



Combination of Fire Assay and Modern Instrumental Techniques for Precious Metals Analysis

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Abstract

The extraction of the precious metals as pure metal or alloys from the primary raw materials (ores, concentrates) and recycling materials is an important issue for ecological perspective. The recycling of materials containing precious metals include e-scrap, automotive catalysts, chemical catalysts, production waste from the electronic and galvanic industries and other numerous waste materials. The production and recycling of non-ferrous metals requires very precise knowledge about the chemical processes to get the composition of the materials.

Due to their high value, the precision and accuracy of the analytical methods for the determination of precious metals is important. The analysis of gold and silver has a tradition, which is based on the miniaturisation of the smelting process and was described by Agricola around 1550 A.D in detail. This century-old traditional technique is still in use in precious metals analysis due to its accuracy. Nowadays, the determination of platinum group metals have to be carried out in addition to gold and silver so that modifications of this existing method are required. In order to get statistically proved results, samples of heterogeneous materials such as e-scrap and complex composites are prepared by means of combinations of mechanical and thermal procedures to get homogeneous samples for analyse.

The samples that have been prepared for analysis are suitable for the combination of fire assay and subsequent measurement either directly or after wet chemical preparatory treatment.

In traditional fire assay, the precious metals are separated and accumulated by using lead flux. The sample-lead flux mixture is fused in a furnace at >1000 °C and finally a lead regulus is obtained. After then lead is removed by means of oxidation in order to get pure precious metal. Nickel sulphide flux is also a useful collector especially for platinum group metals. The precious metals are recovered in concentrated form by a wet chemical separation and then transferred into solutions for



ICP-OES measurement. The use of copper flux is another mean. Ion exchange separation could be made for the precious metal-containing copper, but a relatively complex procedure is included. The more efficient technique is the homogenization of the copper reguli in an induction oven for direct spectroscopic measurement of the precious metals.

The combination of the fire assay technology with instrumental methods such as ICP-OES, spark OES, XRF and GDMS assures a significant lowering of the detection limits of precious metals down to the ppb level. Elements which interfere in the measurement of the precious metals are excluded or minimised by the fire assay process.

Key words: Fire Assay, modern instrumental techniques, precious metals

Introduction

The high value of precious metals (PMs) means that particular demands are placed on the precision of the chemical analysis of these elements. However the fire-assay technique was developed in the 16th century, it is still the most reliable method for the analysis of gold and silver in ores. The analysis process was described by G. Agricola in 1550 in detail in *De Re Metallica* [1] and it still remains the most accurate method for determination of gold in the industry. This technique is based on the extraction and refining of the PMs by means of melting processes. The chemistry of the fusion process is upon oxidation-reduction reaction in which multicomponent systems consist [2]. A flux is used which will convert infusible matter into fusible compounds at a certain temperature. Lithargo (PbO), sodium carbonate (Na_2CO_3), borax glass ($\text{Na}_2\text{B}_4\text{O}_7$) and silica (SiO_2) are the four main reagents commonly used as flux. Other compounds as carbon (C), calcium oxide (CaO), calcium fluoride (CaF_2), potassium nitrate (KNO_3) etc. can also be used as part of the flux. Nowadays fire assay method is also used for the analysis of PMs including platinum group metals (PGMs). Palladium, along with platinum, rhodium, ruthenium, iridium and osmium form a group of elements referred to as the PGMs. The analysis of gold and silver has a tradition but it is needed to modify this existing method for PGMs.

Institut for Materialpruefung Gloerfeld GmbH (IMG) in Willich, Germany offers varieties of material for the analysis by the combination of fire assay and modern analytical techniques. The fire assay is used as a method for extraction and concentration of the PMs. The advantage of using fire assay is the elimination of interfering elements, hence the determinations by modern techniques can be performed without any problems. The materials such as ores, concentrates, intermediates, metallurgical products, sweeps, waste metals, electronic waste, catalysts, fine metals and alloys which happen to be in the category of PMs, are analyzed (**Figure 1**). Precise and reliable measurements of rare earth elements in minerals and all kinds of recycling materials, and the trace elements in pure metals, PMs, semiconductor materials and geological samples are also offered.

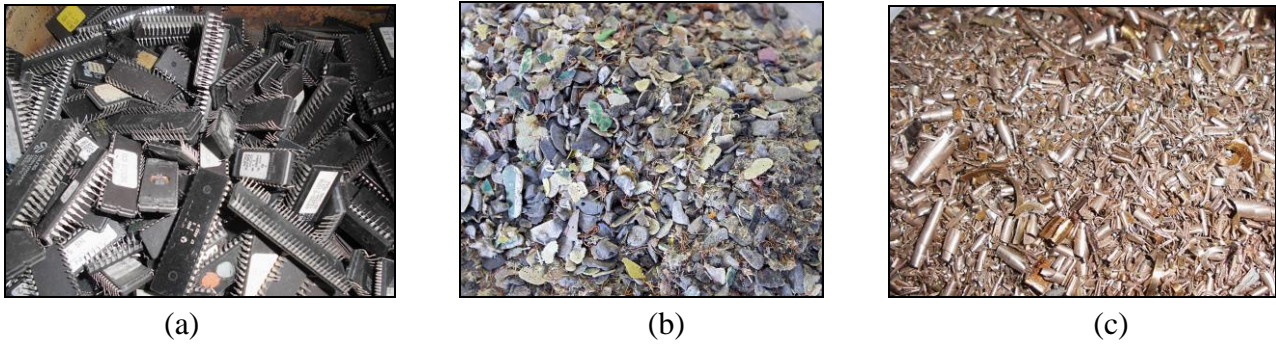


Figure 1. Raw materials e-scrap (a, b) and brass chips (c) as received for sample preparation.

Preparation of Samples

In order to get precise results, pre-treatment of samples must be carried out. Statistically based sampling and preparation of representative homogeneous samples are needed. This is mainly performed on the sites of refinery companies under supervision of independent samplers. IMG cooperates with sampling companies in Germany and abroad. IMG can realize sample preparation in its own sampling division in Willich where the procedure is the same as the refiners do (**Figure 2**).

Depending on the type and amount of the raw sample, the treatment steps include shredding, dividing, incinerating, screening, melting, sawing the metal ingots, grinding of brittle parts etc. by means of shredder, crushers, hammer mills and laboratory mills (**Figure 3**) to obtain homogeneous metallic chips and fine powders less than 160 μm grain size.



Figure 2. (a) Melting the sample mixture in an induction furnace and (b) casting for further treatments for sample preparation at IMG, Willich.



(a)



(b)

Figure 3. Sample preparation units (a) hammer mill (b) shredder to get homogeneous samples at IMG, Willich.

Fire Assay

The choice of analysis method and flux for fire assay procedure requires the knowledge of the matrix elements and the estimated concentration of the PMs. A simple measurement by ICP-OES or XRF gives these information. Based on the PMs present in the sample, the following fire assays can be carried out.

Method of Fire Assay	Collected Precious Metals
Lead collection	Ag, Au, Pd, Pt, (Rh)*
Nickel sulphide (NiS) collection	Pd, Pt, Rh, Ir, Ru, Os
Copper collection	Ag, Au, Pd, Pt, Rh, (Ir, Ru, Os)*

*Under special conditions

General procedure consists an extremely fine state of sample and thoroughly mixed with the flux constituents in a clay crucible. It must be ensured that intimate contact of each PM particle with particles of the melting flux occurs in order to have a sufficiently complete reaction between sample and flux and the simultaneous production of the fine globules of the collecting agent [2]. Crucibles and cupels in furnace for fire assay at (1000 - 1100°C) are shown in **Figure 4** (a, b).

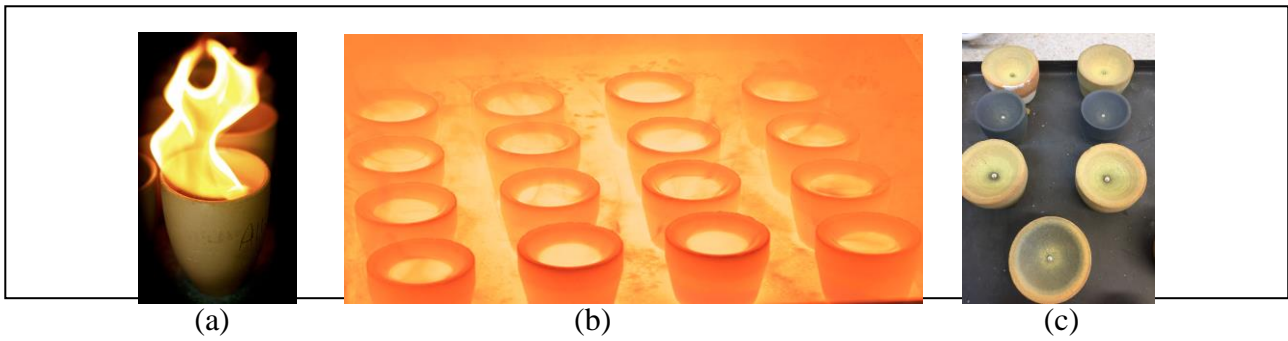


Figure 4: (a) Crucibles and (b) cupels in furnace (c) prills after cupellation.

Lead Collection:

The first step in lead fire assay involves the reduction process in a crucible [4 - 6]. The sample is accurately weighed and mixed with a proper flux in a crucible. The sample-lead flux mixture is fused in a furnace at $>1000\text{ }^{\circ}\text{C}$. As the fusion process progresses, the impurities which combine more readily with oxygen are converted to their oxide states and extracted by the slag, preventing them from entering the metal phase. Generally, metallic oxides are quite soluble in the slag phase, but not the metallic phase. After fusion process, the high density noble metals including gold and platinum group metals (PGMs), which are difficult to oxidize, are settled to the bottom of the crucible and collected in a lead button during the subsequent fusion process [2, 3]. Once the sample is removed from the furnace and cools, the lead button is separated from the slag by crushing the crucible. A mass reduction and purification of the produced lead button is possible by an oxidative melting (scorification).

The produced lead button after fire assay, the determination of the elements can be realized as follows:

- (a) After dissolution in nitric acid, silver and palladium by AAS, ICP-OES or ICP-MS measurement.
- (b) After remelting to form a metallic disc (**Figure 5**), silver, gold, palladium, platinum and rhodium by spark OES or GD-MS measurement.



Figure 5. Metallic discs after remelting of lead buttons after GD-MS measurement.



Extraction of the Precious Metals

The PMs are then extracted from the lead button by an absorption process known as cupellation. Elements which interfere in the measurement of the PMs are excluded or minimised by the fire assay process. In order to control the whole process, standard reference material with known concentration is used along the process together with samples to be analyzed.

During cupellation, the lead in the button oxidizes and is absorbed into the cupel, leaving a PM button known as a prill (**Figure 4 c**). The prill will contain silver, gold and some of the platinum group metals [7].

Analysis of Gold, silver, Platinum and Palladium

The content of the prill containing Au, Pt and Pd is determined after dissolving in nitric acid followed by hydrochloric acid. These PMs in solution can be analyzed by using modern techniques such as:

Atomic Absorption Spectrometry (AAS)

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Silver content can be calculated from mass difference.

Nickel Sulphide (NiS) Collection:

The sample- nickel sulphide flux mixture is fused in a furnace at higher temperature. The melting process in the crucible by a reaction between nickel and sulphur results in finely divided NiS droplets. Since NiS has a high affinity to all PGMs, so after solidification a NiS button containing the PGMs remains [8 - 11]. A concentrate of PGMs will be recovered by dissolving in hydrochloric acid. After filtration, the residue containing the PGMs can be dissolved in a hot aqua regia to obtain a solution for ICP-OES or ICP-MS measurements.

Copper Collection:

Metallic copper can be used for the quantitative collection of PMs by fire assay [12]. By reduction of the copper oxide containing flux, the collecting copper metal is obtained. The melting process in the crucible happens to occur by reaction between copper oxide and carbon as in the lead collection. Copper powder as part of the flux can also be used. After dissolution of the copper button, the collected PMs can be extracted by cation exchange resins, but it is more useful to analyse these elements in the copper matrix. PMs in the resultant copper button can be measured in the following means.

- (a) After dissolving in acids, and determined by by ICP-OES or ICP-MS



- (b) After homogenization by remelting, the metallic buttons can be analysed by XRF, spark OES or GD-MS.

Analysis and Detection

Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES)

Most of routine analysis is accomplished by using of standard wet chemical method or inductively coupled plasma atomic emission. These methods are destructive since the samples have to be dissolved to form a solution [13, 14]. IMG is using three different types of ICP-OES instruments namely axial view plasma with CCD detector (Iris Advantage, Thermo), radial view plasma with CCD detector (Arcos, SPECTRO) (**Figure 6**) and Photomultiplier tubes (Modula, SPECTRO). The combination of these instruments give a wide range of spectra of the analysis.

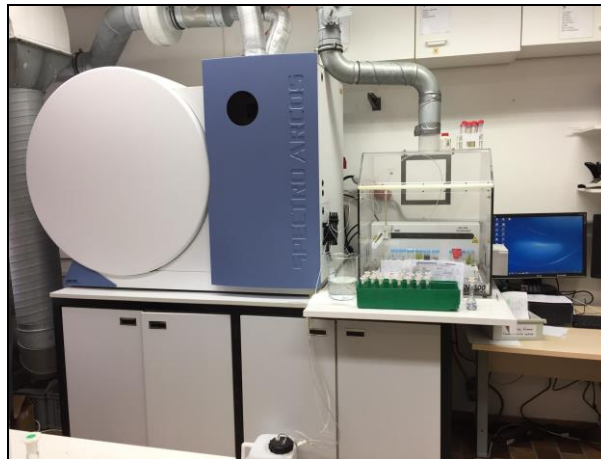


Figure 6. Sample solutions for analysis and ICP-OES system (Arcos, SPECTRO).

Concentration ranges and detection limits:

Depending on the method of fire assay, sample material and the amount of sample, the concentration range from less than 1 ppm up to 50 - 85% can be determined.

Analysis by X-Ray Fluorescence Spectrometry (XRF)

Precious metals including gold, silver and platinum group elements collected in a copper button after fire assay can be analyzed by XRF since it is a rapid and non-destructive technique. After homogenization by a special remelting step, cutting and polishing the surface, the copper discs (**Figure 7a**) is ready for XRF measurement. A wavelength dispersive X-ray fluorescence (WDXRF) spectrometer (4 kW), Axios, Panalytical, Netherlands is used for the analyses (**Figure 7b**). Typical applications are the analysis of reforming catalysts, automotiv catalysts, PGM concentrates, PM containing ceramics, alloys, ashes etc.

Depending on the size of the sample, pre-treatment and elements to be analyzed, the concentration ranges from ca. 10 ppm up to 100% can be analyzed. Calibration curves for the analysis of gold and



platinum present in sample prepared as copper discs is shown in **Figure 8 (a)** and **(b)**. The advantage of using XRF is the reproducibility of the measurements.

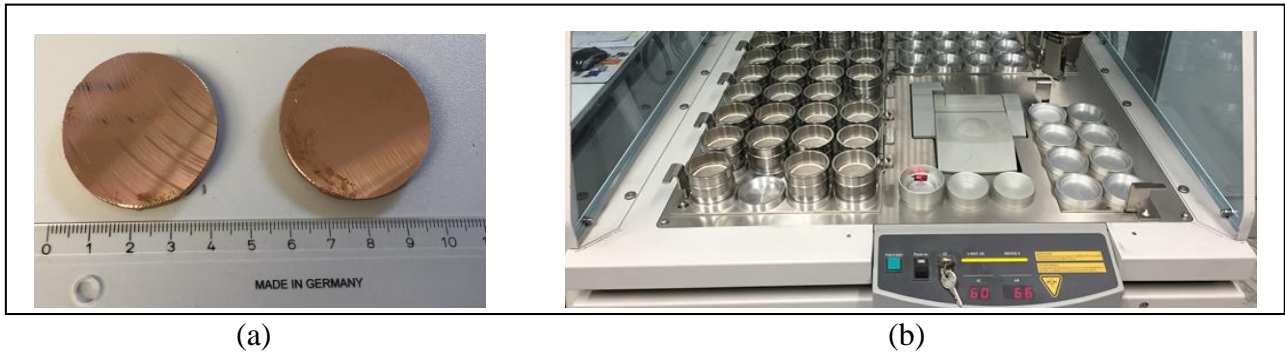
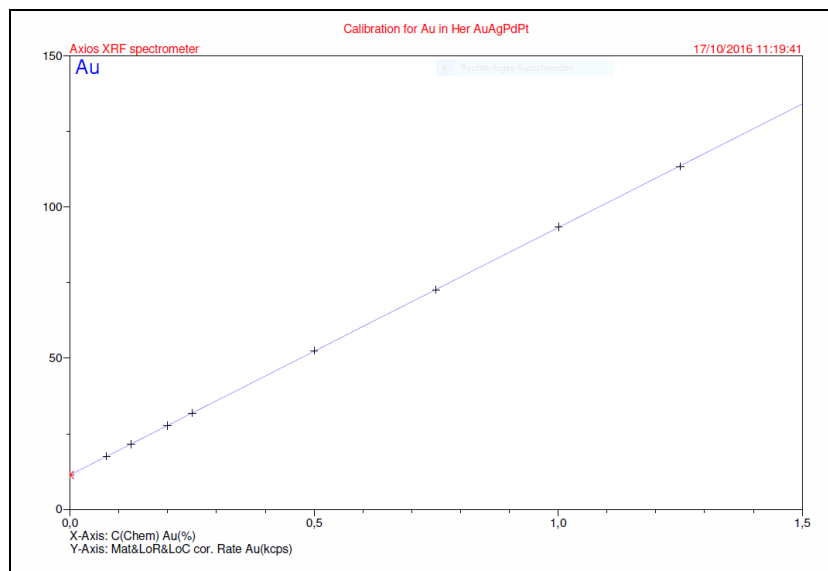
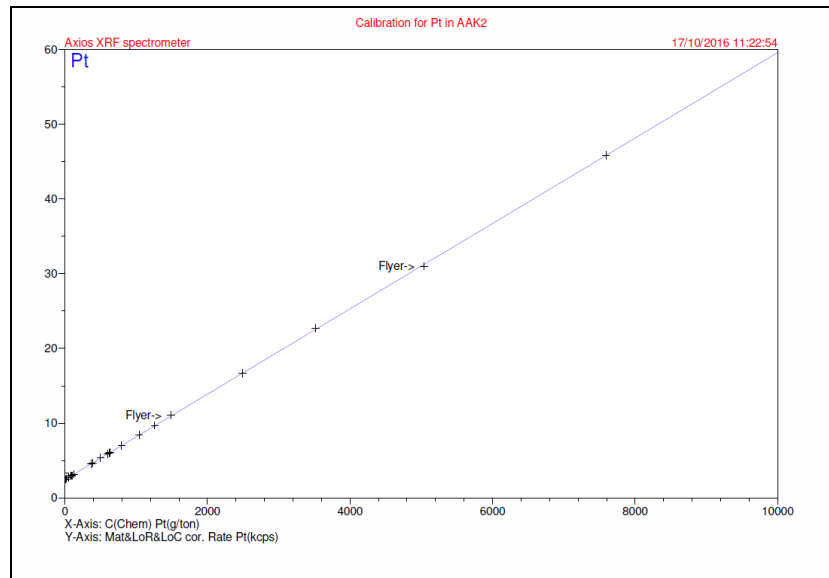


Figure 7: (a) Copper discs (40 mm) for XRF analysis and (b) sample chamber of WDXRF, Axios, Panalytical.



(a)



(b)

Figure 8: Calibration curves for the analysis of (a) gold and (b) platinum present in sample prepared as copper discs.

Analysis by Glow Discharge Mass Spectrometer (GD-MS)

Analytical methods with sufficient sensitivity are needed to determine the PMs and impurities at background levels. Copper and lead buttons from fire assay collection, prepared by the remelting step for XRF, can be directly analyzed by GD-MS. A Thermo Scientific ELEMENT GD PLUS glow discharge mass spectrometer (500 - 1400 V) is used for the analyses (**Figure 9**). Minimum calibration and less sample preparation are needed for the measurements of each and every elements. The calibration of Pd in silver prepared by centrifugal casting and measured by GD-MS is shown in **Figure 10**.



Figure 9. Sample chamber with ion source in GD PLUS GD-MS.

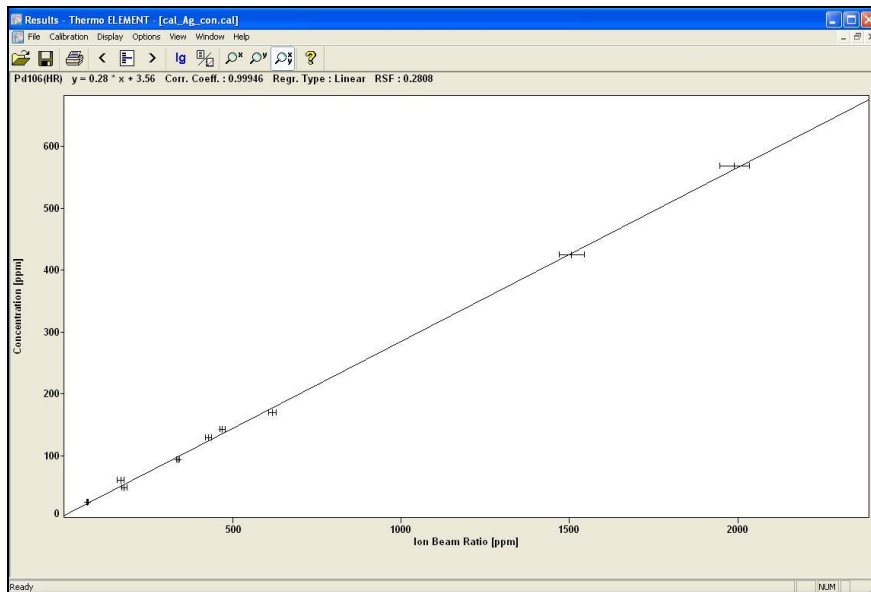


Figure 10: Calibration of Pd present in pure silver sample prepared by centrifugal casting and measured by GD-MS.

The detection limits of PMs are down to three decimals lower comparing with XRF measurements. Therefore, the combination of these two instruments enables us to determine the elements in a range from some ppb to 100%.

GD-MS technique is predestined for trace elements in pure metals. The content of ultra-traces and matrix elements ranges from (ppt - %) are measured by a combination of a dual mode secondary electron multiplier (SEM) and a Faraday collector within a single scan in seconds. For analysis of pure metal powders, presslings can be prepared. Presslings from gold granulates and copper powder in steel discs for GD-MS measurement are shown in **Figure 11** (a, b).



Figure 11: Presslings from (a) gold granulates and (b) copper powder in steel discs for GD-MS measurement.

Conclusion

The combination of fire assay and modern analytical techniques has proved the industry standard process for obtaining gold, silver and platinum group metals (PGMs). The efficiency of the



recovery of precious metals (PMs) is nearly 100%. This combination of analysis is worthwhile to recycle different kinds of recycling materials like e-scrap, automotive catalysts, chemical catalysts, production waste from the electronic and galvanic industries as well as for the analysis of PMs in the primary raw materials (ores, concentrates). It is essential to analyse the content of precious metals for selling, buying or recycling in order to ensure the quality and value of the materials. Well experience with good background of understanding on the analysis in our company IMG produces the accurate and precise assay results.

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