Extraction Chromatograph GC Separation of Precious Metals with 2-octylanaminopyridine

Introduction:

Platinum group metals (PGMs) are divided into primary platinum metals (platinum and palladium) and secondary (ruthenium, rhodium, iridium and osmium). Platinum is found in about 0.01 ppm in the earth’s crust. Palladium is the second most important platinum group metals (PGMs). This metal is often used in place of platinum, where conditions permit, because of its lower price and density. Iridium is found in the earth’s crust in concentration of about 0.001 ppm. This metal is mostly found together with osmium in the alloys osmiridium or syserkite, iridiosmium or Neuyanskite. Rhodium is present at about 0.001 ppm in the earth’s crust. Rhodium metal is known for its stability in corrosive environments, physical beauty and unique physical and chemical properties. It commands a premium price because of its very low abundance in nature. The importance of gold in human life as well as its fascination for scientists has been appreciated right from alchemist times until the present day. This metal is found in about 3.5 ppb in the earth’s crust, often as 75-90% pure native gold that has been released by the weathering of sedimentary and igneous rocks. Gold is one of the most ancient metals used in the arts and jewellery, and it is of growing importance in technology because of its resistance to corrosion. It commands a premium price because of its low abundance in nature. The economy of a nation depends to a significant extent on the size of its gold reserves. Recent advances in analytical chemistry are characterized by great progress towards more powerful methods of separation, equaling in the significance the great forward strides made in instrumental methods of determination. Problems of chemical analysis almost always involve two steps: separation of desired constituent and measurement of the amount or concentration of this constituent by spectrographic, spectrophotometric and polarographic methods, which minimize the need for the separation steps preceding the measurement step. However, with the rapid growth of chemical technology, the analytical chemist is called upon to deal with mixture of increasing complexity. Extraction chromatography enjoys a favored position among the separation technique because of its ease, simplicity, speed and wide scope. It is a potential alternative refining technology as well as ion-exchange process. The most important factor in the reversed phase extraction chromatography extraction of metals is extractant selectivity to the specified metal ions to be recovered.

The literature studies show that, there are problems associated with separation and determination of individual metals from their ore and metallurgical concentrates. The whole analyses of these precious metals are very complicated because they have similar properties and are found together therefore it is desirable to have to have versatile scheme of analysis for extraction and separation of all these precious metals is very important. Hence the extraction and separation of these metals from their ores and metallurgical concentrate using reversed phase extraction chromatographic technique has been proposed. Among the various methods Reversed phase extraction chromatographic method is recent, rapid, versatile and popular technique because the extraction is carried out at micro and macro gram levels. In recent years reversed phase reverse phase extraction technique by using various reagents has becomes most popular so we are using N-n-octylaniline as an extractant which acts as liquid anion exchanger for extraction of these metals. I hope this method will be applied for separation and extraction of these precious metals.

Literature survey:

Ruthenium(III) was extracted with 1, 2, 3-benzotriazole in 1-pentanol [1]. Noble metals were separated by extraction chromatography using tri-octylamine [2] as a stationary phase on paper support. The Rf value of ruthenium(III) was less than rhodium(III) and greater than aluminum(III), osmium(VIII), iridium(III), platinum(IV), palladium(II). A group separation of rhenium and platinum group elements (ruthenium, palladium, osmium, iridium and platinum) were carried out using TEVA [3] as an anion exchange resin. Ruthenium, osmium and iridium were extracted from hydrochloric acid media using cyxen 921 [4], the method was applied for recoveries of metal ions from catalysts The literature survey revealed that osmium(VIII) was extracted with tri-octyl phosphine oxide [5] in a hydrochloric acid media. In this method for elution of metal it requires thiourea and it suffers from interference of cations viz. thallium(III), gallium(III) and indium(III). Rhodium was extracted as rhodium chloride and was separated from palladium and platinum with trioctylamine or aliquot 336 [6] in toluene. In a method metal was eluted with concentrated hydrochloric acid. N, N’-dimethyl-N, N’-diphenyltricynlmalonamide [7], was used for solvent extraction of rhodium but for elution method requires mixture of 4.0 mol/L hydrochloric acid in presence of 0.05 mol/L sodium hypochlorite. Alamine 336 [8] in kerosene was used for selective separation of iridium(IV), ruthenium(III) and rhodium(III) from chloride media. The liquid liquid extraction of iridium(III) from 2.0 mol/L hydrochloric acid solution was carried out by N, N-diethyl-N'-benzoylthiourea
Iridium(III) was extracted from aqueous solution by 4-(non-5-yl) pyridine in chloroform. Solvent extraction behavior of iridium(III) with salicylhydroxamic acid (SHA) in isobutanol from aqueous chloride solution was studied and compared with similar extraction behavior of rhodium(III) and ruthenium(III). Palladium(II) was extracted from hydrobromic acid media by hexadecylpyridinium bromide [12] which gives metal recovery 99%. 1-(2-pyridylazo)-2-naphthol [13] has been used for solvent extraction of palladium(II) but method suffers from interference of nonferrous alloys in the determination of palladium. Cyanex 921 in toluene [14] was used for liquid-liquid extraction of platinum in hydrochloric acid media but it requires higher concentration of acid. Separation of gold(III), palladium(II) and platinum(IV) in chromites was achieved by anion exchange chromatography using inductively coupled plasma-atomic emission spectrometry (ICP-AES) [15]. This method requires more elution time. Presence of ruthenium, osmium and iridium was observed from Ni-Cr-PGE minerals but the separation study has not been carried out [16]. Separation of gold (III), palladium(II) and platinum(IV) in chromites was achieved by anion exchange chromatography using inductively coupled plasma-atomic emission spectrometry (ICP-AES) [17]. This method suffers from the drawbacks viz. it requires more elution time and palladium(II) was not determined. Solid phase extraction of gold(III), platinum(IV) and palladium(II) was carried out using polystyrene-divinylbenzene porous resin (XAD-4) [18]. Platinum(II), palladium(II) and gold(III) were separated by amberlite XAD-7 resin [19] column gave the recovery of elements greater than 95%.

**Significance:**

The proposed method will found advantageous over the other reported methods. The cost of chemical required for synthesis of extractant i.e. 2-octylaminopyridine is low and it will be prepared in the laboratory. The proposed method will be simple, rapid and advantageous over reported method. The proposed method will be effective for quantitative extraction of precious metals. The use of costly and harmful organic solvent is avoided.

**Objectives:**

Preconcentration of the elements of interest may prove sometimes to very useful and advantageous. Enrichment of precious group metals from complex matrix of natural samples by using high molecular weight aniline as extractant is well known but little is known about its use in the extraction of precious metals. In this research investigation, I wish to develop a reversed phase extraction procedure for precious metals from associated elements like base metals and preconcentration of these metals. The extractant like 2-octylaminopyridine is also known as liquid anion exchanger. It is the cheap, can be regenerated and required in low concentration. The method can be applied at a low acid concentration. In moderately weak chloride medium most of the base metals are present in cationic form in the solution where as precious group metal chlorocomplexes are very stables at fairly low chloride concentration and hence separation of precious group can be achieve.

**Methodology adopted:**

The liquid anion exchange separation procedure has potential to separate selectively precious group metals from the large concentration of flux and matrix elements. The reversed phase extraction using liquid anion exchanger such as 2-octylaminopyridine can be carried out in batch extraction. The solution of precious group metals is adjusted to low concentration at this stage these metals forms stable anionic chlorocomplexes while the base metals remains quantitatively in aqueous solution in the cationic form and hence separation will be achieved. The precious group metals in column with reagent back stripped with suitable strippands and determined this metal by spectrophotometrically. The procedure will be developed and condition will be optimized to have maximum separations of precious group metals. After development of these separation methods, it will be applied for the separation of precious group metals from their ores.

**Techniques to be used in study:**

The reversed phase column chromatographic techniques will be used for development of separation methods of precious group metals. Silica gel (60-120 mesh) will be rendered hydrophobic by exposing it to vapours of dimethylchlorosilane in atmosphere of nitrogen. The gel will then washed with anhydrous methanol and dried at 100 °C the silenced silica gel will be impregnated with 2-octylaminopyridine in suitable soluble solvent and dried in a rotary vacuum evaporator to produce uniform coating. Excess solvent will be removed by washing with 2M hydrochloric acid. The impregnated silica gel will be slurred with distilled water and poured into column. Voids present in column will be removed by pressing gently with glass rods. Silica gel will be preferred as support because it is porous and retain a considerable amount of extractant. Each column will be used for number of times without loss of extraction efficiency. After column preparation, individual precious group metals will be added to a column at various
acid conditions and optimum pH and acid condition will be determined experimentally. The method for removal of extracted metal be developed using various strippents. Eluted metals ions will be determined spectrophotometrically in 10 ml fraction. After development of method for extraction and stripping metals, this method will be applied for separation of precious group metals from each other and separation of metals from commercial samples and also from their ores.

**Year wise plan of work and target to be achieved:**

**I Year:**
- To Procure Instruments, Glassware’s and Chemicals.
- Synthesis and Characterization of 2-octylaminopyridine.
- To Develop Extraction Separation Method for Platinum and Palladium.
- The method developed will be successfully apply for the analysis of platinum in the real samples, such as platinum–rhodium thermocouple wire, pharmaceutical sample cisplatin, and catalysts

**II Year:**
- To Develop Extraction Separation Method for Gold, Ruthenium and Rhodium.
- To achieve Mutual separations of these metals.
- To apply these methods for extraction separation of precious metals from real sample.
- Conditions have been identified for attaining some separations of gold, ruthenium and rhodium from other metal ions; these conditions are extended for the recovery of pure platinum and palladium from ore and alloys.

**III Year:**
- To Develop Extraction Separation Method for Osmium and Iridium.
- The method applied for the binary separation of platinum group metals from associated elements and was further extended to the analysis of a synthetic mixture
- Interpretation and tabulation of data with graphical and statistical method.
- Submission of work in the form of thesis.

**Reference:**