- or glutathione-aqueous solution. After re-extraction into an organic solvent methylmercury is measured using GLC-ECD.

GLC-ECD responds to the halide ion attached to the methylmercury ion (it does not measure mercury directly). Because of its superior sensitivity (detection limit of approximately a few pg), this technique is widely used for the determination of methylmercury in various kinds of biological and environmental samples [23].

Methods that use the formation of volatile organomercury derivatives through ethylation, propylation, butylation, hydration and iodination can be used in order to separate organic mercury [23]. These volatile compounds are removed from solution by aeration and then trapped on an adsorbent. From there, they can be desorbed or leached and analyzed.

Methods that are based on differential reduction also exist. Magos [29] described a method based on the rapid conversion of organomercurials first into inorganic mercury and then into atomic mercury. Organomercury compounds are reduced to elemental mercury by a tin chloride-cadmium chloride combination; CVAAS is used as an analytical technique for mercury determination.

3.4.3. Determination of mercury and its compounds in solutions

Mercury compounds occurring in water are presented in Figure 4; they are most often defined by their ability to be reduced to elemental mercury [23].

The stability of mercury in solution is affected by factors such as: concentration of mercury and its compounds, the type of water sample, the type of containers used, the cleaning and pretreatment of the containers and the preservative added [23].

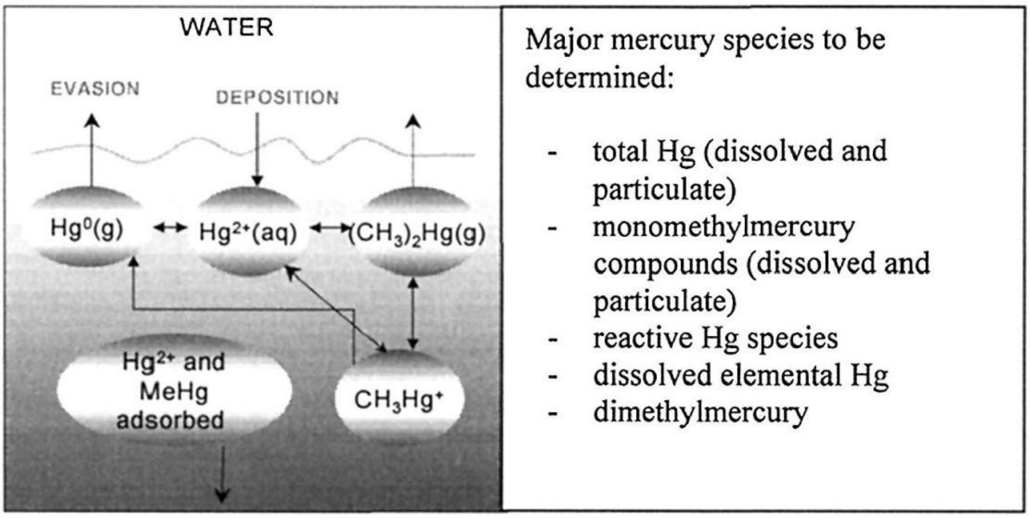

Figure 4: Mercury species and transformation in water [23]

The main steps for determination of various mercury compounds in solution are shown in Figure 5 [23].

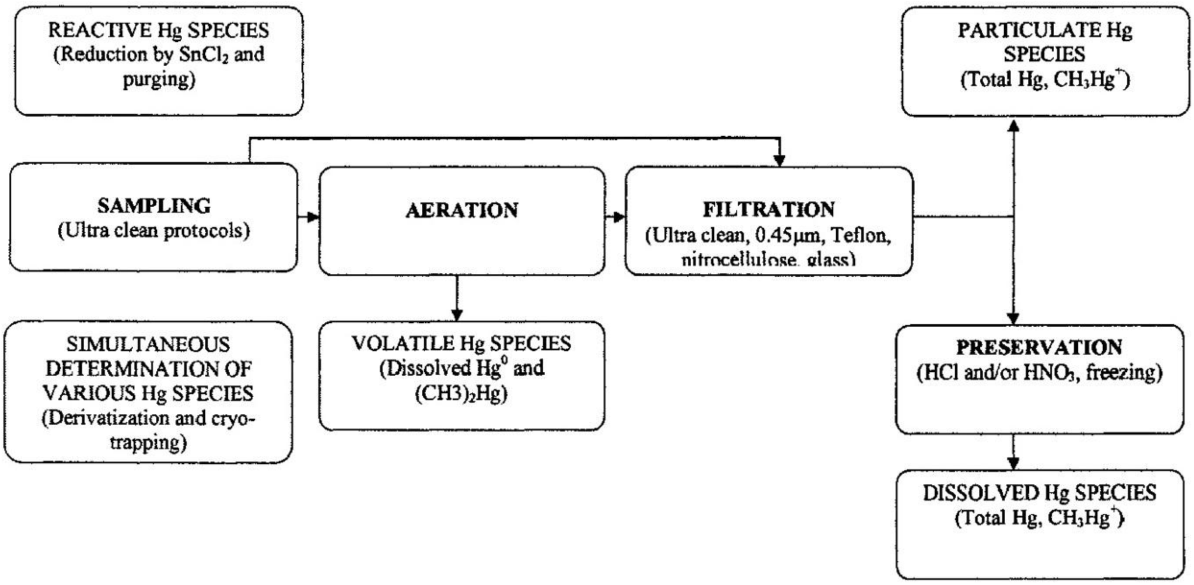

Figure 5: Common steps for determination of total mercury and its compounds in solution [23]

Containers and other sampling equipment used should be made of Teflon, borosilicate glass or silica glass. Teflon has the best performance regarding contamination and loss-free storage of aqueous samples [23]. In order to minimize contamination, water can be pumped through Teflon tubing using a peristaltic pump.

Volatile mercury species such as metallic mercury and methylmercury can be removed from the samples by aeration and collection on absorbents. In order to measure dissolved mercury compounds, removal of particulate materials from the sample is necessary. This is achieved by either filtration or centrifugation. Samples should be processed immediately after removal of the particulate matter. If this is not possible and samples have to be stored for a certain period of time, the mercury present has to be stabilized by adding acid. For the analysis of organomercurials, preservation with oxidative reagents is not advised as organomercurials are converted into inorganic mercury. In this case, hydrochloric acid was found to be the most appropriate acid for storing aqueous solutions [23].

A schematic flow chart for determination of total mercury in natural water samples is shown in Figure 6 [23]. If total mercury is to be measured, the decomposition of all species into Hg^{2+} is mandatory. This can be achieved with oxidizing agents or by using UV irradiation. A combination of the above methods can be used for better results. CVAAS is the most used method for total mercury determination in solutions. ICP-MS and ICP-OES can be used if mercury in the samples is present in traces, due to better detection limits compared to CVAAS.

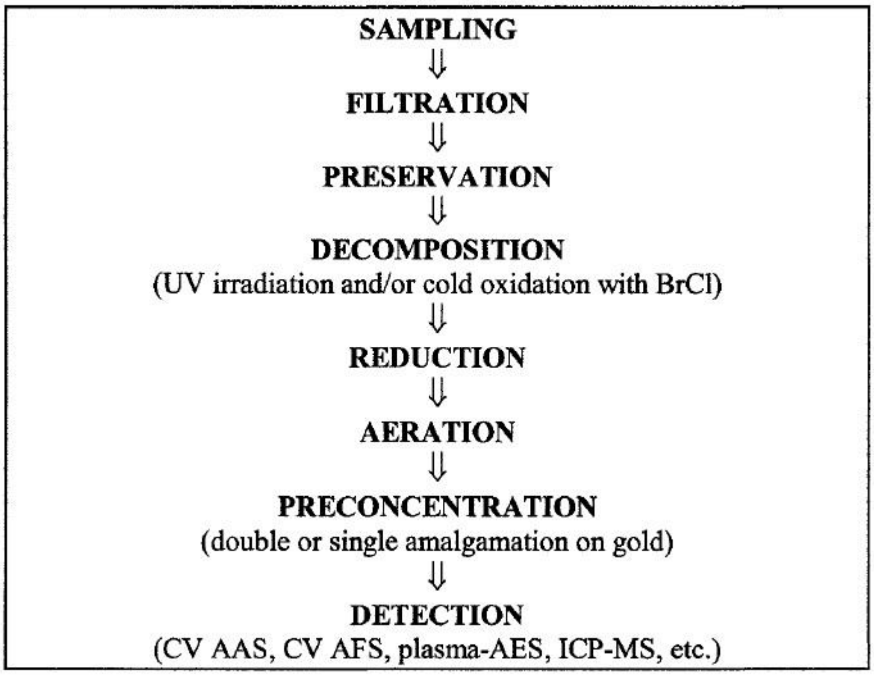

Figure 6: Principal steps for the determination of total mercury in solution [23]

3.4.4. Determination of mercury and its compounds in solid samples

When analyzing solid samples, a preliminary decomposition is needed. Wet procedures using oxidizing agents (hydrochloric, sulphuric, nitric acid) or dry procedures involving combustion/pyrolysis are usually used [23]. The latter can be performed under reductive or oxidative conditions and can be combined with pre-concentration methods for better results e.g. gold amalgamation.

Comparison between acid digestion and thermal treatment of solid filters containing particulate mercury was made [30]. Microwave assisted acid digestion was carried with nitric acid at 160 ºC followed by determination of mercury by CVAAS. Pyrolysis experiments were conducted in a quartz pyrolyzer, at 800-900 ºC, under a nitrogen flow. Acid treatment was found to give better results (about 30%) compared to pyrolysis, due to possible interactions of mercury with the matrix.

3.4.5. Recovery and determination of airborne mercury

One of the methods for removing mercury vapors from gas streams involves using adsorbents. Activated carbon and zeolites [31, 32], as well as sulfur-impregnated activated carbon and zeolites have been studied [33]. Experiments on the adsorption of mercury vapor on sulfur-impregnated adsorbents, conducted by Otani *et al.* [34], showed that the impregnation of sulfur increases the adsorption capacity of active alumina and zeolite by several orders of magnitude.

The removal of mercury vapors by TiO_2 irradiated using various light sources was studied [35]. A mixture of TiO_2 and glass beads was used to increase the effective surface area of TiO_2 for mercury adsorption and UV radiation. A mercury vapor generator, a photochemical reactor, and an on-line mercury analyzer were used to study the effectiveness of the method. Three different commercially available TiO_2 were used and removal efficiencies under different light sources were evaluated (UV black light, UV sterilizing light, fluorescent light and blue light). With one exception, more than 99% of initial mercury was removed. Under blue light, a removal efficiency of only 85% was achieved. Exhaust gas samples were taken out of the photochemical reactor and analyzed to verify that mercury was actually adsorbed onto the TiO_2 surface. This was confirmed for efficiencies close to 100%, no mercury being detected in the gas. Comparisons made with activated carbon shows that TiO_2 performs better for mercury removal while also being much more economical.

Several types of sorbents were analyzed for the removal of elemental mercury from a carrier gas [36]. The capacities and breakthrough times of different sorbents were investigated. Higher capacities were observed for activated carbons at lower temperatures and also for chemically promoted activated carbons, compared to standard ones. Due to low costs, chlorine was suggested as a chemical promoter for carbon sorbents for the removal of mercury. Metal oxides and sulfides are suggested as an alternative, MnO_2, Cr_2O_3 and MoS_2 exhibiting moderate capacities for mercury removal.

Occupational Safety and Health Administration Method ID 140 [37] describes the collection of airborne elemental mercury in a passive dosimeter or active sampling device and further analysis using CVAAS. The passive dosimeter is based on controlled diffusion while the active sampler uses a calibrated sampling pump. Mercury is irreversibly trapped on a solid sorbent such as Hydrar or hopcalite. For quantification of mercury, the sorbent is dissolved with concentrated acids. Tin chloride is added to generate mercury vapors that are driven into the cell of a flameless atomic absorption spectrophotometer.

The method describes that previously, mercury samples were collected on iodine-impregnated charcoal contained in glass tubes. Mercury vapors were released into the beam of an atomic absorption spectrophotometer by thermal treatment. Detection limit for this method is approximately 0.1 µg.

Hopcalite solid sorbent was chosen for mercury vapors sampling in place of the iodine-impregnated charcoal. Analysis of hopcalite used for mercury collection shows its composition consists mainly of oxides of manganese and copper. Hydrar, which has a similar composition, can be used as a substitute.

According to the documentation [37], the advantages and disadvantages of the OSHA method are:

- adequate sensitivity for measuring workplace atmospheric concentrations of elemental mercury;
- small, lightweight, reusable, cost efficient passive dosimeter that requires no sampling pumps;
- stability of the collected mercury sample for at least 30 days;
- simple sample preparation procedures for analysis;
- analyzes can be performed in any laboratory equipped with a CVAAS;
- one of the disadvantages the passive dosimeter has is the inability of collecting particulate compounds; a separate sampling pump and collection media is necessary in this case;
- sample rate is dependent on air velocity, the dosimeter not being recommended in areas where the air velocity is greater than 229 m/min;
- the active device is dependent on a calibrated pump for sample collection.

Inorganic mercury passive samplers validated by OSHA method ID 140 are commercially available. One of such devices is manufactured by the company SKC Inc. It uses Anasorb, a proprietary sorbent, comparable to Hydrar. The passive sampler, according to its specification sheet has high accuracy and sensitivity:

- positive analysis of inorganic mercury;
- limit of detection: 0.01 μg;
- limit of quantitation: 0.04 μg;
- sampling and experimental error: ± 8.6%;
- background: 0.02 μg/200 mg section.

The device is light, easy to us, has the lowest cost per measurement and provides longtime sampling (up to 120 hours). It is supposed to be attached close to the collar when used for personal exposure or close to the desired measuring area in case of room measurements.

An active sampler has more advantages, due to the fact that is programmable. It uses a pump and continuously measures the air flow taken into the device. Temperature in the work area is an important factor, due to the fact that mercury concentrations in the air increase with temperature (Table 3) [37].

Several patents regarding mercury removal from gases were registered over the years.

Brooks registered a patent for removal of mercury from a combustion gas stream and the apparatus used [38]. Mercury in gas stream is oxidized and the resulting compounds are absorbed on adsorbent particles e.g. activated alumina. Catalysts are used to promote oxidation. Thermal treatment is used to desorb mercury from the absorbent which can be regenerated and re-used. In another embodiment, elemental mercury is oxidized using catalysts and the resulting compounds are removed from the stream by scrubbing.

Table 3: Vapor pressure-saturation concentration of mercury at various temperatures [37]

Temperature (degrees C)	Vapor Pressure (torr)	Mercury Concentration (μg/m^3)
0	0.000185	2,18
10	0.000490	5,88
20	0.001201	13,2
24	0.001691	18,3
28	0.002359	25,2
30	0.002777	29,5
32	0.003261	34,4
36	0.004471	46,6
40	0.006079	62,6

Dangtran *et al.* registered a patent for removal of mercury and nitrogen oxides from combustion flue gas [39]. This is achieved by injection of calcium chloride into the combustor and lowering the flue gas temperature. Oxidation of mercury and nitrogen oxides leads to more soluble compounds that are absorbed in a wet scrubber. By cooling the flue gas, mercury removal is enhanced.

Bhat *et al.* registered an activated carbon flue gas desulfurization system for mercury removal [40]. A flue gas treatment system comprising of an electrostatic precipitator and a wet flue gas desulfurization tower is used. Fresh activated carbon is injected into the stream and then collected by the electrostatic precipitator. A part of the reacted carbon collected by the precipitator can be injected back into the stream to minimize fresh activated carbon consumption.

Lovell *et al.* registered a patent for a high-capacity regenerable sorbent for removal of mercury from flue gas and processes and systems for making and using the sorbent [41]. A polyvalent metal sulfide deposited on a phyllosilicate substrate is used to absorb elemental mercury or oxidized mercury species present in flue gas in a wide range of temperatures.

3.4.6. Recovery of mercury by amalgamation

Mercury forms alloys, also known as amalgams, with a lot of metals. Amalgams are easily formed by heavy metals. Most of the lighter transitional metals (with the exception of manganese and copper) are insoluble in mercury [42]. Iron is one example, iron-flasks being sometimes used for mercury storage.

The capacity of mercury to form amalgams is of great interest, many of them having important applications e.g. sodium and zinc amalgams are valuable reducing agents [42]. The ability of mercury to dissolve gold and silver was used to extract these metals from their ores.

Metallic mercury can be neutralized or removed from certain mixtures by forming amalgams. Mercury can then be separated from the amalgamated metals by heating the amalgam in special vessel (a retort). For smaller quantities of amalgams, nitric acid dissolution can be used as an alternative. Although gold and silver combine very well with mercury to form amalgams, because of their price, other metals are required for this process. Considering the availability and price, aluminum is one of the best choices when it comes to removing high quantities of metallic mercury using amalgamation. Aluminum amalgam can be obtained by grinding aluminum pellets or wire in mercury, or by immersion of aluminum wire in a solution of mercury(II) chloride [43].

Oxygen in the air reacts with aluminum, forming on its surface a thin layer of aluminum oxide. The aluminum oxide protects the metal from interacting with mercury; however, small scratches can expose aluminum and lead to the formation of amalgam.

A convenient method to extract mercury available as mercuric chloride in water is described in [43]. An aluminum wire can be immersed in the solution containing mercuric chloride. Aluminum interacts with mercury in the solution, deposits forming on the surface of the wire. Aluminum from the wire will gradually diffuse into the outer coating of mercury to form the amalgam.

3.4.7. Solvent extraction of mercury

Solvent extraction, also known as liquid-liquid extraction, is based on the differential partitioning of soluble complexes between two immiscible phases: an aqueous and an organic one [44]. The component to be separated is distributed between the two phases and a distribution coefficient can be defined at equilibrium:

$$D = (\textit{Concentration in organic phase}) / (\textit{Concentration in aqueous phase})$$

A percentage of the extraction, also known as the extraction factor can be defined. This shows how much component has been extracted:

$$\%E=100D/(V_{aq}/V_{org}+D)$$

The organic phase acts as a diluent for the extractant; acidic solutions are commonly used as the aqueous phase.

Solvent extraction is considered to be one of the most effective, energy-saving and nonpolluting separation techniques for the removal of heavy metals from industrial wastes. In this process, the most important factor is how selective is the extractant to the specified metal ions to be removed [45].

Extractants such as tri-n-butyl phosphate (TBP) [46], dialkylsulphoxides [47-49], trialkyl thiophosphates [50], thiophosphorus compounds [51], dihexyl sulphide [52], octyl(phenyl)-N,N-diisobutylcarbomylmethyl-phosphine oxide (CMPO) [53], Aliquat 336 (tri-octyl methylammonium chloride) [54-56], Alamine 304 [57], Cyanex 923 [58], rhodamine B [59], N-octylaniline [60], dibenzo-18-crown-6 [61], dicyclohexyl-18-crown-6 [62], 1,2-bis(hexylthio)ethane [63], calixarenes [64, 65], triphenylarsine oxide [66] and iodonitrotetrazolium chloride [67] are capable of extracting mercury with good results [58].

For mercury(II) in hydrochloric acid solutions, certain metal species may exist in the aqueous phase: Hg^{2+}, $HgCl^{+}$, $HgCl_2$, $HgCl_3^{-}$ and $HgCl_4^{2-}$. Considering that mercury exhibits a strong tendency to form complexes with ligands containing phosphorus, sulphur or nitrogen as donor atoms, amines can be used to extract these species [68].

Fábrega *et al.* [68] has shown that Aliquat 336 is very efficient for the removal of mercury from hydrochloric acid solutions. Aliquat 336 was dissolved in kerosene and 1-octanol was added in the organic phase, to avoid the formation of a third phase. The experiments were carried at room temperature. Very fast extraction was achieved, mercury being quantitatively extracted within 5 minutes at $pH \geq 1$. Thiourea proved to be a good stripping agent, the efficiency of the process being correlated with the concentration of the agent. There was no formation of precipitates.

The extraction of mercury(II) from hydrochloric solutions using Aliquat 336 was also studied by Cattrall and Daud [54, 56]. Their investigations show that the monovalent trichloromercurate(II) species ($HgCl_3^{-}$) are extracted more strongly than the divalent tetrachloromercurate(II) ions ($HgCl_4^{2-}$). Extraction equilibrium constants have been determined for different systems: mercury in iodide solutions and copper (II), zinc (II) and cadmium (II) in hydrochloric acid solutions. The results show that the extraction order using Aliquat 336 is: $\text{mercury}_{(\text{iodide})} > \text{mercury}_{(\text{chloride})} >$ cadmium > zinc > copper.

The extraction of mercury(II) from hydrochloric acid solutions has been investigated using Cyanex 923 (TRPO), a mixture of four trialkylphosphine oxides that exhibits extraction properties similar to trioctylphosphine oxide [58]. This extractant has also been studied for the separation of trivalent lanthanides and yttrium from industrial wastes [69]. The effects of hydrochloric acid and Cyanex 923 concentrations on the extraction of mercury have been studied. The extraction efficiency decreases with increasing hydrochloric acid concentration in the aqueous phase. An explanation for this is the formation of $HgCl_3^-$ and $HgCl_4^{2-}$ in the aqueous phase with the increase of acid concentration. The authors state that a similar behavior has been observed by Brewer *et al.* [53] when using CMPO and TBP as extractants. As for Cyanex 923, the distribution ratio of mercury increases linearly with an increase in the concentration of the extractant. The effect of other metal ions (zinc, cadmium, calcium, barium, magnesium and iron) on the extraction process has been investigated and it was found that none of these metal ions are extracted into the organic phase. Various stripping agents have been investigated and it was found that $Na_2S_2O_3$ and thioureea strip mercury almost quantitatively in a single stage.

The liquid-liquid extraction of mercury(II) from hydrochloric acid solutions has been studied using bis-2-ethylhexyl sulfoxide as an extractant [49]. In parallel, extraction studies with di-n-octyl sulfoxide and diphenyl sulfoxide have also been carried out. The effect of other metals (zinc, cadmium, calcium, barium, magnesium and iron) on the extraction of mercury has also been investigated; none of these metals were extracted in the organic phase. The nature of the diluent was found to be an important factor in the process. Very little extraction is observed when using chloroform; for aromatic hydrocarbons extraction increases in the order: benzene<toluene<xylene. Diluents such as kerosene and cyclohexane show high extraction for mercury, because of low dielectric constants. Mixtures of 1% thiourea in 1% hydrochloric acid and 4M sodium chloride in 0.1 M sodium hydroxide were found to be a very effective stripping agents (>99.9%), stripping mercury in one stage.

Trialkyl thiophosphates have been investigated for the extraction of silver(I) and mercury(II) [50]. Triiso-octyl thiophosphate and tri-n-butyl thiophosphate were found to be highly selective extractants for silver and mercury(II) ions in nitric acid. Partition coefficients exceeding 100 for silver and 90 for mercury were observed at room temperature.

Tri-n-butylphosphine sulphide and tri-n-octylphosphine sulphide can be used to extract silver(I), mercury(II) and palladium(II) from aqueous acid solutions [70, 71], the last one being more selective in hydrochloric acid systems than in nitric acid systems.

Di-n-butyl thiophosphite (DBTP), di-n-butyl 2-hydroxypropylthiophosphonate (DBPrPS) and di-n-butyl phosphinyl S-methyl dithioformate have been used to study the extraction of mercury [51]. Mercury showed a stronger affinity for the sulphur in the PSH group in DBTP than the P=S in DBPrPS. From the preliminary calculations of the stability constants it was clear that DBTP forms the most stable complexes.

Alamine 304, a high molecular weight tertiary amine, was used to extract mercury in aqueous chloride medium [57]. The effect of Alamine 304 concentration was investigated, at least a 5% solution being necessary to extract the mercury in an equal aliquot of solution. High Alamine 304 concentrations did not improve the efficiency of the extraction however, increases in hydrochloric acid concentration showed a positive effect. More than 98% of the mercury is removed at a concentration of 0.001 M, a maximum being observed at 0.1 M HCl. Equilibrium is reached very rapidly, more than 98% of the mercury being transferred from the aqueous phase to the organic phase in about 30 seconds. Nitric acid, sodium hydroxide and EDTA were found to be good stripping reagents to remove mercury from Alamine 304 xylene solutions.

Dibenzo-18-crown-6 into benzene was used to extract mercury(II) as chloro-complexes from solutions in hydrochloric acid with. The experiments were conducted in the presence of different cations (lithium, potassium, ammonium, calcium and strontium) [61]. The extractability of mercury(II) in the presence of these cations decreased in accordance with their ionic diameter.

3.4.8. Standardized methods for separation and detection of mercury

A series of standardized methods used by USEPA for separation and detection of mercury in different media are specified below. Variations of these methods are currently in use all over the world.

- Mercury species fractionation and quantification by microwave assisted extraction, selective solvent extraction and/or solid phase extraction (EPA Method 3200);
- Mercury in solid or semisolid waste (manual cold-vapor technique) (EPA Method 7471B);
- Mercury in liquid waste (manual cold-vapor technique) (EPA Method 7470A);
- Mercury in aqueous samples and extracts by anodic stripping voltammetry (ASV) (EPA Method 7472);
- Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry (EPA Method 7473);
- Mercury in sediment and tissue samples by atomic fluorescence spectrometry (EPA Method 7474);
- Mercury in water by oxidation, purge and trap, and cold vapor atomic absorption fluorescence spectrometry (EPA Method 1631);
- Methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS (EPA Method 1630);
- Mercury in water by cold-vapor atomic fluorescence spectrometry (EPA Method 245.7);
- Mercury (automated cold vapor technique) (EPA Method 245.2);
- Determination of particulate and gaseous mercury emissions from chlor-alkali plants (air streams) (EPA Method 101);
- Determination of particulate and gaseous mercury emissions from sewage sludge incinerators (EPA Method 101A);

- Determination of particulate and gaseous mercury emissions from chlor-alkali plants (hydrogen streams) (EPA Method 102);
- Determination of mercury in wastewater treatment plant sewage sludges (EPA Method 105).

EPA Method 3200 [72] describes the determination of total mercury and various mercury species in soils and sediments. Microwave-assisted extraction using nitric acid solution or ultrasound-assisted extraction using a mixture of hydrochloric acid and ethanol can be used to extract mercury in the samples. The method offers information about sub-speciation of extractable and non-extractable mercury and analysis of specific mercury fractions.

EPA Method 7471B [73] measures total mercury in soils, sediments, bottom deposits, and sludge-type materials. Digestion of the samples with concentrated acids at elevated temperatures is necessary. CVAAS is used to quantify total mercury in the solutions.

EPA Method 7470A [74] is used to determine the concentration of mercury in mobility-procedure extracts, aqueous wastes and ground waters. All samples are subjected to an appropriate dissolution step prior to analysis. Mercury content is determined using CVAAS.

EPA Method 7472 [75] is based on ASV for quantifying mercury. It can be applied for determinations of dissolved organic and inorganic divalent mercury ions and compounds in drinking water, natural surface water, seawater, in domestic and industrial wastewater, and in aqueous soil extracts. Acid digestion is necessary for solid matrices.

EPA Method 7473 [76] is applied for the determination of mercury in solids, aqueous samples and digested solutions. It can be used in the laboratory or field environments. Mercury is liberated from the samples using controlled heating. AAS is used for measurements.

EPA Method 7474 [77] uses AFS to determine total mercury in sediment and tissue samples. Microwave digestion of the sample is accomplished using nitric and hydrochloric acids. Mercury species are reduced to elemental mercury which is measured using AFS.

EPA Method 1631 [78] describes the determination of mercury in filtered and unfiltered water using oxidation, purge and trap, desorption, and CVAFS.

EPA Method 1630 [79] is applied for determination of methyl mercury in filtered and unfiltered water using distillation, aqueous ethylation, purge and trap, desorption, and CVAFS.

EPA Method 245.7 [80] quantifies mercury in filtered and unfiltered water using CVAFS. Mercury in drinking water, surface and ground waters, marine water, and industrial and municipal wastewater can be determined.

EPA Method 245.2 [81] is applied for the determination of mercury in surface waters and, if potential interferences are not present, in saline waters, wastewaters, effluents, and domestic sewages. Dissolved mercury is reduced to its elemental state, aerated from solution and analyzed by AAS.

EPA Method 101 [82] determines particulate and gaseous mercury emissions from chlor-alkali plants and other sources where the carrier-gas stream is principally air. Particulate and gaseous mercury emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride solution. Mercury is reduced to its elemental form, which is then aerated from the solution and measured using AAS.

EPA Method 101A [83] analyses mercury emissions from sewage sludge incinerators and other sources. Particulate and gaseous mercury emissions are withdrawn isokinetically and are collected in acidic potassium permanganate solution. Collected mercury is reduced to its elemental form, which is aerated and analyzed by AAS.

EPA Method 102 [84] is used for the determination of both particulate and gaseous mercury emissions from chlor-alkali plants and other sources where the carrier-gas stream is principally hydrogen. The procedures are similar to EPA Method 101.

EPA Method 105 [85] quantifies total organic and inorganic mercury content in sewage sludge. The samples are collected after dewatering and before incineration or drying. Digestion in aqua regia followed by potassium permanganate oxidation is performed for a weighted portion of the sample. CVAAS is used to measure mercury content.

3.4.9. Mercury recovery from fluorescent lamps

Considering the environmental implications and the extreme rarity of mercury in the Earth's crust (average crustal abundance of 0.08 ppm [86]), recycling of mercury containing waste and recovery of the contained mercury is very important.

As previously discussed, mercury in fluorescent lamps can be found in elementary form or in different oxidation states, bound to certain components of the lamps: glass, end caps, electrodes, phosphorus powder. Contamination of the waste with mercury is a problem, as mercury interferes with the recycling of important elements such as REMs. Therefore, mercury removal techniques play an important role in developing recycling processes for spent fluorescent lamps.

Durao *et al.* [8] states that three processes are most important for the decontamination of fluorescent lamps waste: a thermal process, a chemical process involving lixiviation by aqueous solutions and stabilization. The first two are the most important, making possible the recycling of mercury.

3.4.9.1. Thermo-desorption techniques for recovering mercury from fluorescent lamps

Thermal processes for the recovery of mercury from fluorescent lamps are described in literature [2, 8, 9, 87]. The material is exposed to high temperatures, above mercury's boiling point, for several hours. Mercury vapors are condensed and collected into decanters. Further distillation steps or additional treatments such as nitric acid bubbling can be used as purification methods [2]. The efficiency of the process is influenced by two main parameters: temperature and desorption time [9].

TDAAS was used to investigate the thermal release of mercury from phosphorus powder and glass of spent fluorescent lamps [3]. A heating rate of 33 ºC/min was used to bring the powder samples from room temperature to 570 ºC. With the help of a constant nitrogen flow, the desorbed vapors were taken to the detection cell of an atomic absorption spectrophotometer and mercury was quantified. Using a thermocouple and monitoring the temperature over the sample, registration of absorbance as a function of the temperature was obtained (Figure 7). Relevant information regarding the interaction force of mercury with the matrix was obtained by studying these thermo-desorption profiles. They show that desorption of elemental mercury occurs at low temperatures, reaching a maximum at 150 ºC. Maximum desorption for Hg_2Cl_2 is reached at 225 ºC, for $HgCl_2$ at 275 ºC and for HgO at approximately 400 ºC. Higher desorption temperatures of mercury were observed for glass samples of spent fluorescent lamps. Mercury desorption was recorded between 240 and 800 ºC with a maximum peak at 618 ºC. Such high temperatures confirm the strong interactions between mercury and the glass components.

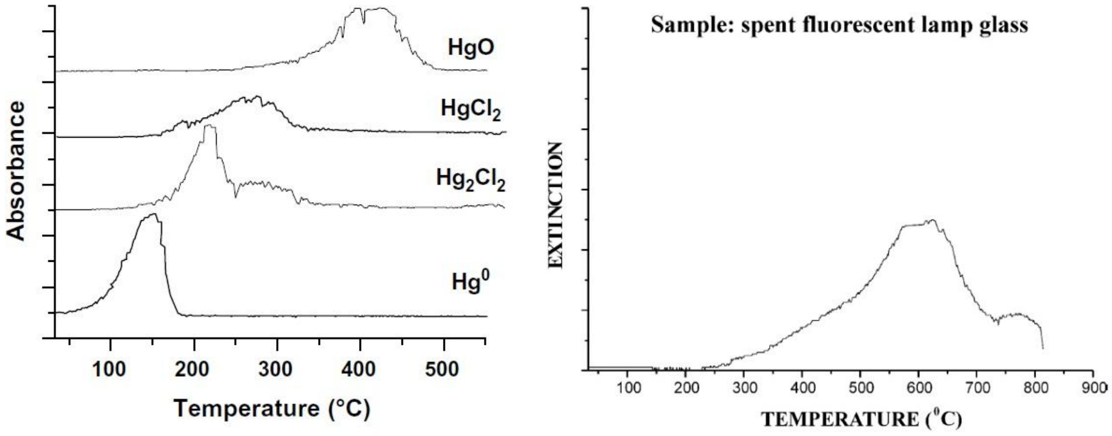

Figure 7: a. Thermograms of fluorescent lamp treated phosphor powder spiked with mercury standards b. Thermo-desorption profile of glass sample of a spent fluorescent lamp [3]

The high temperatures that are necessary to weaken the interactions between mercury and lamp components translate into more energy consumption, specialized installations and the possibility of unwanted chemical or physical transformations. Studies with compounds that lower the temperatures necessary for mercury desorption from phosphorus powders of spent fluorescent lamps have been performed [8]. Sodium borohydride, lithium aluminum hydride, iron powder, citric acid, sodium oxalate and sodium citrate were used as reducing agents in order to lower the heating temperature required for mercury release. Among the tested substances, sodium borohydride proved to be the best, an improvement of 30% compared to the treatment without crushing and reducing agent being observed. Citric acid presented a high capacity to weaken mercury bonds with the matrix as well.

The efficiency of mercury desorption from fluorescent lamps glasses at various temperatures has been studied [2]. Temperatures between 100 and 500 ºC were investigated. Spent fluorescent lamps and a sample taken from a recycling company were used. Good results were observed after only 1 h of exposure at 100 ºC. In this case the mercury concentrations dropped below 4 µg/g for all samples (Figure 8). The remaining mercury was slowly desorbed by increasing the temperature. After thermal treatment at 400 ºC, mercury was not detected in 3 samples, indicating complete removal. Mercury was still found in one sample, even after heating it at 500 ºC, due to strong bounds with the glass matrix.

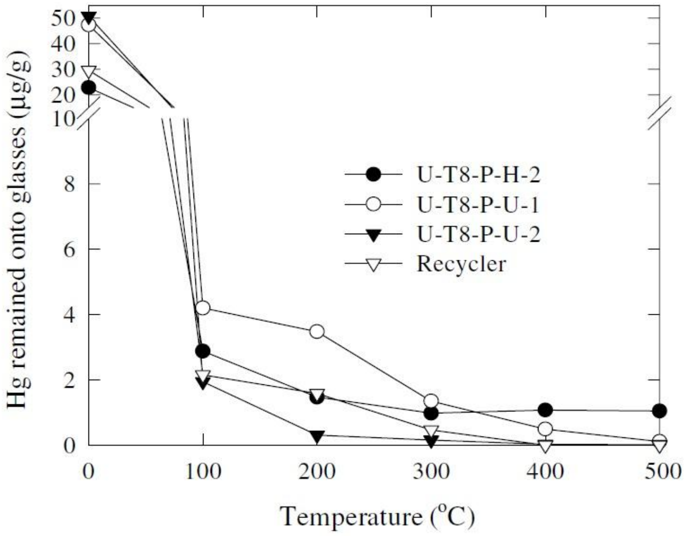

Figure 8: Temperature effect for mercury extraction from fluorescent lamps glasses [2]

Wet-based and dry-based thermal desorption systems for mercury removal from fluorescent lamps exist: Nomura (Japan), respectively MRT (Sweden), AERC and SepaDyne (US). High costs, secondary pollutants and the required treatment of the resulting wastewaters are some of the disadvantages wet-based thermal desorption systems have [9].

A full-scale thermal desorption process comprising a pre-treatment unit and a mercury recovery system can be used for recovering mercury from fluorescent lamps waste [9]. Mercury is thermally separated in the pre-treatment unit then recovered by a condenser in the mercury recovery system. A dry-based system, including a lamp crushing system, was used to recover mercury from different types of lamps (Figure 9). Two heating chambers were used: a pre-heating one that operated under vacuum conditions to vaporize the mercury from the lamps and a post-heating one to make sure that all the mercury was vaporized. The effects of pre-heating temperature and desorption time on the efficiency of the process were investigated. For standard fluorescent lamps efficiencies from 97.08 to 99.22%, with standard deviation and coefficient of variation of 0.74% and 0.75%, were obtained. The two parameters investigated had little influence on the process (2.14% maximum difference). The pre-heating temperature showed higher influence on the process compared to desorption time. Efficiencies between 69.37-93.39% were obtained for CCFLs with standard deviation and coefficient of variation of 8.03% and 9.88%. Pre-heating temperature is an important factor in this case, the efficiency of the process improving with an increase in temperature. For optimum mercury recovery, 525 ºC pre-heating temperature and 8 hours desorption time is required.

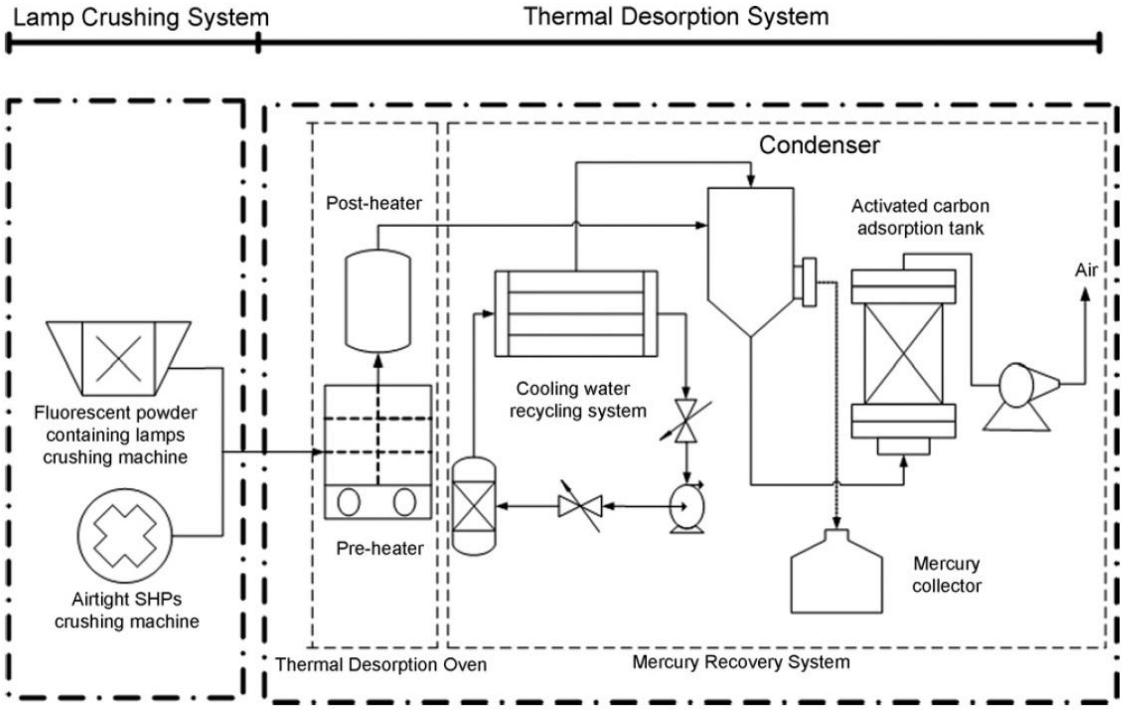

Figure 9: Schematic diagram of full-scale thermal desorption process to recover the mercury from high-mercury-containing lamps [9]

Release of mercury from different materials was studied using a bench scale thermal desorption setup [87]. Pure mercury, cinnabar, amalgam, different types of mercury containing lamps and a mercury/fluorescent powder of a mixed sample originating from a thermal desorption plant were investigated. Results showed a desorption of mercury in the sample from the treatment plant at temperatures between 550-850 ºC, much higher compared to those of the other materials investigated. For those, mercury release temperatures were between 50-250 ºC. Comparison was made for the mixed sample with commercial phosphor powders and desorption temperatures were found to be lower in the latter (30-150 ºC).

3.4.9.2. Acid digestion techniques for recovering mercury from fluorescent lamps

Another method used for the recovering of mercury from spent fluorescent lamps involves leaching of mercury species with acids. For this, the crushed waste is dissolved into acid or a mixture of acids. Extraction can be accomplished with the aid of microwave irradiation, ultrasound or temperature. A separation of the resultant extracts from the remaining sample matrix is needed. Mercury is analyzed and recovered through various techniques: ion exchange, solvent extraction etc.

Strong oxidants such as hypochlorite and nitric acid solutions were tested for the recovery of mercury from the phosphorus powder of spent lamps [88]. Nitric acid was very effective, leading to the dissolution of more than 99% of the mercury. However, the agent was very aggressive and dissolved the whole powder, the goal of the authors (return the powder back in the production process) being rendered impossible. The efficiency of hypochlorite extraction increased with concentration, leaching time and temperature, reaching similar values (over 99%).

The effectiveness of acid digestion compared to thermo-desorption of mercury from spent fluorescent lamps glass has been investigated [2]. Different concentrations of nitric acid solution and a mixture of nitric and hydrochloric acid solution (1:1 volume ratio) were used. CVAAS was used to analyze the mercury content in the samples. The obtained results show that the extraction effectiveness increases with an increase in acid concentrations. Also, higher extraction efficiency was observed for the mixture of nitric and hydrochloric acid. The mixed acids solution managed to extract 36% of total mercury and the nitric acid solution only 28%. These results indicate that acid extraction is not as effective as thermal treatment for mercury recovery from spent fluorescent lamps glass. Comparing these two techniques, heating is much simpler, easier to achieve and leads to better results. It does not require the use of chemical reagents and does not lead to toxic compounds or effluents, making additional treatment unnecessary.

3.4.9.3. Other mercury removal techniques from fluorescent lamps

Other mercury removal techniques have been investigated. Electroleaching was considered for treating the phosphorus coating of fluorescent lamps [88]. The powder, consisting mainly of fluorchlorapatite, was suspended in 1M sodium chloride solution and two graphite electrodes were used. Different pH values were tested, better results being obtained at pH=4. The efficiency of the process in this case reached 99.5%. Compared to chemical procedures, where mercury is recovered as soluble species and further treatment is necessary, this method leads to the recovery of mercury in its elemental form, in one step.

Heterogeneous photocatalysis has been applied for the selective reduction of mercury from fluorescent lamps [89]. In this method UV-VIS photons are absorbed by a semiconductor, their energy promoting the passage of electrons from the valence band of the semiconductor to its conduction band. The species in solution can be reduced by the electrons that reach the surface of the semiconductor. Also, the holes created in the valence band are capable of migrating to the surface, oxidizing species in solution. Thus, one or more redox reactions occur, the semiconductor acting like a catalyst. Crushed lamps originating from a recycling company were used in the experiments. A mixture of hydrochloric and nitric acids and an aqueous solution of sodium hypochlorite were used to bring the mercury into solution. Sodium hypochlorite at pH 5.5 was found to be most effective. Two 18 W UV lamps with a radiation peak value of 360 nm were used. Titanium dioxide was used as a photocatalyst and the reduction was performed in the presence of citric acid in order to avoid interferences of high concentrations of calcium and other metal ions. A solid mixture of different mercury compounds was obtained as depositions on the photocatalyst. More than 99.9% of mercury was recovered this way. After re-dissolving into sodium hypochlorite, metallic mercury was obtained by cementation techniques with iron as a reducing agent.

4. Rare earth metals recycling from industrial waste

4.1. The rare earth metals

The rare earth metals, also known as rare earth elements or rare earths, is one of the largest naturally occurring groups in the periodic table, comprising the 14 lanthanides (cerium to lutetium), lanthanum, yttrium and scandium [42] (Figure 10).

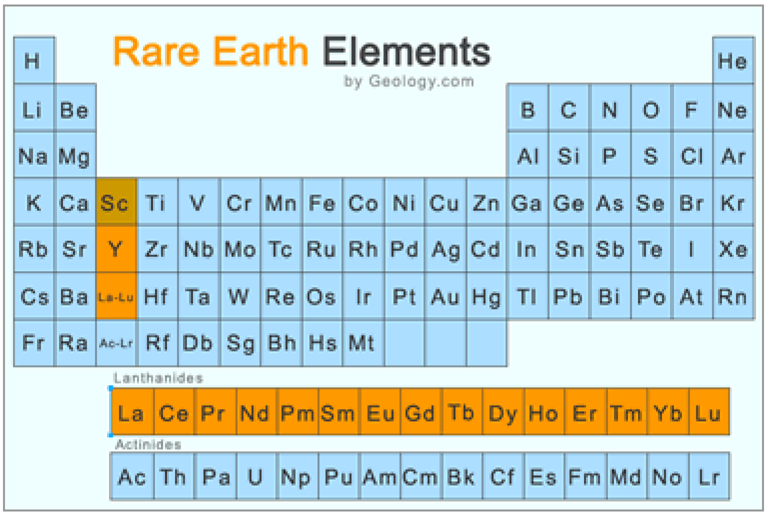

Figure 10: Chemical periodic table delineating the REMs: the lanthanides, lanthanum, scandium and yttrium

The REMs are divided into two groups: the light REMs, also known as the cerium group, and the heavy REMs, also known as the yttrium group. The REMs with atomic mass lower than 153 and radius larger than 95 pm (lanthanum, cerium, praseodymium, neodymium, promethium, samarium and europium) are included in the first group, while REMs with atomic mass higher than 153 and radius lower than 95 pm (gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium) are included in the latter. Yttrium, despite lower atomic mass, is included in the latter group as well, having a comparable ionic radius [42]. Sometimes, a third group known as medium REMs is used to define REMs of intermediate atomic mass and ionic radius, thought this group is rarely well defined [90].

Substantial geochemical fractionation was revealed on the boundary between the two subgroups. Anomalies of cerium and europium were found in natural deposits. The lanthanides undergo regular chemical fractionation in aquatic mediums, a phenomenon also known as the tetrad effect [91] (see 4.4 for more information).

With the exception of promethium, REMs are relatively abundant. Cerium has almost the same abundance as copper and zinc, while the most scarce members of the group, lutetium and technetium, are more abundant than cadmium and selenium [90]. One of the main concerns is the fact that REMs rarely form continuous ore bodies, thus are not often found in concentrated forms. It's not unusual that the concentrations between the most and least abundant REMs in geological deposits to differ by two to five orders of magnitude [95]. Additionally, because they are found together in the same deposits and show similar chemical properties, their individual separation is difficult to achieve. Considering these aspects, some of the REMs that are critical for the development of sustainable future technologies, are relatively expensive.

4.2. Applications of rare earth metals

Due to their nuclear, metallurgical, chemical, catalytic, electrical, magnetic, and optical properties, REMs have a big variety of applications: lighter flints, glass polishing, phosphors, lasers, magnets, batteries, magnetic refrigeration, high-temperature superconductivity, safe storage and transport of hydrogen etc. [95].

Many of these applications are characterized by high specificity, and most REMs have no substitutes that possess the same efficient properties. One example is europium which is used as the red phosphor in color cathode-ray tubes and liquid-crystal displays; no substitute is known, and because of this europium has a relatively high price. The same thing can be said about erbium which is used in laser repeaters for fiber-optic cables that can transmit signals over long distances. Specificity applies even to the most abundant and least expensive REMs such as cerium; cerium oxide is the only polishing agent for glass products, ranging from ordinary mirrors and eyeglasses to precision lenses [95].

Neodymium, samarium, gadolinium and dysprosium revolutionized permanent magnet technology. They made possible the construction of small, lightweight and high-strength magnets that have allowed miniaturization of many electrical and electronic components. These components are used in appliances, audio-video devices, computers, portable disk drives, automobiles, communications systems and military gear [95].

Environmental concerns have led to the use of REMs in automotive pollution-control catalytic converters and to the widespread adoption of energy-efficient fluorescent lamps that use yttrium, lanthanum, cerium, europium, gadolinium, and terbium. Magnetic-refrigeration technology could also help reducing energy consumption and carbon dioxide emissions. Due to their several unpaired electrons, Gd^{3+} through Tm^{3+} ions have unusually large magnetic moments. Alloys that contain REMs and have a very big magnetocaloric effect near room temperature have been developed. These alloys can be used in refrigerators, freezers and air conditioners and, compared to gas-compression refrigeration, have many advantages: they are not flammable or toxic, don't deplete the Earth's ozone layer or contribute to global warming. Because of their relatively low toxicity, REMs are slowly replacing toxic metals like cadmium and lead in rechargeable batteries. La-Ni-H batteries pose fewer environmental problems upon disposal or recycling, have greater energy density and better charge-discharge characteristics [95].

4.3. Rare earth metals in fluorescent lamps

One important application of REMs is the production of luminescent materials, also known as phosphors. Rare earth phosphors are important components of fluorescent lamps [10]. Their role is to convert invisible UV radiation into visible light. The phosphorus powder contained in a standard 40W fluorescent lamp weights between 4 to 6 g, accounting for 2% of the lamp's mass [3]. The CCT and the CRI of the lamp is influenced by the blend of used phosphors. A mixture of three rare earth phosphors (red, green and blue) is used today in high-performance lamps. Such lamps are known as *triband* or *triphosphor* lamps [10].

The powder coating a standard triphosphor fluorescent lamp consists of approximately 55% red, 35% green, and 10% blue phosphors, though variations exists. Also, the amount of REMs in each of these phosphors is not constant. Depending on the manufacturer and application requirements, different quantities of REMs can be used. Yttrium (mainly) and europium constitute the red phosphor. The green phosphor contains approximately 10% terbium, and the blue phosphor less than 5% europium [10].

Ronda *et al.* reviewed the fundamentals and applications of rare earth phosphors [12]. Details regarding the composition, absorption and emission of light are presented. The blue phosphor consists of $BaMgAl_{10}O_{17}$ doped with Eu^{2+}. The photons are absorbed and emitted by the Eu^{2+} ions, due to a 4f→5d and, respectively, a 5d→4f optical transition. $Y_2O_3:Eu^{3+}$ is responsible for the red emission, excitation involving a charge transfer transition from O^{2-} ions to Eu^{3+} and emission involving the f-levels of Eu^{3+}. For green emitting phosphors, Ce^{3+} ions are involved in the absorption, the energy being transferred to the emitting Tb^{3+} ions. $LaPO_4:Ce^{3+},Tb^{3+}$; $(Ce,Tb)MgAl_{11}O_{19}$ and $(Ce,Gd,Tb)MgB_5O_{10}$ are examples of green phosphors that can be used. In the latter, energy is transferred from Ce^{3+} to Tb^{3+} via the Gd^{3+} ion.

The composition of trichromatic phosphors was determined using X-ray fluorescence (XRF) by Wang *et al.* (Table 4) [31]. Rare earth oxides reach up to 27.9% of the total weight of phosphors, proving that fluorescent lamps have high recycling value.

Table 4: Component analysis of rare earth trichromatic phosphors by XRF [96]

Element	Compound	Content (%)
Al	Al_2O_3	27.6
P	P_2O_5	14.4
Ca	CaO	15.1
Ba	BaO	2.0
Y	Y_2O_3	23.2
Ce	CeO_2	2.4
Eu	Eu_2O_3	1.8
Tb	Tb_4O_7	0.2
La	La_2O_3	0.3

The chemical composition of pure tri-phosphor samples was determined by Mei *et al.* using ICP-OES and XRD and is presented in Table 5 [97]. Phosphors particle sizes in the range of 1 to 10 µm were observed, the average being less than 5 µm. Gravity measurements were performed in specific bottles, with the following results: 4.295 (red phosphor), 3.506 (blue phosphor) and 4.062 (green phosphor).

Table 5: The chemical composition of pure tri-phosphor samples [97]

Phosphor	Formula	Element content (%)							
		O	Y	Eu	Al	Mg	Ba	Ce	Tb
Red	Y_2O_3:Eu^{3+}	17.5	67.2	6.5					
Green	$CeMgAl_{10}O_{17}$:Tb^{3+}	42.6			31.3	5.7		9.5	5.3
Blue	$BaMgAl_{10}O_{17}$:Eu^{2}	42.3		1.9	32.4	2.7	12.4		

Phosphorus powder from fluorescent lamps waste was dissolved in concentrated sulfuric acid and ICP-AES was used to determine the amount of REMs in solution [32]. XRD and scanning electron microscopy-energy dispersive spectroscopy (SEM/EDS) were used to analyze the structure of the powder. Yttrium (29.6%), europium (2.3%), lanthanum (10.6%), cerium (5.0%) and terbium (2.6%) were identified in the powder (Table 6). Yttrium and europium were identified as oxides and lanthanum and cerium as phosphates. Due to its low concentration, the structure of terbium was unable to identify. SEM/EDS identified phosphor particles ranging from 5 to 10 µm. Analysis showed that lanthanum and cerium coexist in the same particle and yttrium is present independently in different particles.

Table 6: Elemental content and structure of phosphorus powder from fluorescent lamps waste [98]

Element	Content (%)	Structure
Y	29.6	$(Y_{0.95}Eu_{0.05})_2$
Eu	2.3	
La	10.6	$La_5P_6O_{22.5}$
Ce	5.0	$CePO_4$
Tb	2.6	Unidentified

The chemical composition of phosphor materials originating from a fluorescent lamps recycling plant in Japan was determined by Hirajima *et al.* (Table 7). The waste contained about 80.1% calcium halo-phosphate, 15.1% rare earth phosphors and 4.8% other materials [5].

Table 7: Chemical composition of phosphor materials from the waste fluorescent lamps recycling plant (Itomuka Mining Laboratory (Nomura Kohsan Co., Ltd), Hokkaido (Japan)) [5]

Elements	Content (%)
P_2O_5	21
Cl	0.35
Sb_2O_3	0.9
La_2O_3	2.1
CaO	55
BaO	1.2
CeO_2	1.0
SiO_2	1.9
ZnO	0.13
MnO_2	2.3
Y_2O_3	8.1
Tb_4O_7	0.62
SrO	3.9
Eu_2O_3	0.51
Fe_2O_3	0.47
TiO_2	0.18
HgO	0.00
Others	0.34

Analyses of phosphorus powder collected by brushing from 5000 spent fluorescent lamps of different types revealed the powder contains mostly calcium orthophosphate (61.52%) and calcium sulphate (34.48%). Small percentages of europium oxide (1.62%), yttrium oxide (1.65%) and other impurity metals (0.65%) were identified [33].

XRF analysis of fluorescent powder originating from recycled fluorescent lamps revealed an yttrium percentage of 7.55% in the sample (Table 8) [34].

Table 8: Phosphorus powder originating from recycled fluorescent lamps [34]

Elements	Content (%)
Mg	1.45
Al	<0.001
Si	20.81
P	<0.001
K	<0.001
Ca	25.54
Mn	1.09
Fe	0.7
Ni	<0.001
Cu	<0.001
Zn	<0.001
Y	7.55
Sb	<0.001
Ba	3.04
Pb	0.46

Very high levels of purity are necessary for the REMs used in lighting appliances and this leads to an increase in the manufacturing costs. Depending on the lamp type, the rare earth phosphors can be the most expensive component of a fluorescent lamp [10]. Halophosphors can be used as a cheaper alternative to coat the inside of a lamp. However, they are less efficient and produce a lower quality light.

Halophosphate phosphorus powder recovered from spent fluorescent lamps was characterized. Distillation was used in order to remove mercury. Analysis revealed that the recycling process affects phosphor particle size, a decrease in average particle size from 7.7 µm to 6.5 µm being observed. Also, a difference in the composition of fresh and recovered phosphors was observed (Table 9) [35]. Small amounts of REMs such as lanthanum, gadolinium, terbium and europium were identified in the samples, due to possible contamination with other phosphors in the recycling process.

Table 9: Halophosphate phosphorus powder composition, before and after mercury removal using thermal treatment [2]

Compound	Content before thermal treatment (%)	Content after thermal treatment (%)
CaO	50.9	49.5
P_2O_5	35.7	34.9
Y_2O_3	3.28	3.09
F	2.48	2.43
Al_2O_3	1.21	1.16
SrO	1.14	1.13
Sb_2O_3	1.04	0.91
MnO	0.8	0.82
La_2O_3	0.79	0.97
C	0.63	0.7
BaO	0.54	0.83
Cl	0.5	0.44
Gd_2O_3	0.2	–
Tb_4O_7	0.2	0.16
Eu_2O_3	0.18	0.19
SiO_2	0.14	1.88
ZnO	0.1	0.02
Fe_2O_3	0.05	0.12
Na_2O	0.05	0.33
SO_3	0.04	0.06
HgO	0.03	–
GeO_2	0.02	0.02
PbO	–	0.23
MgO	–	0.09
K_2O	–	0.06

4.4. Rare earth metals separation and determination

The small difference in ionic radius, the preference for interaction with hard-sphere base donor atoms and the dominance of the +3 oxidation state across the lanthanide series, make individual separation of these elements very difficult [36]. Methods such as fractional crystallization or precipitation, ion-exchange, selective oxidation/reduction and solvent extraction were developed for individual separation of REMs. A summary of separation methods for such elements was published by Gupta and Krishnamurthy [37]. Fractional crystallization and fractional precipitation are slow and tedious methods that were used in the past. Especially when the lanthanides were first discovered and separated, up to more than 1000 recrystallizations were not uncommon for separation. Nowadays, solvent extraction and ion exchange are the most useful methods for REMs separation [36].

Ion exchange and solvent extraction separations are based on lanthanide contraction – the decrease in ionic radius across the lanthanide series of elements, from lanthanum to lutetium (Table 10) [101]. This has an effect on the properties of the elements, the strength of cation-anion, ion-dipole and ion-induced dipole interactions increasing with the decrease in ionic radius. Thus, heavy members of the series will create stronger bounds with solute and solvent molecules compared to light members [99], allowing preferential binding to ion exchange resins, or extraction of the complex into the organic phase [101].

Table 10: Lanthanide contraction [101]

Element	Atomic number	Atomic mass	Ionic radius
Lanthanum (La)	57	138.9	1.061
Cerium (Ce)	58	140.1	1.034
Praseodymium (Pr)	59	140.9	1.013
Neodymium (Nd)	60	144.2	0.995
Promethium (Pm)	61		0.979
Samarium (Sm)	62	150.4	0.964
Europium (Eu)	63	152	0.95
Gadolinium (Gd)	64	157.3	0.938
Terbium (Tb)	65	158.9	0.923
Dysprosium (Dy)	66	162.5	0.908
Holmium (Ho)	67	164.9	0.894
Erbium (Er)	68	167.3	0.881
Thulium (Tm)	69	168.9	0.869
Ytterbium (Yb)	70	173	0.858
Lutetium (Lu)	71	175	0.848
Yttrium (Y)	39	88.9	0.88

In certain solvent extraction systems the logarithmic distribution coefficients of lanthanide ions exhibit four separate rounded segments (tetrads) in relation with the atomic number: lanthanum-neodymium, promethium-gadolinium, gadolinium-holmium and erbium-lutetium [92]. The segments are either convex or concave, with M-shaped and W-shaped distribution patterns, respectively [93].

A significant increase in stability, represented by the half (gadolinium) and completely filled (lutetium) 4f electron shell, is observed. Also, a lesser increase in stability is associated with the quarter (between neodymium and promethium) and three-quarter filled (between holmium and erbium) 4f shell. Solvent extractions systems such as di-2-ethylhexyl ortophosphoric acid (HDEHP)/ hydrochloric acid and di-n-octyl ortophosphoric acid (HDOP)/hydrochloric acid are some of the best examples for tetrad effect. When the distribution coefficients or stability constants are plotted against atomic number or ionic radius, clear breaks can be observed at neodymium/promethium, gadolinium and holmium/erbium, and a further discontinuity at lutetium [94].

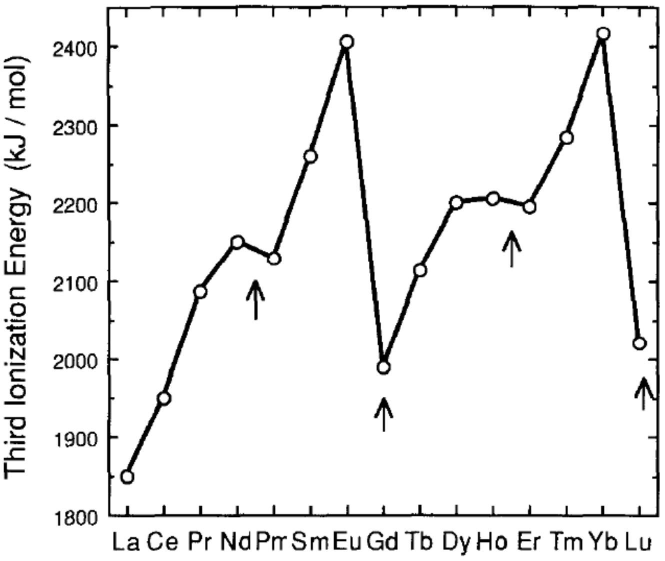

Figure 10: Plot of third ionization energy vs. atomic number for lanthanide elements with arrows denoting the location of the quarter, half, three-quarter, and completely filled 4f electron shell [94]

A series of methods that can be used for REMs separation are presented in Table 11.

Three main steps are required for REMs recovery from waste products: separation of the components containing the REMs, extraction of REMs compounds from these components and the metallothermic reduction of the metals [102].

Table 11: Possible methods for REMs separation

Selective oxidation/reduction	Ce^{3+} can be oxidized to Ce^{4+}, then precipitated as CeO_2 or $Ce(IO_3)_4$ Eu^{3+} can be reduced to Eu^{2+}, then precipitated as $EuSO_4$		
Separation by fractionation	Small scale methods used originally	Fractional crystallization	
		Fractional precipitation	
	Current methods	Ion-exchange	Mobile phases: aqueous solutions of complexing agents (HIBA, EDTA etc.) Stationary phases: low-capacity cation-exchange resins
		Solvent extraction	Solvating type extractants (TBP) Amine extractants Acidic extractants (carboxylic and organophosphorus acids)

4.4.1. Solvent extraction of rare earth metals

Solvent extraction is one of the easiest methods for REMs separation. It is more convenient than ion exchange because it allows both semicontinuous operation and the use of more concentrated feed solutions. Solvating type extractants such as TBP can be used to extract REMs. Kerosene containing TPB is used to extract the metals from nitric acid solutions. The pH, nitric acid concentration, ionic strength, and concentration of the elements in the aqueous phase influence the extraction effectiveness. A complication can occur due to the ability of TBP to extract nitric acid which competes with the lanthanides. To prevent this, the process must be optimized in terms of high pH but low nitric acid concentration. The separation factors between adjacent elements decrease as the total concentration of lanthanides in the feed rises; in contrast, the separation factors between yttrium and the lanthanides increase with dilution [101].

An alternative method for extraction lanthanides from nitric acid media is the use of amine extractants; pH above 2 is required. The amine structure is important, asymmetric compounds giving the highest distribution coefficients [101].

Acidic extractants such as carboxylic and organophosphorus acids give very good results when recovering lanthanides; the extraction depends on the pH of the feed. Organophosphorus acids are more powerful extractants than carboxylic acids and extract the heavy lanthanides even at low pH values. The separation factors between adjacent lanthanides follow the order: phosphinic > phosphonic > phosphoric > carboxylic acids. A 0.1M di-2-ethylhexylphosphoric acid (DEHPA) solution completely extracts all the elements above europium at pH 2; however, this gives problems with stripping, the heaviest elements, ytterbium and lutetium, requiring 20% hydrofluoric or 50% sulfuric acid as strip solutions [101].

Synergistic systems can be used for improved extraction efficiencies. They can be obtained by combining solvating extractants with chelating extractants. Such systems often exhibit extraction strength greater than the sum of the two ligands. Although the diluent may act as a synergist, more often a solute ligand is used. Even though synergistic systems show improved extraction strength, not much enhancement in selectivity for given elements is achieved. The composition of the aqueous phase can also affect the efficiency of the extraction. Other parameters can be modified in order to achieve better separation: the diluent (solvent) of the organic phase, salting out reagents, water soluble complexing agents or various types of solid sorbent materials [99].

4.4.1.1. Solvent extraction of rare earth metals from different waste materials

Rare earths were recovered from waste materials using different solvents and techniques [103].

The extraction of lanthanum, europium and lutetium with bis(4-acyl-5-hydroxypyrazoles) derivatives was achieved [104]. The extraction was performed from sodium nitrate aqueous solutions using chloroform as a diluent.

Narita *et al.* [105] used the bidentate N,N’-dimethyl-N,N’-diphenyl-malonamide (MA) and the tetradentate N,N’-dimethyl-N,N’-diphenyl-3,6-dioxaoctanediamide (DOODA) to extract lanthanides. Comparison of the extraction by MA and DOODA was made with the extraction by the tridentate N,N’-dimethyl-N,N’-diphenyl-diglycolamide (DGA). It was found that the order of the extractabilities in 4M nitric acid solution using 0.1M extractants is MA < DOODA << DGA. It is clear that the introduction of one ether oxygen atom to the principal chain in the diamides leads to an increase in the extraction effectiveness.

The synergistic extraction of REMs with a mixture of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and sec-nonylphenoxy acetic acid was investigated [106]. Scandium, yttrium, lanthanum, gadolinium and ytterbium were extracted from hydrochloride medium using extractants dissolved in n-heptane. The extraction equilibrium was investigated and calculations of the equilibrium constants, formation constants and several thermodynamic parameters were performed.

Vijayalakshmi *et al.* [107] describes a process for the recovery of REMs from xenotime concentrate by sulphuric acid digestion and selective thorium precipitation. Xenotime is a rare earth phosphate mineral which is a rich source of yttrium and heavy REMs. Two types of concentrates which are routinely produced in India were used: a low grade one, typically assaying 57% light REMs, 27% yttrium oxide and 15.6% heavy REMs, and a high grade one, assaying 38% light REMs, 41.8% yttrium oxide and 20.55% heavy REMs. Dissolution of more than 98% metal values has been achieved, using sulphuric acid as a leaching agent. Thorium was removed by selective precipitation with ammonia and sodium pyrophosphate. This also facilitated the precipitation of lighter REMs along with thorium, enriching the heavy REMs in the filtrate. The REMs have been recovered and separated from other impurities (such as iron, uranium, sulphate and phosphate) by oxalate precipitation. Oxides were obtained by calcination of the oxalates; REMs were purified by dissolving the oxides in hydrochloric acid followed by solvent extraction. About 99% recovery of REMs can be achieved using these processes.

Leaching of REMs from computer monitor scraps in order to recover the metals from the obtained liquor has been investigated [108]. The experiments were carried out under mechanical agitation, with controlled temperature, using hydrochloric and sulphuric acids as leaching agents. Energy-dispersive X-ray spectrometry, AAS and XRD were used to characterize the samples. By determining the europium and yttrium content in the sample and on the leached residue, the recovery of the metals was calculated. Several parameters were investigated: influence of the leaching agent, acid/sample ratio, time of leaching, solids percentage and temperature. Sulphuric acid was far more efficient and selective than hydrochloric acid, reaching 97% europium and yttrium recovery, compared to only 30% for hydrochloric acid. Leaching efficiency improved gradually with the increase of the acid/sample ratio and with time. Regarding temperature, maximum leaching was attained at 60 ºC. Solids percentage is recommended to be less than 20%. The optimum parameters selected were: 1.5 hours of leaching, acid/sample ratio of 1500 g/kg, solids percentage of 20% and room temperature. In this case a dissolution of 96% of total europium and yttrium was possible.

In order to obtain pure yttrium and europium, the authors suggest solvent extraction, followed by the precipitation of the metals and calcination of the precipitate. Because yttrium presents similar behaviour to the heavy lanthanides group and europium belongs to the medium group, the separation by solvent extraction can be easily achieved. DEHPA can be used as an extractant for yttrium. Europium, which will remain in the raffinate, can be further removed through selective precipitation or by solvent extraction.

Morais and Ciminelli developed a solvent extraction process for the recovery of high-grade lanthanum oxide from chloride solutions containing light REMs: lanthanum, praseodymium and neodymium [109]. DEHPA and HEH(EHP) (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) were used as extractants. Several parameters were investigated: the nature and concentration of the extractants, contact time, acidity, REMs concentration in the extraction stage and hydrochloric acid concentration in the stripping stage. The process required 22 stages (8 for extraction, 8 for scrubbing and 6 for stripping) leading to a high-grade oxide (>99.9% lanthanum oxide).

A comparison of three organophosphorus extractants in the separation of samarium and gadolinium was conducted [110]. Gadolinium and samarium oxides were dissolved into hydrochloric acid solution and DEHPA, EHEHPA (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester) and DTMPPA (di-2,4,4-trimethylpentyl phosphinic acid; Cyanex 272) were tested as possible extractants. High purity n-dodecane was used as a diluent. The results show that separation of the two metals from hydrochloric acid solutions can be achieved with good results using DEHPA and EHEHPA; satisfactory separation was not attained using DTMPPA. DEHPA achieved the highest separation factors. Using this extractant has other advantages as well: lower feed ratio and a reduced number of stages. However, EHEHPA is more favourable in the stripping stage, permitting the use of a more dilute hydrochloric acid solution.

Cyanex 925 (a mixture of branched chain alkylated phosphine oxides) in n-heptane was used to extract lanthanides and yttrium from nitrate medium [111]. Several parameters were investigated: the ionic strength of the aqueous phase, the concentration of the extractant in the organic phase and the temperature. It was observed that the extraction efficiency increases with increasing nitrate and extractant concentrations. An extraction mechanism was proposed and the equilibrium constants have been calculated for yttrium, samarium, neodymium and erbium. Separation of yttrium from the light lanthanides and also the light and heavy lanthanides can be achieved. Nitric acid solution was used as a stripping agent. Stripping agent concentration studies have been made, observing an increase in the percentage stripping of yttrium with increasing acidity; at pH=2 the value is almost 100%.

Nuclear technology has played a big role in the development of solvent extraction techniques for industrial-scale separations of metals. After World War II a lot of studies have been conducted on solvent extraction of lanthanides from different mixtures, many of them having applications in the nuclear field.

One particular case is the separation of the trivalent actinides from the trivalent lanthanides; this is necessary because some lanthanides have very high neutron absorption cross sections and act as neutron poisons. Efficient separation of these elements is therefore critical in the preparation of nuclear fuels or in the transmutation of actinides into shorter lived nuclides [99]. Solvating extractants like malonamides (the DIAMEX process) or phosphine oxides (the TRUEX and TRPO processes) are the most commonly used [112].

Another example is the SANEX process. A considerable amount of research has been performed in order to find the optimum extractants for large-scale separations. Four chemical systems have been explored: SANEX 1, based on the preferential extraction of trivalent actinides over lanthanides using tris-pyridine and α-bromocapric acid in tert-butylbenzene; SANEX 2 which uses 4,6-di-(pyridin-2-yl)-2-(3,5,5-trimethylhexanoylamino)-1,3,5-triazine, α-cyanodecanoic acid and N,N'-dimethyl-dibutyltetradecylmalonamide with TPH as diluent; SANEX 3 which uses the 2,6-bis-(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine family of extractants containing the propyl group and SANEX 4 based on S donors dithiophosphoric acids [113].

The TALSPEAK (trivalent actinide/lanthanide separation by phosphorus reagent extractants and aqueous komplexes) process is based on the extraction with an acidic organophosphorus extractant from an aqueous phase containing a carboxylic acid buffer and a polyaminopolycarboxylate complexant [112]. The complexant holds back the trivalent actinides, allowing the extraction of the lanthanides into the organic phase. Different components are used in the TALSPEAK system: di(2-ethylhexyl) phosphoric acid (HDEHP), lactic acid and diethylenetriamine-N,N,N’,N’’,N’’-pentaacetic acid (DTPA). Each component plays a certain role: HDEHP – lanthanide extractant, DTPA – actinide holdback reagent and lactic acid – buffer, catalyst, solubility enhancer, complexant and secondary extractant [112].

Nash published a review of the basic chemistry and developments in trivalent f-elements separations [99]. Different methods that can be used for intragroup lanthanide separations are shown in Figure 11. Solvent extraction with HDEHP and cation exchange using α-hydroxyisobutyric acid are used with great results in the separation process. Regarding intergroup separations, Figure 12 shows a representation of americium/europium separation factors (as a representative of lanthanide/actinide group separation factors) for several separation methods.

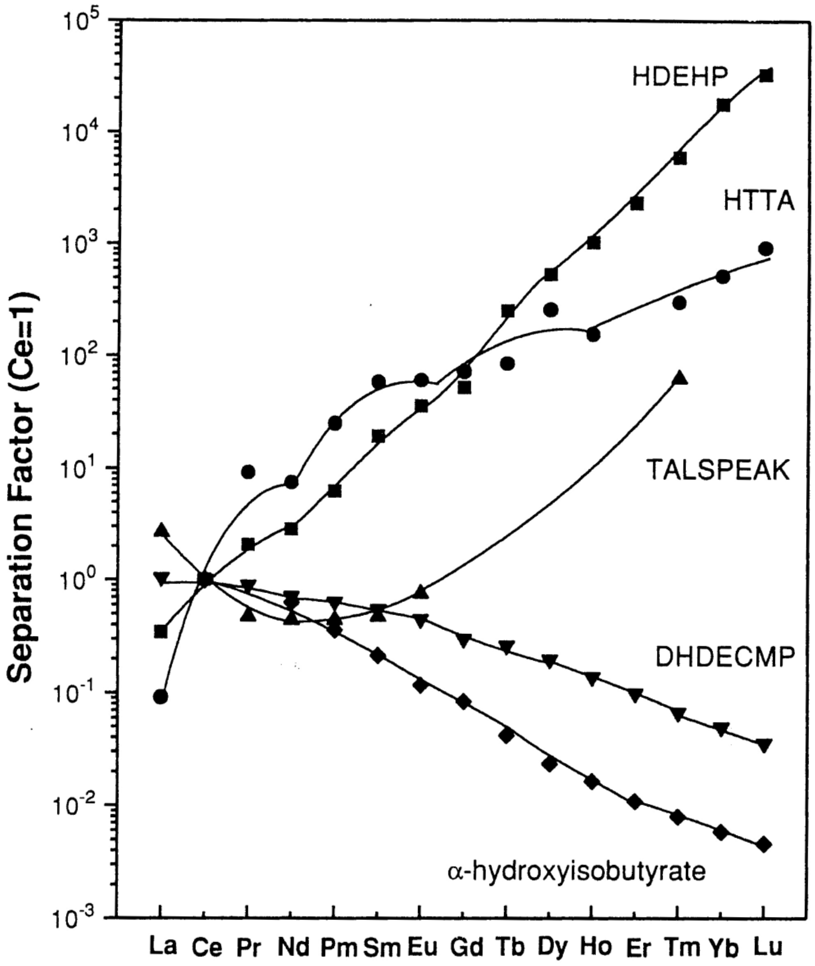

Figure 11: Interlanthanide separation factors (relative to Ce=1) for different methods [99]

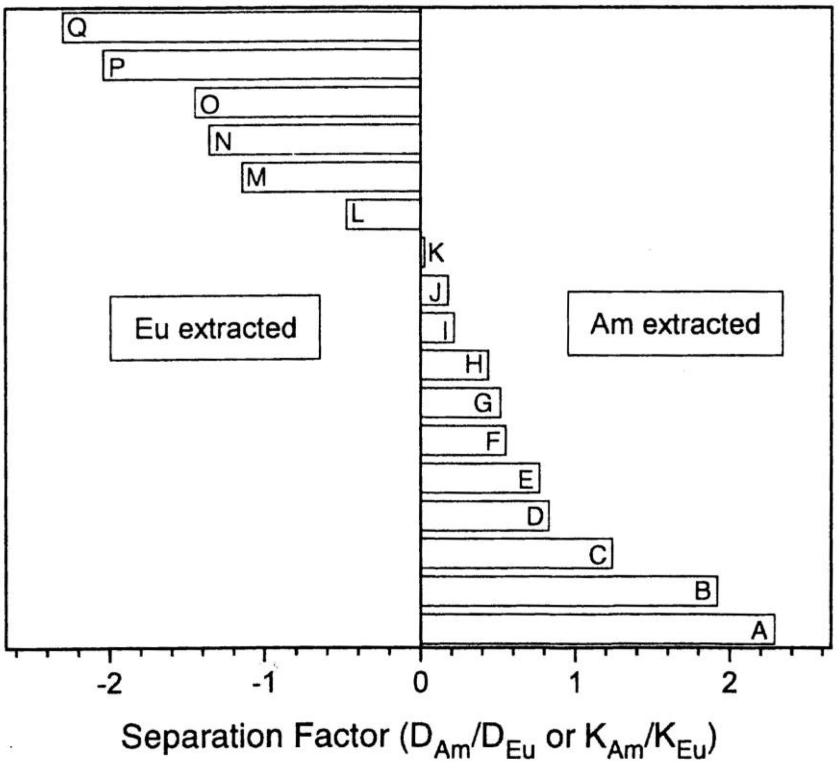

Figure 12: Histogram representation of americium/europium separation factors (as a representative of lanthanide/actinide group separation factors) for several separation methods [99]

A – HBMPPT/DPPHEN (thiopyrazolone/diphenylphenantroline)
B – 30% Alamine 336/xylene/11M LiCl
C – 1,10-phenantroline/nanoic acid/decanol
D – DHDECMP/NaSCN
E – Dowex 1/10M LiCl/ 87 ºC
F – Dowex 50/ammonium- α-hydroxyisobutyric acid as elutriant
G – 5% TBP/hexane/1M NaSCN-4M $NaClO_4$ (pH 4-5)
H – Dowex A1
I – DHDECMP/diisopropylbenzene/1M HNO3
J – TTA/benzene
K – Biorex 70
L – TTA/$CHCl_3$
M – Dyoctylphosphoric acid
N - Dybutylphosphoric acid
O – Bis(2-ethylhehyl)phosphoric acid
P – 2-ethylhexyl(phenylphosphonic) acid/diethylbenzene/1M lactic acid-0.05 M DTPA-pH 3
Q – TALSPEAK – 0.3M HDEHP/diisolpropylbenzene/1M lactic acid

4.4.1.2. Solvent extraction of rare earth metals from fluorescent lamps

Leaching, conversion and solvent extraction of REMs from fluorescent lamps have been carried using various compounds. [96-98, 103, 114, 115].

Experiments for the recovery of europium and yttrium from the phosphorus powder of spent fluorescent lamps using solvent extraction were carried [103]. A conceptual flow sheet for the recovery of these metals and some salts from spent fluorescent lamps was proposed (Figure 13). The lamps were washed with tap water and the aluminum caps were removed mechanically. In order to minimize mercury emissions, the lamps were broken under aqueous acetone. The phosphorus powder was separated by brushing, under a water stream. The water was filtered and the collected powder was dried at 110 ºC. A sulfuric and nitric acid mixture was used to leach the metals. During a 4 hours digestion at 125 ºC and 5 MPa pressure, a large percent of the metals was leached into solution (96.4% yttrium and 92.8% europium). Calcium was removed by precipitation as oxalate and potassium thiocyanate was used to convert yttrium and europium sulphate to thiocyanate. Trimethyl-benzylammonium chloride was the solvent chosen to extract the metals from the thiocyanate solution. A maximum in extraction was attained at 80ºC. It was observed that the efficiency of the processes increases with an increase in the organic solvent ratio. Extraction percentages of 98.8% (yttrium) and 96.5% (europium) were achieved using a 2:1 solvent:water molar ratio. The metals in the organic phase were recovered as nitrate salts using N-tributylphosphate in nitric acid. An increase in the acid concentration was observed to increase stripping efficiency. At 125 ºC and a concentration of 1 M nitric acid, a stripping extent of 99% was achieved. The two nitrates were separated by dissolving in ethyl alcohol, in which only yttrium nitrate is soluble. The metals were obtained by thermal reduction using hydrogen at 850 ºC (for europium) and 1575 ºC (for yttrium). A metal separation factor of 9.4 was achieved and economic estimations showed that the method can be applied industrially.

Red ($Y_2O_3{:}Eu^{3+}$), blue ($BaMgAl_{10}O_{17}{:}Eu^{2+}$) and green ($CeMgAl_{10}O_{17}{:}Tb^{3}$) phosphors were efficiently separated using solvent extraction by Mei *et al.* [30]. Artificial mixtures were used in the experiments. 2-thenoyltrifluoroacetone (TTA) dissolved in heptane was used to extract the blue powder at alkaline pH. Potassium sodium tartrate (PST) and Na_2CO_3 were used as regulators. In a second step, chloroform was used to extract the green phosphor into the organic phase, leaving the red phosphor in aqueous phase. A small quantity of 1-pentanol improved the separation efficiency. Extraction with single phosphor samples was first carried. Results show that the blue phosphor can be extracted selectively into TTA at pH values from 7 to 11, reaching a maximum at pH=10.34. The blue and green phosphors can be extracted into chloroform, with more than 90% recovery at pH values from 7 to 11, leaving the red phosphor in the aqueous phase. Due to similarity in chemical composition and crystal structure, blue-green phosphor mixtures are very difficult to be separated completely. TTA was used to extract the blue phosphor. Optimum results were achieved at pH 10.3, TTA 2.5 g/L, solid/liquid 30 g/L and PST 1%.

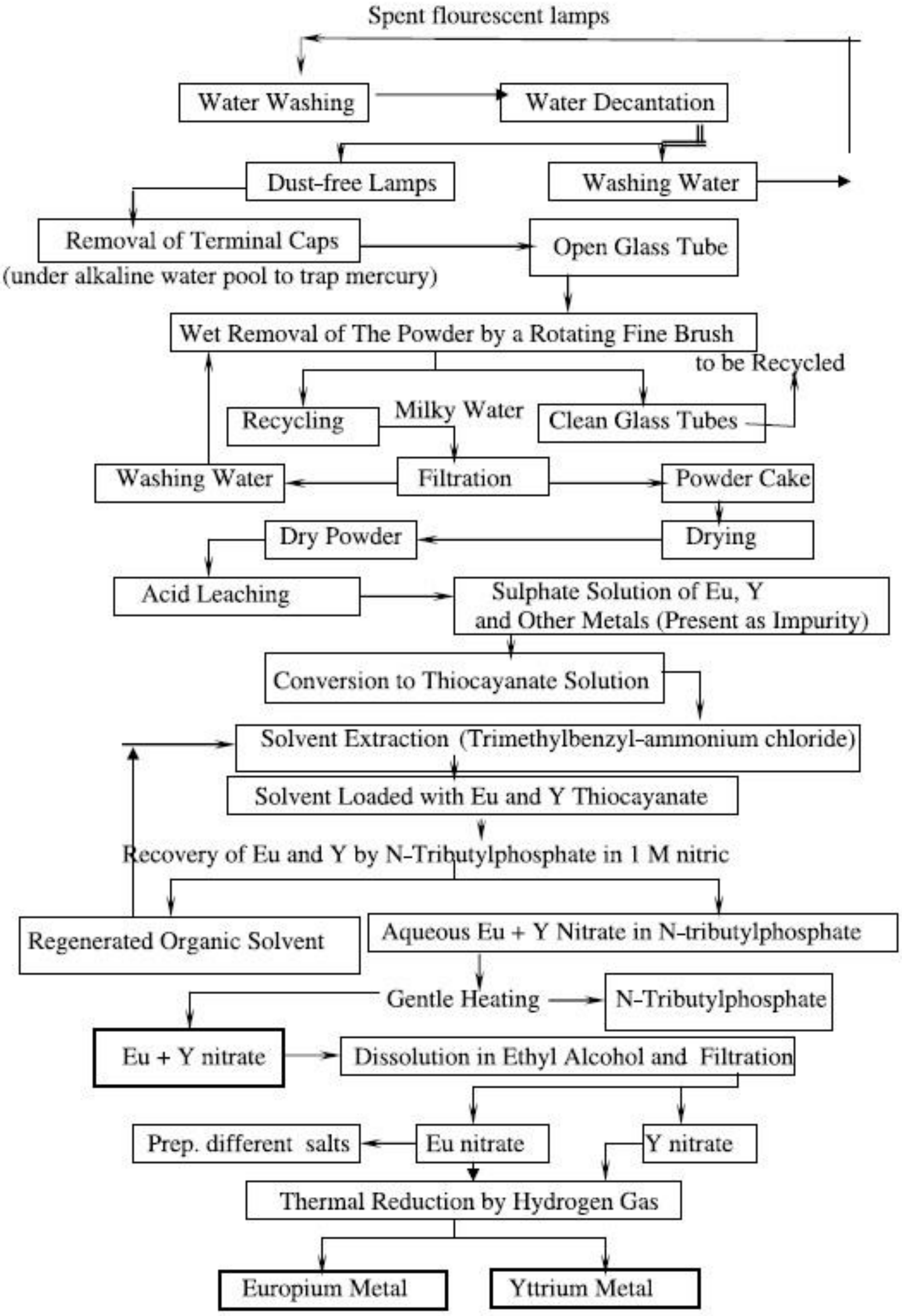

Figure 13: A conceptual flow sheet for the recovery of europium, yttrium metals and some salts from spent fluorescent lamps [103]

Extraction of red phosphor from three phosphor mixtures was carried at room temperature and the optimal conditions were found to be: neutral pH, PST concentration from 0.5% to 1.0%, 1-pentanol/chloroform (by volume) in the range of 0.2-0.5%, solid/liquid 5-30 g/L. The separation of red, blue and green phosphors was carried out according to Figure 14. Regarding grades and recovery of the separated products: red was 96.9% and 95.2%, blue was 82.7% and 98.8%, green was 94.6% and 82.6%. Testing with UV radiation revealed that the colors and emissions of separated phosphors are very close to that of commercial pure phosphors.

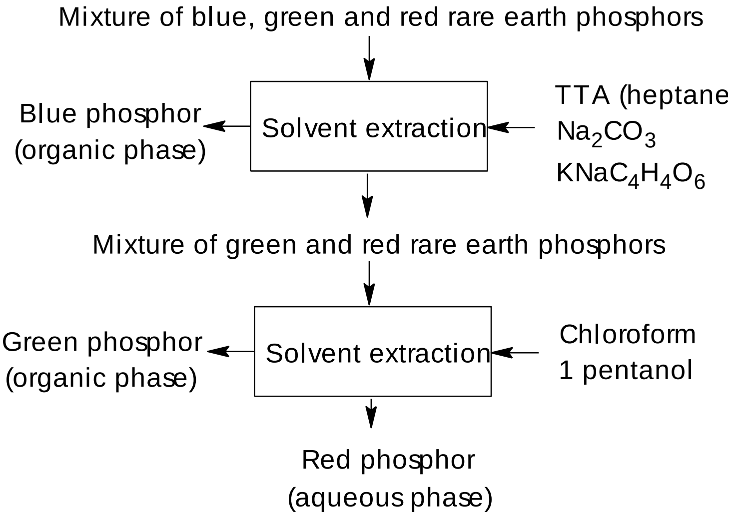

Figure 14: The separation flow sheet of red, blue and green phosphors [97]

Supercritical fluid extraction using carbon dioxide was investigated, as a method of recycling spent fluorescent lamps [32]. REMs extraction from phosphorus powders was carried with tri-n-butyl phosphate (TBP) complexes with nitric acid and water. Several advantages are stated when comparing this method with traditional solvent extraction: improved extraction efficiency due to rapid mass transfer in supercritical fluid, rapid and complete removal of the solute from the solvent and effective dissolution and extraction of metal oxides with TBP complexes with nitric acid and water. Disadvantages are stated as well: an excess amount of water can form water droplets in the supercritical fluid. A possible distribution of the metals in these droplets lowers the effectiveness of the extraction. This was prevented by controlling the TBP:nitric acid:water molar ratio in the complexes.

TBP complexes with nitric acid and water were prepared and extractions at atmospheric pressure and under supercritical conditions were performed. For the extraction at atmospheric pressure, an aliquot of each of the TBP complexes was placed in a glass vessel and heated, and then the phosphorus powder was added. Nitric acid solution (1M) was used to back-extract the metal ions in the sample and their content was determined by ICP-AES. The extraction efficiencies of yttrium and europium at 323 K, for 120 minutes, were 37.4% and 36.8%. For lanthanum, cerium and terbium they were less than 3% for all experiments. The incomplete dissolution of phosphorus powder into the TBP complexes explains the low efficiencies. An extraction at the same rate was observed for yttrium and europium. For the extraction under supercritical conditions a special apparatus was used. The main parts consist of a reaction cell, a high-pressure cell, a syringe pump, a liquid CO_2 cylinder, a pre-heating coil, a back-pressure regulator and collection cells. The experiments were conducted at 333K and pressure of 15 MPa. Under these conditions the extraction efficiencies of yttrium and europium improved significantly, reaching 99.7% and 99.8%. Unfortunately, for lanthanum, cerium and terbium they were less than7%. Yttrium and europium were again extracted at the same rate.

Leaching of metals from fluorescent lamps waste with nitric acid, followed by the recovery of REMs using solvent extraction was achieved [39]. The solvent chosen was 2-ethylhehyl phosphonic acid mono-2-ethylhehyl ester (PC-88A) in kerosene. Equations corresponding to the equilibrium processes were established for both divalent (calcium, strontium, barium) and trivalent (lanthanum, cerium, europium, yttrium, terbium and aluminum) metals present in the samples and an overall flow chart was proposed (Figure 15). The focus was the selective recovery of europium, terbium and yttrium. Through simulation the authors established that the effective separation and recovery of these REMs is possible in two steps, in a counter-current mixer-settler cascade. Recovery percentages from the leaching solution and the corresponding metal purities were: 97.8% for yttrium (98.1% purity), 58.1% for terbium (85.7% purity) and 52.8% for europium (100% purity).

Yang *et al.* recovered REMs from simulated phosphorus powder using solvent extraction [40]. The simulated powder consisted of 56.62% aluminum oxide, 32.72% rare earth oxides (yttrium, europium, gadolinium, cerium and terbium), 4.57% barium oxide, 3.94% magnesium oxide and 2.09% other constituents. Bifunctional ionic liquid extractants, prepared from Aliquat336 and two commercial organophosphorus acid extractants, P204 and P507, in n-heptane were used to extract the metals. High concentrations of aluminum nitrate in the aqueous phase proved to be an efficient salting-out agent, facilitating extraction and retaining constant ion strength at the same time. To prevent the formation of a third phase, isooctanol was added. Stripping was carried with nitric acid solution and it was observed that the stripping percentage increases with an increase in acidity, reaching nearly 100% at 0.02 M. A recovery of 95.2% was possible using a countercurrent extraction system comprising up to seven stages, phase ratio V_o:V_w=4:1 and pH=0.56. Comparison with neutral organophosphorus extractants such as P350, TBP and Cyanex923 at different initial values of pH and temperature has been made. It was observed that the system shows higher extraction efficiencies compared to P350 and TBP, but lower than Cyanex923. The extraction efficiencies decrease in the order: Cyanex923>Aliquat336-P204=Aliquat336-P507>P350>TBP.

For REMs extraction from the simulated phosphorus powder, the extractants showed good efficiency, approaching that of P350 at the same concentration.

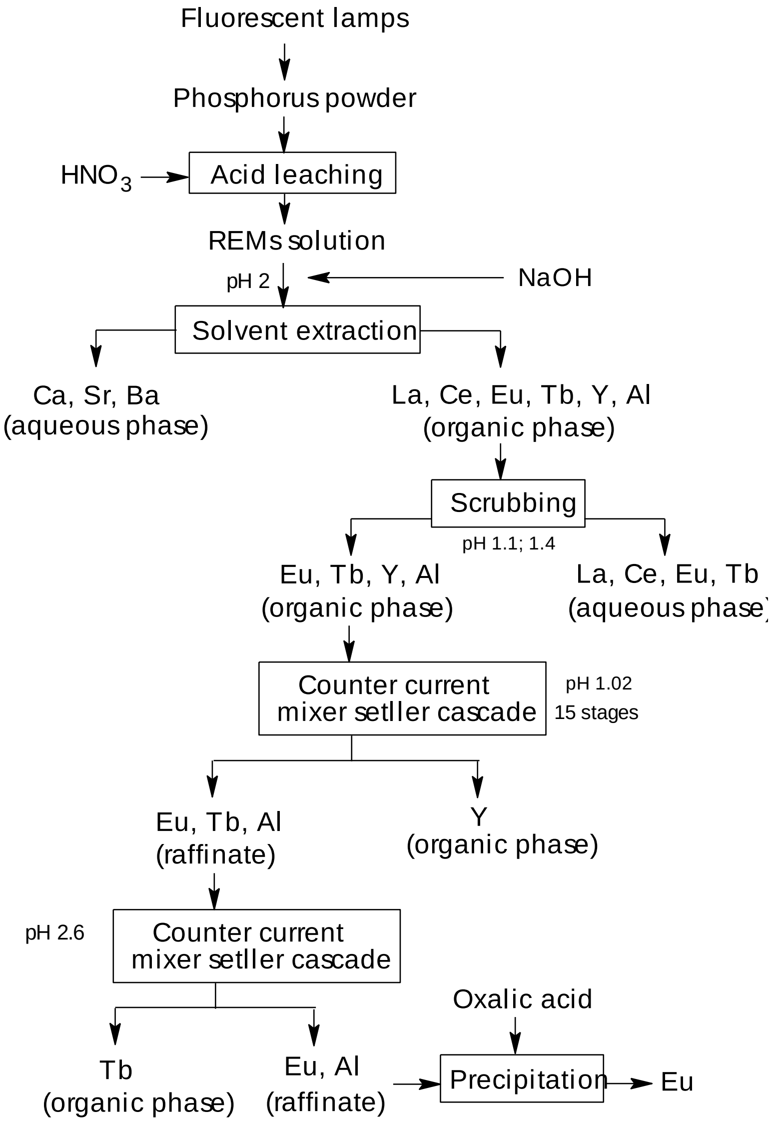

Figure 15: Recovery of REMs from phosphorus powder using solvent extraction [39]

4.4.2. Leaching and precipitation of rare earth metals from phosphorus powders

Acid leaching of metals contained in the phosphorus powder of spent fluorescent lamps was performed, in order to recover yttrium [34]. Different conditions (temperature, concentration, solid/liquid ratio) and leaching agents were investigated. Nitric acid, hydrochloric acid, sulphuric acid and ammonia were among the reagents tested. Ammonia gave poor results for leaching yttrium and nitric acid led to toxic vapors. Hydrochloric and sulphuric acid proved to be efficient leaching agents, extracting more than 80% of yttrium. The latter one also led to the precipitation of calcium, barium and lead which were found in the samples. In this way, a preliminary purification can be achieved considering the low solubility of calcium, barium and lead sulphates. Yttrium was recovered from solution by precipitation with oxalic acid. A process simulation at laboratory scale was conducted. The chosen leaching conditions were: solid/liquid ratio of 20%, temperature of 90 ºC and sulphuric acid concentration of 4N. More than 90% of yttrium was leached and 80% of this was recovered as oxalate. Simulations made revealed that about 7 tons of high purity yttrium oxalate can be produced each year, which can be transformed into yttrium oxide by heating it at 800-1000 ºC. If other components such as glass, ferrous and non-ferrous materials are also exploited, the process described shows a positive return on investment.

Leaching of trichromatic phosphorus powders with hydrochloric acid followed by precipitation with ammonia/oxalic acid, in order to obtain the contained REMs, has also been tested [31]. Several parameters were investigated in the leaching process: pH, solid/liquid ration, stirring intensity and temperature. The optimum leaching conditions were found to be: hydrochloric acid concentration 4M, solid/liquid ratio 100 g/L, stirring at 600 rpm, temperature of 60 ºC, 60 minutes time. 89.85% of the total rare earths were leached, yttrium accounting for 96.28%. The influence of the pH on ammonia precipitation was investigated and an optimum in efficiency was found at pH=8. A second precipitation step was carried with oxalic acid. Acid concentration and precipitation time were both investigated and optimum conditions were found to be: oxalic acid 6.25 g/L and precipitation time of 3 hours. The sedimentation was in this case almost 95%. After roasting, washing and drying, the samples were analyzed by XRF. The results showed that yttrium and europium oxides account for 92.10% and 7.25% respectively, the rest being impurities.

4.4.3. Gravity-based processes for recovery of rare earth metals from fluorescent lamps

Dense medium centrifugation was studied as a pre-concentration method of phosphorus powders collected from spent fluorescent lamps [38]. Through this method, concentrated phosphors can be obtained and can be further processed for the recovery of REMs. Low-density calcium halophosphate phosphors were separated from high-density REMs phosphors using di-iodomethane as organic dense-medium. The addition of sodium oleate, in order to modify the particle surface properties, improved the selectivity of the process. Also, an increase in rotation speed and pulp concentration improved the separation. A sink fraction assaying 48.61% REMs phosphors was collected, with a recovery and Newton's efficiency of 97.34% and 0.84 respectively. More than 90% of calcium halophosphate phosphors were recovered as float product.

Because of the high cost and negative environmental effects of di-iodomethane, alternative methods were investigated. Flotation was used to separate calcium halophosphate and trichromatic rare earth phosphors from fluorescent lamps waste [5]. The experiments were conducted using pure calcium halophosphate, red, green and blue phosphors, a mixture that resembles the powder found in fluorescent lamps waste and phosphorus powders previously discarded as waste products. The authors investigated the effects of dodecyl ammonium acetate, sodium dodecyl sulfate and sodium oleate on the floatability of materials. The influence of sodium meta-silicate on the separation characteristics, at different pH ranges, was also studied. Dodecyl ammonium acetate, sodium dodecyl sulfate and sodium oleate were used as collectors, hydrochloric acid and sodium hydroxide for pH correction, and sodium meta-silicate as a dispersant in the flotation of the pure phosphors mixture. Maximum efficiency for pure phosphors was achieved at pH<5 for dodecyl ammonium acetate, at pH 9-10 for sodium dodecyl sulfate, and at pH>9 for sodium oleate. For the artificial mixture good results were achieved at pH 2.5 using dodecyl ammonium acetate and at pH 9.6 using sodium dodecyl sulfate. Using dodecyl ammonium acetate, 82% red and 90% green phosphors were recovered in tail. About 90% rare earth phosphors were recovered in tail with sodium dodecyl sulfate. Low efficiencies were obtained with sodium oleate, even when adding sodium meta-silicate. A two stage flotation method for processing phosphorus powders from spent fluorescent lamps was tested. The overall process efficiency (η) was 0.43 for dodecyl ammonium acetate and 0.27 for sodium dodecyl sulfate flotation. Complete dissolution of blue phosphor was observed for dodecyl ammonium acetate flotation. However, a significant amount of the other phosphors is recovered in the second stage, leading to a decrease in efficiency.

4.4.4. Ion exchange techniques

Ion exchange techniques can be used for small scale separations of REMs.

Aqueous solutions of complexing agents are used as mobile phases and low-capacity cation-exchange resins are used as stationary phases. Hydroxyisobutyricacid (HIBA) [117, 118], mandelic acid [119], oxalic acid [120], glycolic acid [121], lactic acid [122] and ethylendiaminetetraacetic acid (EDTA) [123] have proved to be very useful eluents for the separation of lanthanides [124].

Pourjavid *et al*. used HIBA as an eluting agent for separation of medium lanthanides: samarium, europium, gadolinium, terbium and dysprosium [124]. He states that HIBA is the most popular eluting agent amongst different hydroxycarboxylic acids, providing a good degree of separation between adjacent lanthanides in ion chromatography. Positive complexes are formed by the lanthanide ions with HIBA, lowering their affinity for the cation-exchange resin. A reduction in their retention is thus achieved. The degree of complexation increases with the atomic number; this affects the charge of the complex. Lanthanides that form the most stable complex with HIBA spend more time in the eluent and elute first while lanthanides that form a weaker complex spend more time in the resin and elute later. A good separation of the ions was achieved using isocratic elution with 0.25 M HIBA at pH 4.0. The elution order was: dysprosium, terbium, gadolinium, europium, samarium. Using oxalic acid as a complexing agent leads to the formation of anionic lanthanide ions; in this case the lanthanides can be separated by anion-exchange. The elution order will be however reversed compared to cation-exchange separations, because the strongest complexes are the most negatively charged.

4.4.5. Methods for the determination of REMs

Usually, analysis of a sample that contains REMs is a destructive process, a dissolution step being necessary to bring the metals into solution. Two kinds of separation are important: separation of the REMs as a group from the matrix components and individual separation of REMs. Chromatographic techniques can be applied for the latter, being characterized by low costs and great sensitivity. Many of them can be used for a complete analysis of REMs content in less than 30 minutes, not including the time required for sample dissolution and preconditioning [125].

ICP-MS, ICP-OES, XRF and NAA are the most common techniques for quantification of REMs [24]. ICP-MS has the advantage of isotopic measurements but, compared to ICP-OES, provides lower detection limits and simpler spectra. When analyzing REMs special attention has to be paid in order to minimize spectral interferences. Because of rapid multi-element detection, ICP-OES is often used for REMs determinations despite the inability of direct solid samples analysis.

XRF has the advantage of direct analysis of materials, but the detection limits achieved for REMs are not as great compared to the other methods. NAA is a very sensitive method but it’s usually complicated, has high costs and is affected by spectral interferences [24].

4.4.6. Patents regarding treatment of spent fluorescent lamps

Patents regarding the recovery of components from spent fluorescent lamps have been registered. [115]. Cleaning using an ultrasound bath, dry cleaning methods using steel, sodium carbonate or calcite grains and sedimentation methods have been suggested, among others, for the recovery of the phosphorus powder (Table 12).

Table 12: Summary of patents dealing with treatment of spent fluorescent lamps [115]

Process	Raw material	Equipment	Product	Reference
Mechanical dismantling	Lamps	Drum; rotating fracture blade; rotary diamond disc	Glass; Al; Cu; etc.	US 2006214039 US 5092527 DE 4030732 KR 950014962
Binder removal by burning	Lamp fragments	Oven (500–520 ºC)	Fluorescent powder	US 2006214039
Coating removal by dry cleaning	Lamps	Ball mill; tube mill; oscillating mill; barrel polisher: use of steel grain or NaCO3 or calcite	Fluorescent powder	JP 2001081449
Coating removal by cleaning	Burned lamp fragments	Ultrasound bath	Fluorescent powder	US 2006214039 JP 2001081449
Recovery of fluorescent powder by sedimentation	Burned lamp fragments	Tank	Fluorescent powder	US 2006214039 US 20020063509

Patents regarding the recovery of REMs from phosphorus powders have been registered as well. Otto *et al.* [126] describes some of the most important ones. Many of these use acids to leach the REMs, followed by their precipitation with various reagents. The method proposed by Otto *et al.* comprises six steps: mechanical separation of coarse components, separation of the halophosphate, extraction in acids of easily soluble rare earth fluorescent substances (mainly Y and Eu oxide), extraction in acids of rare earth fluorescent substances which dissolve with difficulty (rare earth phosphates), breakdown of the remaining components which contain rare earths (for example rare earth aluminates) and final treatment. The REMs are precipitated from the solutions obtained in the various process steps either with oxalic acid as oxalates or with ammonia as basic salts. The oxalates are heated to form oxides. Figure 16 shows the sequences of the recycling process.

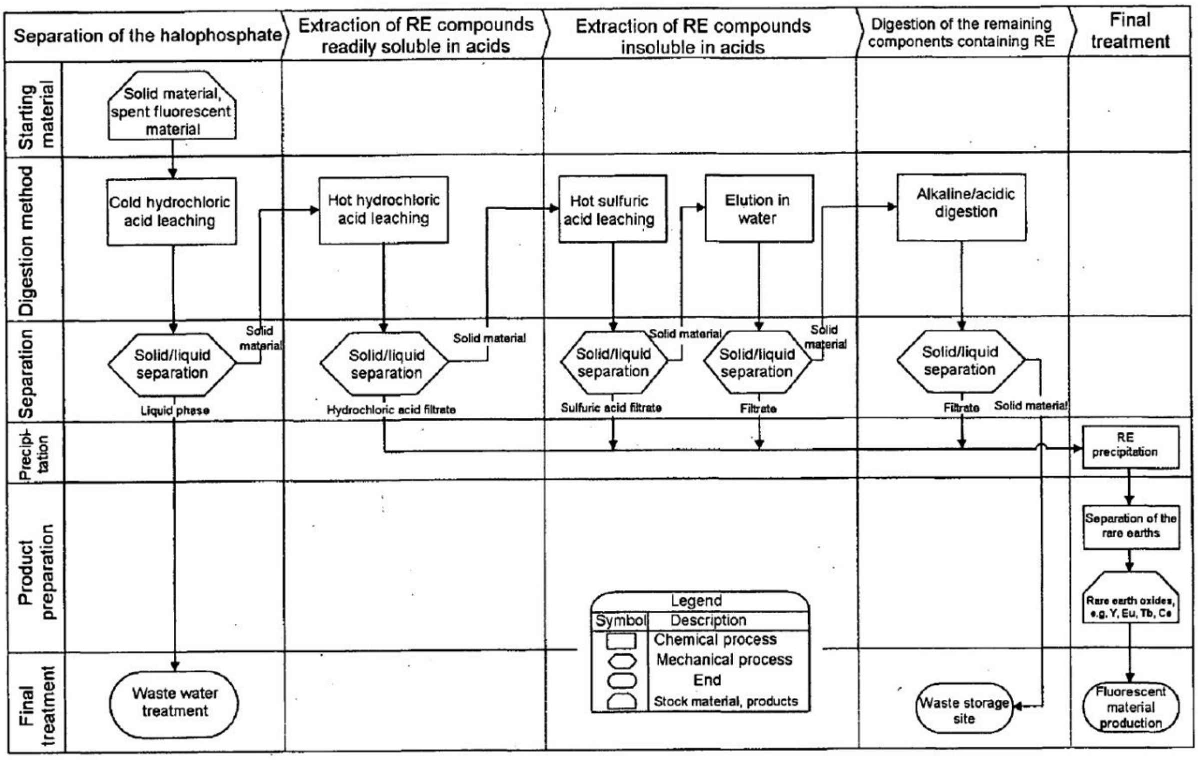

Figure 16: Process scheme for fluorescent material recycling [126]

5. Conclusions

Increase usage of fluorescent lamps around the world, environmental concerns and the rising need for raw materials make the development of an effective recycling process a high priority. Mercury is a component of all fluorescent lamps and because of this spent fluorescent lamps are classified as hazardous waste. According to environmental regulations, such waste cannot be landfilled without lowering mercury content below a certain limit. Special treatment is thus necessary. Moreover, fluorescent lamps contain REMs, elements with important applications in numerous fields.

Different techniques meant to remove mercury and to recover yttrium, europium, terbium and other REMs from fluorescent lamps have been investigated. Possible flow sheets have been proposed by researchers. Although most of the methods discussed showed good results, they don't seem to have applications on larger scale processes and some of them were not tested on real crushed lamps. Parts of the experiments described in these publications were carried in the laboratory on clean lamps, carefully treated material or pure samples that imitate the composition of phosphorus powders. In reality, the waste that needs to be recycled is a mixture of crumpled materials, full of impurities and a separation step is needed before applying certain recovery methods.

Although certain methods had very good results in the laboratory for recovering mercury and REMs, when applied at a larger scale and on complex mixtures they may not necessary show the same efficiencies. One has to keep in mind that fluorescent lamps composition is not the same. Depending on the manufacturer and the year of production, mercury and REMs content can vary greatly, making fluorescent lamps waste a heterogeneous material.

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