THE ANALYSIS OF PLATINUM METALS IN PLATINUM CATALYSTS BY THIN LAYER CHROMATOGRAPHY

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ABSTRACT

THE ANALYSIS OF PLATINUM METALS IN PLATINUM CATALYSTS BY THIN LAYER CHROMATOGRAPHY

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In this study, the matrices of fresh and spent catalysts were previously characterized by using x-ray diffraction spectrometry, x-ray fluorescence spectrometry and optic emission spectrography.

In the dissolution of platinum catalysts, aqua regia was generally used. However, the complete dissolution of TUGSAŞ Pt-sieve catalyst samples were achieved in two steps; aqua regia treatment and NaOH fusion. Alumina-supported rhenium catalyst standard was only dissolved by applying $Na_2B_4O_7$ or Na_2O_2 + Na_2CO_3 fusion.

TLC method as a novel one was investigated for the determination of platinum metals in catalyst and the obtained results were compared by FAAS method.

In Atomic Absorption Spectrometry, lanthanum chloride was used for the controlling of the interferences due to aluminum, platinum metals and rhenium. In the end of optimum conditions studies, 1500-5000mg/L buffer solution was added to both standards and sample solutions. The reproducibilities of the method as RSD % for Pt, Pd and Rh are 1.42, 1.58 and 1.99 respectively.

Initially, N,N-diethyl-N'-benzoylthiourea (DEBT) as chelating agent and metal chelates were synthesized in the TLC method. Their characterization were made by using XRD, DTA, IR and UV-vis. spectrometry and their chromatographic behaviours were investigated by thin layer chromatography.

Re(IV) chelate was synthesized because of the presence of rhenium in catalysts, but the analysis of rhenium by the investigated TLC method could not be accomplished.

Enrichment and separation of metal chelates from inorganic matrix were achieved in a single step by extraction of precipitated metal chelates to organic phase.

The elements found as contamination except copper

and iron did not cause any problem with platinum metals in highly acidic medium. By adding 3 M hot H_2SO_4, copper and iron chelates which precipitated at pH 0 - 4, were decomposed and the residual chelates of PGM were taken into organic phase by extracting with $CHCl_3$. Chloroform extracts of metal chelates were injected and were developed in HPTLC-silica gel plate with benzene. After the development of chromatogram, the spots were evaluated by in situ measurement method using dual-wavelength densitometry in zig zag scanning mode. The reproducibilities of Pt, Pd, Ru, Rh and Ir as RSD % are 2.4, 0.8, 1.2, 1.3 and 1.1 respectively.

When the results of Pt, Pd and Rh found in platinum catalysts obtained by two methods were compared, TLC was found to be an alternative method among the various spectrometric and electroanalytic methods used for trace metal determinations.

Keywords: Platinum Metals, Platinum, Palladium, Ruthenium, Rhodium, Irridium, Rhenium, Recovery, Thin Layer Chromatography, Atomic Absorption Spectrometry, Metal Chelates, Scanning Densitometry, Complexation, Retardation Factor.

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ÖZ

İNCE TABAKA KROMATOGRAFİSİ İLE PLATİN KATALİZÖRLERİNDEKİ PLATİN METALLERİNİN ANALİZİ

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Bu çalışmada, öncelikle çalışılacak taze ve kullanılmış katalizör örneklerinin matriksleri x-ışını kırınım spektrometresi, x-ışınları floresans spektrometresi ve optik emisyon spektrografı ile belirlenmiştir.

Platin katalizörlerinin çözünürleştirilmesinde genelde kral suyu kullanılmıştır. Ancak TUGSAŞ elek numuneleri iki aşamada; kral suyu işlemi ve NaOH eritişi ile. Alumina bazlı renyum katalizör standardı da yalnız $Na_2B_4O_7$ veya Na_2O_2 - Na_2CO_3 eritişleri ile çözünürleştirilebilmişlerdir.

Katalizörlerdeki platin metallerinin tayininde ince tabaka

kromatografisi yeni bir yöntem olarak geliştirilmiş ve karşılaştırma yöntemi olarak FAAS seçilmiştir.

Atomik absorpsiyon yönteminde, örneklerin çoğunda substrat olarak bulunan aluminyumun yanında, aynı ortamda birden fazla platin metalinin ve renyumun bulunmasıyla oluşacak girişimlerin azaltılması için lantanyum klorür tampon çözelti olarak kullanıldı ve optimum şartların taranması sonucu standardlara ve örnek çözeltilerine 1500 - 5000 mg/L tampon çözeltisi eklendi. Yöntemin tekrarlanabilirliği % BSS değerleri ile Pt, Pd ve Rh için sırasıyla 1.42, 1.58 ve 1.99 olarak elde edildi.

İnce tabaka kromatografisinde öncelikle şelat yapıcı N,N-dietil-N'-benzoiltiyoüre (DEBT) ve metal şelatları sentezlendi. Karakterizasyonları XRD, DTA, IR, UV-vis. spektrometrisi ve kromatografik davranışları ince tabaka kromatografisi ile yapıldı.

Örneklerde renyuma rastlandığı için Re(IV) şelatı sentezlendi ancak geliştirilen kromatografik yöntemle renyum tayini yapılamadı.

Metal şelatlarının çöktürülerek elde edilmesi ve daha sonra organik faza ekstraksiyonu ile, zenginleştirilmesi ve inorganik matriksten ayrılması tek bir basamakda sağlanabilmiştir.

Demir ve bakır hariç örneklerde bulunan diğer kirletici

elementler örneklerin çalışıldığı asidik ortamda problem yaratmamaktadır. Platin metalleri ile pH 0-4 aralığında çöken demir ve bakır şelatları 3M sıcak H_2SO_4 ilavesiyle ortamdan uzaklaştırımış. Geriye kalan platin metali şelatları kloro-form ile ekstre edilerek organik faza alınmışlar; HPTLC silika jel plakalarına damlatılan çözeltiler benzende yürütüldükten sonra, lekeler plaka üzerinden direkt olarak çift dalgaboylu, zig zag taramalı densitometri ile okunmuştur. Bu yöntemin tekrarlanabilirliği Pt, Pd, Ru, Rh ve Ir metalleri için sırasıyla 2.4, 0.8, 1.2, 1.3 ve 1.1 % BSS dir.

Katalizörlerde bulunan platin metallerinden Pt, Pd ve Rh elementlerinin her iki metodla elde edilen sonuçları karşılaştırıldığında ince tabaka kromatografisinin eser element tayinlerinde kullanılan çeşitli spektrometrik ve elektroanalitik yöntemlere karşı alternatif bir metod olabileceği gösterilmiştir.

Anahtar Kelimeler: Platin Metalleri, Platin, Paladyum, Rutenyum, Rodyum, İridyum, Renyum, Geri Kazanım, İnce Tabaka Kromatografisi, Atomik Absorpsiyon Spektrometrisi, Metal Şelatları, Taramalı Densitometri, Kompleksleşme, Geciktirme Faktörü.

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CHAPTER I

INTRODUCTION

1.1- Importance of Platinum Group Metals

The world's natural supplies of platinum group metals (PGM) are limited. They are derived from only three areas in the world, i.e. sulfide deposits in Canada, Russia and South Africa.

These sources have in common a low PGM grade (2 to 10 ppm), and in general a very close association between the PGM minerals and the base metal sulfide minerals.

The world consumption of PGM by industry has increased by a factor of 50 between 1930 and 1980. The vast increase in consumption has been matched by the growth of the secondary metal industry. Therefore, palladium and platinum with their associated metallic elements ruthenium, osmium, rhodium, iridium and rhenium used in products are recovered for recycling. The major uses of the metals today are as follows: electrical and electronic industry 40 %, chemical and

pharmaceutical (catalysts) 30 %, auto-exhaust catalyst 10 %, petrochemical industry 10%, fabricated ware (glass and porcelain decoration jewellery and dental alloys) 10% [1].

1.2- Types of Catalyst

Platinum group metal catalysts can have, as their main constituent, a single active metal, a doped metal or a combination of different metals. In most cases, PGM catalysts have a wider range of application than non-precious metal types (Ni, V, Mo, Zn etc.) and are less complicated to use [2]. The unsupported metals and metal alloys are used in a wide variety of forms for laboratory studies and industrial catalysis. These catalysts include single crystals, metal films, wire and foil, which form a group of clean surface catalysis, and colloidal metals, metal blacks and metal powders in which the surface is variously contaminated by the reaction products formed during manufacture. Catalysts are found in two different types.

Unsupported catalysts; for special catalytic reactions, the PGM and compounds are employed by themselves in particularly activated form, without the use of any supporting material. Platinum black, platinum dioxide, palladium black, rhodium(III)-oxide, platinum-rhodium gauzes, platinum-rhodium oxide are the examples of this type.

Supported catalysts consist of a precious metal in concentration from 0.1 to 10 % of substrates which can be more or less inert or supports possessing large surface area. The most common supports are active carbon (C) mostly in powder form with very large surface, aluminum oxide (Al_2O_3) mostly in moulding but also in powder form in various modifications such as α- and γ-phases, a particularly high pure support silica (SiO_2) in moulding or powder form and calcium carbonate ($CaCO_3$) in the form of powder with a relatively small specific surface area .

Some various supports such as aluminum silicates, barium sulfate, asbestos and fused quartz wool are also used[2].

Supported catalysts are usually found in the form of cylinders, spheres or granules with particle size of 0.079 - 0.635 cm. With bimetallic catalysts, the active components are dispersed together on the support material. The relationship between performance and support is extremely complex. Among the physical properties of a support that may influence performance are total surface area, specific surface area, average pore size, pore size distribution and particle size.

Supported platinum metal catalysts have a number of advantages over unsupported catalysts. They are used in vast, covering the refining and chemical industries as well as pollution control. The support permits greater efficiency in use of the metal

by increasing the active metal surface and by facilitating metal recovery [3].

Unsupported metal is used less efficiently than supported metal and recovery losses are likely to be higher.

The dissolution of alumina supported catalysts depends upon various forms of alumina that it contains. The amount of acid-insoluble α-alumina is usually small in fresh reforming catalyst. Spent reforming catalysts that are usually recycled because of their platinum content, may be contaminated with a variety of metallic impurities and carbon. In addition, because of high-temperature applications of some of these catalysts, part of the acid-soluble γ-alumina may be converted into α-alumina [4].

1.3- Methods Used in the Determination of PGM and Re from Catalysts

The six elements (Pt, Pd, Rh, Ru, Os, and Ir) in the platinum group metals and rhenium are all hydrogenation catalysts. Palladium and platinum catalysts have been widely used for decades. Rhodium and ruthenium are also excellent hydrogenation catalysts, but their merits are not so widely appreciated yet. Iridium and osmium have found still less use. Osmium hydrogenation catalysts do not appear to have exceptional merit. Iridium, on the other hand, makes a fair

catalyst and its lack of use stems partly from neglect and partly from the fact that some platinum metal has usually proved more suitable whenever a comparison was made. Metallic rhenium is only a weak catalyst in hydrogenation reactions [3].

Platinum group metals and rhenium are also used as effective industrial catalysts. The following Table 1.1 shows the major industrial applications for catalysts in USA during 1978 [1].

Table 1.1. Major Applications of Catalysis in USA During 1978

APPLICATION	CATALYSTS	PRODUCTION CAPACITY $x10^6$ t	CATALYST VALUE $x10^6$ $
Petroleum Refining	Pt, Pd, Ir, Si, Al, Re, Cr, Mo, W, Ni	434	364
Fertilisers	Pt, Pd, Rh, Fe, Ni, Cr, Zn	27	44
Bulk Chemicals	Pd, Rh, V, Bi, Mo, Ag, Cu, Ni, Fe, Co	65	43
Plastic	Cr, Fe, Al, Ti, Sn	18	116
Fine Chemicals	Pt, Pd, Rh, Ru, Ni, Cu	-	90
Fats and Oils	Ni, Cu	28	24
Pollution Control	Pt, Pd, Rh	-	230

Platinum-bearing catalysts have the ability to reform or rearrange the molecular structure of hydrocarbons in the petroleum industry. Later, platinum and platinum-palladium-bearing catalysts were used in the form of catalytic converters in automobiles from 1975 models onward, to achieve satisfactory control of exhaust emission [4].

Reforming catalysts (~ 0.3 or ~ 0.6 % Pt) and the emission-control catalysts (0.03 - 0.11% Pt) contain the platinum as a deposit on a substrate consisting mainly of γ-alumina, or, in the case of octafining catalysts, of γ-alumina plus silica. Rhenium (~ 0.3 or ~ 0.6% Re) is frequently present in reforming catalysts and palladium (0.015 - 0.04% Pd) in emission-control catalysts.

The high price of platinum metals requires that the metal or compound be utilized to the full extent and that it is completely recovered after use. The petroleum industry regenerates catalytic activity by the controlled oxidation of the carbonaceous deposits on the catalyst [1].

The aim of regeneration and recovery is to recycle the active platinum catalyst metal centres. The catalyst is not chemically attacked by the reactants. The catalyst particles can be separated from the product by filtration or centrifugation or without separation, the catalyst activity can be regenerated in situation [1].

In order to recycle the active platinum catalysts, the first step is to determine the platinum content of the catalyst. For the recovery the literature on determining platinum metals and rhenium in catalysts is not extensive. X-ray fluorescence approach was described by Lincoln and Davis for reforming catalysts [5]. Conrad and Evans [6] suggested the distillation of the platinum as the chloride, followed by the spectrophotometric procedure using p-nitroso-dimethyl-aniline. Dissolution of the catalyst in hydrochloric acid, followed by a spectrophotometric stannous chloride, was used by Maziekin et al. [7]. A gravimetric method based on the precipitation of platinum with dimethylphenyl-ammonium bromide was suggested by Kuebler [8]. A method of determining platinum in catalysts, based on the interaction of platinum with nitrite, was suggested by Fishel and Simion [9]. Spectrophotometric analysis of palladium on the catalyst based on active carbon, silica gel, asbestos and kieselguhr with palladiazo, chelating agent, was suggested by Sierra et al. [10]. Dissolution of Rhodium on either carbon or Al_2O_3 catalyst supports in hot mineral acids, followed by colorimetric method ($SnCl_2$), was suggested by Friedrich et al. [11]. For measurement of platinum and rhenium dispersion on supported and unsupported catalysts, chemisorption of hydrogen was used in 1973 [12]. For the determination of rhenium in the presence of platinum in bimetallic catalysts, spectrophotometric method with α-furil dioxime reagent was suggested by Wiele et al. [13]. A polarographic method was used to determine Rhenium in low percentage Al-Re catalysts by Rubinskaya et al. [14] in 1975.

Differential spectrophotometry in conjunction with stannous chloride method in reforming and emission-control catalysts was suggested by Kallman [4] in 1976. The palladium metal in fresh or spent petroleum hydrocracking catalysts was determined by coulometric reduction of the palladium (IV) azide complex to the palladium(II)azide complex at a platinum gauze electrode in phosphate media [15]. Marsh and Butler [16] determined the platinum and ruthenium on an alumina supported catalysts in the presence of barium by instrumental neutron activation analysis. Dissolution of a catalyst and separation of the noble metals from the substrate material platinum and palladium were measured using atomic absorption spectrophotometry by Potter [17].

Conventional and portable XRF equipment was suggested to analyze ruthenium in catalytic surfaces by Bramstedt [18]. Total Rh (heat-treated rhodium oxide and all other forms of Rh) on alumina supported catalysts was determined by AAS, following sodium peroxide fusion by Bramstedt et al. [19]. Rhodium in Pt-Rh loaded automotive catalyst was determined by GFAAS following dissolution in sulfuric and hydrochloric acids by Potter [20]. Dissolution of aluminum-platinum catalyst in HCl + HNO_3 + H_2SO_4, followed by flame AAS was suggested by Rozanska et al. [21]. Palladium in phenol hydrogenation catalysts was determined by flame AAS using standard addition by Talalaev [22]. In the analysis of the worked-out catalyst, ruthenium was extracted by chlorination and was determined with thiourea photometrically in the chloride distillate by Grinberg et al. [23]. Direct-current

plasma emission spectrometric analysis was used to characterize the effect of alumina-magnesium matrix at the platinum group metals in solutions from automobile catalyst by Fox [24]. An atomic absorption method of determining Pd in benzoic acid hydrogenation catalyst used in producing caprolactam was developed by Igoshina et al. [25]. Platinum and rhodium in catalysts were determined by inductively coupled plasma atomic emission spectrometry, following sodium peroxide fusion and HCl dissolution by Motonori [26]. For the determination of rhenium in the presence of various catalyst elements, polarography was used after dissolution in NaOH by Kim and Shiryaeva [27]. The determination of platinum, palladium and rhodium in silica-alumina based catalyst by acid pressure decomposition/ICP-AES, eliminating aluminum interference by precipitation of Pt, Pd and Rh with 2-mercapto benzathiazole was investigated by Motonori [28]. A procedure has been developed for the sorption-voltametric determination of rhenium in products of the processing of spent Al-Pt-Re catalysts by Kim et al. [29]. Rhenium and platinum in used catalysts have been determined by electromigration-spectrophotometry after dissolution of the corresponding membrane segments in concentrated HCl by Bochkova et al. [30]. As it is seen on Table 1.2, various spectrophotometric and electroanalytic techniques have been used in the determination of PGMs and rhenium; but, the investigation about the chromatographic analysis of these metals had not been encountered in the literature from 1970 to nowadays.

Table 1.2. Methods Used in the Determination of PGMs

ELEMENT	DETECTION LIMIT (µg/mL)	PRECISION (% RSD)	WORKING RANGE	METHOD	REF.
Pt		0.4	10 - 100 µg	UV-vis. Spect. FAAS Differential spect.	9 21 4
Pd	0.045 0.02	0.21 - 0.33 0.036 0.013		UV-Vis. Spect. Coulometry FAAS FAAS	10 15 22 25
Re		±5 0.03 0.2	2E-5 - 2E-4 M	Chemisorption UV-vis. Spect. Polarography Polarography Sorption-voltametry	12 13 14 27 29
Rh		0.08 1.5 4		Cobrimetry FAAS GFAAS	11 19 20
Ru		5.7	0.5-2.5 M	XRF Photometry	18 23
Re, Pt				Electromigration spect.	30
Pt, Pd		~ 1%		AAS	17
Rh, Pt		0.3 - 0.9 Pt 0.01 - 3 Rh		ICP - AES	26
Pt, Pd, Rh		0.2 - 0.7		ICP-AES DC-plasma ES	28 24
Ba, Ru, Pt		3.7 %Ba 1.9 %Pt 1.9 %Ru		NAA	16

1.4- Thin Layer Chromatography and Densitometry

Thin layer chromatography (TLC) is a mode of liquid chromatography in which the sample is applied as a small spot or streak to the origin of a thin sorbent layer supported on a glass, plastic or metal plate. The mobile phase moves through the stationary phase by capillary action or by gravity or pressure. TLC separations take place in the " open " layer with each component having the same total migration time but different migration distances. The mobile phase in TLC consists of a single solvent or a mixture of organic and / or aqueous solvents. Numerous fixed sorbents have been used, including silica gel, cellulose, alumina, polyamides, ion exchangers and chemically bonded silica gel [31]. Positions of separated zones on thin-layer chromatograms are described by the R_f value of each substance, where

$$R_f = \frac{\text{Distance travelled by the spot center of solute 'a'}}{\text{Distance travelled by solvent front}}$$

R_f values range from 0.0 for a zone not leaving the point of application to 1.0 for zones migrating at the solvent front. When R_f data are tabulated, it is more convenient to report $R_f \times 100$ or hR_f values.

Thin layer chromatography is a relatively new discipline and most chromatography historians date the advent of modern TLC from 1958. TLC has been regarded traditionally as a simple, rapid and inexpensive method for the separation, tentative identification and visual semi quantification of wide variety of substances. Despite the widespread use of TLC worldwide over the past 30 years, the technique usually has not been considered to be highly efficient or quantitative. But modern high-performance or high-efficiency TLC rivals high performance liquid chromatography (HPLC) and gas chromatography (GC) in its ability to resolve complex mixtures and to provide analyte quantification. High performance thin layer chromatography (HPTLC) has come about as a result of improvements in the quality of sorbents and consistency of plate manufacture use of optimized techniques and equipment for sample application, plate development, detection reagent application and densitometric scanning [32].

Quantitative determinations of different classes of substances on thin-layer plates by optical scanning (Densitometry) have been carried out for about 30 years. During the past 20 years, chromatogram photometers for reflectance, transmission and fluorescence measurements have been commercially available. There are highly sophisticated instruments for avoiding errors due to the irregularities of the sorbents, solvent and the chromatographic process itself, which operate in a single-beam, double-beam or single-beam-dual wavelength.

Quantitative in situation TLC is a very flexible analytical method and the separations of different compounds from each other and from the interfering matrix are effected in a single procedure directly followed by the quantitation [33].

The purpose of a scanner is to convert the spots on a layer into a chromatogram consisting of a series of peaks similar in appearance to a gas or high performance liquid chromatogram. The positions of the scanner peaks on the recorder chart are related to the migration distance of the spots on the layer and the peak heights or areas are related to the concentrations of the substances in the spots. The signal that is measured represents the absorption of transmitted or reflected light that passes through the spot. In addition to absorption (or fluorescence) by the solute, light is diffusely scattered by the layer particles, leading to differences in the theory of densitometry and solution spectrometry [31].

Detection limits with commercial scanners and high performance plates are typically low nanogram levels for compounds that absorb visible or UV light strongly and low picogram amounts for compounds that fluoresce strongly [31]. The relationship between the signal value and the concentration of a compound is linear only at very low concentration, but for high concentrations, Kubelka-Munk equation (Equation 1.1) is used because of diffusion of light by the particles in the layer. The

Kubelka-Munk theory assumes that the transmitted and reflected components of the incident light are made up only of rays propagating inside the sorbent in a direction perpendicular to the plane of the plate surface. All other directions lead to much longer pathways and, therefore, much stronger absorption. Consequently, they contribute only negligibly to the total amount of transmitted or reflected light. The restriction to propagation in only the forward and reverse direction does not apply to light exiting the medium, and at the plate/air boundary, light is distributed over all possible angles with the surface. By assuming that the scatter coefficient of the sorbent is unchanged by the presence of the sample, equation 1.1 can be derived [31, 34].

$$\frac{(1-R)^2}{2R} = \varepsilon \frac{c}{S} \qquad (1.1)$$

R= light reflected from the plate surface

ε= sample absorption coefficient

c= Spot concentration

S= Plate scatter coefficient

Linearity may be enhanced by plotting log area versus log concentration rather than area versus concentration or using

an internal standard with properties similar to the analyte and plotting the peak area ratio versus concentration [35].

To carry out a densitometric analysis, several standards and adequately purified samples are applied to the same plate, development and detection are carried out and the spots are scanned.

Thin layer chromatography has found wide spread use in clinical laboratories, in drug industry and many biochemical and biological studies. Nowadays, it also finds widespread use in the industrial laboratories and in the analytical chemistry for quantitative trace metal analyses by densitometry despite the ability of a great number of established methods such as atomic absorption spectrometry, plasma emission spectrometry, x-ray fluorescence spectrometry, polarography and voltammetry.

1.5- Thin Layer Chromatography of Metal Chelates

In quantitative trace metal analysis, the analytical signal is affected from interferences because of matrix effects or contaminant elements in direct methods.

Both separation and enrichment can be possible in a single operation step simultaneously, by liquid-liquid extraction

for trace metal analyses. After complexation of metal ions in aqueous solution with organic reagents and separation from interfering inorganic matrix by extraction under enrichment into nonpolar organic solvents, they can be monitored by spectrophotometric or fluorometric measurements. All analytical operations lead to the chromatography of metal chelates as a powerful analytical method for trace metal determination (Figure 1.1) [36].

Generally, the following advantages can be utilized in the chromatography of metal chelates for trace metal analysis:

1. Relatively simple sample preparation (complex-formation at appropriate pH-value),

2. Elements to be determined can be enriched before determination by extraction of their complexes,

3. Interfering inorganic matrix remain in aqueous phase during extraction,

4. Because of chromatographic separation, several elements can be identified and determined quantitatively in a single analytical step (multi-element analysis),

5. Sensitive detection of the metal chelates using UV-

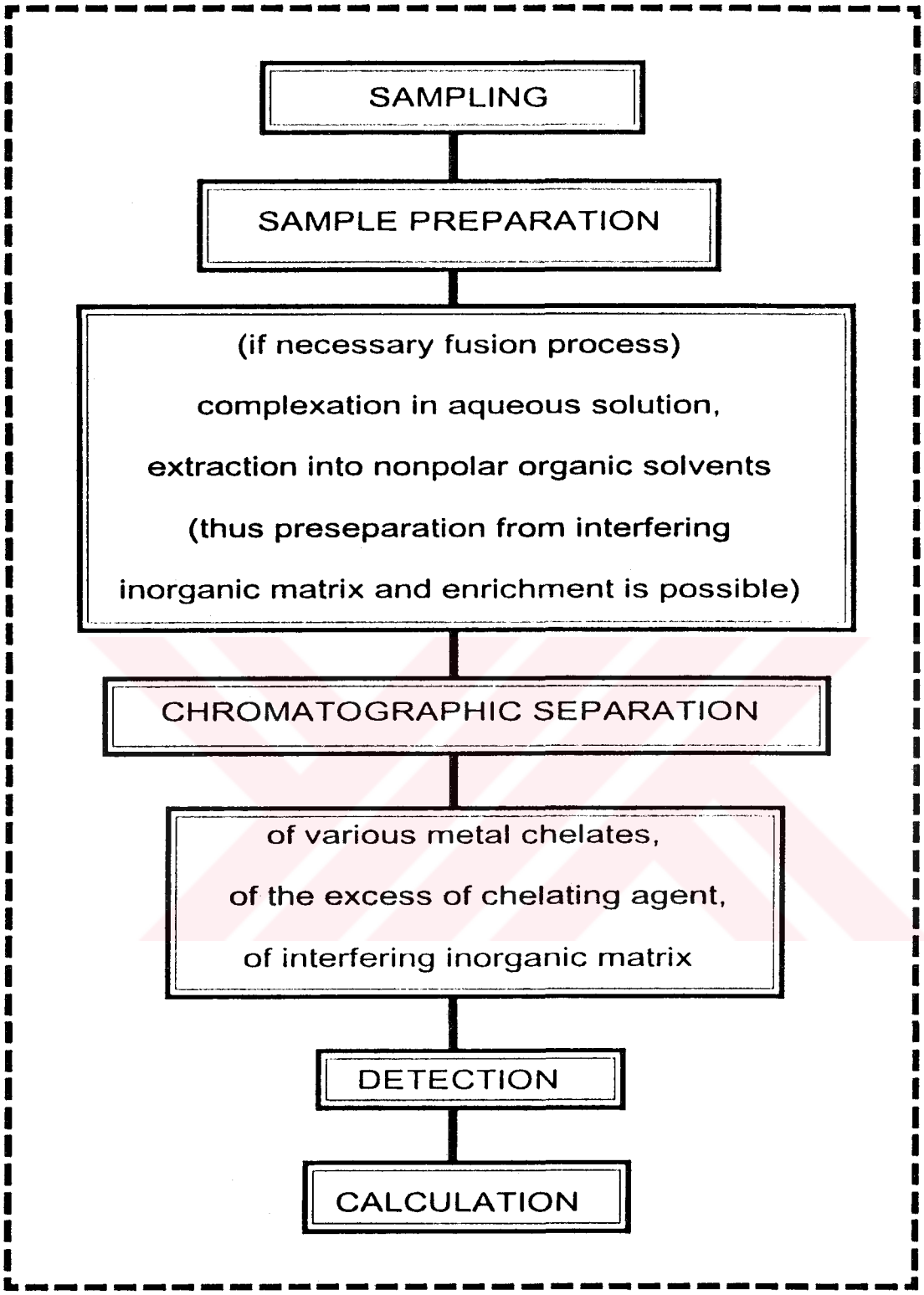


Figure 1.1. Trace Metal Analysis by the Chromatogphy of Metal Chelates

photometry (high extinction coefficient of the chelates) is possible,

6. Short analysis time, simple and rapid procedure.

Therefore, chromatography of metal chelates is a highly efficient analytical technique and it is able to replace other well known analytical methods of trace metal determination.

For separation of metal chelates, generally the same chromatographic techniques like liquid chromatography (LC), gas chromatography (GC) are used as for the analysis of organic substances. Adsorption chromatography is the most important one of the various liquid chromatographic separation techniques. Especially for chromatography of metal chelates, silica gel and alumina have been used more successfully as stationary phases in TLC because of their good separation qualities.

Unfortunately not all elements can be used without problems in chromatography. Certain difficulties like decomposition of the chelates before or during elution, may appear as well as incomplete separation of the various complexes or strong tailing in chromatograms may appear. These difficulties often reduce the good qualification of chromatography of metal chelates for trace metal analysis. Therefore, only certain complexing agents which form chelates that can be separated chromatographically and determined analytically, can be used successfully [36].

Relation Between Complex Chemical Properties and Chromatography of Metal Chelates:

The well known complexing agents in analytical chemistry for photometric, gravimetric and volumetric determinations, in spite of their wide range of application, do not form metal chelates which can be chromatographed successfully. Several reasons are responsible for that;

1. Lack of solubility of the formed chelates in nonpolar solvents,

-thus it is not possible to enrich the metal ions from aqueous solution by extraction,

-thus only limited fractions of the chelates carried out in adsorption chromatography on silica gel phases,

2. Lack of stability of the chelates during contact with the stationary phase,

3. Decomposition of the chelates during elution,

4. Strong tailing, because of reaching equilibrium between adsorption and desorption of the chelates on the stationary phase slowly,

5. In spite of successful chromatographic behaviour for individual analytes, not enough differences in chromatographic retention for the mixture.

A close relationship exists between the chromatographic behaviour and the complex chemical properties of the metal chelates because these are responsible for type and intensity of interaction with stationary and mobile phases. The active site of silica gel is the end positioned with silanol groups (-SiOH) [37]. They form a weak linkage with each neighbouring molecule with one of the following interactions;

1. dipole - dipole,

2. dipole - induced dipole,

3. π - complex - linkage to double bondings of the metal chelate,

4. hydrogen bonding between the silanol group (as proton donor) and the functional groups of the ligand with a free electron pair (as a proton acceptor),

5. polar electron donor bonding of the silanol anion ($-SiO^-$) with the central atom of the complex.

The interaction between adsorption of the chelate onto the surface of the stationary phase depends on the properties of the chelates. These are dipole moment, basicity of the coordination sites, metal-specific properties of the central atom like its affinity to oxygen or sulphur, coordination number, steric structure of the chelate including additional ligands like water, solvent molecules or oxygen.

The power of interaction between the mobile phase and the stationary phase is very important for retention of complexes, because mobile phase and analyte compete for the active sites of the stationary phase.

Elements coordinated to ligands with oxygen as coordination site (oxygen affinic elements) can be chromatographed less successfully than those with sulphur on polar stationary phases [36].

Moreover, most of these complexes are less soluble in aqueous as well as in nonpolar organic solvents.

Tailing can be reduced by addition of strongly polar substances (H_2O, acids) or complexing agents to the mobile phase. This can be solved by ligand-derivatisation, but substitution is restricted, because too big substitutents would level out chromatographic retention, or decrease the solubility in organic solvents by gravimetric effects.

Therefore, low polarity of the metal-ligand bonding is a prerequisite for successful application of a chelate to adsorption chromatography. If the linkage is too polar, tailing or decomposition of the complex appear, or no elution of the substance takes place. The chromatographic behaviour can be improved by substitution of oxygen with sulphur as coordination site. The metal-sulphur bonding is more covalent, thus the enthalpy of adsorption of the complexes decreases on the stationary phases [36].

Numerous complexing agents with N-, S-; S-, S-; or S-, O- coordination sites are suitable for chromatography of metal chelates [38 - 61].

Metal chelates must have the following conditions and prerequisites;

1- Formation of stable neutral metal chelates,

2- Control of complex formation by pH-variation or by masking reagents,

3- Formation of well defined chelates with clear stoichiometry,

4- Five-membered chelate-rings between metal and

ligand possess the highest stability. But four- and six-membered chelate-rings reduce stability,

5- Chelating agents with N-, O-, S- or Se- atoms as coordination sites has good chemical properties for complex formation. In addition these ligands are stable under normal circumstances for analytical applications,

6- The metal chelates should have high solubility in the mobile phase,

7- The ligand must not be too large,

8- The chelating conjugated-π-system should cover the complete ligand for sensitive photometric detection (high extinction coefficients).

The most investigated chelating agents in chromatography are the dithiocarbamates, dithiozonates, β-diketones (thioketone), oxinates, thiooxinates and thionates. These are summarized in Table 1.3. with the references. They all show more or less excellent chromatographic properties. The chromatographic separation of important heavy-and noble-metals succeed as well as the separation of toxic metals with these ligands.

According to their structure the N,N-disubstituted acylthioureas are used successfully as ligands for the chromatography of their metal chelates [61]. They have a great similarity with monothio-β-diketonates with respect to their complex chemistry. They form stable, crystalline chelates with numerous metal ions, which are coordinated to both chalkogen atoms (S and O) so that chelate-6-rings result.

For the TLC-separations of the chelates the N-pyrolidino-; N,N-diethyl; N,N-dimethyl- and N,N-di-n-propyl-N'-benzoylthioureas are the best qualified ligands. The great advantage of these chelating agents in comparison to other sulphur containing ligands are their unusual stability against oxidation. Solutions of dialkyl-benzoylthioureas are totally stable under normal conditions and therefore can be handled without difficulties. Besides, the dialkyl-benzoylthioureas are excellent reagents for pH-selective precipitation and extraction and therefore are qualified for liquid-liquid extraction of metal ions. Within these N,N-diethyl-N'-benzoylthiourea (DEBT) is one of the widely used chelating agent [61]. So it is possible to separate the platinum metals from such important interfering metals like Cu, Fe or Ni by liquid-liquid extraction forming their metal chelates and moreover, to separate individual platinum metals and to carry out their fine purification. By extraction high enrichment-factors are possible.

Table 1.3. Investigated Chelating Agents in TLC

CHELATING AGENTS	INVESTIGATED ELEMENTS	DL	REMARKS	REF
DITHIOZONE	Pd, Pt, Ag, Au Mn, Cu, Ni, Co, Zn, Cd, Hg, Pb Co, Ni, Cu, Hg Co, Ni, Zn, Hg	0.5 ng	Separation and Identification Toxicological analysis Separation Zn, Co in soaps and in vitamin B12, Hg in human urine	38 39 -40 41 42
DITHIOCARBAMATES	Cu, Cd, Hg, Pb, Bi, V, Cr, Mn, Fe, Co, Ni, Pd, Ag, Zn Cd, Hg, In, Tl, Sn, Pb, As, Sb, Bi, Te Co, Ni, Cu, Zn, As Cu		Separation Separation Separation Separation	43 44 -45 46 47
OXINE	Mg, Ca, Cr, Mn, Fe, Co, Ni, Pd, Zn, Al, Pb, Bi		Separation	48
THIOOXINE	Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Zn, Hg, Sn, Pb	5 - 20 ng	Separation	49 -50
THIOOXINE DERIVATIVES	Tl, Sn, Pb, As, Sb, Bi, Te		Control of R_f Values	51 -52
1-HYDROXY -2- PYRIDINE THIONE (HPT)	Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt Rh, Pd, Ir, Pt	0.1 - 1 ng	Separation Separation of 7 elements in a single run	53 54

Table 1.3. Investigated Chelating Agents in TLC (Continued)

CHELATING AGENTS	INVESTIGATED ELEMENTS	DL	REMARKS	REF
HPT DERIVATIVES	Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Zn, Hg, Tl, Bi, Te		Separation	55
β-DIKETONES	Ca, Be, Cr, Mn, Fe, Co, Ni, Cu, Zn Cr, Fe, Co		Separation (binary and ternary solvent mixture) separation	56 57
MONOTHIO-β-DIKETONES	Co, Ni, Rh, Pd, Cu Co, Ni, Cu, Zn, Hg, Pb, Cd	10 ng Co, 50 ng Ni, Cu, Rh Pd	Trace Co in presence of Cu, Ni Det. of Rh and Pd traces Separation	58 59
β-DITHIOKETONES	Mn, Co, Ni, Zn, Rh, Pd, Pt		Separation	60
N,N-DIALKYL-N'-BENZOLY THIOUREAS	Co, Ru, Rh, Pd, Os, Ir, Pt, Cu, Hg	0.5 ng Pd 2ng Pt, Cu		61
PYRIDINE-2-ALDEHYDE-QUINOLYHYDROZONE	Ni	34-195 ng Ni	Separation	62
1-2-PYRIDYLAZO -2-NAPHTHOL	Fe, Co, Ni, Cu		Separation	63
1-2 -DIKETO-BIS-THIOBENZHYDRAZONES	Zn, Cd, Hg, Pb		Separation	64
TETRAKIS (P-TOLYL) PORPHIN	Mg, V, Ni, Pd, Cu, Zn		Separation	65 - 66

Silica gel is the best qualified phase for these chelates. Thereby resolution depends on the humidity of the silica gel material. The chelates of the platinum metals, Co(II), Cu(II) and Hg(II) show excellent chromatographic properties. As mobile phases pure solvents like benzene, toluene and chloroform are used.

1.6. Objective of the Present Work

The platinum group metals supplies are very limited and their consumption in the world by many industries have been increased very much. Therefore, the recovery and recycling of these metals become very important. In this respect, precise determination of platinum group metals in different matrices requires dependable methods.

Determination of platinum group metals in catalyst matrices whether fresh or used were carried out by different spectrophotometric and electroanalytic methods such as AAS, XRF, NAA, polarography in literature. In most of these methods, the controlling of interference of aluminum and noble metals was required for obtaining precise results. Therefore, one of the objectives of this study was to improve the TLC method which was not used before in this field, and to compare the results with that obtained by AAS that is a conventional method for trace metal analysis.

As catalyst samples both fresh and used, alumina and active carbon supported and also platinum sieve (unsupported) types are chosen. The control of the interfering effect of aluminum and contamination elements and determination of PGMs are carried out using scanning densitometer in TLC method.

It is also aimed to carry out the complexation of metal ions with organic reagents in aqueous solution and separation of metal chelates from the interfering inorganic matrix by extraction into nonpolar organic solvents. So that enrichment by the extraction will result better sensitivity in TLC determinations.

In this respect, in the petrochemical industries and refineries, the TLC method will be proposed for the control of PGMs content of the catalysts that gradually exhausts during the process. In order to support this proposition the reproducibility, sensitivity and applicability of TLC will be compared with AAS and accuracy of the method will be given with the analysis results of calibration standards.

CHAPTER II

EXPERIMENTAL METHODS AND MATERIALS

2.1- Synthesis of Chelating Agent and Metal Chelates

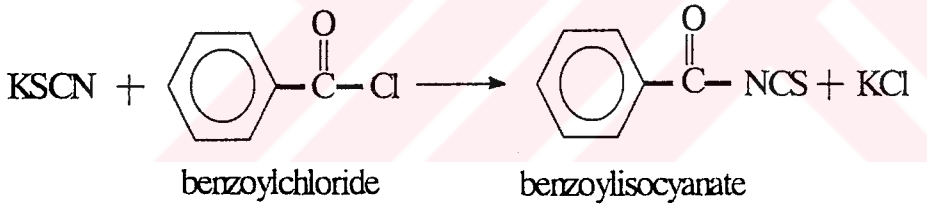
The synthesis of N,N-Diethyl-N'-Benzoylthiourea (DEBT) as chelating agent and metal chelates which have been used in the separation and determination of platinum metals and also contamination elements found in catalyst matrices were performed by following the procedure given in literature [67] with some modifications.

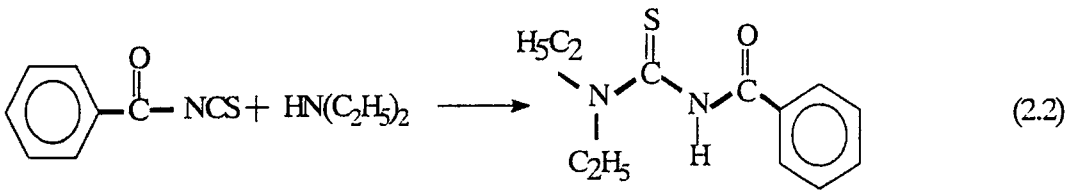
In the formation of metal chelates, two different methods are followed: extraction of chelate precipitate from solid phase formed in aqueous solution and extraction of metal ion in the form of metal chelate, directly to organic phase containing chelating agent. These two methods have been described below.

2.1.1- Synthesis of DEBT

0.1 mol of potassium thiocyanate (Merck) was dissolved

in 100 mL anhydrous acetone (Merck, blue band) by stirring and heating in a reflux condenser. 0.1 mol (approx. 11.6 mL) of benzoyl chloride (Merck) was added drop by drop to the mixture after heating was stopped. The reaction mixture was stirred about 30 min. at room temperature. Then the precipitate of potassium chloride was removed by filtration and the orange coloured filtrate was reacted with 0.1 mol (approx. 10.5 mL) of diethylamine (Merck). The reaction mixture was crystallized in 1 M HCl solution which was cooled with ice. Then the supernatant solution was removed by filtration and the residue was recrystallized with ethanol (99%, absolute) [67]. Synthesis of DEBT in two steps is shown with chemical equations 2.1 and 2.2.



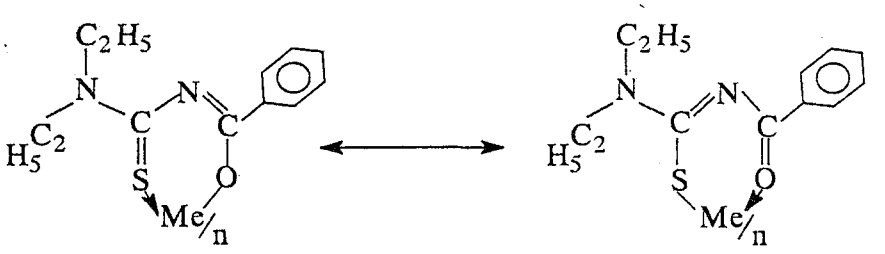


2.1.2- Precipitation and Extraction of Metal Chelates From Solid Phase

Metal ion solutions of Pt(II), Pd(II), Ru(III), Rh(III), and Ir(III) were prepared from K_2PtCl_4 (47 % Pt, Sigma), $RhCl_3.3H_20$ (38% Rh, Merck), $PdCl_2$ (60 % Pd, Merck), $RuCl_3.H_2O$ (38 % Ru, Sigma), and $IrCl_3.3/2\ H_2O$ (65 % Ir, Sigma) in 1 M HCl. Fe(III) and Cu(II) were prepared from $FeCl_3.6H_2O$(Merck) and $CuCl_2.2H_2O$ (Merck) in distilled water. Re(IV) solution was made from rhenium heptaoxide (76.9 % Re, Aldrich Company) reducing by 0.1 M $SnCl_2$ in 1 M HCl [68, 69, 70].

A 0.1 M DEBT solution, which was insoluble in water ,was prepared in ethyl alcohol and was added to the 0.01 M aqueous metal solution in stoichiometric ratio (ligand slightly in excess) by stirring vigorously at the suitable pH values (Please see Table 3.3) [67, 71]. Formation of metal chelates can be expressed in general with the following equation 2.3. Also, open formula of metal chelates are given below (eq. 2.4). In addition, molecular structure of metal chelates as square planar and as octahedral are given in Appendix A.

$$M^{n+} + nHL \longrightarrow ML_n + nH^+ \qquad (2.3.)$$



(2.4.)

The ratio of metal ion solution to ligand solution, in volume, was 4:1. This results in a solution where metal ion concentration is 0.008 M and ligand concentration is 0.020 M. For a ML_2 type complex, this molar ratio is in excess for ligand. Ru, Rh, Ir and Pt metal complexes were heated for complete precipitation. Temperatures varying from 40 °C to 90 °C (Please see Table 3.3), were attained for the precipitation of these chelates. Heating was not required for the formation of Pd and Re chelates.

The extraction recovery was tested by analysing the aqueous layer for metal ions with AAS. The completeness of precipitation of metal chelates in aqueous solution was shown by checking the solubility of chelates in water [72].

For the characterization of chromatographic and the absorption properties on silica gel plates, the precipitated chelates were extracted into chloroform. The aqueous part which contained the precipitate, varied in volume from 1 to 5 mL. This part was extracted in a 20 mL test tube, using $CHCl_3$ exactly in the same volume as the aqueous part; so that after a successful extraction

using a vortex mixer for 5 minutes, the anaylte concentration in the organic phase was same as the original aqueous phase. A portion of the organic layer was removed using a dropper with a long and fine end. Then, the organic layer was dried over anhydrous Na_2SO_4 before further use. Chloroform used for extraction was presaturated with water, and no measurable change was obtained in its volume.

In the other part of study, the precipitated metal complexes were filtered and were recrystallized two times by ethanol. Crystals were dried with P_2O_5 in vacuum desiccator. Further analysis with XRD, DTA and IR were carried out by using this precipitate.

2.1.3- Solvent Extraction of Metal Chelates From Liquid Phase

In literature, the extraction of metal ion into an organic solvent in which ligand is dissolved is a common way to enrich the metal ion [73]. So it seemed that preparing metal chelate samples in this way for chromatographic analysis was a practical procedure.

500 mg/L metal ion in 1 - 4 mole / L HCl solutions were reacted with ligand solution in toluene in different molar ratios (metal/ligand) between 1/4 and 1/24 (Please see Appendix B), at

various temperatures (up to 80°C) in the constant temperature water bath by stirring vigorously. The constant temperature water bath used in this study shown in Figure 2.1 was designed by us and constructed in 1009 Ordudonatım Ana Tamir fabrikası, Kayseri. The duration of reaction was also optimized by following the product yields.

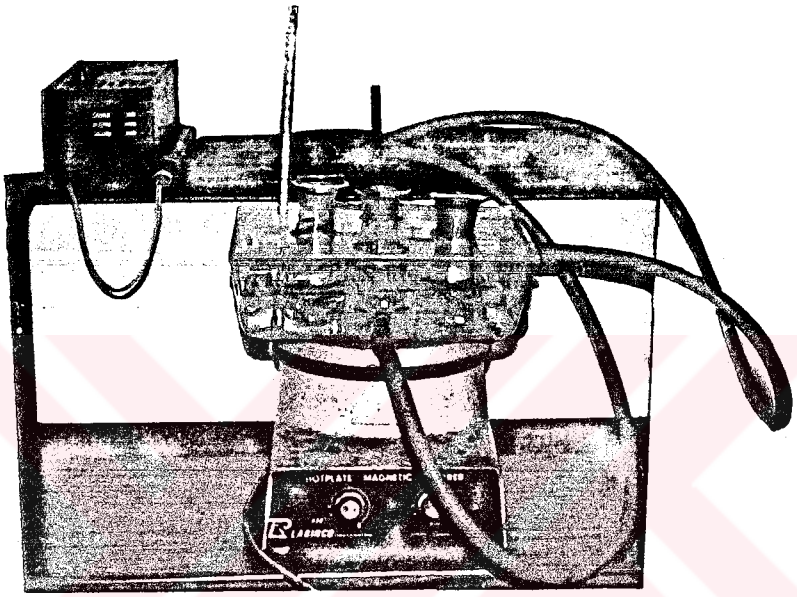


Figure 2.1. The Constant Temperature Water Bath

In order to check the completeness of metal chelate formation in organic phase, the aqueous solutions were analysed for their metal ion content. For this, the same volume of samples were taken from both aqueous phase and from organic phase to keep the mole ratio constant at certain time intervals during the reaction and the determination of all metals except Ir in aqueous solution were done by AAS. During the analysis with the available hollow cathode lamps, two different atomic absorption

spectrophotometers were used. Because of the unfitting socket of hollow cathode lamps, Hitachi Model Z-8000 AAS for the determination of Pt and Pd and Perkin Elmer 403 Model AAS for the determination of Ru and Rh were used. Determinations of Ir was done by Hitachi Model 150-20 UV-visible spectrophotometer due to the lack of its hollow cathode lamp for AAS. The analysis conditions for each elements are given in Table 2.1 [74].

Table 2.1. Instrumental Conditions for the Analysis of Metal Ions Remained in Aqueous Solutions

METAL	LIGHT SOURCE	CURRENT (mA)	λ (nm)	SLIT (nm) WIDTH	ATOMIZER
Pt	HCL	12.5	265.9	0.4	Air - Acetylene
Pd	HCL	10	247.6	0.4	Air - Acetylene Graphite tube
Ru	HCL	10	349.9	0.2	Air - Acetylene
Rh	HCL	5	343.5	0.2	Air - Acetylene
Ir (UV-vis)		-	441.2	-	

HCL: Hollow Cathode Lamp

2.2- Dissolution of Metal Chelates in Water and in Some Organic Solvents

To control the quantitative precipitation of the analytes, solubilities of the metal chelates were determined in the following way.

Approximately 5 mg of each of metal chelates (Pt, Pd, Ru, Rh, Ir and Re) were added to 25 mL of hot water which was heated in reflux condenser; the mixture was cooled to 25^{0}C and stirred for 30 minutes at this temperature. Then the mixture was filtered by a gooch crucible and the residue was weighed after drying at 110^{0}C.

The dissolution of metal chelates in various organic solvents was determined comparing the areas obtained using densitometer. One mg of metal chelate was added to one mL of the organic solvent. One µL of each solution was applied to silica gel plate and was developed in benzene.

2.3- Characterization of Metal Chelates

To verify the stoichiometry and to determine chemical properties of the synthesized chelating agent and metal chelates, UV-visible absorption, XRD, DTA, IR and chromatographic analysis have been performed.

2.3.1- Structural Characterizations

Structural characterization of ligand and metal chelates have been conducted by the following techniques:

a) Infrared Analysis (IR):

A Nicolet 510 FT-IR spectrometer, in Chemistry Department (METU), in the 4000-400 cm^{-1} range for group and finger print region frequencies was used for structural characterization of ligand and metal chelates. 1 mg of finely ground sample was intimately mixed with about 150 mg of dried potassium bromide powder by using an agate mortar. The mixture was then pressed in a special die at 700 - 800 kgf/cm^2. The pellet was investigated by FT-IR.

b) X-Ray Diffraction Analysis (XRD):

For the characterization of crystalline solid metal chelates in any mixture, x-ray diffraction powder patterns were obtained. X-ray diffraction patterns of randomly oriented powder samples (alone and mixed with starch) were recorded by Siemens F Model diffractometer with Philips PW1010 Model generator using Cu K_α radiation in Martin Trömel Lab. (Erciyes Univ.). Under computer control, the detector is scanned through each reflection while the intensities are recorded and stored. The x-ray

powder program was used for the evaluation of each reflection, zero point correction, background correction and for the indexation of crystalline powder patterns of substance according to Bragg equation ($n\lambda = 2d\sin\theta$).

c) UV - Absorption Analysis

For the investigation of characteristic absorption bands of chelating agent and metal chelates, samples were examined by using Hitachi 150 - 20 Model double beam UV-visible absorption spectrophotometer, in Chemistry Department (Erciyes Univ.), in the range of 190 - 400 nm with 10 mm quartz cells. Working solutions were prepared from 1.6×10^{-5} to 8×10^{-5} M for PtL_2, from 5×10^{-6} to 6×10^{-5} M for PdL_2, from 5×10^{-6} to 6×10^{-5} M for RhL_3, from 8×10^{-6} to 2×10^{-5} M for RuL_3, from 5×10^{-6} to 6×10^{-5} M for IrL_3 and from 2.5 to 20 mg Re/L for Re(IV) chelate from the 4×10^{-3} M stock solutions for PGM chelates and 100 mg Re/L for Re(IV) chelate by diluting with chloroform in 10 mL volumetric flasks. Chloroform was used as blank. In Re(IV) chelate, reagent blank was used as blank, which was 0.1 M $SnCl_2$ ni1 M HCl, diluted according to procedure used.

d) Thermal Gravimetry and Differential Thermal Analysis:

For the control of thermal stability and purity of DEBT and metal chelates, their thermal analysis were carried out on

Shimadzu DT-40 Thermal analyzer with simultaneous DTA-TG module using sampling weight as 5 -10 mg and a heating rate of 10 $^{0}C\ min^{-1}$ under N_2 atmosphere in Martin Trömel Lab. (Erciyes Univ.). The temperature ranges investigated were between 25 - 1000 ^{0}C. α-Al_2O_3 was used as reference.

2.3.2- Chromatographic Properties

In general, because of the similarities of chemical properties of metal chelates, determination of each platinum metal by classical methods was done with great difficulty. However, following the separation of platinum metals as their metal chelates from the interfering matrix, their quantitative determination would be possible chromatographically by applying on silica gel plates even though the chelates have similar properties. Therefore, chromatographic behaviours of these metal chelates were studied.

In the examination of the chromatographic behaviours of metal chelates and ligand, silica gel $60F_{254}$ -HPTLC and -TLC and alumina -$60F_{254}$ plates, as stationary phases; chloroform, benzene, xylene and toluene as mobile phases were used.

Flat bottom and twin trough chambers for ascending technique and horizontal developing chamber for horizontal technique were used during the investigation of the

chromatographic properties of metal-DEBT chelates. Their qualitative and quantitative analysis were done by using Shimadzu CS -9000 Model TLC - dualwavelength flying spot scanner, in Martin Trömel Lab. (Erciyes Univ.), as shown in Figure 2.2.

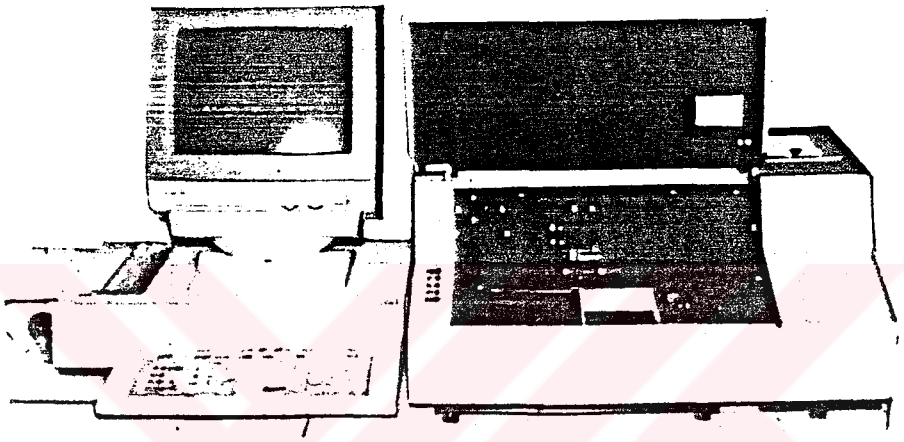


Figure 2.2. The View of Shimadzu CS-9000 Model TLC-Scanner

Its features are high reproducibility; reflection, transmission and fluorescence as photometric modes, baseline correction mode; linear or polynomial working curves; measuring wavelength from 200 - 700 nm; Kubelka - Munk correction single or dualwavelength; linear, zig zag or trace scanning in quantitation. In its optical system, the monochromator is of the Monk Gilleson type with 600 lines / mm. The entrance slit is fixed while the exit

slit has selectable width and height (Figure 2.3) adjusted by rotating the exit slit turret.

As shown in Figure 2.3, in the optical system of scanner the filters mounted immediately before the entrance slit of the monochromator is to cut high orders in the visible region or stray light in the fluorescence photometry. The light leaving the exit slit of the monochromator is reflected upward by a concave mirror (M3) and downward by a plane mirror (M_4) to form 1:1.25 image of the exit slit on the sample surface. In case of the reflection photometry, light scattered of the sample surface is detected by the reflection photomultiplier (PM_R), while a part of light immediately before falling on the sample is detected by the monitoring photomultiplier (PM_M) as reflected from the window plate. The ratio between outputs of two detectors is converted to provide absorbance signal. On the other hand, in case of transmission photometry, the photomultiplier (PM_T) is put to operation in place of the reflection photomultiplier (PM_R) to detect light passing through the sample [75].

The size of the measuring beam in scanning densitometer is defined by the slit width in the direction of scanning and the slit height in the orthogonal direction as shown in Figure 2.4.

The beam dimensions are important in linear scanning mode. The influence of the measuring beam dimensions on the

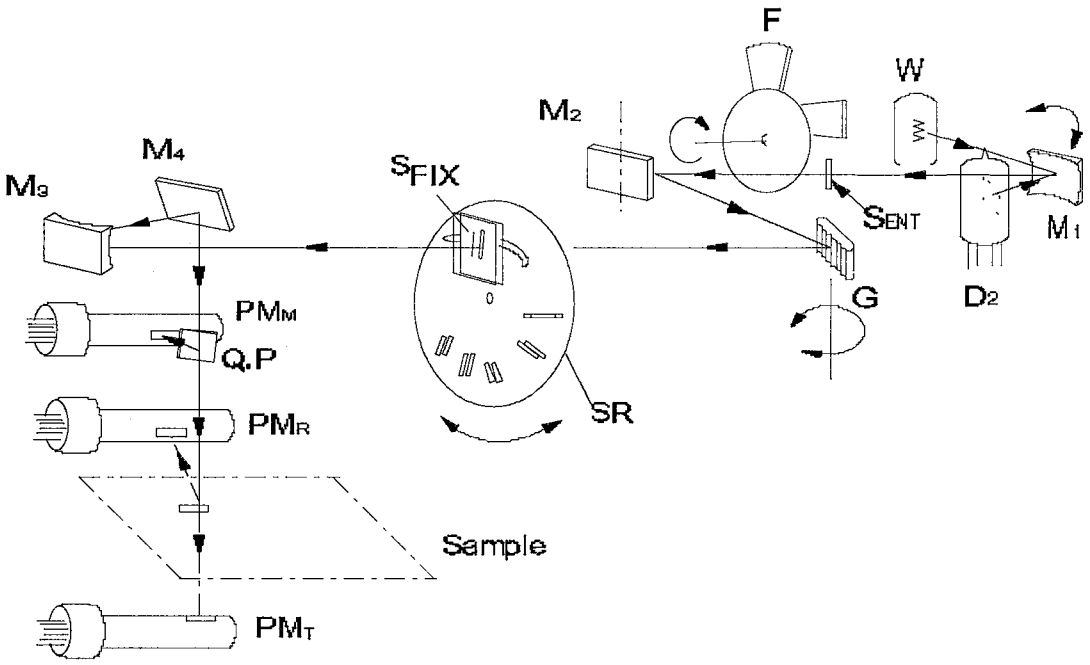


Figure 2.3. The Optical System of TLC-scanner

M_1:	Light source selecting mirror	D_2:	Deuterium lamp
M_2:	Collimating mirror	F:	High order cut off filter
M_3:	Concave mirror	G:	Grating
M_4:	Planar mirror	PM_M:	Lamp energy monitoring photomultiplier tube
S_{FIX}:	Fixed exit slit	PM_R:	Reflection and fluorescence photomultiplier
S_R:	Rotating exit slit	PM_T:	Transmission photomultiplier
W:	Tungsten lamp	QP:	Quartz window plate
S_{ENT}:	Entrance slit		

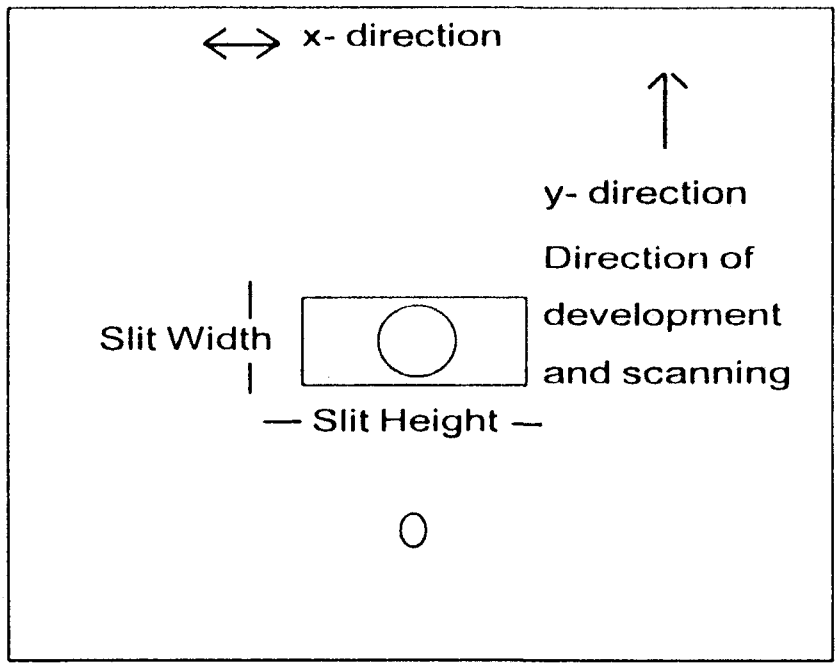


Figure 2.4. Enlargement of an HPTLC-plate Showing the Orientation of the Slit Width Respect to the Direction of Scanning

recorded signal in the reflection mode is shown in Figure 2.5. The signal declines only slightly as the slit width is increased. A more dramatic change is observed with changes in the slit height. When the slit height is large compared to the diameter of the spot, the signal becomes weak because the light flux reflected by the blank area of the plate is increased [34].In the zig zag scanning mode, the beam dimensions are fixed and is the smallest one (0.4 x 0.4 mm).

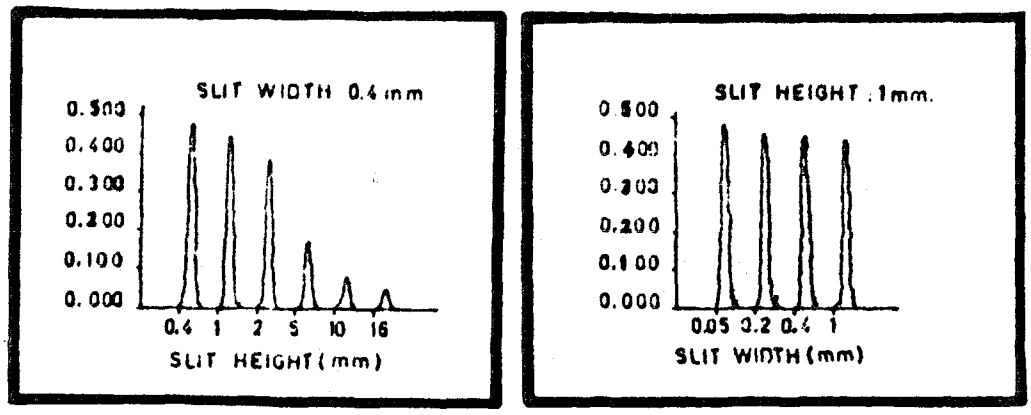


Figure 2.5. Variation of Signal as a Function of the Slit Dimensions in Linear Scanning Mode Operated in the Reflection Mode

For the detection of R_f values of DEBT and metal chelates, the sample solution of ligand, DEBT and its metal chelates were prepared in $CHCl_3$ at a concentration of about 100 - 200 µg/mL. 1 µL portion of each sample solution was placed on the start line located at 10 mm from edge of chromatographic plate. The chamber had been pre-equilibrated with solvent for at least 10 minutes before inserting the plate. To obtain highly reproducible results in determining the hR_f values, experimental conditions were standardized. The layer was developed at room temperature for a distance of 4 cm for HPTLC-plate and a distance of 6 cm for alumina-plate. For identification of spots, the chromatogram was air dried and the hR_f values were compared

with that of the standards. The quantitation of spots were done with Shimadzu CS-9000 model TLC-dualwavelength flying spot scanner in reflection mode by dualwavelength zig zag scanning at the selected wavelength.

2.4- Determination and Verification of Metal Chelate Compositions

In the determination of formula of Pd(II), Ru(III) and Re(IV) chelates, Job's and mole ratio method were used [76].

In Job's method, equimolar solutions of $4x10^{-5}$ M of perrhenate ($HReO_4$) and chelating agent for Re(IV) and $1x10^{-3}$ M of Pd(II) and Ru(III) and chelating agent for Pd(II) and Ru(III) chelates in 1 mL total volume were treated as described in Section 2.1.2. to prepare the metal chelates.

In mole ratio method, into separate containers, 0.5 mL of 1 $x10^{-3}$ M Pd(II) and Ru(III) solutions and 0.5 mL of 4 $x10^{-5}$ M perrhenate solution were placed. Onto these solutions, varying volumes (0.25-2.5 mL) of equimolar chelating agent were added, keeping the total volume constant; 3 mL for Pd(II) and Ru(III) chelates and 4 mL for Re(IV) chelate. Re(IV) chelate was measured at 390.8 nm in spectrophotometer. For Pd(II) and Ru(III) chelates, 1 µL of each solution in each method was injected to silica gel plate using Hamilton microsyringe and the measurements were taken at 20 nm by scanning densitometer.

2.5. Analysis of Catalysts

2.5.1. Catalyst Matrices

Catalyst matrices used in this study were obtained from the petroleum refiners, namely Aliağa (AL1F), Orta Anadolu (OAF and OA7R), ATAŞ (AT1S-AT4S) and TUPRAŞ (TUF, TU7R and TU9R) and from petrochemical complex of Aliağa (AL2F and AL3F) and nitric acid production complex of IGSAŞ (IGS) and TUGSAŞ (TG1S and TG2S). In addition, two active carbon based catalysts (AC1 and AC2) synthesized in Heraeus laboratory, Germany, were analysed.

Catalyst samples used in petroleum refining are either fresh or spent catalysts, samples used in petrochemical industry were all fresh and samples used in nitric acid production were spent catalysts. TUGSAŞ samples were taken from two different places; one of them was scrapped from the vapour pipes present in the production system, the other one was taken from the acid deposition tank.

Except TUGSAŞ samples and active carbon supported catalysts which are in the form of coarse particles, all others are in the form of cylinders or spheres as shown in Figure 2.6. The diameter of spheres are 4.04 mm (AL3F) and 1.76 mm (AT1S) and the dimensions of cylinders are 4.38 x 4.37 mm (AL2F), 3.33

x 3.25 mm (IGS) and 5.50 x 1.52 mm (TUF, OAF, AL1F) (height x diameter). As it was seen in this figure, the color of matrices has been darkened in spent catalysts. This shows that catalyst particles have been contaminated during the chemical process.

Figure 2.6. The Form of Collected Catalyst Matrices

The informations about the source of samples and the some properties of these matrices were given in Table 2.2. The explanations of fresh (F), spent (S) and regenerated (R) expressions used for the catalysts in the table are as follows: Fresh, not used in process yet; spent, not completely exhausted;

Table 2.2. Informations About Collected Catalyst Matrices

CATALYST	AREAS OF USE	% PGM (w/w)
Alumina Sup.		
TUPRAŞ (TUF, TU7R, TU9R)	Reforming	0.375 Pt, 0.375 Re
ATAŞ (AT1S-AT4S)	Reforming	0.22 Pt, 0.44 Re
Orta Anadolu (OAF,OA7R)	İncreasing the octane number of gasoline	0.35 Pt
Aliağa		
AL1F	Platforming	0.375 Pt, 0.375 Re
AL2F	Combustion	0.1 Pd
AL3F	Hydrogenation of ethylene	? Pd
IGSAŞ (IGS)	Nitric acid production	? Pt,? Re
Pt-Sieve		
TUGSAŞ	Nitric acid production	
TG1S		14-21 Pt, 0.09-0.03 Rh
TG2S		3.5 Pt, 0.2 - 0.4 Rh
Synthetic Active Carbon Based		
AC1		32.73 Pd
AC2		58.16 Pt, 3.39 Pd

regenerated, from time to time, catalyst in production was washed with pressurized water before completely exhausted. The number in regenerated catalyst shows how many times the catalyst was regenerated.

The PGM contents of the catalysts given in Table 2.2 are approximate values, AC1 and AC2 on the other hand were the calibration standards synthetically prepared in Heraeus Laboratory.

2.5.2- Standard Catalyst Materials

For the control of the accuracy of analysis methods, alumina based platinum, palladium and rhenium standards were used. Platinum on 1/8- inch alumina pellets (Pt 0.5%), rhenium on 1/8-inch alumina pellets (Re 0.5% unreduced) and palladium on alumina (Pd 1%) as catalyst standards purchased from Aldrich Chemical Company, Inc., were used as the standard in all qualitative and quantitative analysis.

2.5.3- Characterization of Catalyst Matrices

To control the supporting material and contamination elements which occurred during chemical process, the methods were developed for the quantitative analysis of platinum metals

and the matrix composition. For the matrix identification, three methods were used. The detection of supporting material in catalyst material was performed by XRD analysis and the platinum metals and contamination elements were examined by XRF and by OES.

a) X-Ray Diffraction Analysis (XRD):

The instrument, instrumental conditions and evaluation procedure were described in Section 2.3.1. Samples were ground finely in agatha mortar and spread over oiled plexyglass sample holder. The powder patterns were measured from 5^0 to 45^0 θ. By using ASTM indexes, the elements or compounds found in catalyst matrices were determined.

b) X-Ray Fluorescence Analysis (XRF):

X-Ray fluorescence spectra of powder samples were recorded by JOEL JSDX-MODEL X-Ray wavelength dispersive spectrometer in Geological Engineering Department (METU). A tungsten X-Ray tube was used with a LiF analyzer crystal (220). The tube was operated at 50 kV and 30 mA.

Catalyst samples were initially ground in an agate mortar to a sufficient mesh size. Then 8 drops of 4% binder was added to samples. Pellets were prepared by pressing and were

allowed to dry overnight. The spectra were recorded with a scanning rate of 2°/min.

Catalyst standards of platinum, palladium and rhenium were prepared by mixing known amounts of the promoter powders with γ-Al_2O_3 powder to give a homogeneous mass. The uniformity in the distributions was checked by recording the spectra of different weights. By using these spectra, metal amounts as percentages were determined in accordance with peak heights of the standards.

c) Optical Emission Spectrography (OES)

Three spent catalysts (OA7R, TG2S and TU7R) were analysed by Jarrell Ash Model Optical Emission Spectrograph in Maden Tetkik Arama Enstitüsü (MTA) for the semiquantitative determination of contamination elements.

2.5.4- Dissolution of Catalysts

Catalyst matrices were dissolved for the separation of platinum and contamination elements from the supporting material in catalyst. The catalyst materials were dried in oven at 110° C to get rid of volatile hydrocarbons and moisture. For dissolution of catalysts and standards except TUGSAŞ and active carbon

supported samples, several procedures were tested. In each procedure, one gram of accurately weighed finely ground sample was used. These procedures are as follows:

i. Decomposition by 4 times with only 4 mL aqua regia

ii. Leaching by 3 mL H_3PO_4 + 2 mL H_2SO_4 then, decomposition by 2 times with 4 mL aqua regia

iii. Decomposition by 10 mL of a mixture of HCl + HNO_3+ H_2SO_4 (3+1+1)

iv. Leaching by 5 mL (1+1) H_2O+H_2SO_4 solution and decomposition by 2 times with 4 mL aqua regia [17, 21, 4].

All alumina supported samples and standards except rhenium standard were dissolved according to the last procedure. Then the solution was filtered into volumetric flasks and diluted to the volume for the determination of the PGMs and rhenium in catalysts and PGMs in standards. Rhenium standard could only be dissolved by the procedures given below.

Platinum sieve TUGSAŞ samples containing very large amount of platinum were dissolved in two steps, completely. First step; approximately 50 mg of weighed samples were leached by 3 mL of aqua regia, 5 times for platinum metals. Then the

insoluble part (probable contaminants) after filtration was dissolved by NaOH fusion. For this, 10 mL of 30 % NaOH (saturated) solution was evaporated to the dryness in nickel crucible. Then the insoluble part of the samples were added and heated in oven at 800 °C for one hour. The leached mixture was dissolved in 100 mL of water at 70 - 80 °C and 10 mL of concentrated HCl were also added for complete dissolution. Finally, this solution was evaporated down to 50 mL.

Two synthetic active carbon based catalysts were heated in oven at 600 °C for 2 hours for decomposition of carbonaceous deposits. Then 5 times, 3 mL aqua regia were added for leaching of platinum metals, heating solution on hot table at near boiling temperatures. The solution was filtered through blue ribbon filterpaper, and diluted to 50 mL by washing 3 times with 3 mL of hot 1M HCl solution.

Rhenium catalyst standard was dissolved by alkali fusions in two ways;

Procedure 1: The sample with a mass of 50 mg was mixed with 400 mg of Na_2O_2 and 200 mg of Na_2CO_3 in a platinum crucible and the surface of the mixture was covered with a layer of Na_2CO_3. The crucible was placed into the cold furnace and heated to 600 - 650 °C for 1 hour to avoid an immediate violent reaction. The fusion of the sample was then continued for 1 hour at 600 - 650 °C. The melt was cooled and leached from the

crucible walls with 100 mL of H_2O, by throughly washing the reaction mixture. The solution was boiled to remove the excess of Na_2O_2. After cooling, the solution was filtered through a paper filter and the residue was washed on the filter with hot water to a total filtrate volume of 250 mL. Then the solution was evaporated down to 50 mL [77].

Procedure 2: Sodium tetraborate was used for the basic flux. 500 mg of sample was mixed with 2.5 g of $Na_2B_4O_7.10H_2O$ in a platinum crucible. The crucible was then placed into the cold furnace and heated to 850°C slowly to avoid a violent reaction. The fusion of sample was then continued for 30 minutes at 850 °C. The melt was cooled and leached with 200 mL of water and 3 mL of concentrated HCl. Then the solution was evaporated down to 50 mL.

2.5.5- Determinations of Pt, Pd and Rh in Catalysts Matrices

For the quantitative studies, the methods used were Atomic Absorption and Thin Layer Chromatographic methods.

2.5.5.1- Procedure For AAS

Standards and reagents:

Platinum solution: 980 mg Pt/L in 5% HCl, Sigma

Palladium solution: 1010 mg Pd/L in 5 % HCl, Sigma

$RhCl_3.3H_2O$ (38% Rh, Merck): 1000 mg Rh/L in 1 M HCl

Buffer Solution: Lanthanum (10000 mg/L) stock solution containing 11.85 g La_2O_3 and 24 mL HCl per liter.

All the other chemicals were of analytical reagent grade. Triplet distilled water was used in all solution preparation.

Concentration ranges for calibration solutions of each metal at working wavelengths were selected with respect to linear range of signal versus concentration of each elements. Calibration solutions containing from 0 to 90 μg/mL for platinum, from 0 to 30 μg/mL for palladium and from 0 to 50 μg/mL for rhodium were prepared freshly before use. All of them were prepared in 10 mL-volumetric flasks. For controlling aluminum effect in alumina based catalysts, Al solutions at concentrations in the range of 0-5000 mg/L and containing fixed concentrations of 40 mg/L of Pt and Re and 15 mg/L of Pd were prepared. Sets of these solutions containing the various concentrations of buffer (1500-5000 mg La/L) were tested. For active carbon based and platinum sieve catalysts, two sets of Pt standards at concentrations in the range of 0-500mg/L and 0-300 mg/L and containing fixed

concentrations of 4 and 15 mg/L of Rh and Pd respectively. When no buffer was used, water was used as blank. Otherwise, the same concentration of buffer was added to standards, test solutions, samples and blank.

Instruments and operating conditions:

Platinum and palladium determinations were made using Hitachi Z-8000 Model Atomic Absorption Spectrophotometer in Biochemistry Department (Erciyes Univ.). Rhodium determination was made using Perkin Elmer 403 Model Atomic Absorption Spectrophotometer in Çinkur, Kayseri. All instrumental conditions used in this study were the same as given in Table 2.2.

2.5.5.2- Procedure For TLC

Standards and reagents:

All solutions were prepared using the same procedure given in Section 2.1.2. DEBT was synthesized as described in Section 2.1.1. All other chemicals were of analytical reagent grade.

The instrument and instrumental conditions were described in Section 2.3.2.

0.5 - 2 mL of dissolved sample solution were reacted with 100-500 µL of 0.1 M DEBT and the solution was heated depending upon the metal to precipitate the metal chelate. 2-3 mL of hot 3M H_2SO_4 was added to decompose the contaminating elements (Fe and Cu). After cooling, the precipitated mixture containing only PGMs was extracted with 1-3 mL of chloroform for one minute. Then the mixture was let to stand at least for thirty minutes in order to have distinct layers of organic and aqueous phases.

After that, one microliter portion of each sample solution of metal chelate from the organic phase was placed on the start line located at 10 mm from the edge of the HPTLC plate by using a Hamilton microsyringe. Each sample was applied three times. The plates were preconditioned for 2 hours in the development chamber with H_2SO_4 (43% w/v) and benzene. The height of the rise of mobile phase from the starting line was 4 cm. Then the plates were dried in air.

The chromatograms obtained were scanned in reflection mode and quantitative evaluation were made by comparison with the calibration standards. Scanning was done in the dual wavelength with zig-zag mode.

CHAPTER III

RESULTS AND DISCUSSIONS

3.1- Synthesis of DEBT and Metal Chelates

3.1.1. Characterization of DEBT

Chelating agent, DEBT, used in the determination of Pt, Pd and Rh in the catalysts by TLC analysis, was synthesized according to the procedure described in Section 2.1.1.

The verification of the structure and the purification of DEBT crystals was controlled by taking IR and UV-absorption spectra and by the examination of chromatographic properties (densitometer), thermal properties (DTA-TG) and crystallographic parameters (XRD).

FTIR spectra of DEBT given in literature [67] and that of the synthesized reagent in this study resemble to each other as shown in Figure 3.1. The characteristic absorption bands for N-H, C-H and amide I (C=O), amide II and III at 3276, (3066 - 2936),

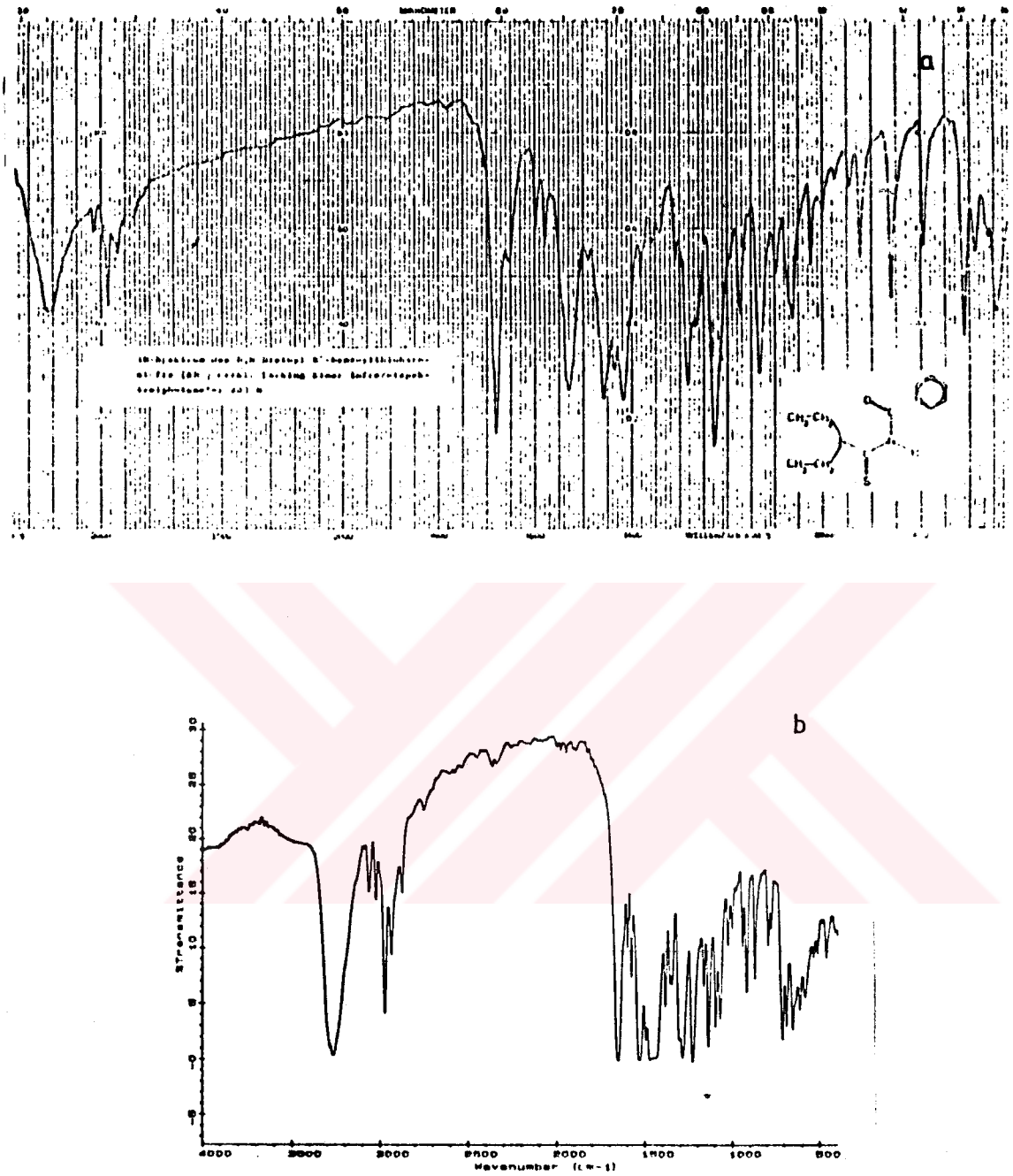


Figure 3.1. The Infrared Spectra of DEBT from

a) literature [67] b) this study

1656, 1538 and 1309 cm^{-1} respectively appearing in both of the spectra, support the formation of DEBT.

UV-absorption bands obtained are also very similar to that of given in literature (Table 3.1).

Table 3.1. UV - Absorption Properties of DEBT

	λ_{max} (nm)	ε_{max}(L/mol.cm)
Literature (67)	242 281 346	10560 17110 900
This Study	241.2 282.0 341.2	10971 18524 1092

A characteristic UV-spectrum of DEBT is given in Figure 3.2. DEBT has a very weak absorption band above 300 nm. However, molar extinction coefficients of ligand in near UV-region are between 10000 - 19000 L/ mol.cm having two strong but broad absorption bands at 241.2 nm and 282 nm.

The chromatographic properties of DEBT on HPTLC using silica gel as stationary phase and benzene (B), toluene (T), chloroform, xylene (X) and carbontetrachloride as mobile phases

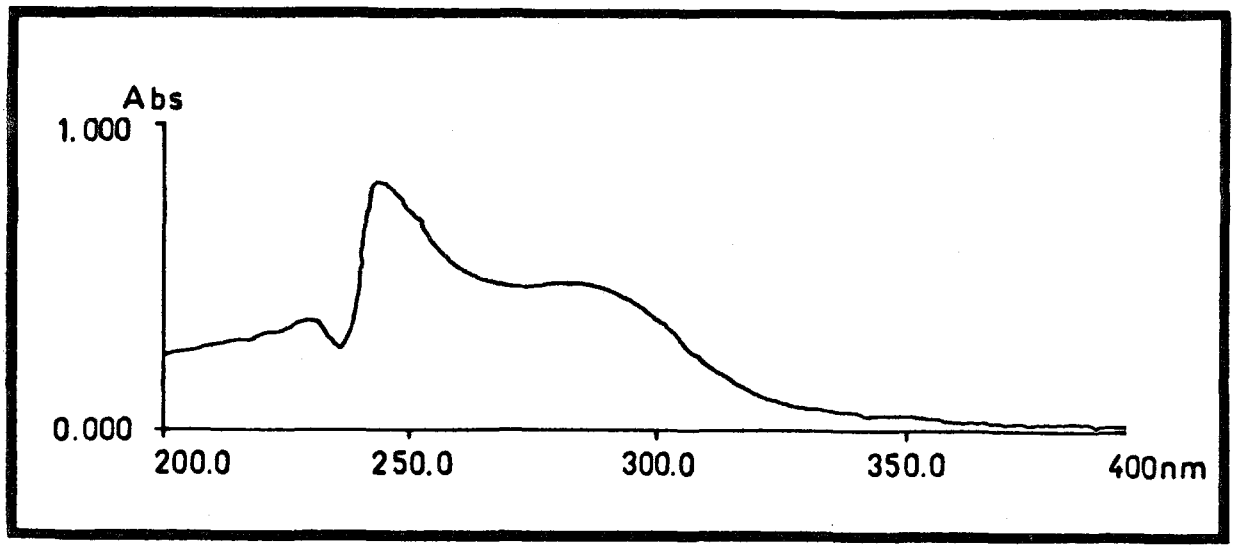


Figure 3.2. UV-Absorption Spectrum of DEBT

were studied. Silica gel was preferred as stationary phase because it is the common sorbent used for inorganics in TLC, and therefore the results obtained could be easily compared with the results given in literature [32]. Pure solvents of medium polarity like toluene, xylene, benzene and chloroform were chosen because DEBT was insoluble in highly polar and nonpolar solvents. To show this, carbontetrachloride was used in this series as an extremely nonpolar solvent. The obtained hR_f values were the same as the data given in the literature (Table 3.2). The values of Synder's solvent strength in Table 3.2 as measured by the semiempirical parameter (ε), increases with the polarity of the solvent showing ability to form hydrogen bonds. Although the values in the Table 3.2 are for alumina, they can be used inter-changably with reasonable reliability for silica gel as well [31].

Table 3.2. The hRf Values of DEBT with Various Solvents on HPTLC-silica gel

	CCl_4	Xylene	Toluene	Benzene	$CHCl_3$
ε^0	0.18	0.26	0.29	0.32	0.40
Literature (66)	-	6	-	10	-
This Study	0	6	8	10	55

The chromatograms in these mobile phases were shown in Figure 3.3.

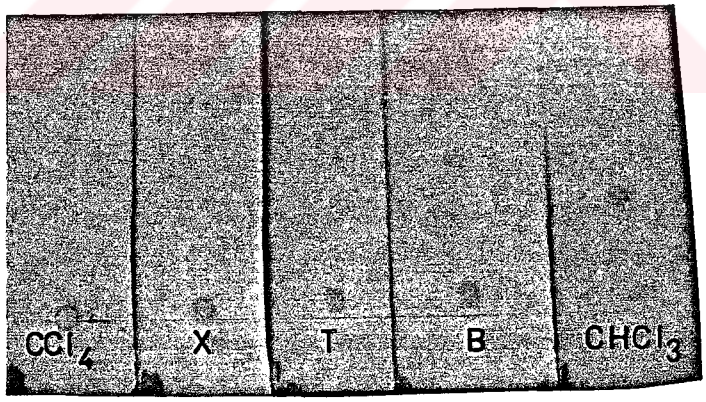


Figure 3.3. Chromatograms Showing The Positions of DEBT in Different Mobile Phases
X: Xylene T: Toluene B: Benzene

The polarity of the mobile phase needed to achieve adequate hR_f values is determined by that of the solutes studied. The greater the polarity of the solvent, the greater the distance of the development on the chromatographic plate.

Benzene was preferred as the mobile phase in spite of the high hR_f in chloroform because the migration rates of PGM chelates are higher than that of DEBT in this study and with the use of chloroform, the hR_f values which are almost the same as solvent front would be obtained.

Portions of 1.0 mL alcoholic solution of 0.1 M ligand were extracted separately with 5 mL of chloroform, carbontetrachloride, toluene, benzene, xylene and cyclohexane. For the control of extraction, 1 µL of each organic layer was injected to HPTLC-plates and were developed in benzene and their areas were compared. Chloroform and CCl_4 were lower phases so the evaporation possibility was limited because aqueous phase acts as a cover. The results are given by the chromatograms in Figure 3.4.

In order to show the reasonable solubility of DEBT in organic solvents studied, 5 mg of ligand was subjected to dissolution by water and the organic solvents separately and the chromatographic plate were prepared in a similar way.

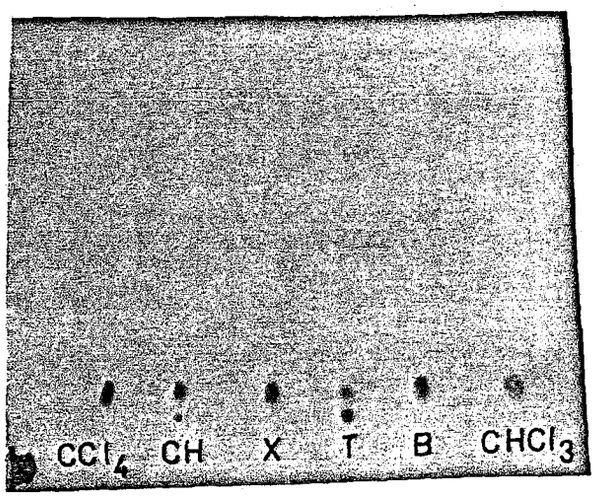


Figure 3.4. Chromatograms Showing Extraction of DEBT in Different Extractants
CH: Cyclohexane X: Xylene T: Toluene
B: Benzene

This chromatogram was shown in Figure 3.5. When the areas in these chromatograms were compared the greatest area was obtained with chloroform.

Then, comparing the areas and considering the lower evaporation, chloroform was selected as the best solvent for the extraction.

In addition to these, to control whether chelating agent would be present in synthesized and purified metal chelates, XRD powder pattern of DEBT for the determination of its some

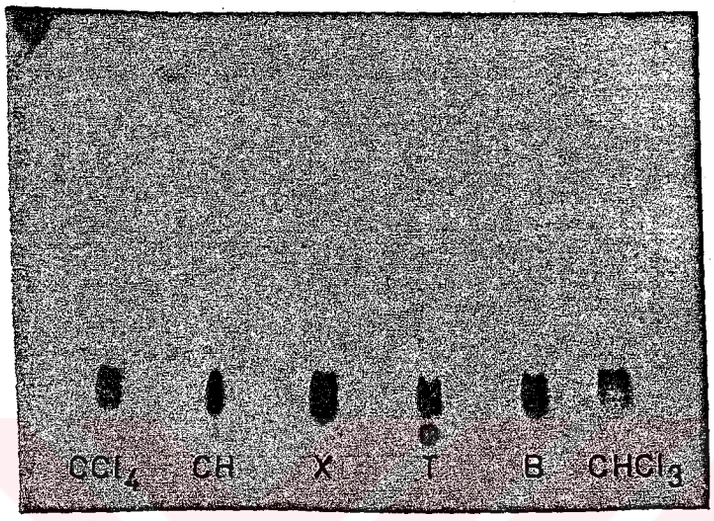


Figure 3.5. Chromatogram Showing Solubility of DEBT in Different Solvents
CH: Cyclohexane X: Xylene T: Toluene
B: Benzene

crystallographic cell parameters was also investigated. Powder pattern of DEBT, shown in Figure 3.6, was evaluated but could not been indexed due to the texture effect.This effect has been observed when crystallites are in the form as needle or sheet (layer). In sample preparation, the sample holder is filled with ground sample and then the sample surface has been smoothed.

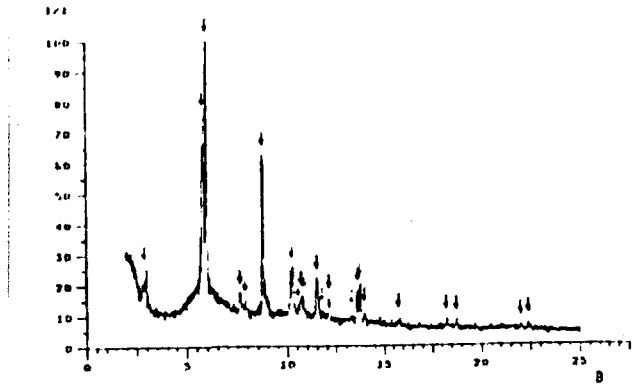


Figure 3.6. Powder Pattern of DEBT

When the sample is exposed to x-ray beam, the larger surfaces of crystallites will be exposed to diffraction more than the small surfaces. Therefore, the intensities of reflections of these surfaces are measured in higher magnitudes than normal state. This effect has been observed in different ratios in each sample preparations. To prevent this effect in relation to orientation of crystallites, amorphous reagent or substances having isometric crystallites were added to this kind of substances. For DEBT, although starch as an amorphous reagent and NaCl as an isometric crstallite were added, no sufficient improvement was observed in x-ray pattern.

For the controlling of its thermal stability and purity of DEBT, thermal analysis was employed and the TG-DTA curve is shown in Figure 3.7. Its TG curve shows that above 143.4 ^{0}C,

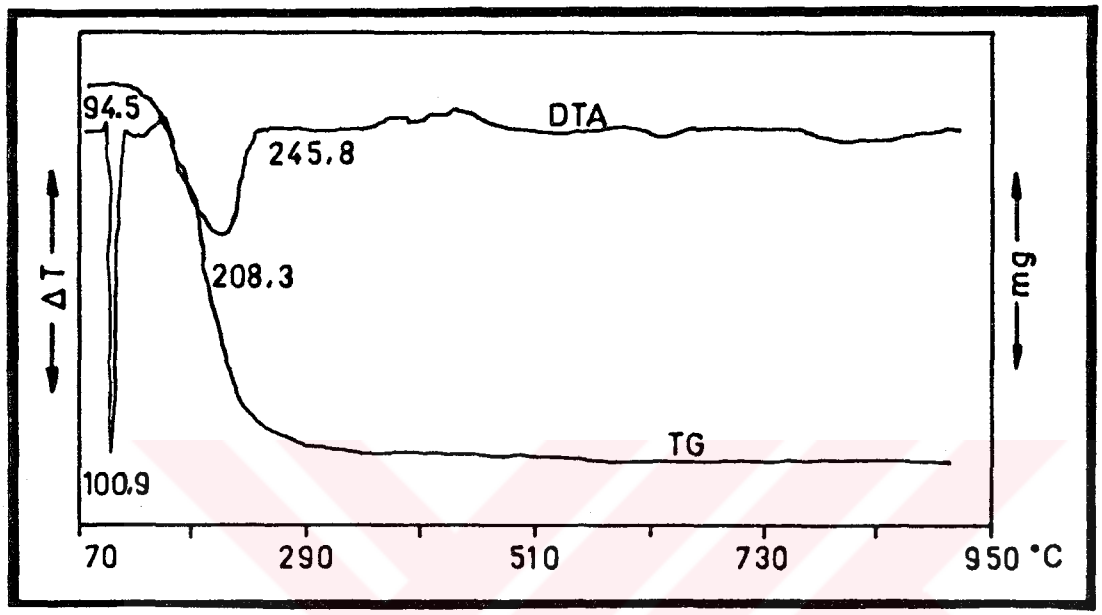


Figure 3.7. DTA and TG Curve of DEBT

it starts to lose mass. It decomposes completely in the temperature range of 143.4 - 373.8 ^{0}C in which one endothermic peak at 208.3 ^{0}C was observed successively on the DTA curve. Its melting point was also observed on DTA curve. The sharp peak at 100.9 ^{0}C belongs to melting point. Melting starts at 94.5 ^{0}C and ends up 100.9 ^{0}C. The melting point value determined by digital melting point apparatus in this study was 98 ^{0}C which is the same value as given in literature [67]. The sharpness of the peak and the

more precise melting point value obtained with DTA shows the purity of chelating agent.

3.1.2. Preparation and Extraction of Metal Chelates From Solid Phase

Metal chelates of platinum metal group, iron and copper were synthesized as described in Section 2.1.2. Iron and copper were also studied because these were the most probable interfering elements in the pH range of study. The experimental parameters for the precipitation of metal in aqueous solution were given in Table 3.3. The maximum yields of all these metals were obtained in the given pH ranges.

The extraction efficiency of the precipitated metal chelates into benzene, toluene, xylene, cyclohexane (CH), decaline (D), acetone (A), carbontetrachloride and chloroform were tested using densitometer. As the best solvent for the extraction, chloroform has been selected because the extraction was very easy, fast and the evaporation loss was eliminated by the presence of aqueous layer over the organic layer. As an example, densitogram of Pd(II) was given in Figure 3.8. The greatest areas obtained with $CHCl_3$ were also supported that it was the best solvent for complete extraction.

In order to control the completeness of extraction,

Table 3.3. Experimental Parameters For The Preparation of Chelates [71]

METAL	pH	COLOR	REMARKS
Pt(II)	1 - 7	yellow	Complexation at 40°C
Pd(II)	1 - 7	orange	Room Temperature
Ru(III)	1 - 3	brown	Complexation at 60°C
Rh(III)	1 - 5	yellow	Complexation at 70°C
Ir(III)	2 - 7	yellow	Complexation at 80-90°C
Re(IV)*	1 - 4	green	Room Temperature
Cu(II)	0 - 7	green	Room Temperature
Fe(III)	2 - 4	red	Room Temperature

*: Not found in literature, optimized values

chloroform extracts of metal chelates were separated and the metal concentrations in aqueous phase were determined by FAAS for Pt, Pd, Ru and Rh and UV-visible spectrometer for Ir (Table 3.4).

Table 3.4. Extraction Efficiency of PGM Chelates into Organic Layer, Mean ± 95 % Confidence Interval (n:5)

	Pt	Pd	Ru	Rh	Ir
%	98.1±0.3	97.9±0.2	93.7±0.4	93.7±1.4	98.6±0.4

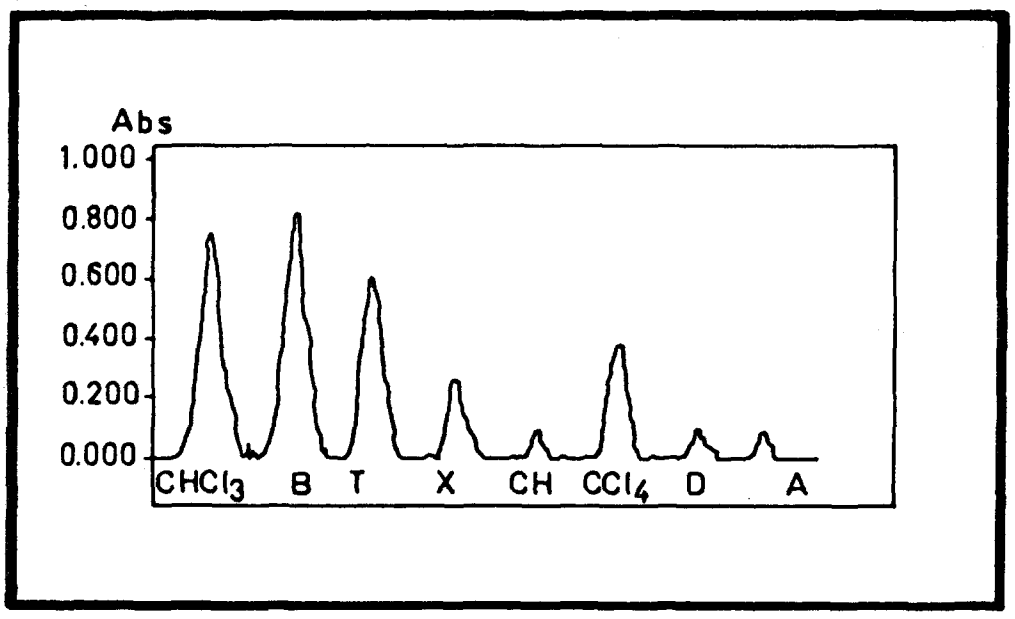


Figure 3.8. Densitometric Scan of Pd(II) After Extraction
B: Benzene T: Toluene X: Xylene
CH: Cyclohexane D: Decaline A: Acetone

The percent values were obtained for five parallel samples and the confidence interval was given at 95% confidence level.

DEBT is a very good reagent for selective extraction for the PGMs due to high extraction values. In literature, it was given that the metal chelates of DEBT have very high complexation stability [78] and there was no problem of dissociation of these chelates in aqueous solutions and organic solvents. The high stability of these metal chelates and their high extraction efficiency in organic layer renders the use of this reagent practicable in an analytical procedure.

3.1.3. Solvent Extraction of Metal Chelates From Liquid Phase

Very effective separations of PGMs by the selective extraction with DEBT are possible controlling the extraction parameters [73].

The solvent extraction of Pd, Pt, Ru, Rh and Ir with DEBT in toluene has been studied by controlling the various parameters such as acidity, reagent and ligand concentration, reaction time and temperature.

Platinum metals in hydrochloric acid solutions formed anionic complexes with very high stabilities. Chloro and chloro / aqua complexes of Ir(III) and Rh(III) are especially very stable [79]. They form metal complexes with chelating agents if they have greater tendency to form these metal chelates as compared to their chloro/aqua complexes. PGM have high tendency towards the formation of DEBT chelates in the increasing order of Ir, Rh, Ru, Pt and Pd. However, reactions take place very slowly. The concentration of ligand and the reaction temperature are very important parameters to control the rate of reactions. By increasing concentration of ligand and reaction temperature, extraction rate and yield are increased.

The rate of formation of the PGM chelates determines

the rate of extraction. The rate of reaction between metal ion and DEBT in the aqueous phase, rather than the rate of transfer of DEBT from the organic solvent to water, determines the rate of metal extraction. The rate of extraction tends to rise with the value of the extraction constant [80]. The extraction rate of different metals was affected relatively by the change in acidity from 1 to 4 M HCl. However, the slight effect of varying acidity on the rate is well established in literature [80]. The effect of acidity and ligand concentration show that the reaction takes place largely between metal ions and DEBT in the aqueous phase.

The change of yield for PGM's with the change of the investigated parameters were given as tables in Appendix B. All the mole ratios are given as Metal:Ligand. As a summary of these tables for Pd, 25 ^{0}C and 1:4 mole ratio are sufficient. In platinum extraction, 60 - 80 ^{0}C and 1:8 and 1:12 mole ratios can be used for the best result. 60- 80 ^{0}C and 1:6, 1:9 and 1:12 mole ratios for Ru, 70 - 80^{0}C and 1:12 and 1:18 mole ratios for Rh and 80^{0}C and 1:9, 1:12 and 1:24 mole ratios for Ir give the highest yields. The best conditions for the extraction of all PGMs, simultaneously, will be obtained at 80^{0}C in 2 M HCl but in different mole ratios. The extraction yields calculated from the concentration of metal ion remained in aqueous solution (c_{oM}(rest)) were given in Table 3.5 and change of c_{M}(rest) with time of extraction was shown in Figure 3.9.

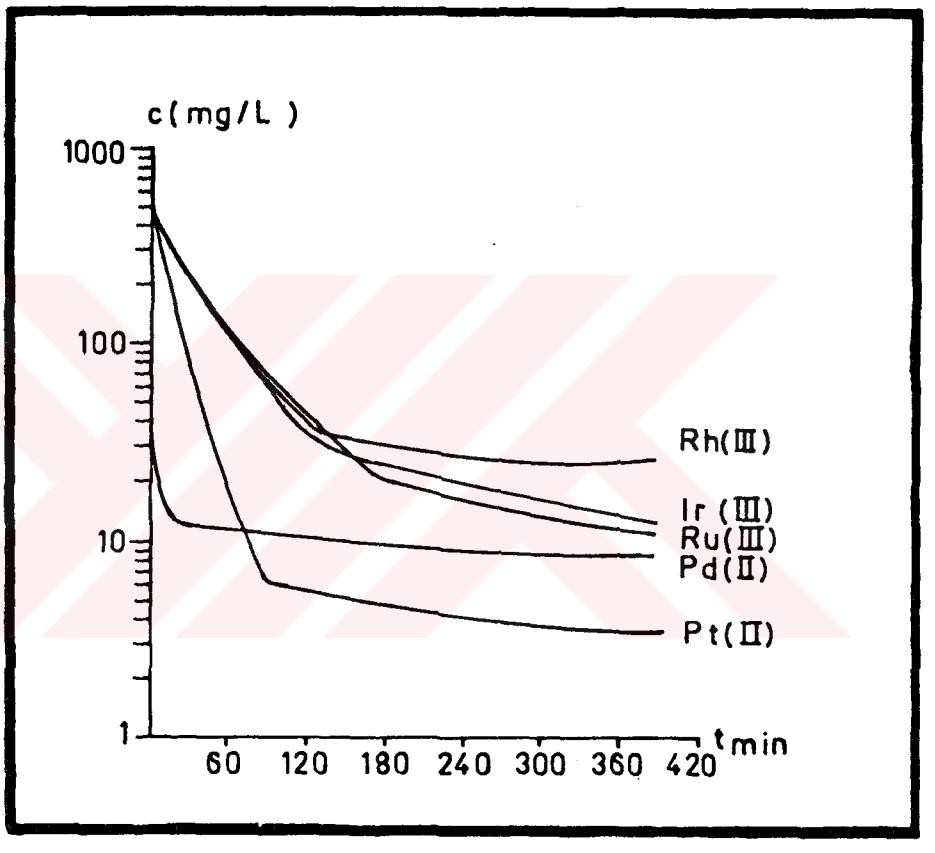


Figure 3.9. The Change of Solvent Extraction With Best Values With Time For Pd(II), Pt(II), Ru(III), Rh(III) and Ir(III)

Table 3.5. The Best Values Obtained With Solvent Extraction of Metal Chelates From Liquid Phase, at 80°C in 2M HCl for All PGMs (stock solutions: 500 mg metal/L)

	M:L	t_{min}	C_M(rest) (mg / L)	Ext.yield (%)
Pd(II)	1 : 4	30	11	98
Pt(II)	1 : 8	90	6	99
Ru(III)	1 : 9	180	22	96
Rh(III)	1 : 18	120	36	93
Ir(III)	1 : 12	420	12	98

The percent yields obtained by two different extraction techniques discussed so far were comparable for all the metal chelates. The extraction to organic solvent after forming precipitate of chelate in aqueous solution is a much easier and rapid process as compared to the extraction of the metal ions in aqueous solution into organic solvent containing the chelating agent. The extraction from solid phase also requires less amount of ligand than the extraction by liquid phase. Therefore this extraction process was used throughout of the work.

3.2. Dissolution of Metal Chelates in Water and in Some Organic Solvents

As it was stated previously, the solubility of metal chelates in water and in several organic solvents are very low due to high stability constants (10^{12} - 10^{16}) [81]. In order to show this experimentally, metal chelates were subjected to dissolution by water as described in Section 2.2. The direct determination of undissolved amount by filtration could not be performed due to formation of high suspension of metal chelates in aqueous solution and sticking of particles on the inner surface of the round bottom flask during filtration. Therefore, the filtrate was extracted with chloroform to control the solubility with densitometer. However, no spot for the metal chelates was detected on chromatogram after development with benzene.

The dissolution of these metal chelates in chloroform, benzene, toluene, xylene, cyclohexane, decaline, acetone and carbontetrachloride as extractants were also studied. From the comparison of areas, it was found that the best one is chloroform, having medium polarity, as in DEBT. Also, the densitometric scans of Pd(II) chelate as a representative example of the dissolution were shown in each extractants (Figure 3.10).

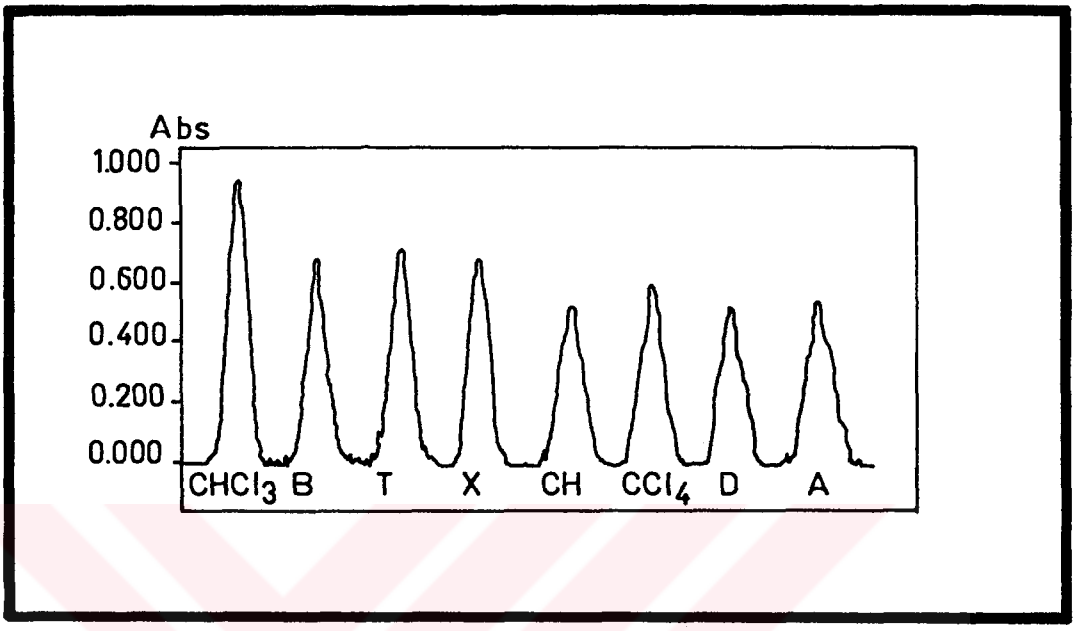


Figure 3.10. Densitometric Scan of Pd(II) Chelate in Various Solvents

3.3. Characterizations of Metal Chelates

Metal chelates were characterized by using the same methods used in chelating agent characterization. The information obtained is given below.

3.3.1. Structural Characterizations

IR Spectrometry:

The IR spectral bands correspondingly to C=N, C-H, N-H and C=O bonds of the chelating agent and complexes are presented in Table 3.6 and also the spectra of Pt and Ru chelates were given as example in Figure 3.11.

Table 3.6. IR Spectral Bands of DEBT and Metal Chelates

	DEBT	$Pt(DEBT)_2$	$Pd(DEBT)_2$	$Ru(DEBT)_3$
νN-H	3276	-	-	-
νC=O	1656	-	-	-
νCH_3	2877, 2974	2872, 2972	2869, 2979	2870, 2978
νCH_2	2936	2930	2929	2936
ν=C-H	3020, 3066	3066, 3090	3065, 3086	3062, 3086
νC=N	-	1588	1587	1586

All complexes have similar IR spectra, which indicates that these complexes have similar structures and there is no significant dependence on the central metal ion. The absorption peaks of C-H bonds appearing in the spectra of chelating agent are also present in the complexes but their positions are slightly shifted. The characteristic IR bands of $-N(CH_2CH_3)_2$ group,

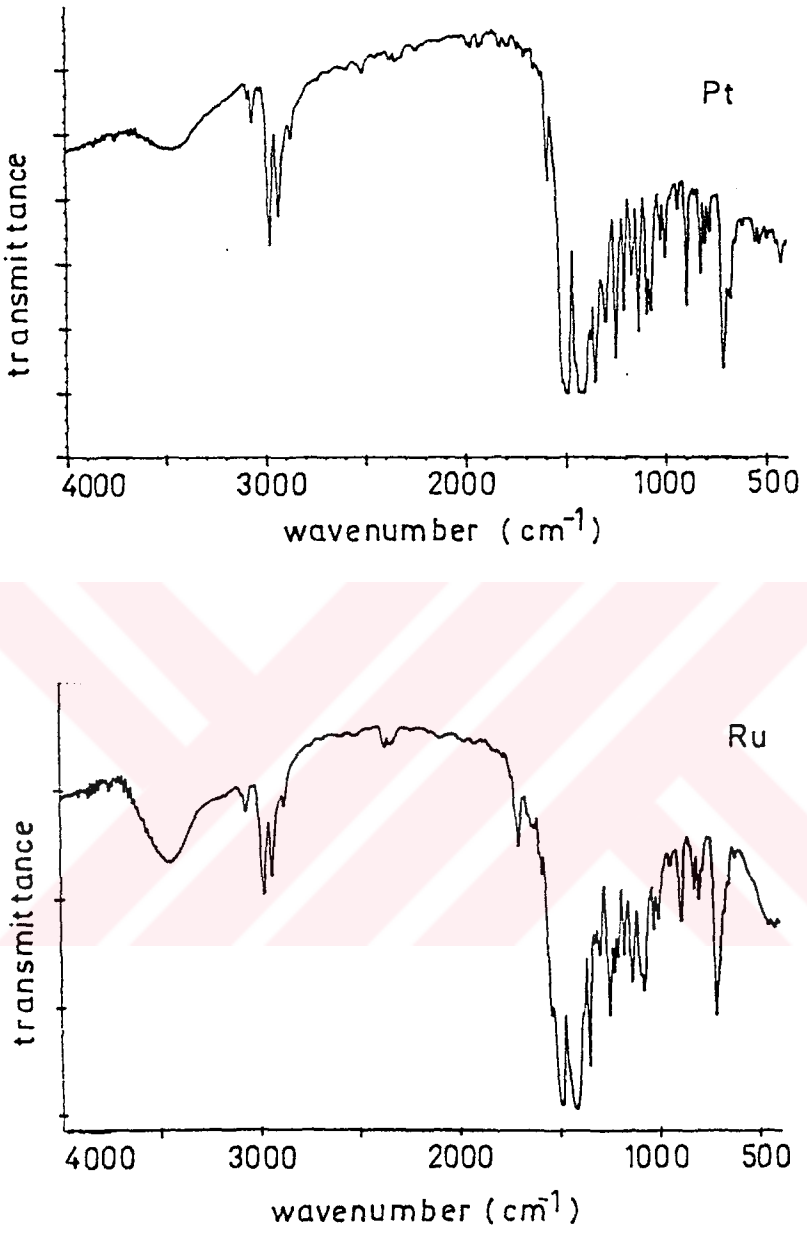


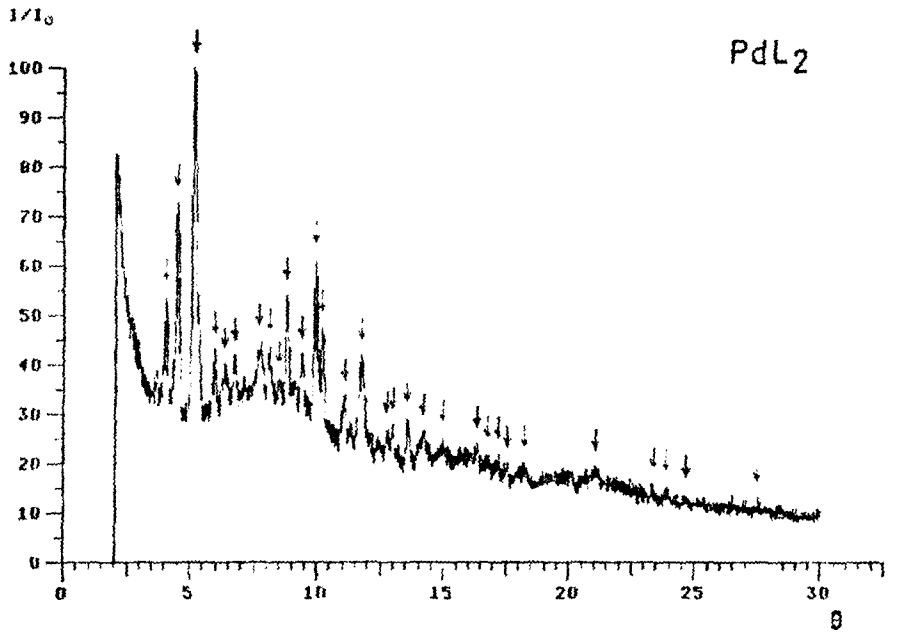
Figure 3.11. Infrared spectra of Pt- and Ru- DEBT Chelates

appearing at 2877 and 2974 cm^{-1} (ν -CH_3) and 2936 cm^{-1} (ν–CH_2) in the spectrum of the ligand, remain almost unchanged in the spectra of the complexes. In the complexes of DEBT, -$N(CH_2CH_3)_2$ group and aromatic ring displayed slight shifts (5 -20 cm^{-1}) on complexation. The small change in the -$N(CH_2CH_3)_2$ band indicates that this group does not take part in coordination. In the aromatic ring upon the formation of the metal-ligand bond the C-H vibration is shifted to higher frequencies.

The positions of the amide I, II and III bands of DEBT (1656, 1533 and 1309 cm^{-1}) arising from the carbonly group of the benzamide moiety disappeared in the complexes as shown in Figure 3.11. The vibration band of secondary amide at 3276 cm^{-1} also disappeared in the complexes. Similar features and discussion were also valid for IR spectra of Pd and Ru complexes.

XRD Spectrometry:

Besides IR spectrometry, XRD analysis technique was used to investigate the powder pattern of metal complexes as shown in Figure 3.12. It was seen that metal complexes are iso-structural because of the similarities of their XRD powder pattern. The powder patterns of metal chelates could not be indexed due to the high texture effect as it was seen in DEBT. This effect, was tried to be eliminated by adding starch and NaCl; however, no improvement was observed on patterns. List of the d-values and diffraction angles of Pd and Pt chelates are given in Appendix C.



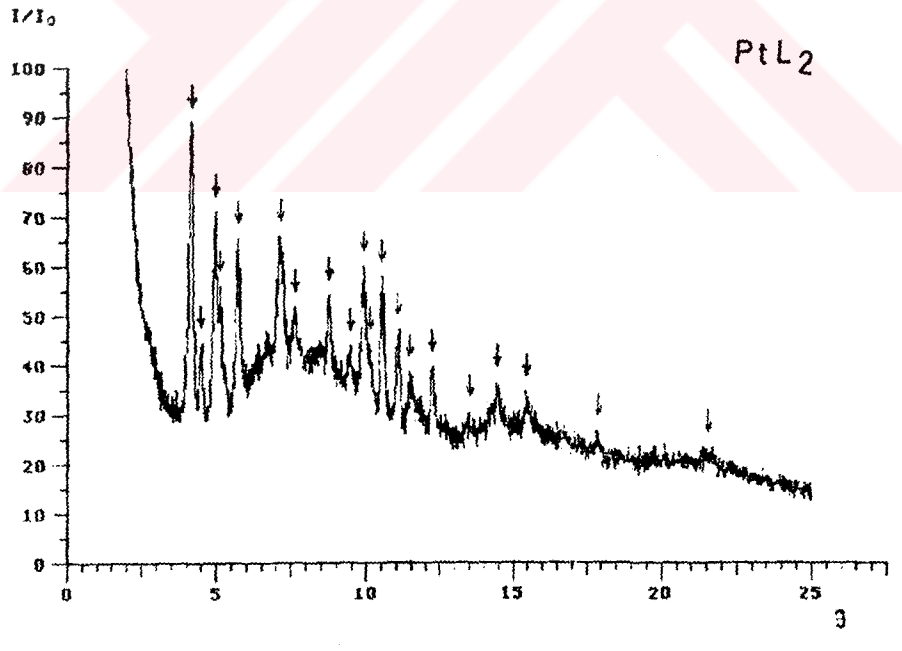


Figure 3.12. XRD Powder Pattern of Pd and Pt Chelates

UV - vis. Absorption Spectrometry:

The important UV-absorption bands of the complexes in chloroform are listed in Table 3.7 and their absorption spectra are given in Figure 3.13. No absorption band was observed in the visible region for any of the compounds. When Table 3.1 is also examined, it is clear that the spectra of the complexes are similar regarding the absorption wavelengths, although absorptivities are different. Re(IV) chelate is an exception. As a result, no spectrum could be obtained for the chelates in the presence of excess ligand in solvent. Because of this reason, excess chelating agent used was separated from chloroform extracts of metal complexes either by reacting with 0.1 M NaOH or by chromatographic separation.

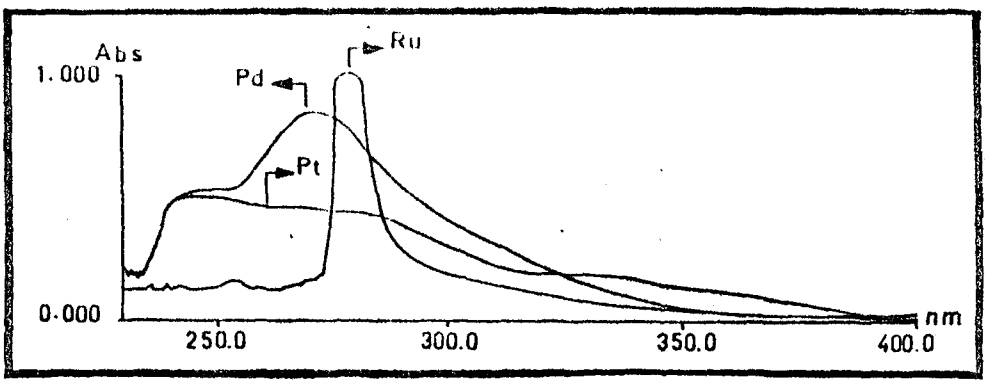
The absorption maxima of the chelating agent remain either unchanged or suffer slight shifts in the complexes. This is because the spectra of complexes are attributed mainly to ligand and it appears reasonable to assign the high energy absorption bands to π - π^* transitions. The weak absorption peak of ligand at 346 nm is due to n - π^* transition which appears in the spectra of some complexes.

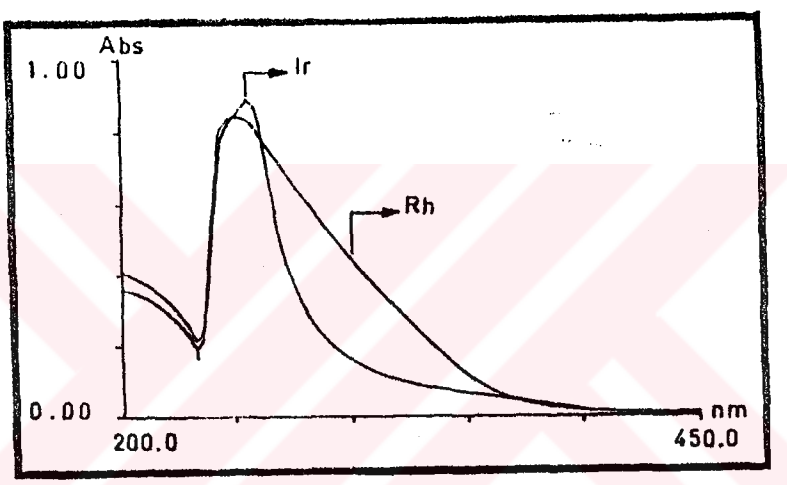
DTA - TG Analysis :

The thermal investigations of metal chelates have been

Table 3.7. UV Absorption Bands Of Metal Chelates

	λ_{max}(nm)	λ_{max}(nm)	ε_{max}(L/mol.cm)	ε_{max}(L/mol.cm)
CHELATE	Ref.,[67]	This Study	Ref.,[67]	This Study
PtL_2	249	248.8	35320	28017
	275	265.0	32327	25515
	280	278.2	33120	25206
	330	325.6	12240	9725.8
PdL_2	244	244.5	37150	39642
	272	273.0	54603	52872
	377	378.0	2600	4868
RuL_3	275	274.6	47500	41372
RhL_3	-	248	-	22111
IrL_3	-	254.5	-	21405
ReL_x	-	390.8	-	22500





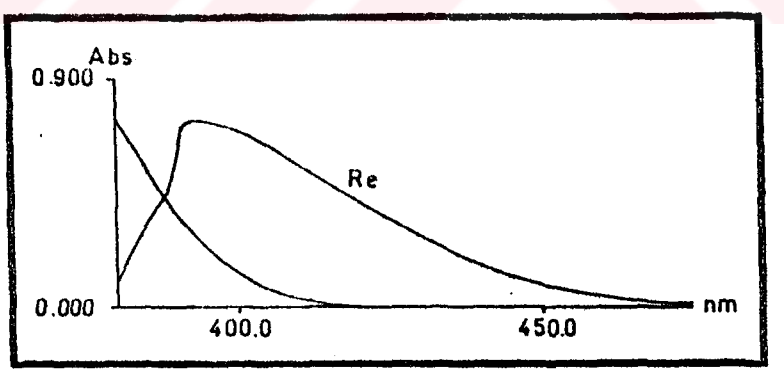


Figure 3.13. UV- Absorption Spectra of Metal Chelates

carried out between 25-1000°C. The initial studies were carried out with digital melting point apparatus. The melting point of crystallized metal complexes were compared with the literature values [67]. The data are given in Table 3.8. The experimental values confirmed the literature values. The further thermo analytical studies were proceeded by DTA-TG analysis.

The results for Pd(II), Pt(II) and Ru(III) chelates are summarized in Table 3.9 and TG-DTA curves of these metal chelates were shown in Figure 3.14 (a-c).

As it is clear from the results, the TG curves of the present complexes do not show the presence of water molecules either in or out of the coordination sphere; because, the TG curves indicate that above 170°C the compounds start to lose mass. The formal sharp endothermic peaks at 160.2°C and 169.8°C in Pd(II) and Pt(II) chelates, respectively, correspond to their melting points. In the DTA curve of $Ru(DEBT)_3$, the temperature observed as melting point on digital melting point apparatus which agreed with literature was seen as decomposition peak on DTA curve. Since the data of DTA analysis is more dependable, we can say that $Ru(DEBT)_3$ chelate decomposes at about 190°C without melting.

The compounds decomposed in two steps, appearing successively on the DTA curve and obvious weight loss occurs

Table 3.8. The Melting Points of Metal-DEBT Chelates [67]

METAL CHELATES	$m.p._{obs}$ (°C)	$m.p._{lit}$ (°C)
$Fe(DEBT)_3$	108	110 -112
$Ni(DEBT)_2$	138	137
$Cu(DEBT)_2$	119	117 - 118
$Pd(DEBT)_2$	155	156
$Pt(DEBT)_2$	163	164 - 165
$Ru(DEBT)_3$	195	194 - 196
$Rh(DEBT)_3$	158	159
$Ir(DEBT)_3$	173	174

Table 3.9. Thermoanalytical Data of the Complexes Studied

COMPOUND	Melting Point Peak (°C)	DECOMPOSITION		
		Temp. Range (°C)	Weight Loss (%)	
			Calcd.	Obs.
$Pt(DEBT)_2$	169.8	197 - 365 365 - 480	52.57 18.03	52.71 18.86
$Pd(DEBT)_2$	160.6	223 - 365 365 - 790	60.65 15.25	59.79 15.06
$Ru(DEBT)_3$		174.8 - 308 311 - 1000	65.02 22.23	65.62 22.26

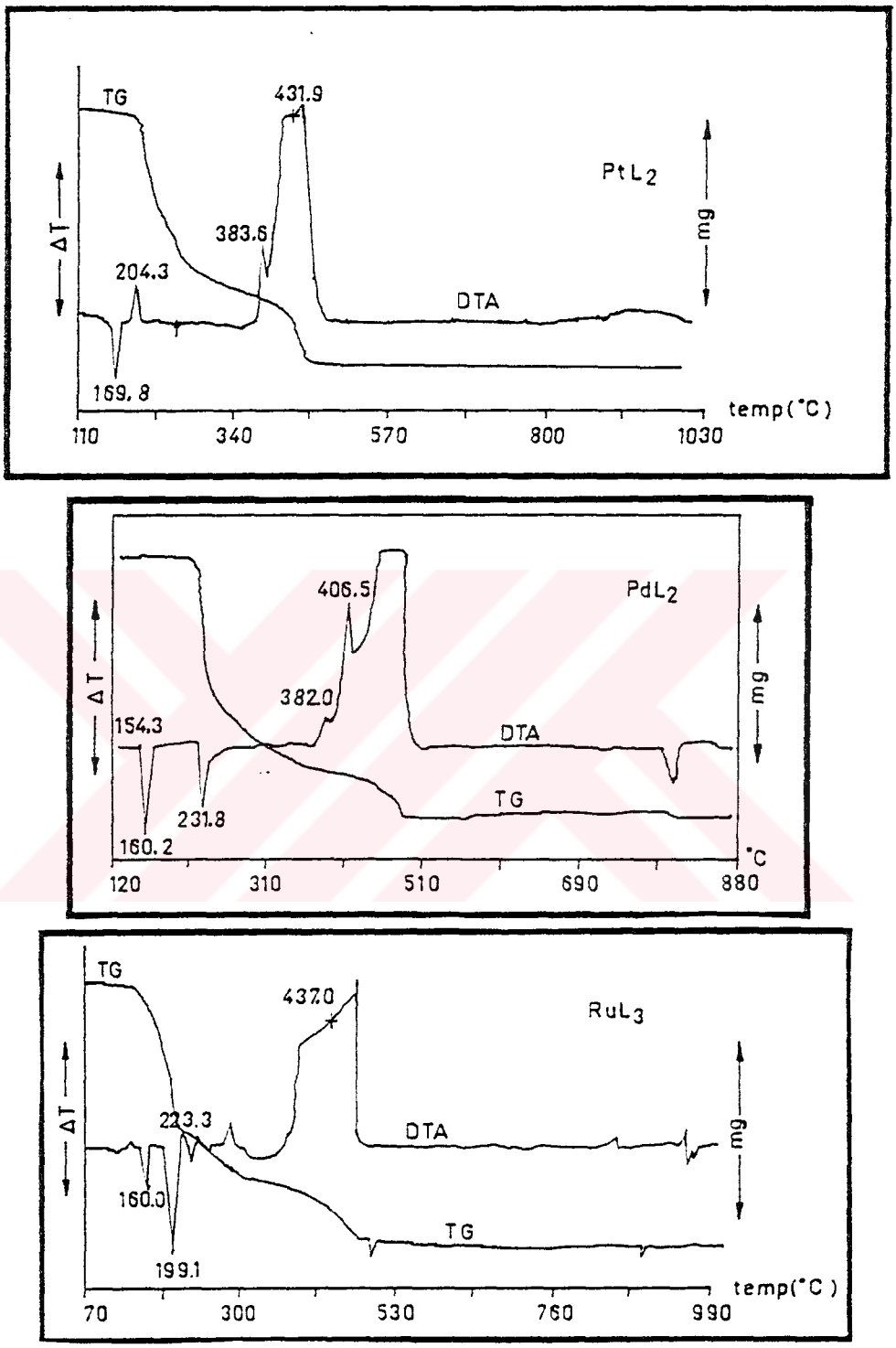


Figure 3.14. DTA-TG Curve of Metal Chelates

a) PtL_2 b) PdL_2 c) RuL_3

on the TG curve. The total weight loss of Pd(II), Pt(II) and Ru(III) chelates when heated was found to be 25.15 %, 28.43 % and 12.12 % which is nearly equal to the calculated values, 24.10 %, 29.40 % and 12.75 % respectively. The calculated values were obtained by assuming that at the first stage, the hydrocarbons, amines and CN groups; then at the second stage CO_x and SO_x are removed. The final residues obtained corresponded to metal or metal oxide. This observation has been confirmed by x-ray powder patterns of the decomposition products. The residue products of these metal compounds were PdO, Pt and RuO_2 + Ru at 750°C, 485°C and 1000°C respectively.

3.3.2- Chromatographic Properties

The experiments were done at room temperature by applying constant humidity in the chromatographic chamber.

A representative result of the development of metal chelates with individual solvents on an alumina plate and high performance thin layer of silica gel by the ascending method are given in Table 3.10. In general, silica gel plates were better than alumina. In the case of alumina, after development of plate, the evaporation of mobile phase was very slow and the migration rates of Pt(II), Pd(II) and Ru(III) were very high which were not preferable, since obtaining complete resolution would not be possible in this case. In this study, preliminary works were

Table 3.10. The hR_f Values of PGM Chelates in Different Mobile Phases

a) On Silica Gel $60F_{254}$ HPTLC (n=5, confidence interval at 95% CL, 50 % relative humidity)

Developer Solvent (ε^0)		hR_f					
		PtL_2	PdL_2	RuL_3	RhL_3	IrL_3	ReL_2
Xylene (0.26)	Exp	44.1±0.3	46.2±0.2	0/9 ±0.1	0/8	0/7	0
	Lit [67]	42	44	0/12	0/8	0/7	0
Toluene (0.29)		54.3±0.3	56±0.4	0/14±0.3	0/12	0/11	0
Exp. Benzene	Exp	64.1±0.2	66±0.2	0/29±0.2	0/23	0/22	0
	Lit [67]	64	69	0/32	0/23	0	0
(0.32)		84.2±0.3	82±0.3	0/56±0.2	1.5±0.03	0.6±0.01	0

b) On Alumina $60F_{254}$ Neutral (type E) Plates (Exp.)

Developer Solvent (ε^0)	hR_f						
	DEBT	PtL_2	PdL_2	RuL_3	RhL_3	IrL_3	ReL_2
Xylene (0.26)	8	68	74	0 / 46	0	0	0
Toluene (0.29)	10	80	83	0 / 63	0	0	0
Benzene (0.32)	18	88	90	0 /83	0	0	0
Chloroform	72	98	100	0 / 97	0	0	0

carried out with silica gel-TLC plates; HPTLC plates were used for further quantitative studies because HPTLC plates are more expensive. HPTLC plates were preferred to TLC plates because the former has the advantages of short migration distance and separation time, smaller sample volume and high sensitivity.

According to results obtained, the chelates may be examined in three mobile phase groups with respect to their chromatographic behaviours. In the first group, all the metal chelates did not migrate from the sample spot when cyclohexane and carbontetrachloride were used as solvent. Therefore, these were not included into Table 3.10. In the second group, Pt, Pd and Ru chelates could be developed to a moderate distance with benzene, toluene and xylene. In the third group in which chloroform and binary mixtures were included, all the metal chelates had similar migration rate, except Rh, Re and Ir and moved up the almost same distance as the solvent front. The results obtained with benzene-acetone binary mixtures were not given in Table 3.10 because they were almost the same as chloroform.

With the moderately polar developing solvents such as benzene, toluene and xylene, the separation of PGMs chelates was achieved successfully. The retention values for xylene and benzene given in literature are in agreement with experimental values. Within these three solvents, the evaporation rate of

benzene was fastest after chromatographic run. Therefore, it was selected as the developing solvent.

The reproducibility of hR_f values was studied using HPTLC - plates at different humidity medium with benzene. The procedures of sample application, sample size as well as the sorbent layer thickness did not appreciably affect the reproducibility of hR_f values. The factors affecting the mobility of substances included the degree of sorbent saturation with water vapour or constant humidity supplied with H_2SO_4 solutions and with the vapours of the mobile phase. Therefore, chromatographic separations were carried out under equilibrium conditions, when the surface of the sorbent being saturated with both moisture and the organic solvent vapour.

The dependence of chelate retention on the duration of sorbent in contact with 33 %, 38 %, 43 % and 54 % H_2SO_4 (w/v) solutions and solvent vapours were examined. The dependence of retention on humidity is presented in Figure 3.15. Percent relative humidity at different percentages of H_2SO_4 solutions were tabulated at Table 3.11. When variation of hR_f, values with relative humidity at 2 h developing time was examined, it was observed that hR_f values were constant within 30 to 50 % relative humidity and increased largely after 50 %.

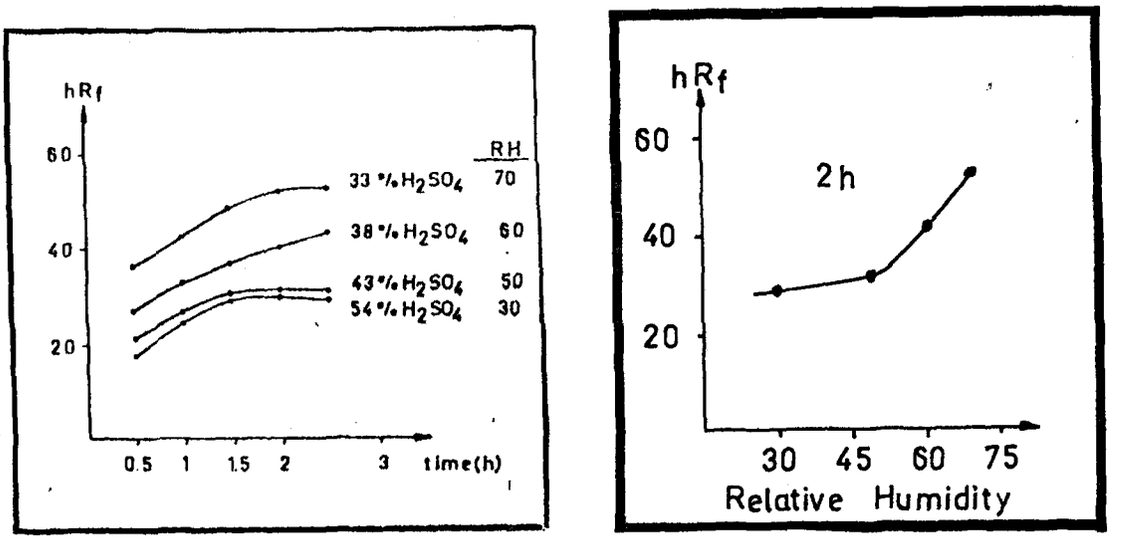


Figure 3.15. Dependence of the hR_f Values of $Ru(DEBT)_3$, 25°C

a) On Time at Different Relative Humidity %

b) on Relative Humidity

Table 3.11. Relative Humidity Using H_2SO_4 Solutions at 25 °C [67]

w / v % H_2SO_4	27	33	38	43	49	54
Relative Humidity	80	70	60	50	40	30

It was found that the saturation with 1.5 to 2 hours sufficed to establish the corresponding equilibria and to obtain reproducible results. Longer contact times did not affect the chelate mobility. Therefore, 50 % relative humidity and 2 h developing time were preferred throughout this study.

Under these optimized chromatographic conditions, the reproducibility of the hR_f values as RSD obtained in HPTLC silica gel plate using benzene as solvent was better than 0.2 %. Typical chromatogram and densitogram of mixtures of metal chelates after saturation with 43 % H_2SO_4 for 2 h obtained by development with benzene were given in Figure 3.16(a-f). The separation of Pd, Ru, Rh and Pt in (a), Pt, Ru and Rh in (b), Rh, Pd, and Ru in (c) and Ir, Pt and Co in (d), Rh, Ni, Co and Cu in (e) and Rh, Ru and Cu in (f) were given. The separation of two, three or four metals in the same mixture would seem to be possible. But Pt and Pd were not separated in this type of spot application because of the closeness of their hR_f values. By using automatic sample applicator in line mode, their separation would become possible. Ru(III), Rh(III) and Ir(III) complexes have two hR_f values because of their structural isomers. The higher hR_f values correspond to trans isomers and the smaller one belong to cis isomers. The trans isomers of metal complexes exhibit higher hR_f values than the corresponding cis isomers, provided that single-component solvent systems were used. These differences in hR_f values of cis and trans isomers may originate from the differences in dipole moments, solubilities, ion-pair formation

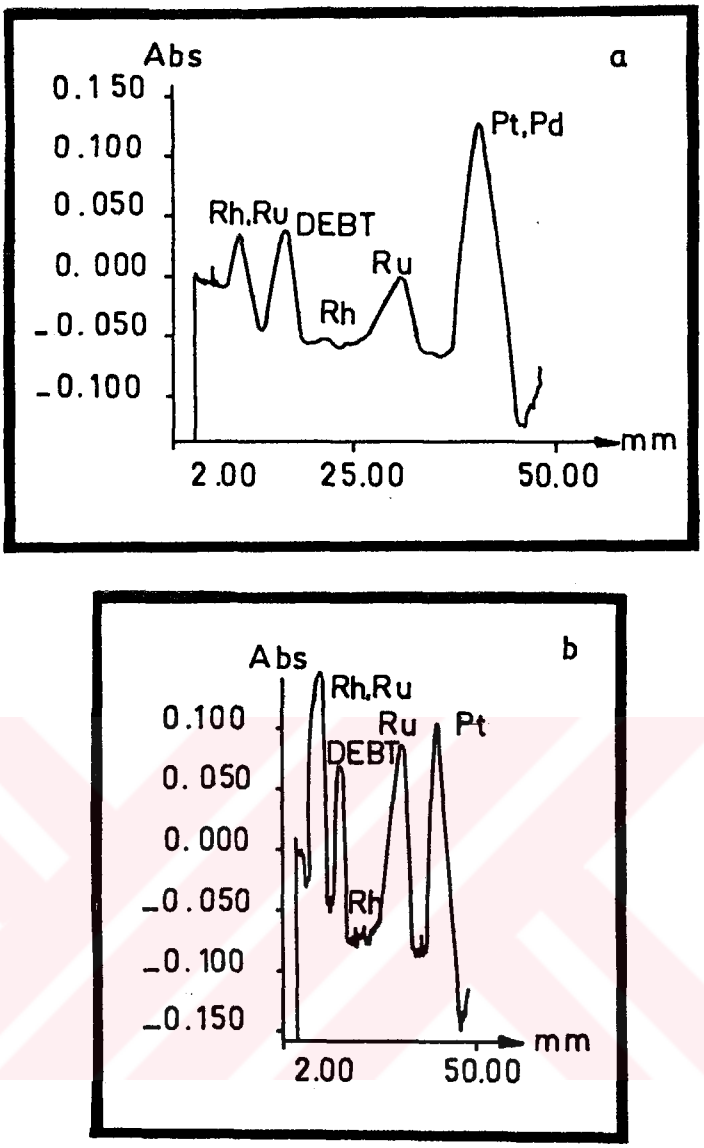


Figure 3.16. Densitogram of Mixtures of Metal Chelates

Stationary Phase:HPTLC-silica gel 60

Mobile Phase: Benzene

Solvent Front: 4 cm

Rel. Humidity: 50%

Detection λ: 280 nm

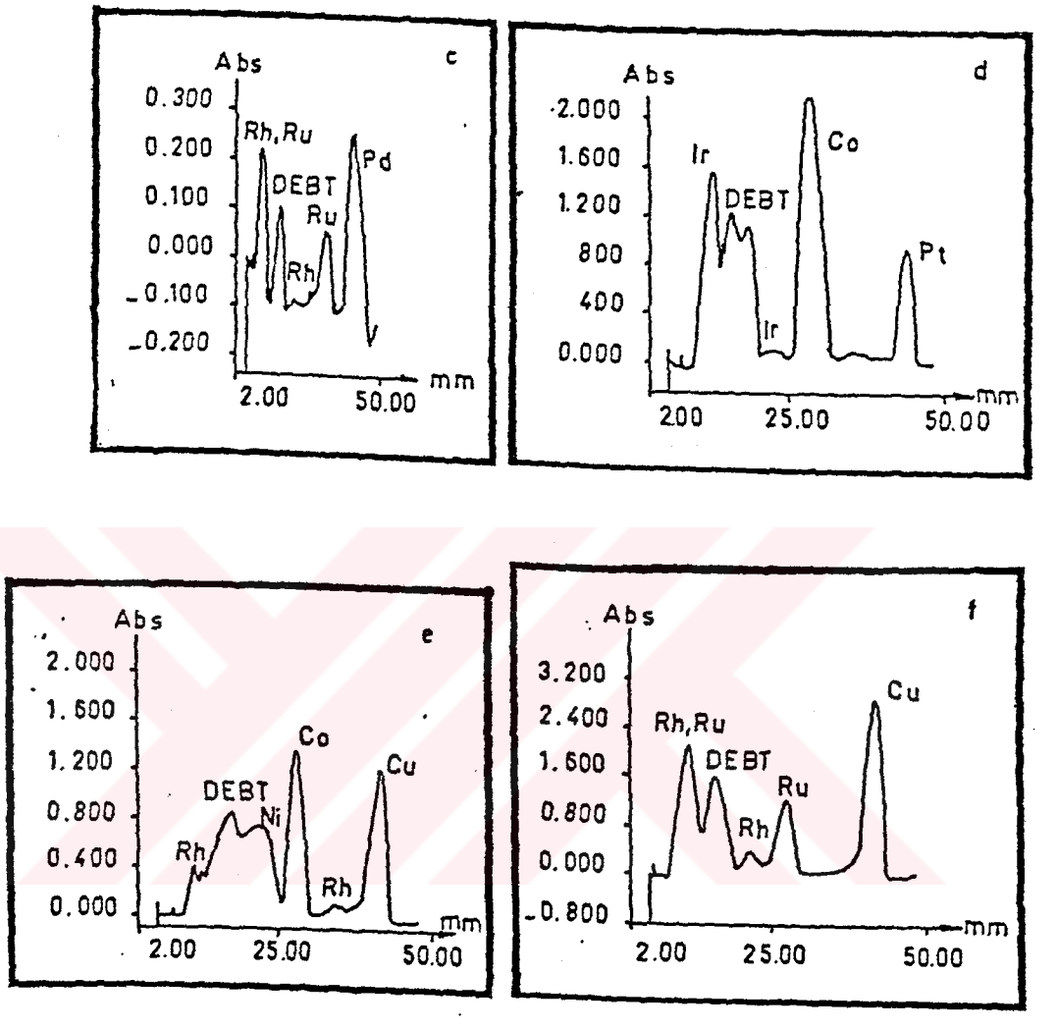


Figure 3.16. Densitogram of Mixtures of Metal Chelates (cont'd)

between the complex cation and anion present in the developer, stability of the complexes, steric hindrance, adsorptivity and symmetry [82,83].

To control which kind of wavelength scanning procedure was better, $Pd(DEBT)_2$ was chromatographed on HPTLC-plate and was scanned at 280 nm (sample λ) and 210 nm (reference λ) by the single and dualwavelength mode . The formal wavelength, is defined as the wavelength where the analyte exhibits maximum absorption and the background exhibits relatively low absorption. In the latter one, background shows a relatively high absorption and the analyte shows relatively low absorption. The absolute difference between these two wavelengths could be less or equal to 100 nm and no background correction would be required to this mode. In the measurement, first scanning is done at reference wavelength and data is stored into memory. Then, at the formal wavelength , the same lane coordinates is scanned and the difference between the signals obtained at these two wavelengths are sent to the recorder as output and stored in memory [34, 75]. The data demonstrated that dual wavelength mode would provide a more stable baseline compared to single wavelength mode (Figure 3.17); and so dual wavelength scanning was preferred to single wavelength mode.

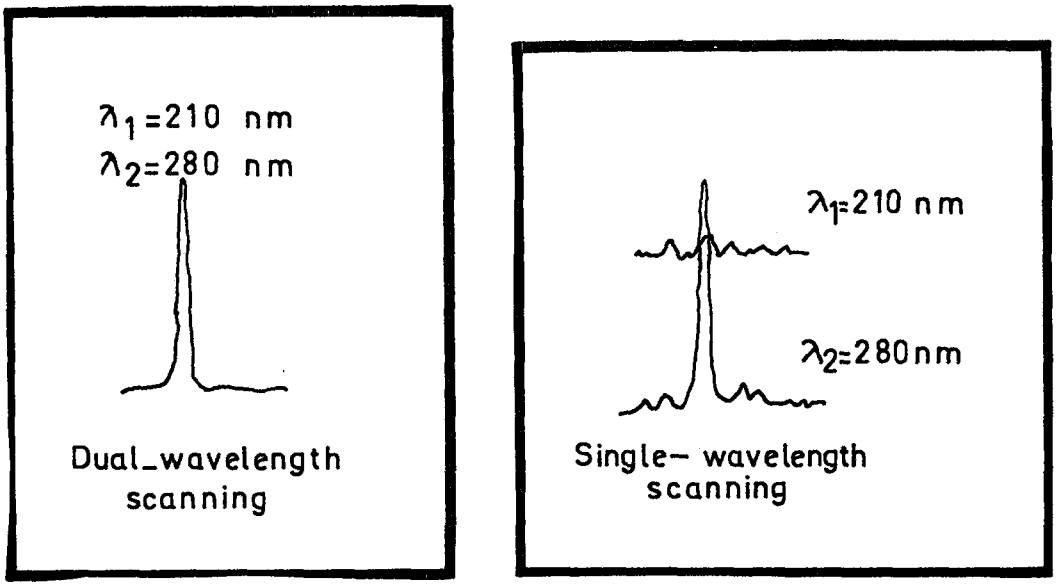


Figure 3.17. Densitogram of a Spot
a) by Dual Wavelength Scanning
b) by Single Wavelength Scanning

During scanning in densitometry, two modes of scanning could be used. In the linear scanning mode, the slit height of the light beam is adjusted to the maximum width of the spot and linear scanning is done along the y-direction within the adjusted range. In the zig zag scanning mode, the flying spot system is used that is each spot is scanned by predetermined small increments by zig zag movements in the x-direction and along the y-axis. The zig zag scanning eliminates errors caused by irregular shape of a chromatographic spot which can not be reproducibly measured with a linear scanning method. The densitogram of $Pd(DEBT)_2$ obtained for the concentration range

of 6.0-60 ng/μL showed that zig zag scanning was more sensitive and gave more successful results compared to linear scanning mode. The chromatogram and the calibration curves obtained from the densitograms were shown at Figure 3.18. More reliable calibration curve was obtained with zig zag mode. So, zig zag scanning mode was decided to use in all studies.

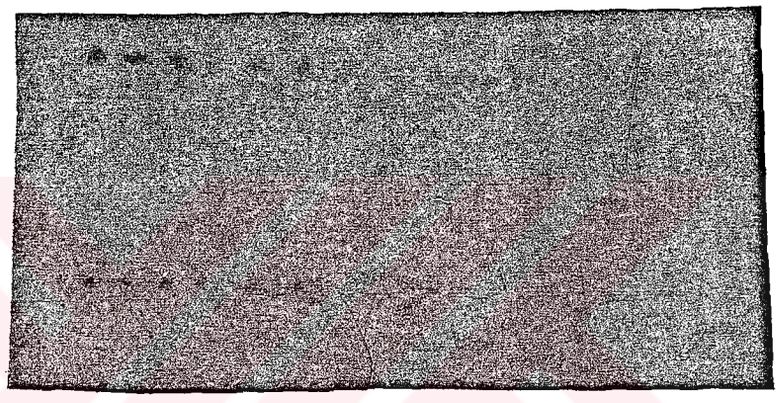
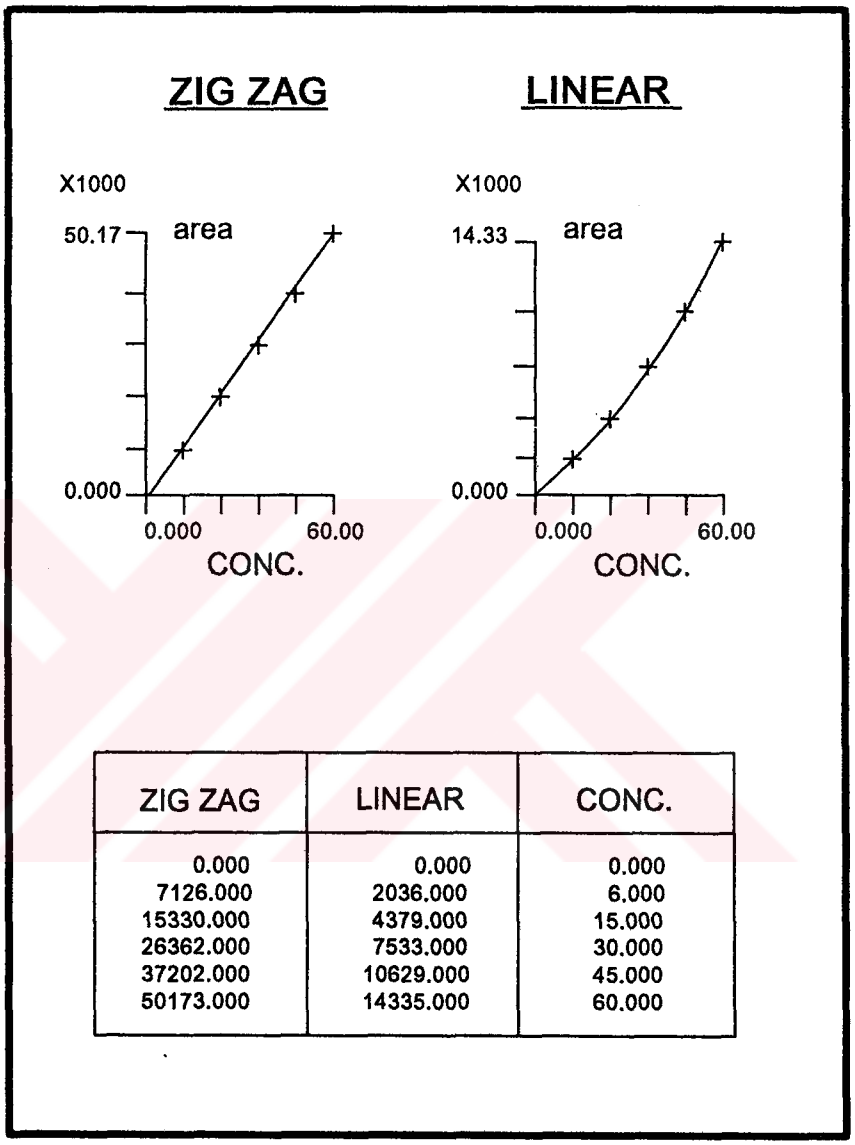


Figure 3.18 a) Chromatogram of Pd(II) Chelate Containing Calibration Standards

In order to establish the optimum experimental conditions for the quantitative determinations, standard solutions of the metal chelates in chloroform were prepared and applied to adsorbent layer as described in Section 2.3.2. Calibration standards were prepared in different concentrations and spotted as a fixed constant volume of 1 μL. Firstly, the maximum absorption wavelengths of metal chelates given in Table 3.12 were determined.



ZIG ZAG	LINEAR	CONC.
0.000	0.000	0.000
7126.000	2036.000	6.000
15330.000	4379.000	15.000
26362.000	7533.000	30.000
37202.000	10629.000	45.000
50173.000	14335.000	60.000

Figure 3.18- b)Calibration Curve of Pd(II) Obtained From Linear Scan and From Zig zag Scan

The UV-absorption spectra of metal chelates obtained from densitometry were given in Figure 3.19. The plot of peak area versus ng of metal per spot (each spot consists of 1 μL sample) was linear up to 78 ng Pt, 42.6 ng Pd, 80.9 ng Ru, 20.6 ng Rh and 30.8 ng Ir with correlation coefficients of 0.997, 0.999, 0.997, 0.997 and 0.999, respectively, when the linear regression is applied. Above these values, the slope of the curves decreased slowly deviating from linearity.

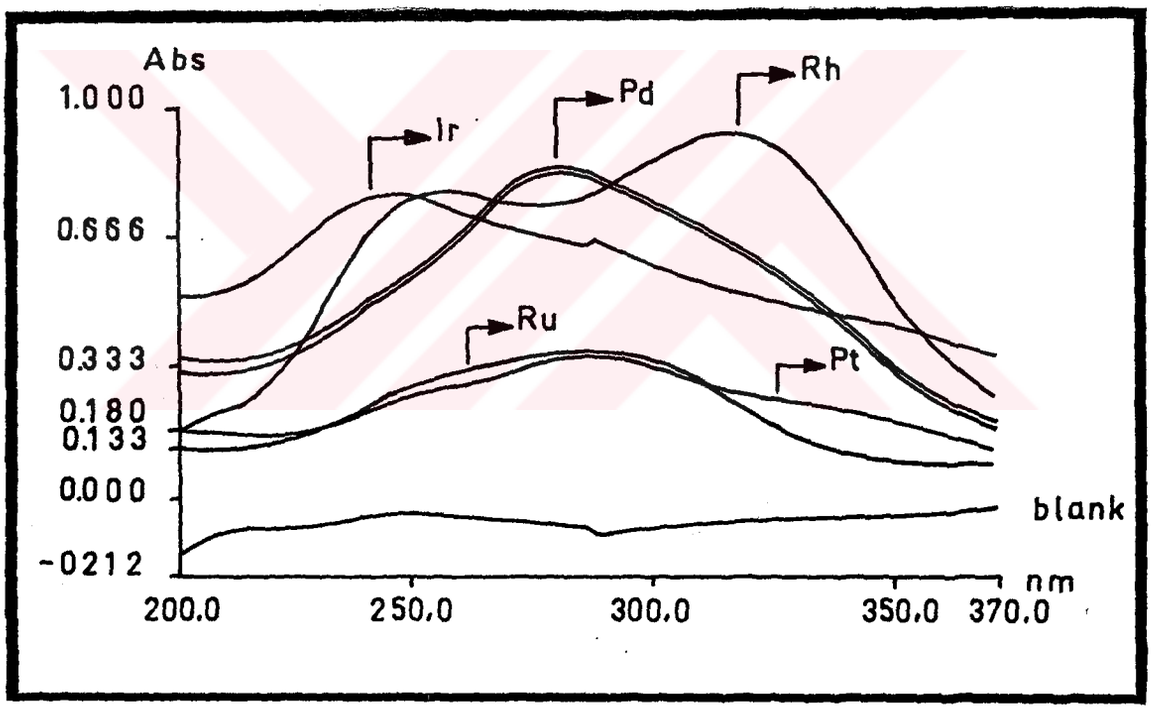


Figure 3.19. UV-Absorption Spectra of Metal Chelates in Densitometry

The calibration plots of Pt, Pd, Ru, Rh and Ir as area versus concentration were shown in Figure 3.20. From the slopes of the calibration graphs, as the lower concentration limits, 7.8 ng Pt, 2.1 ng Pd, 4.9 ng Ru, 1.6 ng Rh and 2.3 ng Ir could be detected instrumentally. The working ranges for each metal were given in Table 3.12.

Table 3.12. The Precision of the Chromatographic Measurements

Element	λ(nm)	Working Range ng/μL	Precision		DL(ng)
			2s	RSD(%)	
Pd	280	2.1-42.6	0.02	0.8	0.3
Pt	285	7.8-78.0	0.8	2.4	3.0
Ru	275	4.9-80.9	0.2	1.2	1.2
Rh	255, 315	1.6-20	0.09	1.3	0.7
Ir	260	2.3-30.8	0.08	1.1	0.5

The quantitative evaluation of chromatograms in routine analysis depends largely on the stability of the colour intensity of spots. It was found that the peak areas for chelates with DEBT did not change during 24 hours after preparation of the chromatogram, apart from variations caused by slight variation of instrument sensitivity. The loss in the spots was represented as the difference in areas which increases as concentrations of metal increased

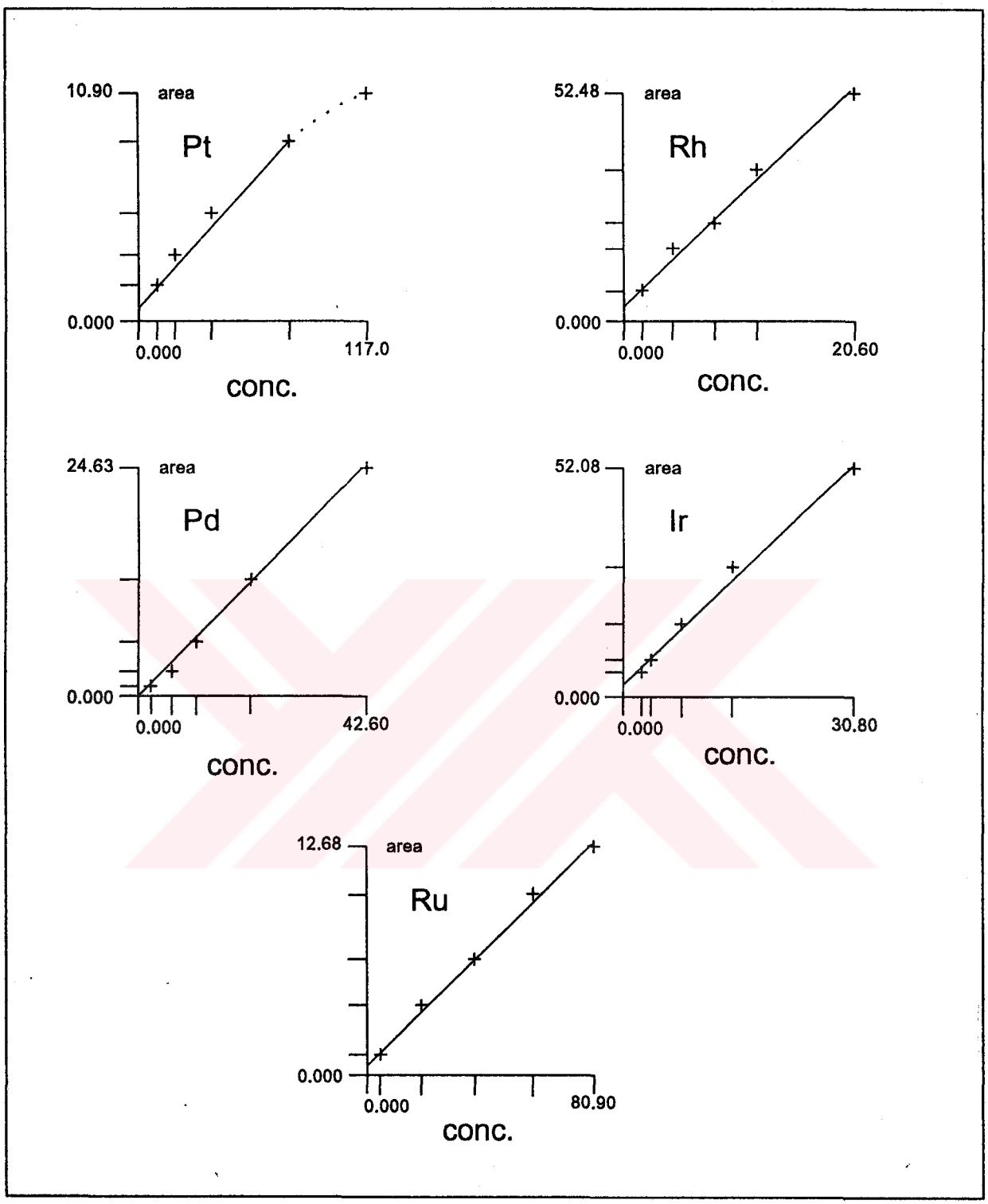


Figure 3.20. The Calibration Curves of Metal Chelates With DEBT

and approximately 15 % loss was observed in each 24 hours (Figure 3.21). Due to loss of color areas, all chromatograms were scanned during one hour after development with solvent.

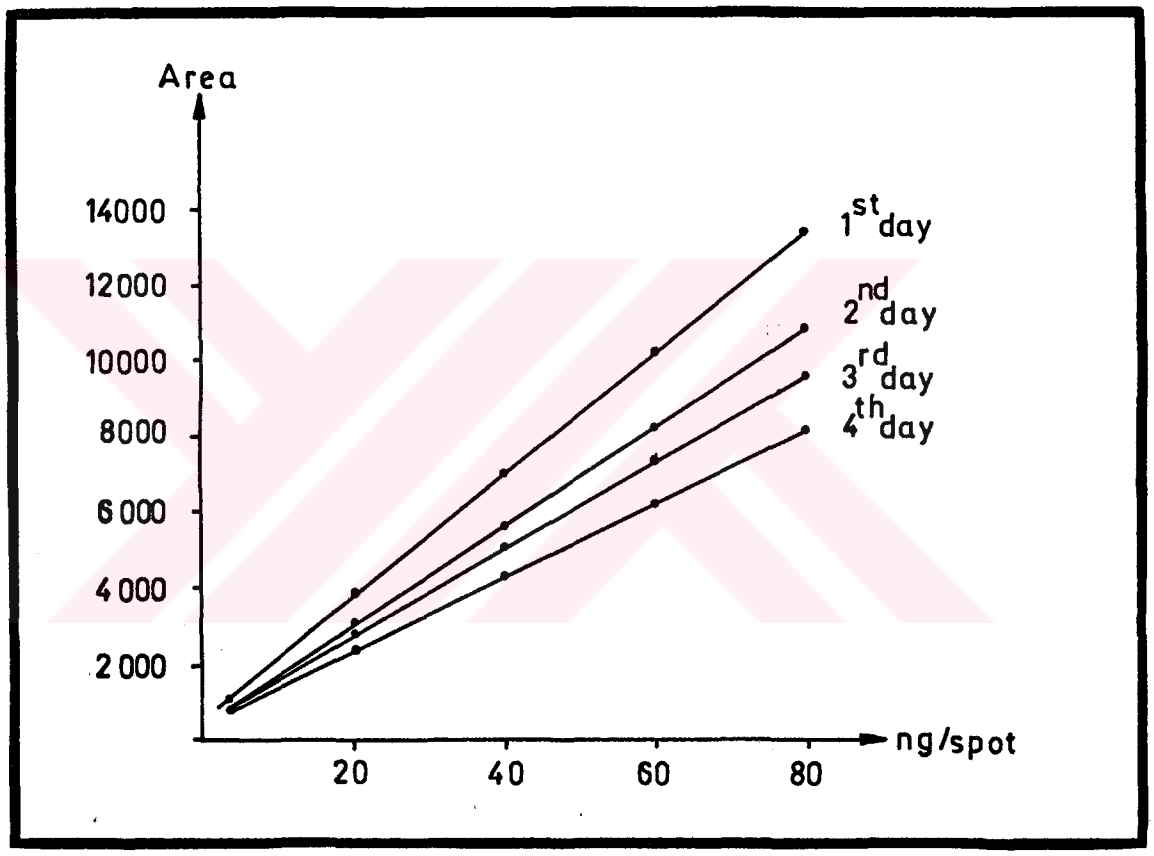


Figure 3.21. Time Effect on the Spot Intensity of the Ru(III) Chelate With DEBT

The precision of the whole procedure including the extraction and the chromatographic process under optimum conditions for each metal chelate was given by the reproducibility of the spot. The precision of the chromatographic method for 10 replicate measurements at levels of 7.8 ng/μL Pt, 2.1 ng/μL Pd,4.9 ng/μL Ru,1.6 ng/μL Rh and 2.3 ng/μL Ir which are the lowest concentrations could be used+ in the calibration curves, were given in Table 3.12. Detection limits for each element was calculated from the precision by taking 3s values as detection limit. The optimum experimental conditions used in chromatographic analysis were given in Table 3.13.

Table 3.13 Optimum Experimental Conditions for TLC Method for PGM Chelates With DEBT

Stationary Phase:	HPTLC-silica gel
Mobile Phase:	Benzene
Relative Humidity:	50 %
Development Run:	4 cm
Scanning λ:	280 nm
Scanning Type:	Zig-zag, Dualwavelength
Max. Time Duration After Development:	1 Hour

3.4. Determination and Verification of Metal Chelate Compositions

Most of the Pt catalysts are found as Pt-Re catalysts. In literature, there is no study about Re-DEBT chelate. Therefore, it would be an original study to prepare this chelate and confirm its composition. For this purpose, Re(IV)-DEBT chelate was studied besides the verification of the formulas of Pd(II) and Ru(III) chelates. These two were selected as representatives of metals with (+2) and (+3) oxidation states.

In literature, the composition of platinum DEBT-metal chelates has been determined potentiometrically [78]. Using Job's method of continuous variation and mole ratio method, the compositions were verified in this study. These metal chelates have two different compositions, that are 1:2 and 1:3, according to their oxidation state. Pd(II) for the metals having oxidation state (II) and Ru(III) for the metals having oxidation state (III) were chosen as examples.

The densitograms of the Pd(II) complex were given in Figure 3.22 a and b. The results obtained by Job's method of continuous variation and by the mole ratio method were illustrated in Figure 3.22 c and d and Figure 3.23, respectively.

In order to apply Job's method, the ligand and chelate should absorb at two different wavelengths which are not close

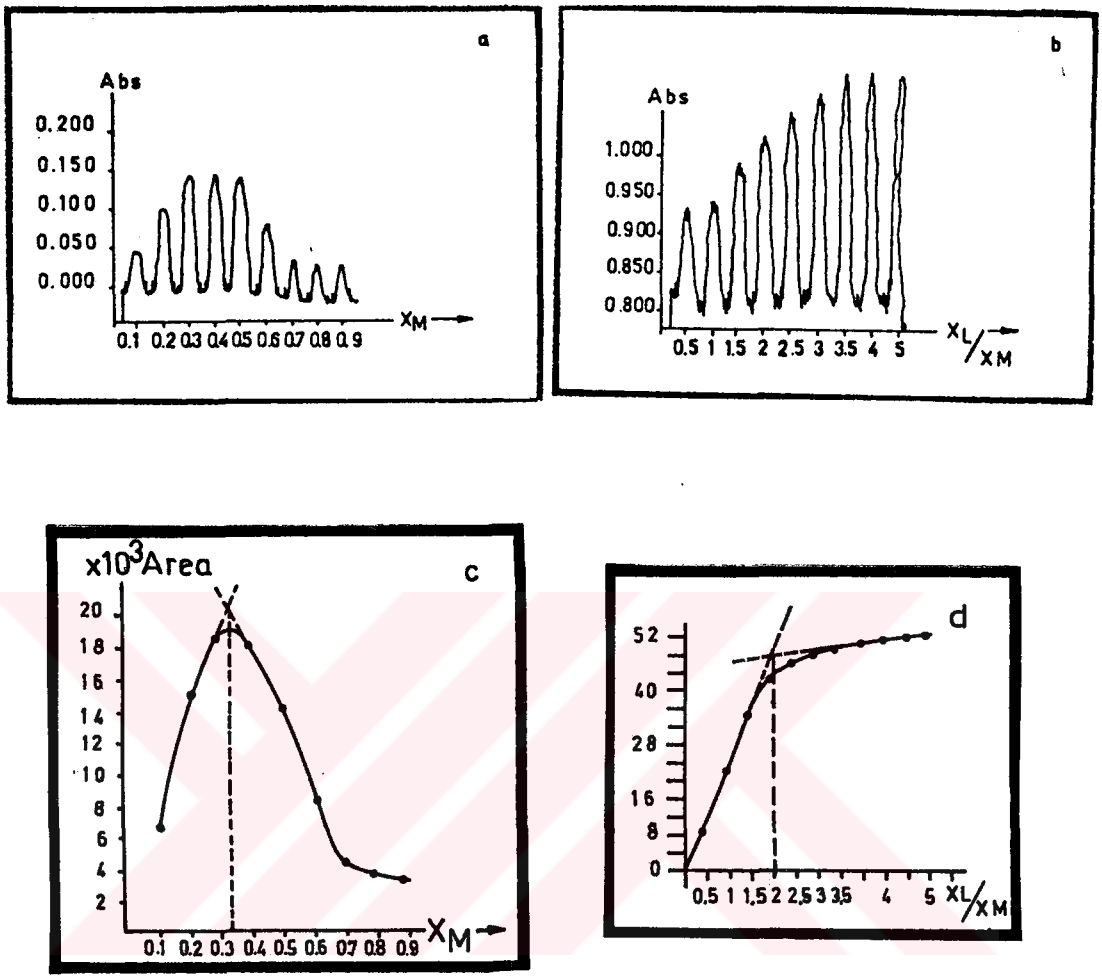


Figure 3.22. Composition Study for Pd(II)-DEBT Chelate

a) Densitogram About Job's Method

b) Densitogram About Mole Ratio Method

c) Job's Method Data for Pd(II) Chelate

d) Mole Ratio Method Data for Pd(II) Chelate

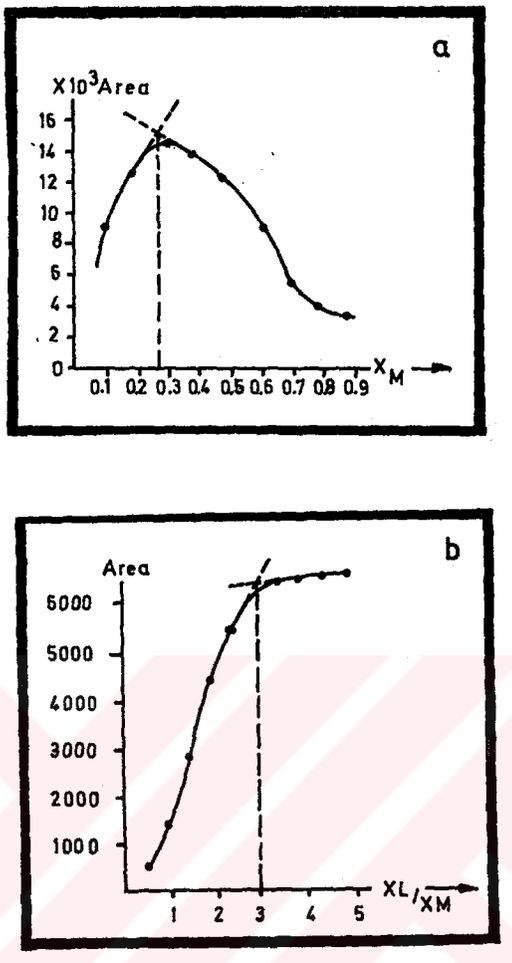


Figure 3.23. Composition Study for Ru(III)-DEBT Chelate

a) Job's Method Data for Ru(III) Chelate

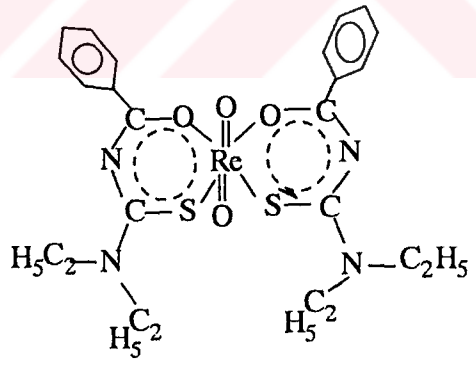
b) Mole Ratio Method Data for Ru(III) Chelate

to each other. Because of the closeness of maximum absorption bands of PGM chelates and DEBT, these two methods could not be applied spectrophotometrically. Since in chromatography, chelating agent and metal chelates had different migration distances, these methods had been studied easily by using

scanning densitometer. Both of the methods confirmed a ratio of 1:2 metal to ligand for the metals having oxidation state(II), like Pd and a ratio of 1:3 metal to ligand for the metals having oxidation state (III), like Ru.

These two methods were also applied to the chelate of Re(IV)-DEBT which does not exist in literature to determine the composition of the chelate. Both of the methods confirm a ratio of 1:2 metal to ligand in Re(IV)-DEBT chelate (Figure 3.24).

Depending on the structure of some Re(IV) chelates in literature [84], the structure of the metal chelate may be proposed as below. A further study for the establishment of the structure is needed.



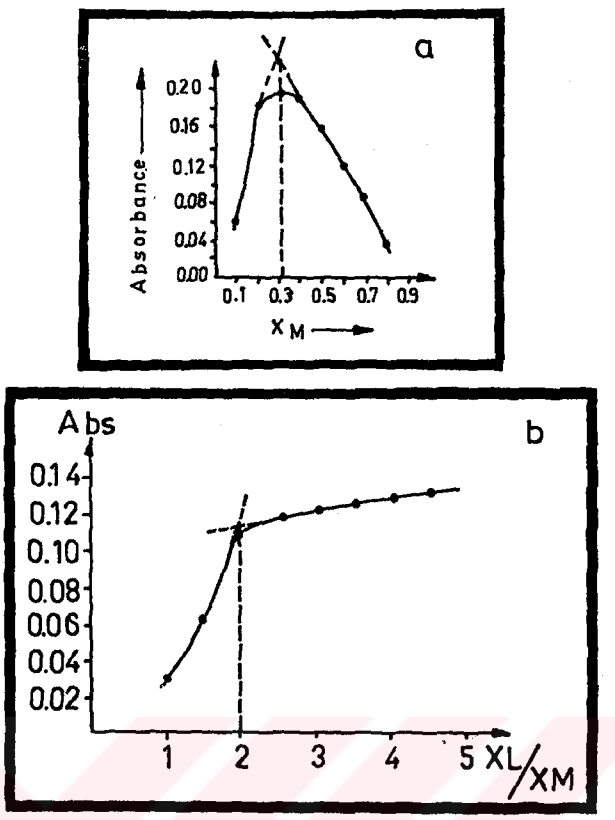


Figure 3.24. Composition Study for Re(IV)-DEBT Chelate
a) Job's Method Data for Re(IV) Chelate
b) Mole Ratio Method Data for Re(IV) Chelate

3.5- Analysis of Catalysts

3.5.1- Characterization of Catalyst Matrices

The informations about the supporting material, PGMs content and the contamination elements in all catalyst matrices used in the present study given in Section 2.5.1 were not exactly

known. Therefore, samples were investigated by XRD and XRF and OES analysis techniques.

3.5.1.1-Structural Characterization by XRD

Spectrometry

X-Ray diffraction spectrometry was used especially to determine the supporting material. For this purpose, the powder patterns of all catalyst samples were taken from 5 to 45 degrees (θ). The powder pattern of catalysts containing palladium were amorphous, therefore no peaks were observed. As an example XRD powder pattern of IGS is shown in Figure 3.25 and the others are given in Appendix D.

As a result of the detection of various phases of Al_2O_3 (16-394, 21-10, 29-63, 23-1009, index file number) and AlOOH in all samples except in Pt - sieve catalysts (TG1S and TG2S) and active carbon based catalysts (AC1 and AC2), the supporting material was determined as alumina. In Pt -sieve catalyst matrices, only platinum from the PGMs and iron were detected. In synthetic active-carbon based catalyst samples, only Pd, Pt and carbon peaks were observed [85]. Besides catalyst samples, XRD powder pattern of platinum, palladium and rhenium catalyst standards were also studied for comparison. In all samples and standards

except in Pd-standard, by XRD method, base metals and contamination elements could not be clearly detected because of the large amount of alumina.

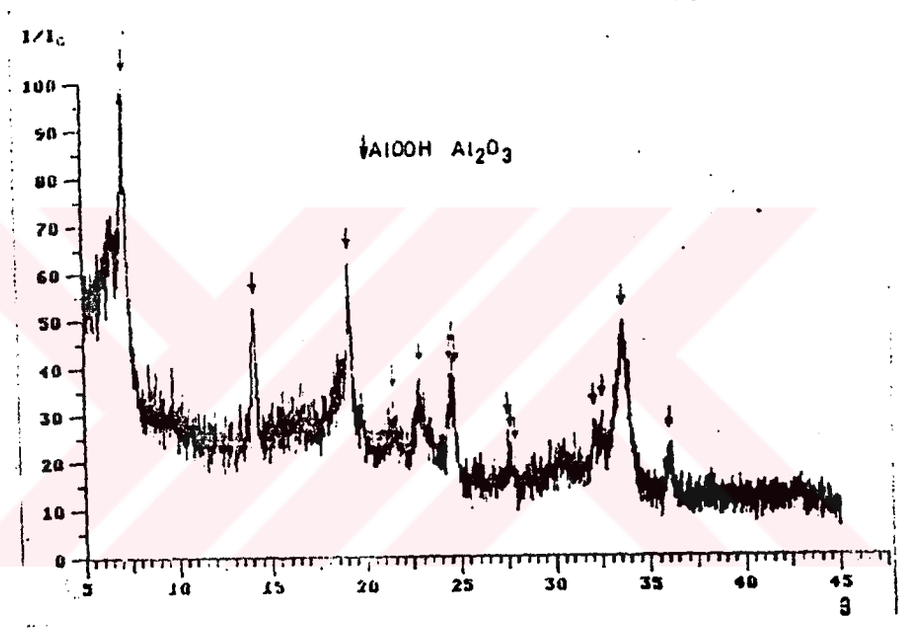


Figure 3.25. XRD Powder Pattern of IGS

Therefore, a more detailed qualitative and semiquantitative determination of PGMs, rhenium and contamination elements that were probably present in the catalysts was carried out by using XRF and OES.

3.5.1.2. Analysis of Chemical Compositions by XRF Spectrometry

All PGMs and rhenium were searched by XRF. The XRF spectra of alumina supported catalyst standards (platinum, palladium and rhenium) and all catalyst matrices except AT2S, AT3S and active carbon supported were obtained. The spectra of IGS and TG1S were given as examples in Figure 3.26 (a and b) and the others were given in Appendix E.

The compositions of all catalyst matrices are given in Table 3.14. Catalysts (AL2F and AL3F) named as Pd - catalysts, consist of only palladium. Pt - sieve catalyst matrices (TG1S and TG2S) were found to consist of much higher platinum than 0.5 % Pt and small amount of rhodium as the base metal and iron, copper, nickel and zinc as the contamination elements. Except Pt - sieve and alumina supported Pd catalysts, all other samples contain rhenium in varying amounts. Ruthenium, osmium and iridium were not found in catalysts. In spent catalysts, iron and copper were found as contamination elements. The spectra of standards showed that they have only the element of standard. Comparing the peak heights in the spectra to that of the calibration standards of platinum and palladium (0.5%, 0.25% and 0.125%) and rhenium catalyst (0.5% and 0.25%). The metal contents were roughly determined. Platinum and rhenium levels in spent catalysts were lower than the fresh ones. IGS had the lowest

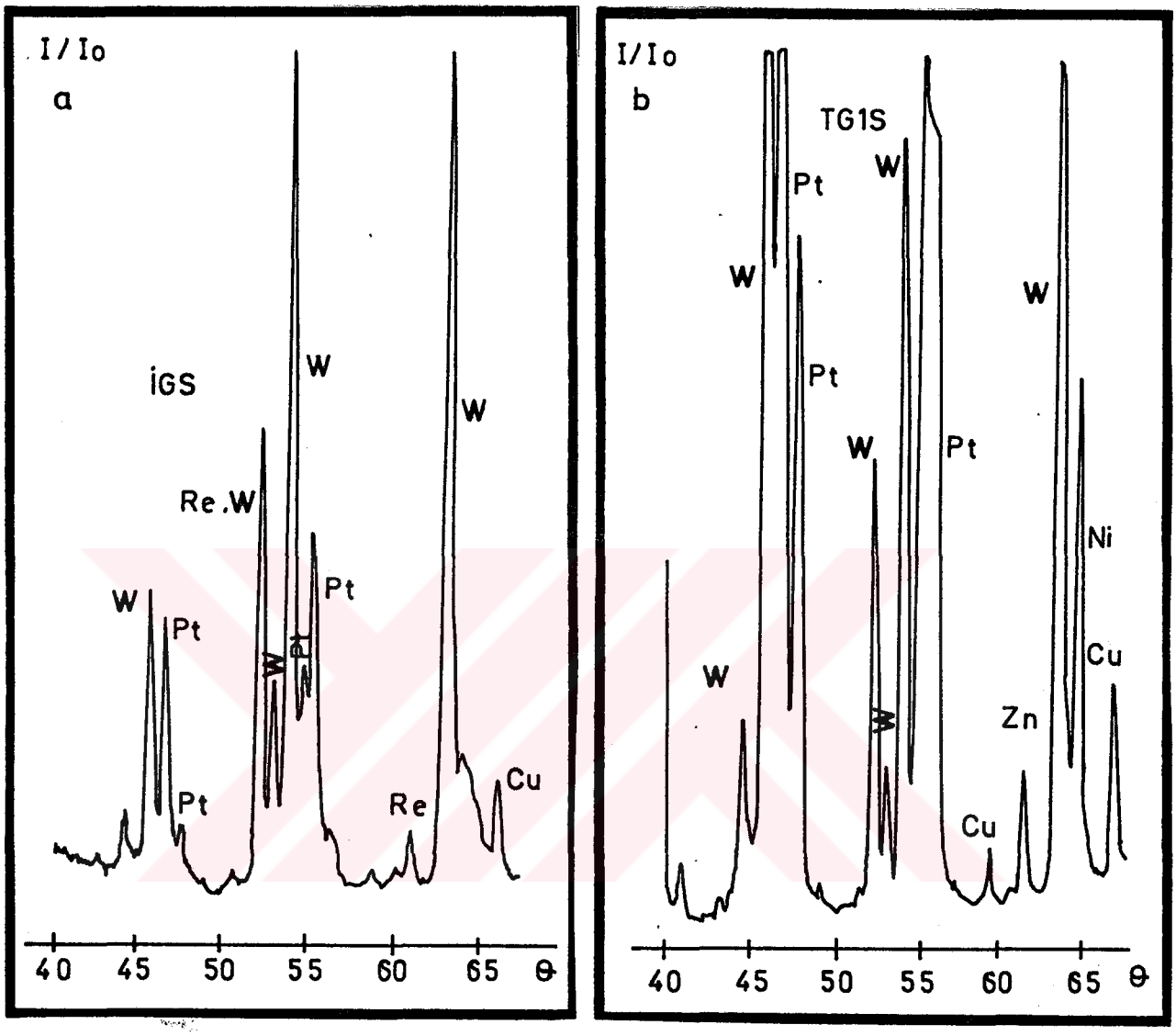


Figure 3.26. XRF Spectra of a) IGS b) TG1S

Table 3.14. The Compositions of Catalyst Matrices Determined By XRF Spectrometry (w/w%)

SAMPLE	Pt	Pd	Rh	Re	Fe	Cu	Ni	Zn
TUF	0.125-0.25	-	-	0.25-0.5	-	-	-	-
TU7R	0.125-0.25	-	-	0.25-0.5	-	-	-	-
TU9R	0.125-0.25	-	-	0.25-0.5	-	-	-	-
OAF	0.5-0.25	-	-	-	-	-	-	-
OA7R	0.5-0.25	-	-	-	+	+	-	-
AT1S	0.125-0.25	-	-	0.5-0.25	-	+	-	-
AT4S	0.125-0.25	-	-	0.5-0.25	-	+	-	-
AL1F	0.5-0.25	-	-	0.5-0.25	-	-	-	-
IGS	<0.125	-	-	<0.25	+	+	-	-
TG1S	>0.5	-	+	-	+	+	+	+
TG2S	>0.5	-	+	-	+	+	+	+
AL2F	-	<0.125	-	-	-	-	-	-
AL3F	-	<0.125	-	-	-	-	-	-

+: Present but values could not be determined due to lack of standards

content of Pt and Re which were lower than 0.125%. Pt - sieve samples (TG1S and TG2S) had the highest amount of Pt that was more than 0.5%. The platinum and rhenium content in the other matrices were between 0.25 - 0.5% respectively. As a summary, the sequences for the metal contents in the thirteen catalysts studied are given below:

Platinum Sequence: TG1S >> TG2S >>Pt 0.5% > OAF > OA7R > AL1F >Pt 0.25% >TUF > TU9R >TU7R >AT1S >AT4S >Pt 0.125% >IGS

Rhenium Sequence: Re 0.5% >TUF >TU7R >AT4S >AT1S >AL1F >TU9R >Re 0.25% >IGS

Palladium Sequence : Pd 0.125% >AL2F >AL3F

3.5.1.3. Semiquantitative Analysis For Contamination Elements By OES

Three kinds of sample with alumina supported and Pt-sieve catalysts (TG1S and TG2S) were selected as examples from the spent catalysts which would probably have contamination elements. The results were given in Table 3.15. The elements given in the table were the contaminants which had the concentrations above the detection limits. The highest

Table 3.15. The Contamination Percentage (w/w %) of Elements in Spent Catalysts Determined by OES

	Cr	Co	Ti	Cu	Mn	Ni	Mg	Ca	Fe	Si	Al
TG2S	>1	0.02	0.15	0.04	0.2	>1	0.04	0.1	10	>10	0.7
OA7R	0.02	-	0.07	-	-	0.01	-	-	0.15	0.15	>10
TU7R	0.02	-	0.07	0.15	0.03	-	-	-	~1	0.07	>10

contamination was observed in spent catalyst. The number and level of contaminant elements were lower in regenerated catalysts.

So, by these three methods, XRD, XRF and OES, sufficient information about supporting material, base metals and contamination elements generally found in catalyst matrices have been obtained.

3.5.2. Dissolution of Catalysts

The dissolution studies were carried out with both catalyst samples and available catalyst standards. Alumina supported platinum and palladium catalyst standards, palladium and platinum

- rhenium catalyst samples, Pt-sieve catalyst and synthetic active-carbon based catalysts were dissolved according to the procedures given in Section 2.5.4 and these methods were summarized at Table 3.16.

Table 3.16. Dissolution Methods Used for Catalyst Matrices

Samples	Dissolution Methods				
			Fusion		
	H_2SO_4 (1:1)	Aqua Regia	NaOH	$Na_2B_4O_7$	Na_2O_2 +Na_2CO_3
Alumina Supported Pt-Re, Pd	+	+			
AluminaSupported Pd, Pt, Std.	+	+			
Active Carbon Supported		+			
Pt-Sieve		+	+		
Alumina Supported Re Std.	-	-	-	+	+

All alumina supported catalysts and standards except Re-standard and also active-carbon synthetic catalysts were easily dissolved in aqua regia after removal of alumina support by H_2SO_4 treatment. On the other hand, platinum sieve samples (TG1S and TG2S) were dissolved only partially by leaching with

aqua regia. Then, sodium hydroxide basic flux was applied for insoluble part containing heavy metal oxides. In this way, the sample was completely taken into solution.

The procedures for dissolution of rhenium in Pt-Re catalysts given in literature were tested for the alumina supported Re-standard catalyst. It did not dissolve in H_2SO_4 : H_2O (1+1) solution, followed by 25% sodium formate dissolution [4]. As a second procedure, dissolution in 20% H_2O_2 and 30% NaOH by heating that is recommended in literature was tried [14]. Again it was not successful. Finally, it was dissolved completely by alkali fusion which was tried in two different ways as described in Section 2.5.4. In procedure 1, with Na_2O_2 and Na_2CO_3 mixture, rhenium in oxide form was oxidized probably to heptavalent state which is the highest oxidation state of Re, then complete dissolution took place [77]. In procedure 2, after several trials, with sodium tetraborate fusion the whole sample was taken into solution presumably without any change in oxidation state.

The percent dissolution of the samples in aqua regia were tested by filtering from gooch crucible and weighing the insoluble part. Results were given below.

TUF 100%	AT3S 100%	AT4S 100%	OAF 100%
OA7R 99%	TU7R 100%	TU9R 95%	AT1S 95%
AT2S 97%	AL1F 100%	AL2F 99%	AL3F 93%
IGS 99%	TG1S 59%	TG2S 23%	

As it was seen that TUF, TU7R, OAF, AT3S, AT4S, AL1F, IGS, AL2F and OA7R were completely dissolved in aqua regia and clear solutions were obtained. Alumina supported catalysts contain mostly acid-soluble γ-alumina but also rarely a little α-alumina and during the industrial process, γ-alumina can be converted to α-alumina at high temperatures which was acid insoluble as it was stated in Section 1.2. That was the reason why AL3F and AT1S, AT2S and TU9R could not be dissolved completely. The dissolution of Pt-sieve catalysts in aqua regia was low because they are spent catalysts (TG1S and TG2S), so they contain large amount of silica and heavy metal oxides. Synthetic active carbon based catalyst (AC1 and AC2) containing Pd and Pt were easily dissolved in aqua regia.

After the dissolution of PGMs on active carbon supported catalysts (AC1 and AC2), carbon powder remained in the filter papers were dried and weighed. The percentages of the insoluble carbon powder were found as 67.36 ± 0.08% for AC1 and 38.82 ± 0.07% for AC2. When these results were compared with the values reported by Heraeus Laboratory it was found that PGMs in these samples were almost dissolved completely. The percent error in the dissolution method was 0.3% and 0.2% for AC1and AC2, respectively.

3.5.3. Determinations of Pt, Pd and Rh in Catalyst Matrices

3.5.3.1. Analysis By AAS

Platinum group metals used extensively in catalytic systems in various industrial applications are often coated on alumina. The economical recovery of these metals largely depends on their accurate determination.

Totally seventeen samples were examined by atomic absorption spectrometry. Fourteen different samples contain platinum. Two of them are platinum sieves (TG1S and TG2S containing Pt (4-21%) and Rh (0.02-0.09%)) and eleven of them are Pt-Re alumina supported catalysts which have less or equal to 0.375% Pt and 0.375% Re. Also, two fresh alumina based-palladium catalyst matrices (AL2F and AL3F) are available and they have been reported to have approximately 0.1% Pd. From the two synthetic active carbon supported catalyst samples, AC1 contains only palladium (32.73%). During the study, one of the catalyst with active carbon support (AC2) has palladium and platinum (58.16% Pt and 3.39% Pd). The interference of Al existing in large amounts in alumina supported catalysts and the interference of one platinum group metal to another were to be controlled.

Lanthanum chloride salt is a common reagent in absorption spectrometry for controlling inter - element interferences in the determination of the platinum group metals. By the addition of lanthanum salt to the samples and the standards, suppression of the analyte signal because of Al and Pt in the determination of Pd and Rh is largely controlled [17, 24, 29]. By adding lanthanum to the solution containing these matrices, signal value is increased to a value very close to true result. Therefore, lanthanum chloride was used as buffer in this method in alumina-based Pt-Re, active carbon based Pt-Pd and Pt-Rh containing Pt-sieve catalyst matrices.

In the determination of Pd, in only palladium containing active carbon based catalyst (AC1) and in the determination of Pt, in the platinum sieve samples (TG1S and TG2S) and AC2, no buffer solution was added to the samples and the standards for the control of analyte signal. Because the interference of Rh which was in very low amount compared to Pt in TUGSAS samples and the effect of low amount Pd (0.3% in diluted sample solution) in AC2 would be negligible.

To evaluate the interference effect of Al on the alumina based catalyst, Pt on the Pt-sieve samples and Pt and Pd on the active carbon catalyst samples a series of test solutions were prepared from standard solutions, each containing one of Al, Pt and Pd contaminants at the concentration ranges that could be present in the final diluted sample solution (Table 3.17).

Table 3.17-Element Concentration Ranges in Interference Effect

Catalyst	Element Conc. mg/L	Inter Element Conc. Range, mg/L
Pt-Re alumina supported	Pt 40	Re 40 Al (0 - 5000)
Pd alumina supported	Pd 15	Al (0 - 5000)
Pt-sieve	Rh 4	Pt (0 - 500)
Active carbon supported	Pd 15	Pt (0 - 300)

Relative enhancement is defined as the observed value divided by true value of analyte signal. Therefore, a relative enhancement of 1.0 indicates no enhancement, 1.2 indicates a 20 % enhancement and 0.8, a 20 % suppression of analyte signal.

In the determination of alumina based catalysts, when

no buffer solution was added. The analyte signal decreased with increasing concentration of matrix element. The analyte signal was depressed down to 0.89 and 0.85 relative enhancement for Pt and Pd respectively (Figure 3.27 and 28) when Al concentration reached to its maximum value.

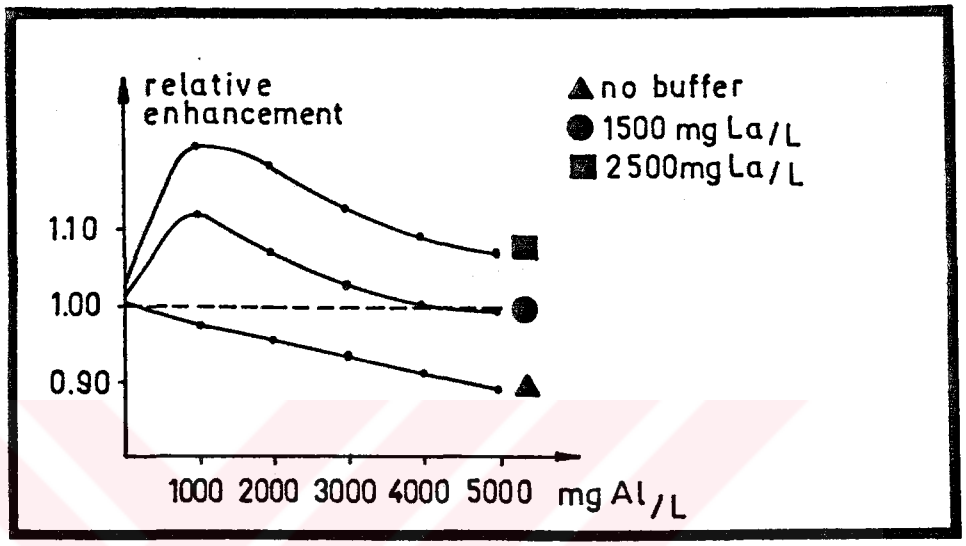


Figure 3.27. Effect of Al on Determination of Pt

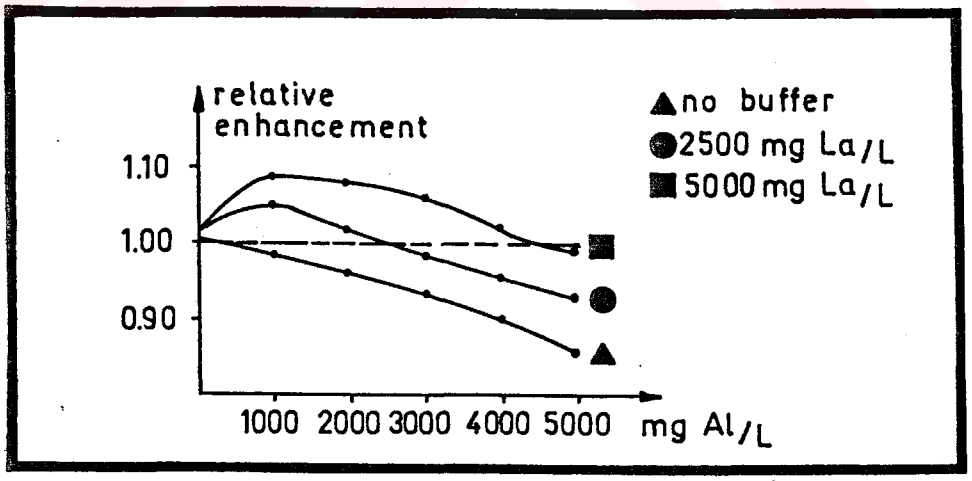


Figure 3.28. Effect of Al on Determination of Pd

The aluminum interference was examined by addition of 1500 and 2500 mg/L buffer solution for Pt and 2500 and 5000 mg/L for Pd, respectively. In the absence of aluminum, an increase in analyte signal was observed when the buffer was added. As it was seen from the figures, the possible aluminum matrix effect (5000 mg/L) could be controlled with 1500 mg/L for Pt and with 5000 mg/L for Pd in the determinations in alumina supported catalysts.

In Pt-sieve catalysts, the Pt-concentrations varying between 40-300 mg/L would create an interference effect in the determination of rhodium. Matrix effect of Pt in the range of 0-500 mg/L were studied in the presence of 1500 and 2500 mg/L buffer solution (Figure 3.29). Without buffer, the

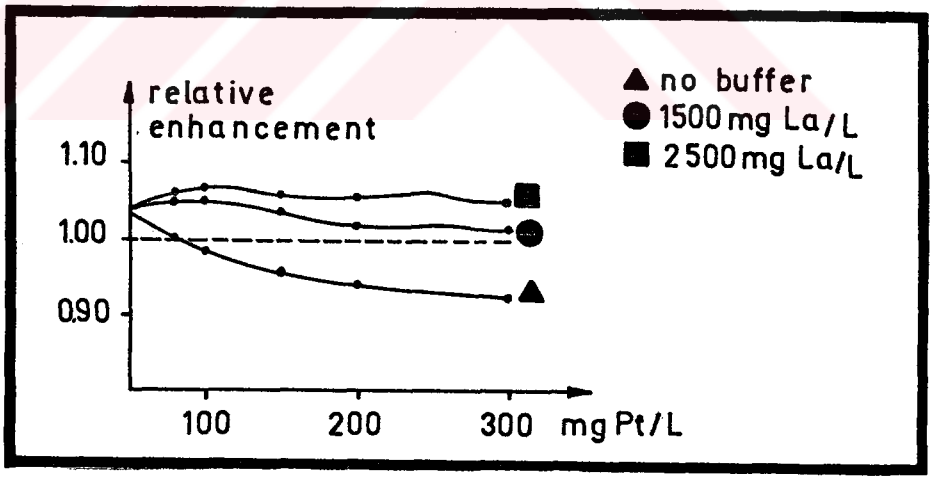


Figure 3.29. Effect of Pt on Determination of Rh

observed relative value was 0.92 at 300 mg/L matrix element. The addition of 1500 mg/L lanthanum salt overcame this suppression. In the presence of 40 mg/L matrix element which corresponded to samples in which Rh content was relatively high compared to Pt, (TG2S), it seemed that there was no need of addition buffer solution, because upon addition of buffer the enhancement in the analyte signal was higher than the required.

In the determination of Pd in AC2, the analyte signal became independent to matrix by the addition of 1500 mg/L lanthanum salt (Figure 3.30.).

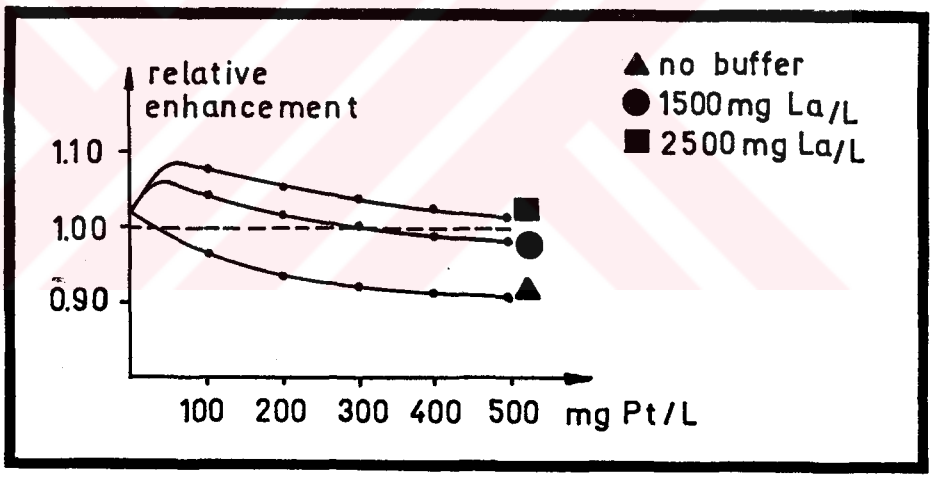


Figure 3.30. Effect of Pt on Determination of Pd

As the result of the studies for the matrix effects, 1500 mg/L buffer solution of lanthanum salt was used for Rh, Pt and Pd determinations in the Pt-sieve, Pt-Re alumina and active carbon

supported catalyst samples. Only, 5000 mg/L lanthanum solution was used for the analysis of Pd on alumina supported catalyst matrices.

The calibration curves of Pt, Pd and Rh, in the presence and absence of buffer were shown in Figures 3.31, 3.32 and 3.33 The range of correlation coefficients for the curves were 0.993-0.999. The data of calibration curves are summarized in Appendix F.

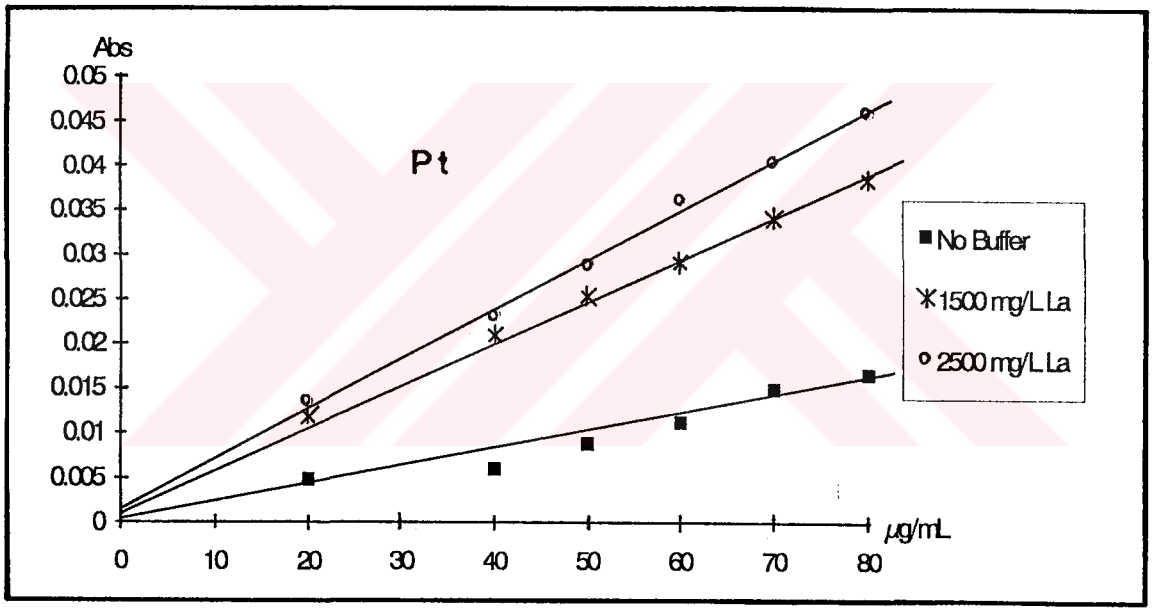


Figure 3.31. Calibration Curve of Pt in AAS Method

Palladium, platinum and rhodium determinations in catalyst samples were studied by three parallels from each of the catalyst samples using buffer of 1500 or 5000 mg/L lanthanum

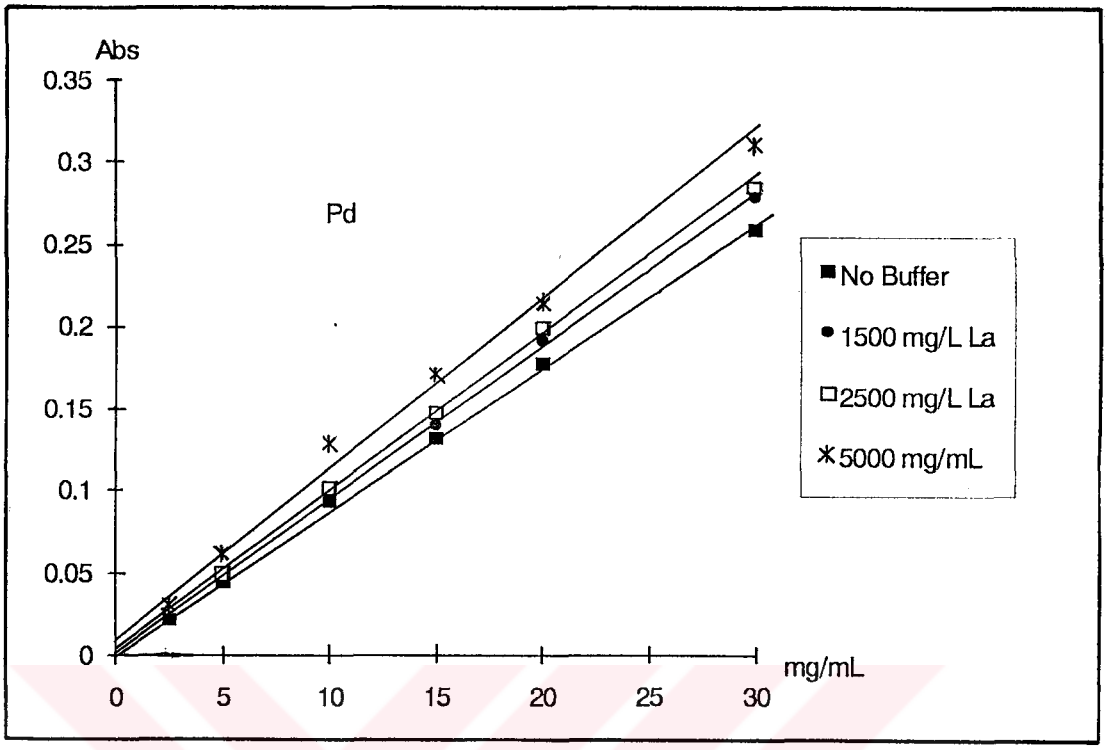


Figure 3.32. Calibration Curve of Pd in AAS Method

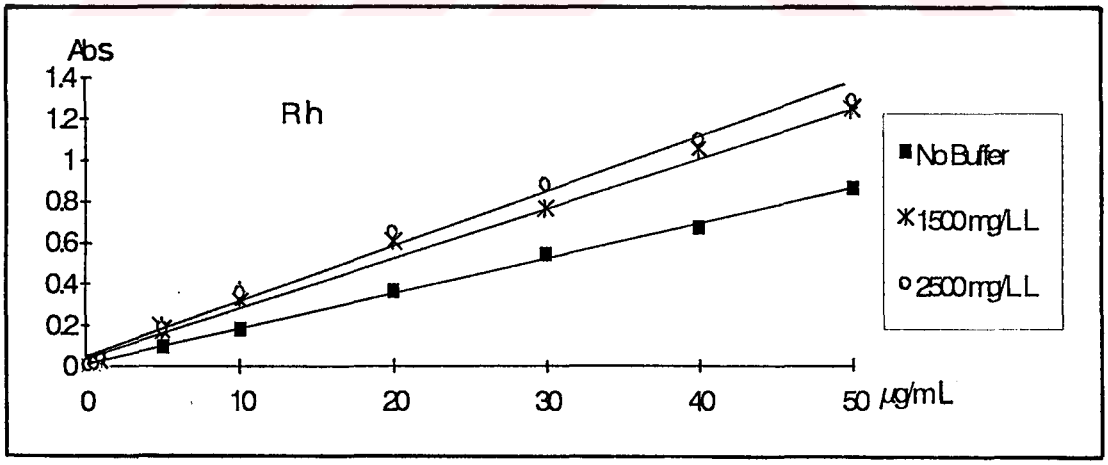


Figure 3.33. Calibration Curve of Rh in AAS Method

in calibration standards and in samples. By the addition of lanthanum, the relation between the analyte signal and analyte concentration becomes independent of the matrix.

The results of Pd, Pt and Rh values in all catalyst samples and precision of the method for each metal are reported in Table 3.18. The precision of the AAS method for the analysis of catalysts calculated as RSD % was in the range of 0.17 - 5.86 for Pt, 0.75 - 4.03 for Pd and 3.54 and 10.53 for Rh.

The precision of measurement for each metal was evaluated by 10 replicate measurements of the sample pool solution prepared by mixing randomly 10 different sample solutions. The data are presented as RSD % in Table 3.19.

Table 3.19- The Precision and Detection Limits of Pt, Pd and Rh with AAS Method (n=10)

Element	Precision		DL_{3s} (mg/L)
	2s(mg/L)	RSD %	
Pt	1.36	1.42	0.005 - 0.004
Pd	0.53	1.58	0.002 - 0.003
Rh	0.007	1.99	0.04

Table 3.18. The Data Set of Pt, Pd and Rh in Catalysts Obtained By AAS Method (n:3)

SAMPLE	$\overline{x} \pm s$, %(w/w)		
	Pt	Pd	Rh
TUF	0.32 ± 0.01	-	-
TU7R	0.26 ± 0.01	-	-
TU9R	0.25 ± 0.01	-	-
OAF	0.35 ± 0.01	-	-
OA7R	0.22 ± 0.01	-	-
AT1S	0.20 ± 0.01	-	-
AT2S	0.20 ± 0.01	-	-
AT3S	0.21 ± 0.01	-	-
AT4S	0.21 ± 0.01	-	-
AL1F	0.39 ± 0.01	-	-
AL2F	-	0.09 ± 0.01	-
AL3F	-	0.03 ± 0.01	-
IGS	0.10 ± 0.01	-	-
TG1S	19.39 ± 0.22	-	0.02 ± 0.01
TG2S	4.65 ± 0.05	-	0.06 ± 0.01
AC1	-	32.58 ± 0.21	-
AC2	57.68 ± 0.46	3.38 ± 0.03	-
Pd, std (1%)	-	0.96 ± 0.04	-
Pt, std(0.5%)	0.54 ± 0.01	-	-

The detection limit of each metal calculated by taking 10 replicate measurements of the blank and finding the corresponding concentrations of the 3s values.

3.5.3.2. Analysis By TLC

Platinum metals in catalysts whether fresh or spent have been determined by various spectrometric and electroanalytic techniques (Table 1.2). In most of these methods, the elimination of matrix effect of aluminum and interference of one platinum metal to another was a serious problem. Therefore, the application of thin layer chromatographic separation of metal chelates of PGMs seems to be very attractive, particularly for the simultaneous determination of trace metal ions. Quantitative evaluation of the amount of metal chelates separated on thin layers of adsorbent may be performed by various instrumental methods. Among these, scanning densitometry being a recent technique in TLC is the most rapid, reliable and powerful one for in situ measurements.

In this part of the study, the experiment with scanning densitometry for the determination of PGMs in catalyst samples were carried out with the metal-DEBT chelates which were prepared and their properties examined previously as explained in Sections 2.1.2, 2.3.2, 3.1.2 and 3.3.2.

To control the effect alumina support, that is the effect of Al on chromatographic process, 1 g Al_2O_3/50 mL stock solution was prepared by dissolving γ-Al_2O_3 with the same procedure used for alumina supported samples and Al-DEBT chelate was prepared according to the procedure given in Section 2.5.5.2. After application on plate, no spot was observed except the DEBT spot. The chromatogram and densitogram of Al(III) was shown in Figure 3.34. The result showed that aluminum did not react with DEBT to form a chelate. The precipitate obtained by the reaction of DEBT with aluminum in aqueous solution belonged to only chelating agent because DEBT was insoluble in water.

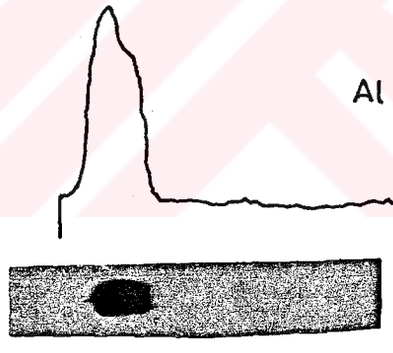


Figure 3.34. Chromatogram and Densitogram of Al(III)-DEBT Chelate

In the spent catalyst matrices, many contamination elements like Co, Cr, Mn, Ni, Cu, Fe, Ti, Si, Ca, and Mg were detected by XRF and OES. In literature, almost 20 metals were

studied with DEBT and within these metal chelates Cr, Mg, Ca, Ti and Si were not included. The presence of Cr, Mg, Ca, Ti and Si had no effect on separation of PGMs. In order to show that these metals do not form chelates with DEBT; their chelates were tried to be prepared under the same experimental conditions as PGMs. When chromatographic separations were run ,no spot was observed for chelates except for the DEBT spot. The reason of the precipitate obtained in these chelate formation studies was same as explained in Al-DEBT chelate study.

Among the others, Fe(III) and Cu(II) were the only contaminants that were precipitated together with PGMs during complexation below pH 3. Other metals like Mn, Zn, Ni and Co could only be precipitated at higher pH values (near to neutral region) [70]. Iron and copper interferences were eliminated by adding 3M hot H_2SO_4 after complexation and good stirring. So that the interfering chelates were decomposed and platinum metal chelates were distinctly separated from all contaminants [67].

A solution of 500 mg/L Fe(III) and Cu(II) ions was reacted with DEBT, then 2 mL of 3M hot H_2SO_4 was added and stirred. Finally, 1 µL of chloroform extract was applied to plate. The chromatogram and densitogram of Fe and Cu chelates were given in Figure 3.35.

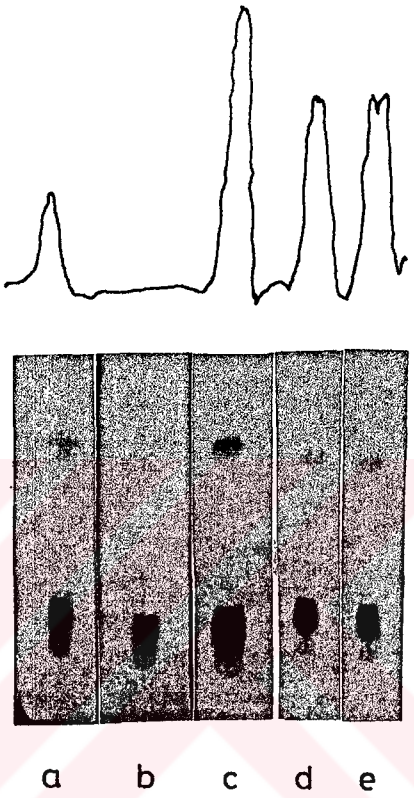


Figure 3.35. Chromatogram and Densitogram of

a) Fe and Cu Chelates

b) Fe and Cu Chelates After H_2SO_4 Addition

c) Fe, Cu, Pd and Pt Chelates

d) Fe, Cu, Pd and Pt Chelates After H_2SO_4 Addition

e) Pd and Pt Chelates

In the lane (a), Fe and Cu chelates were present. Fe chelate has no hR_f value due to its decomposition on silica gel plate, but Cu chelate has a good chromatographic behaviour and its hR_f value is 75. When hot H_2SO_4 was added to Fe and Cu chelates, no spot was seen at the hR_f value of Cu chelate (lane (b) in Figure 3.35). When 50 mg/L Pd and Pt were added to the solution of Fe and Cu, and the chromatographic process was repeated after forming their chelates, a spot belonging to Cu and PGM chelates were obtained (lane c). This was shown by the increase in the area compared to (a). The last step was repeated after H_2SO_4 treatment. The decrease in area in lane (d) support the decomposition of Cu-chelate. The resultant area obtained was almost the same as the area for 50 mg/L PGMs (lane e). Although the closeness of hR_f values of Cu, Pt and Pd chelates, by the addition of hot H_2SO_4, this problem was overcome.

Platinum in catalyst samples were oxidized to Pt(II) and mostly to Pt(IV) state after dissolving by aqua regia. However, in the optimization studies for chromatography in Section 2.3.2, Pt(II) solution was used for platinum. In literature, Pt(IV) solution was reacted with DEBT at 60-70 ^{0}C for complexation and at this temperature range, Pt(IV) was reduced to Pt(II) by excess chelating agent which acts as reductant [67]. To control the conversion of Pt(IV)-DEBT chelate to Pt(II)-DEBT chelate, three kinds of platinum solution in the same concentration were prepared;

i. from K_2PtCl_4 Pt(II),

ii. from alumina supported Pt catalyst which was dissolved by aqua regia following H_2SO_4 (1+1) solution leaching (Pt(IV)) with aluminum,

iii. from platinum wire leaching by aqua regia (Pt(IV) without aluminum).

All of them were reacted with DEBT and were injected to silica gel plate under the same experimental conditions. Their hR_f values are the same(Figure 3.36) and their peak areas are very close to each other. So, platinum in all catalysts were studied as Pt(II)-DEBT chelate, regardless the initial oxidation state of Pt.

Calibration curves of Pd, Pt and Rh were quite reproducible in terms of slope and linearity from plate to plate, but standards were always run in the same plate with samples to obviate the effects of any variations when using the method.

After the control of interferences of supporting material and contamination elements, all samples were analyzed with respect to the procedure given in Section 2.5.2. Hot 3 M H_2SO_4 solution was added only to spent catalyst samples to eliminate the Cu effect. Three parallels for each catalyst samples were run and precision of the method for each element was calculated.

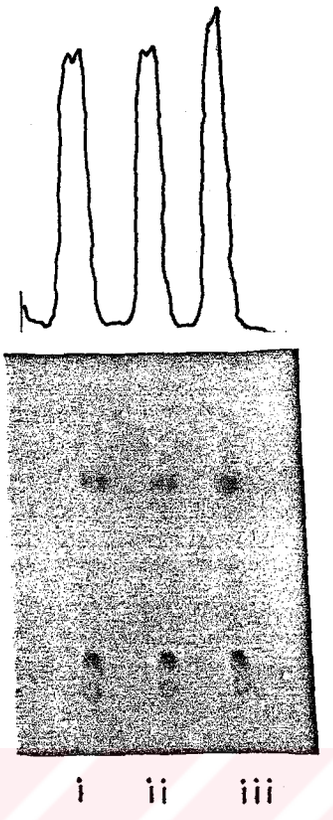


Figure 3.36. Chromatogram and Densitogram of Pt Chelates

i. from K_2PtCl_4

ii. from alumina supported Pt catalyst

iii. from platinum wire

The results are presented in Table 3.20. The precision of the method as RSD % was in the range of 0.38 - 7.08 for Pt, 0.69 - 3.22 for Pd and 4.48 and 7.45 for Rh.

All the values in percentages are in agreement with the expected values except AC2. Both the percentages of Pt and Pd in AC2 are higher than expected. The reason for this, the hR_f

Table 3.20. The Data Set of Pt, Pd and Rh in Catalysts Obtained By TLC Method (n:3)

SAMPLE	$\bar{x} \pm s$, %(w/w)		
	Pt	Pd	Rh
TUF	0.31 ± 0.01	-	-
TU7R	0.24 ± 0.01	-	-
TU9R	0.24 ± 0.01	-	-
OAF	0.35 ± 0.01	-	-
OA7R	0.22 ± 0.01	-	-
AT1S	0.21 ± 0.01	-	-
AT2S	0.20 ± 0.01	-	-
AT3S	0.21 ± 0.01	-	-
AT4S	0.22 ± 0.01	-	-
AL1F	0.39 ± 0.01	-	-
AL2F	-	0.09 ± 0.01	-
AL3F	-	0.03 ± 0.01	-
IGS	0.11 ± 0.01	-	-
TG1S	19.75 ± 0.08	-	0.02 ± 0.01
TG2S	4.76 ± 0.04	-	0.07 ± 0.01
AC1	-	32.77 ± 0.12	-
AC2	61.26 ± 0.46	4.08 ± 0.03	-
Pd, std (1%)	-	0.97 ± 0.02	-
Pt, std(0.5%)	0.54 ± 0.01	-	-

values of Pt and Pd are so close that their separation by spot application was not successful. Then the area obtained for Pt is the sum of the areas of Pt and Pd because Pd-chelate can be formed easily under experimental temperature of Pt-chelate at 40°C. Similarly, a certain contribution of Pt in the determination Pd could be expected even the formation of Pt-DEBT chelate were not favourable under the experimental conditions of Pd-chelate formation at room temperature.

CHAPTER IV

CONCLUSIONS

One of the aims of this study was to establish the TLC method as a new application technique for the determination of PGMs in platinum catalysts besides many electroanalytical and spectrophotometric methods which are commonly used in this field.

Among the most investigated chelating agents, DEBT was selected as the ligand for chromatography for metal chelates. Recently investigated DEBT was totally stable under normal conditions and therefore was handled without difficulties. It was an excellent reagent for pH-selective precipitation and extraction of metals and therefore it was qualified for liquid-liquid extraction of metal ions. It formed stable, crystalline chelates with metals, especially with PGMs.

Metal chelates, including chelates of PGMs and transition metals were formed easily and they were as stable as DEBT under normal conditions. The solubilities of metal chelates in

highly polar and nonpolar solvents were very low, but in medium polarity solvents, they dissolve easily. So, they were easily and highly extracted to organic layer of chloroform after precipitation in aqueous layer during complexation. They showed good chromatographic behaviour on silica gel plate with different solvents such as benzene, xylene, toluene and chloroform.

For the characterization of DEBT and PGM chelates, UV-visible absorption, IR, XRD, DTA and TLC analysis were used.

By IR analysis, the purification of PGM chelates was controlled with respect to the disappearance of the vibration bands of N-H and C=O bonds of DEBT in metal chelates. The similarities in the spectra of metal chelates also showed that they had similar structure.

Besides IR spectrometry, the powder patterns of PGM chelates obtained by XRD analysis showed that metal chelates were isostructural. The difference between the powder patterns of DEBT and metal chelates also supported the purity of metal chelates.

In UV-visible analysis, the absorption maximum of chelating agent remained either unchanged or suffered slight shifts in the complexes except Re(IV). The different spectra of Re-chelate was attributed to its different structure.

In addition, the investigation of thermal analysis showed that PGM chelates decomposed at two steps. But, the decomposition of DEBT was completed in one step. The decomposition curves of metal chelates were similar. The residual products were obtained as metal oxide and metal. The sharpness of melting point peaks of DEBT and metal chelates also strengthened their pureness. So, by all these methods, the purification of chelating agent and metal chelates were controlled besides their characterizations.

PGM chelates and Cu, Co chelates and DEBT had good chromatographic behaviour on silica gel plate with benzene, toluene, xylene and chloroform. By controlling the humidity with various percent H_2SO_4 solutions, high reproducibility for the retardation factor as 0.2% was obtained. The separation and simultaneous determination of Pt, Pd, Ru, Rh, Ir (PGMs) and Cu and Co was possible in the same mixture. However, in our chromatographic system, complete separation of Pt and Pd and determination of Cu in the presence of rhodium and ruthenium could be obtained. Because, these elements have very similar chromatographic properties and their separation with the spot sample applicator technique which was the one used in our system could not be possible. The problem with Cu was solved by removing Cu-chelate from the medium with hot H_2SO_4 treatment. For the separation of Pt from Pd, a better sample application system with an automatic sample applicator in line is required; because narrow-band sample application provides the

highest resolution. Also, optimum precision in densitometric chromatogram evaluation is achieved by this type of sample application. In this case, used sample application volume, utilizing TLC or HPTLC layers, is in the range of .1 - 20 µL and the band length is freely selectable.

The scanning of all spots in one lane using densitometer was possible at one wavelength because the spectra of metal chelates and DEBT contained very broad bands. In the quantitative analysis by scanning densitometry, for a more stable baseline, dualwavelength and for more sensitive and successful results, zig zag scanning were preferred. Because of the loss of color and therefore the change of composition of chelates, all chromatograms were scanned within one hour after development of the chromatogram with solvent. The calibration plots of PGM-DEBT chelates obtained were linear at working ranges with the correlation coefficients ranging between 0.997 and 0.999 when the linear regression was applied. The minimum detectable quantities (MDQ) which were the lowest concentrations corresponding to the smallest detectable peaks, were estimated for Pt, Pd, Rh, Ru and Ir as 7.8, 2.1, 4.9 1.6 and 2.3 ng/µL of solution, respectively. Detection limits for Pt, Pd, Rh, Ru and Ir calculated from the precision by taking 3s values, were 3.0, 0.3, 0.7, 1.2 and 0.5 ng, respectively.

The chemical formulas of Pd(II) and Ru(III) chelates as the representatives of PGMs with (+2) and (+3) oxidation states

which were determined potentiometrically in literature, were reestablished by Job's and mole ratio methods which were applied chromatographically as a new application of TLC-densitometry. Although rhenium is not a PGM, it is one of the base metals found in bimetallic platinum catalysts. So the composition of newly synthesized Re(IV)-DEBT chelate was determined and found as 1:2 by Job's and mole ratio methods, spectrophotometrically.

Platinum catalysts which are used in chemical, pharmaceutical, auto-exhaust and petrochemical industries, are found in two types; supported and unsupported. The supporting materials can be alumina, active carbon, silica or rarely calcium carbonate. The unsupported catalysts are found as sieve, metal powder, metal black and metal films. The platinum metals in spent catalysts must be recovered or recycled because of the limited supplies of PGMs in the world and the high increase in their consumptions. In order to recycle the active platinum catalysts, platinum metal content in the catalysts must be determined. In this study, fresh and spent catalyst samples were studied. Their supporting material was determined by XRD analysis, the base metals and the contamination elements in spent catalysts were determined by XRF and OES. In the catalyst samples studied, active carbon and alumina were the supporting material. Pt, Pd, Rh and Re were determined as base metals and Fe, Cu, Co, Ni, Cr, Si, Mn, Mg, Ca and Ti as the contamination elements.

The dissolution of alumina supported catalyst samples and standards except Re-standard were done by dissolving aqua regia following H_2SO_4 (1+1) solution leaching. Pt-sieve catalysts were completely dissolved by aqua regia and NaOH fusion. The dissolution of alumina based Re standard was accomplished by either $Na_2B_4O_7$ fusion or Na_2O_2+Na_2CO_3 fusion. Active carbon supported catalyst samples were dissolved easily by aqua regia.

In the determination of platinum metals in catalyst, the proposed method of TLC was compared with AAS method that is the conventional method for trace metal analysis. The interference effect of aluminum and one platinum metal to another must be controlled in AAS method. For this, lanthanum chloride as buffer solution were added to standard and sample solutions. However, in TLC method, the presence of aluminum in any concentrations was not a problem because it did not form a complex with DEBT. The presence of more than one platinum metals did not also affect the results because PGM-DEBT chelates have different hR_f values. Apart, only the effect of Fe and Cu as contamination elements were controlled by adding hot H_2SO_4 solution because they form chelates with DEBT at highly acidic medium as PGMs. The contamination elements of Co, Mn, Ni and Zn could only form chelates above pH 5. The other possible contaminants did not form chelate with DEBT.

The main objective of this study was to propose TLC-

densitometry as a method for the determination of PGMs in catalyst samples. In order to support this idea the precision and accuracy of the system were determined and compared with that of obtained by AAS. When the RSD values of measurements for each element in both of two methods were compared, no significant difference was seen as shown in Table 4.1. The comparison of accuracies of two methods using catalyst standards for Pt, Pd and Re with alumina support and calibration standards for Pt-Pd and Pd with active carbon support (AC1 and AC2) was given in Table 4.2.

Table 4.1- The Comparison of Precision of TLC Method With AAS Method

ELEMENT	PRECISION (RSD %)	
	TLC	AAS
Pt	0.38 ~ 7.08	0.17 ~ 5.86
Pd	0.32 ~ 3.22	0.75 ~ 4.03
Rh	4.48 ~ 7.45	3.54 ~ 10.53

The comparison of the results of Pt, Pd and Rh determined by TLC and AAS method showed that there was no significant difference between the results except AC2. The reason of this difference as explained before, is that the separation of the spots of Pt and Pd chelates of which hR_f values are very close

Table 4.2- The Comparison of Accuracy of TLC Method With AAS Method

ELEMENT	Pt (%) Exp. Result (Given Values)*		Pd (%) Exp. Result (Given Values)*	
	AAS	TLC	AAS	TLC
Pt - alumina Supported	0.54 ± 0.02	0.54 ± 0.02		
Standard	0.5	0.5		
Pd - alumina Supported			0.96 ± 0.07	0.97 ± 0.04
Standard			1	1
AC1			32.58 ± 0.42	32.77 ± 0.23
			32.73	32.73
AC2	57.68 ± 0.92	61.26 ± 0.92	3.38 ± 0.06	4.08 ± 0.06
	58.16	58.16	3.39	3.39

*: Values provided by Aldrich Company

was not possible by spot sample application technique. In spite of the low difference in precision and accuracy of both of the methods, the TLC method has several advantages over the AAS method when the time of analysis, the consumption of chemicals and the simplicity of the methods are compared. The main

advantages of TLC over the other methods are due to simultaneous determination of metals and being interference free via the selective complexation of metals. It is believed that TLC method will become an alternative method against many spectrophotometric and electroanalytical techniques used in analytical chemistry.

In future work four objectives can be suggested.

The problem of unresolved Pt-Pd peaks can be solved if the instrument is equipped with automatic sample application in line. In this way, the reproducibilty of the measurements will be improved and with a better resolution a lower minimum detection will be obtained.

In the chromatographic system studied, the calibration data and working parameters can be stored, but the evaluation of a chromatographic run should be done daily, since it is not possible to store the experimental data. If a computer system for data collection is equipped with the system using the data file, more reproducible results can be obtained.

At the beginning of this study, it was also aimed to develop a method for the recovery of platinum group metals from spent catalysts. The enrichment of PGMs by extraction following the selective and easy chelate formation inspires that this can be

possible. However feasibility of the recovery process should be examined as an engineering problem, since plant feasibility and economical aspects would also be important.

Rhenium which is a distinct element investigated in this study, has some differences in its chelate structure and its chromatographic behaviour. As a near future study, it is aimed to examine its structure and thin layer chromatographic properties in more detail.

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APPENDICES

APPENDIX A

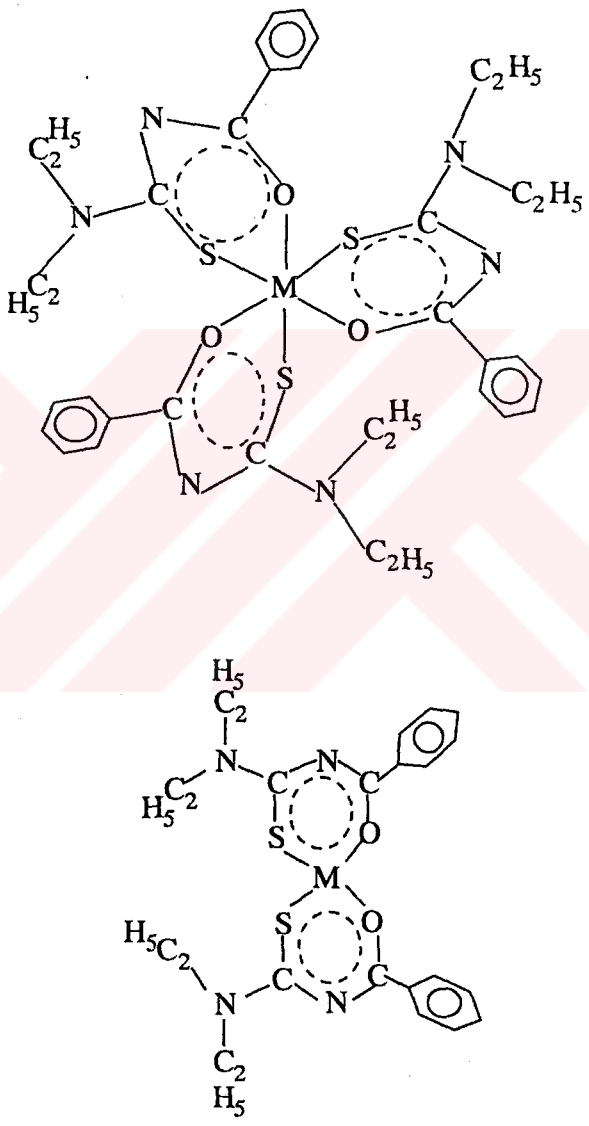


Figure A1. Molecular Structure of Metal Chelates

APPENDIX B

Table B.1. Solvent Extraction for Ir(III)

C_{HCl} (mol/L)	L:M	T (°C)	TIME (min)	Extraction Yield %
1	9.1	80	420	98
1	12:1	80	420	98
1	24.1	80	360	98
2	9:1	80	420	96
2	12:1	80	420	98
2	24:1	80	420	98

Table B.2- Solvent Extraction for Pt(II)

C_{HCl} (mol/L)	L:M	T (°C)	TIME (min)	Extraction Yield %
1	4:1	40	150	81
1	4:1	60	150	86
1	4:1	80	120	87
1	8:1	40	90	82
1	8:1	60	120	87
1	8:1	80	90	87
1	12:1	40	120	83
1	12:1	60	120	83
1	12:1	80	90	84
2	4:1	40	150	84
2	4.1	60	90	84
2	4:1	80	60	85
2	8:1	40	90	86
2	8:1	60	150	91

Table B.2- Solvent Extraction for Pt(II) (cont'd)

C_{HCl} (mol/L)	L:M	T (°C)	TIME (min)	Extraction Yield %
2	8:1	80	90	99
2	12:1	40	120	93
2	12:1	60	90	97
2	12:1	80	90	99
4	4:1	40	150	79
4	4.1	60	150	83
4	4:1	80	150	87
4	8:1	40	180	85
4	8:1	60	120	91
4	8:1	80	120	95
4	12.1	40	180	86
4	12:1	60	150	97
4	12:1	80	120	97

Table B.3- Solvent Extraction for Pd(II)

C_{HCl} (mol/L)	L:M	T (°C)	TIME (min)	Extraction Yield %
1	4:1	25	10	100
1	4:1	80	10	100
1	6:1	25	30	100
1	6:1	80	30	100
1	9:1	25	15	100
1	9.1	80	15	100
1	12:1	25	15	100
1	12:1	80	30	100
2	4:1	25	10	100
2	4:1	80	30	98
4	4:1	25	30	100
4	4:1	80	15	94

Table B.4- Solvent Extraction for Ru(III)

C_{HCl} (mol/L)	L:M	T (°C)	TIME (min)	Extraction Yield %
2	6:1	60	300	93
2	9:1	60	300	95
2	12:1	60	240	95
4	6:1	60	300	86
4	9:1	60	240	87
4	12:1	60	240	90
2	6:1	80	240	94
2	9:1	80	180	96
2	12:1	80	180	96
4	6.1	80	300	90
4	9:1	80	240	92
4	12:1	80	180	95

Table B.5- Solvent Extraction for Rh(III)

C_{HCl} (mol/L)	L:M	T (°C)	TIME (min)	Extraction Yield %
2	9.1	70	180	84
2	12:1	70	180	89
2	18:1	70	120	92
1	9:1	70	300	78
1	12:1	70	240	82
1	18:1	70	180	84
2	9:1	80	180	86
2	12:1	80	180	91
2	18:1	80	120	93
1	9:1	80	240	83
1	12.1	80	240	83
1	18:1	80	180	86

APPENDIX C

Table C.1.The Data of The Powder Pattern of DEBT

$[I] / [I_0]$ rel. Int.	θ	d [Å]
32.7	2.91	15.1674
100.0	5.82	7.5935
80.1	5.98	7.3829
4.5	7.65	5.7823
9.5	7.91	5.5966
65.6	8.77	5.0478
45.7	10.24	4.3312
3.2	10.54	4.2093
12.0	10.68	4.1531
5.5	10.82	4.1025
24.9	11.52	3.8564
5.6	11.78	3.7703
6.2	12.12	3.6681
6.4	13.26	3.3567
17.1	13.57	3.2812
14.2	13.72	3.2473
7.2	13.94	3.1965
6.4	15.78	2.8310
6.3	18.24	2.4605
7.9	18.72	2.3998
4.0	22.02	2.0543
6.4	22.40	2.0214

Table C.2. The Data of The Powder Pattern of $Pt(DEBT)_2$

$[I] / [I_0]$ rel. Int.	θ	d [Å]
100.0	4.16	10.6017
15.9	4.48	9.8421
62.8	4.96	8.8974
27.0	5.13	8.6092
33.7	5.74	7.6960
46.8	7.15	6.1840
16.3	7.64	5.7906
20.4	8.75	5.0605
12.2	9.45	4.6889
30.1	9.92	4.4704
12.0	10.13	4.3782
36.3	10.54	4.2093
20.8	11.06	4.0130
8.8	11.47	3.8711
14.0	12.23	3.6353
15.3	13.48	3.3024
4.7	14.46	3.0835
6.4	15.46	2.8885
17.5	17.87	2.5092
26.2	21.54	2.0976

Table C.3. The Data of The Powder Pattern of $Pd(DEBT)_2$

$[I]/[I_0]$ rel. Int.	θ	d [Å]
17.3	4.03	10.9516
44.5	4.50	9.8179
100.0	5.15	8.5722
8.7	5.94	7.4379
11.5	6.34	6.9707
9.0	6.74	6.5590
15.6	7.73	5.7245
9.2	8.10	5.4670
2.1	8.48	5.2182
17.1	8.80	5.0351
12.6	9.38	4.7219
36.2	9.93	4.4655
18.5	10.18	4.3546
7.9	11.04	4.0210
27.6	11.73	3.7879
2.6	12.75	3.4888
3.9	13.00	3.4243
5.9	13.56	3.2838
14.2	14.21	3.1377
14.0	14.97	2.9805
5.2	16.35	2.7355
6.7	16.77	2.6685
5.2	17.21	2.6033
4.2	17.54	2.5554
12.8	18.21	2.4648
6.9	21.08	2.1408
5.5	23.40	1.9396
5.7	23.91	1.9005
3.9	24.66	1.8457
4.0	27.53	1.6664

APPENDIX D

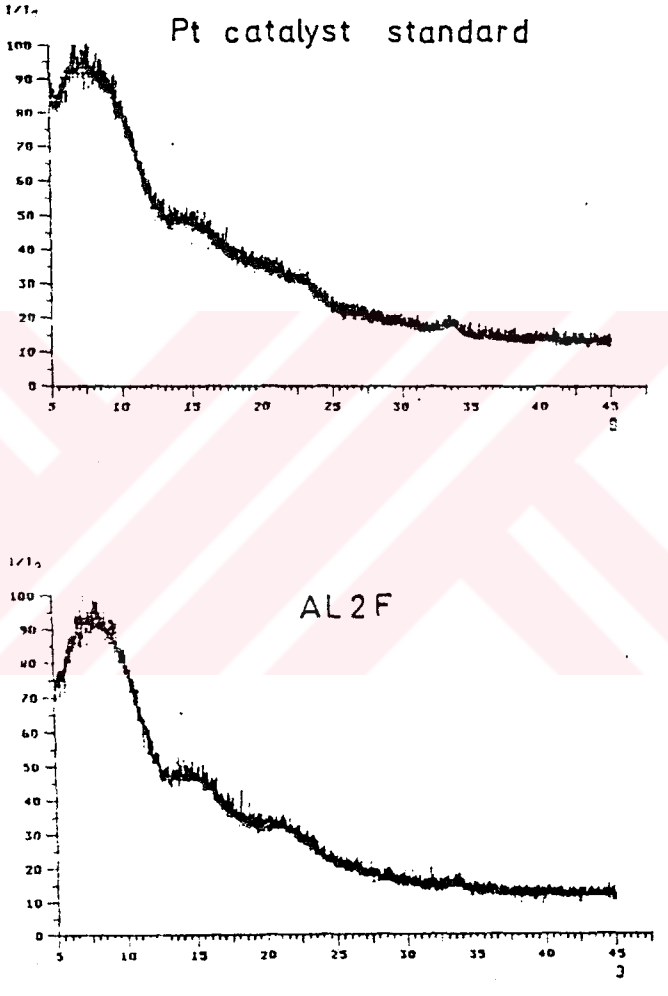
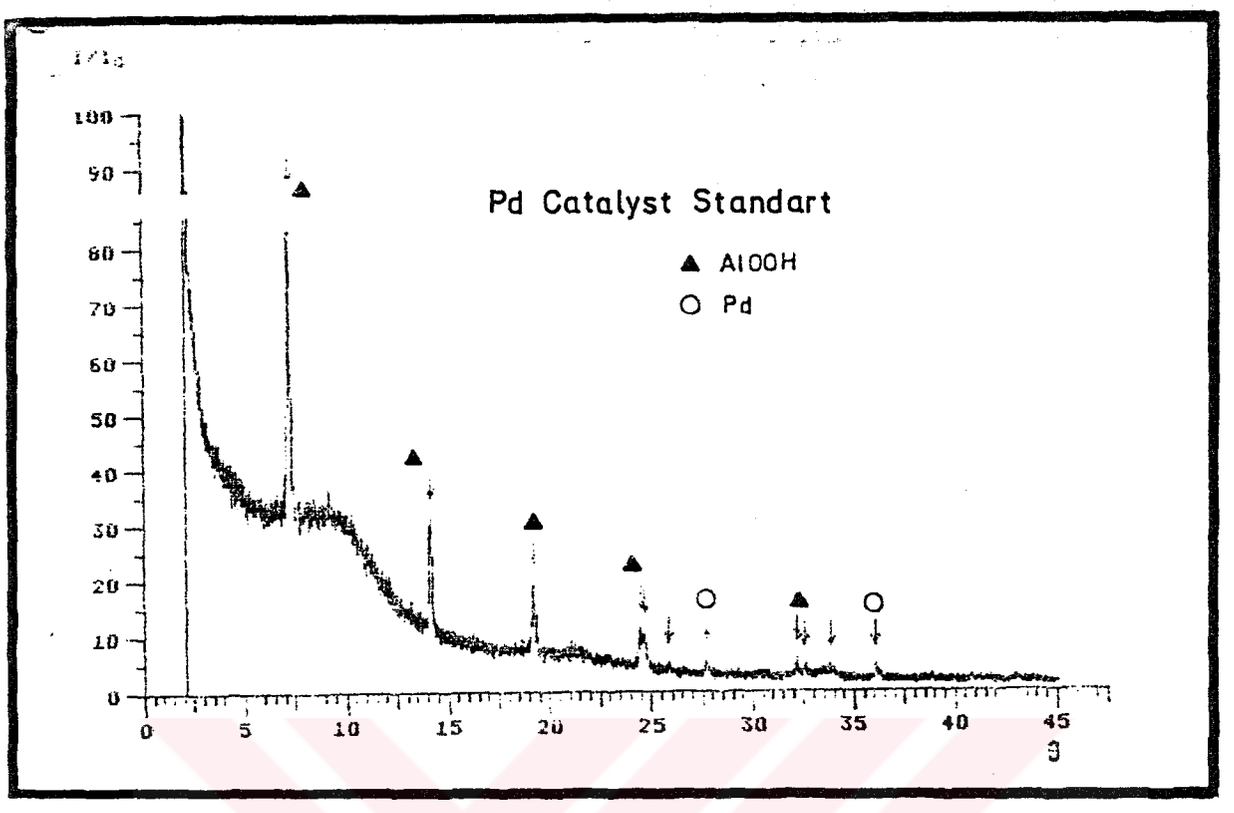


Figure D1. X-Ray Diffraction Powder Patterns of Catalysts Samples



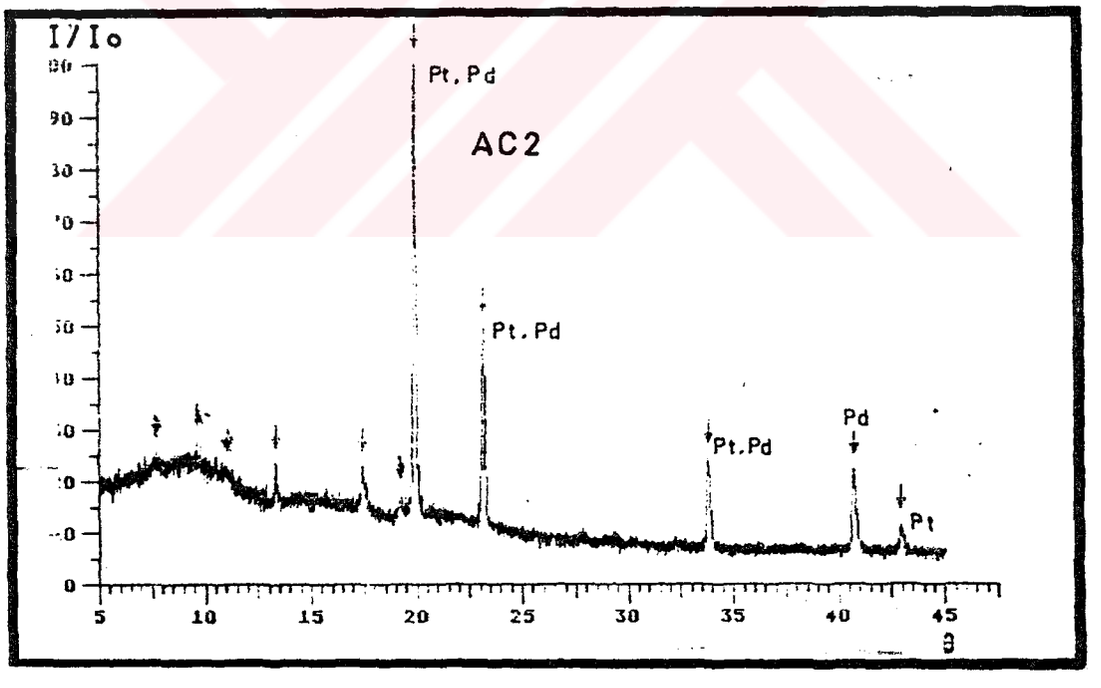
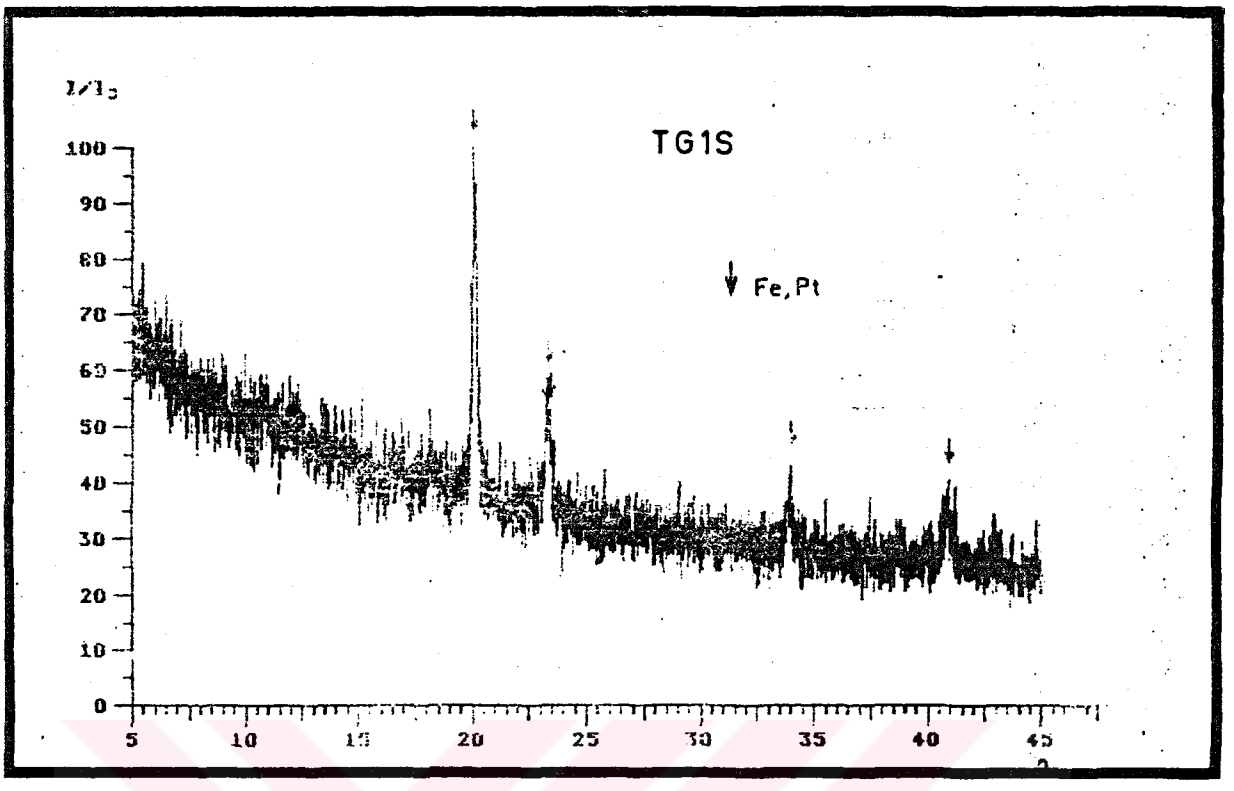


Figure D1. Continued



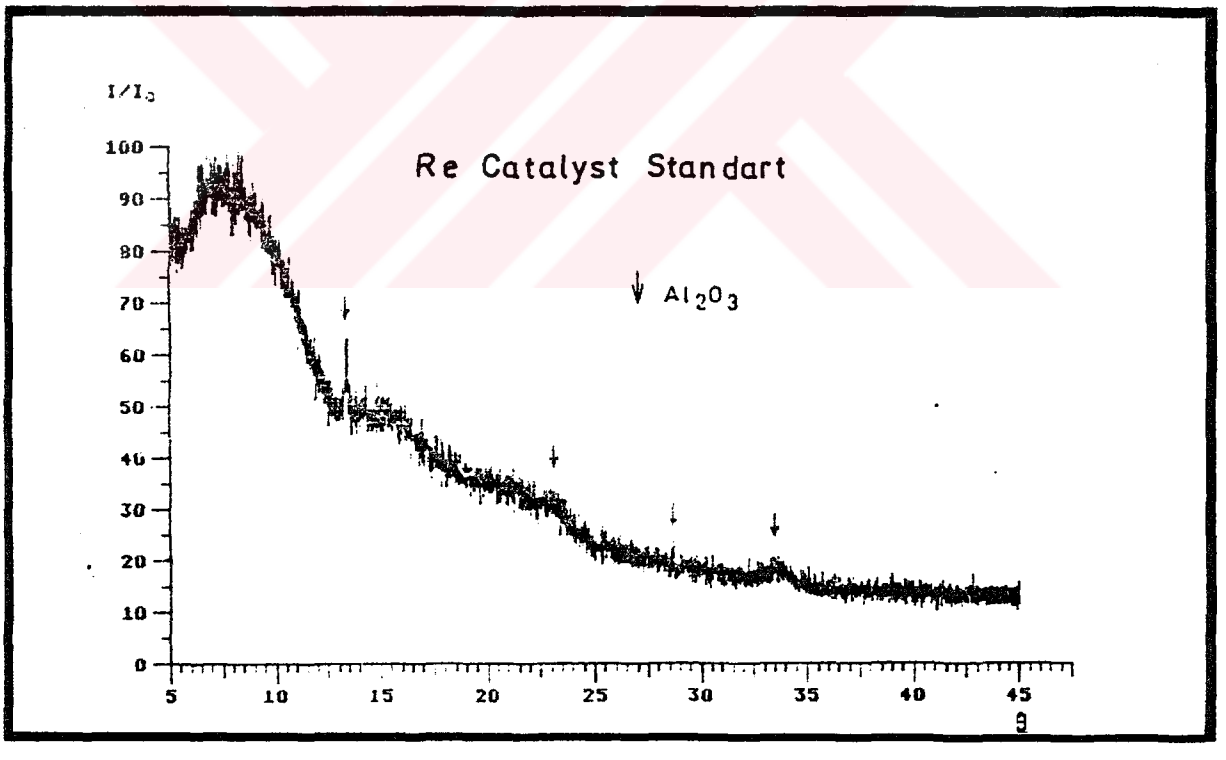


Figure D1. Continued

APPENDIX E

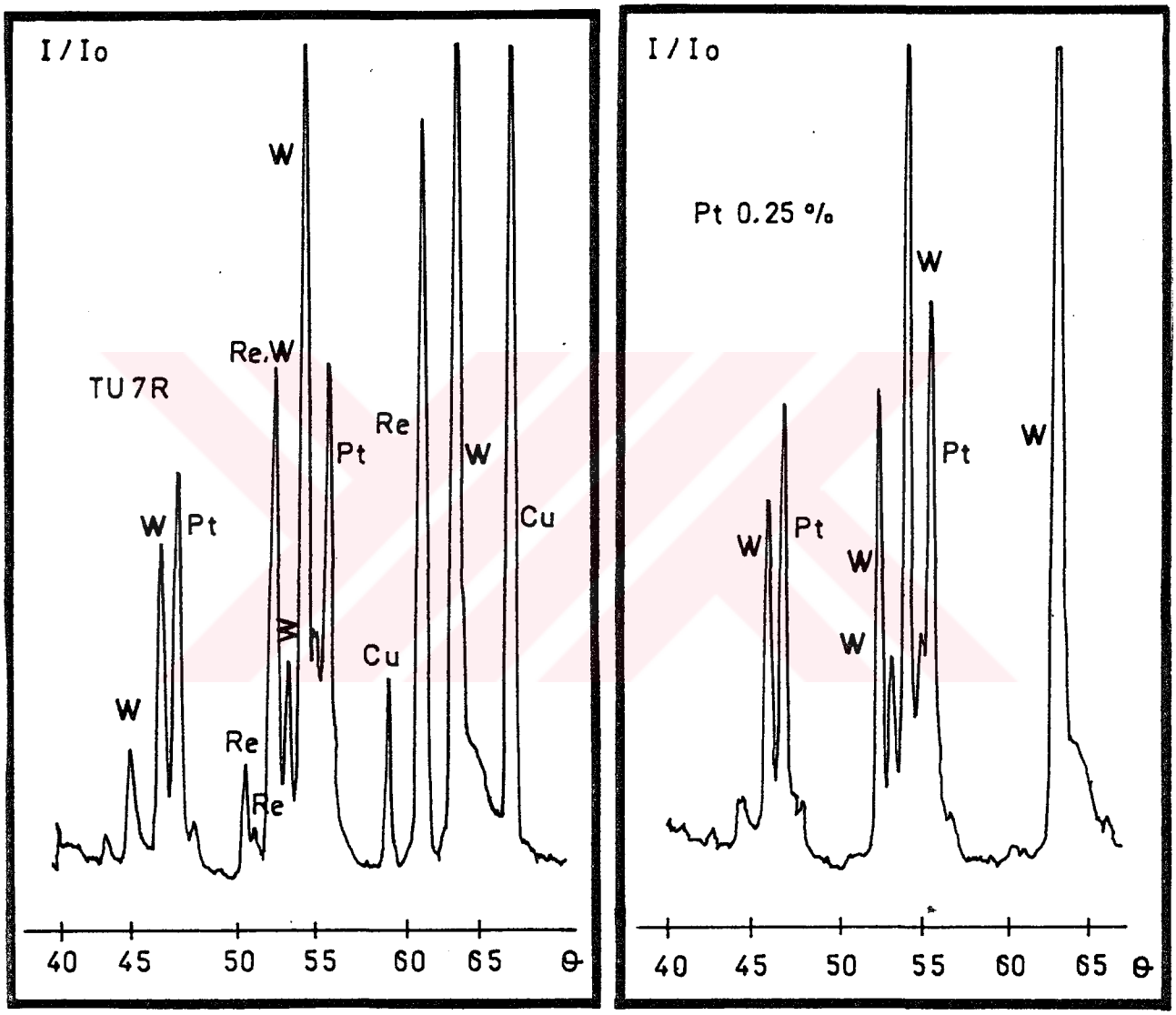


Figure E1. X-Ray Fluorescence Spectra of Catalsyst Samples

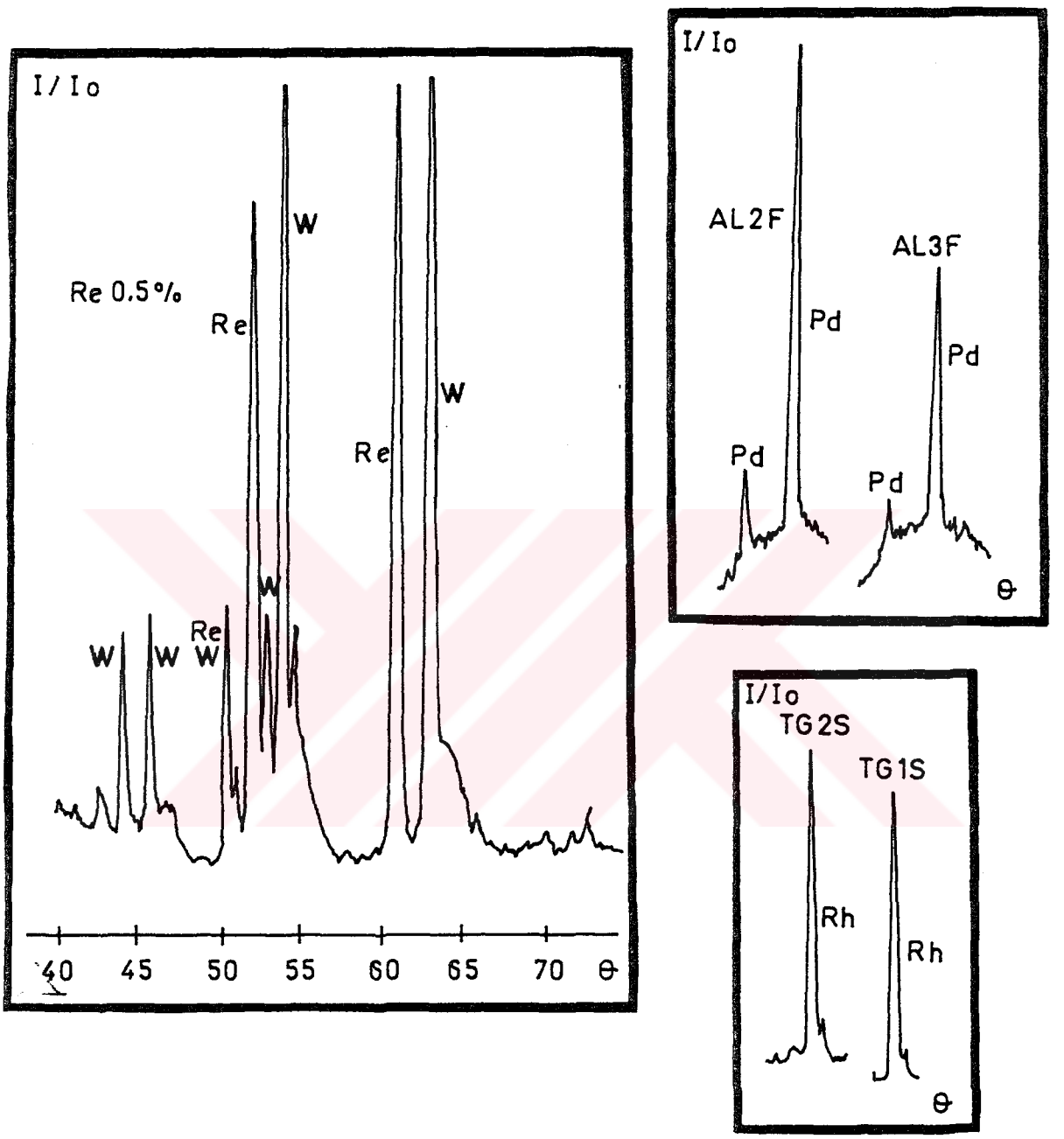


Figure E1. Continued

APPENDIX F

Table F.1. The Data Set For Calibration Curve of Rh

STANDARD NUMBER	CONC. GIVEN (mg/L)	CONCENTRATION FOUND, (mg/L)		
		No Buffer	1500 mg/L La	2500 mg/L La
1	0.1	0.06	-0.49	-0.13
2	0.5	0.21	0.3	0.3
3	1	0.74	0.8	0.85
4	5	5.01	5.79	5.32
5	10	9.43	11.53	11.63
6	20	20.38	22.92	22.88
7	30	31.09	29.16	31.7
8	40	38.92	40.63	40.14
9	50	50.17	48.56	47.42

Table F.2. The Data Set For Calibration Curve of Pt

STANDARD NUMBER	CONC. GIVEN (mg/L)	CONCENTRATION FOUND, (mg/L)		
		No Buffer	1500 mg/L La	2500 mg/L La
1	20	20.29	18.78	18.75
2	40	42.02	39.55	40.21
3	50	51.42	55.06	52.83
4	70	70.76	65.58	69.00
5	80	77.84	79.43	78.52
6	90	88.73	91.61	90.7

Table F.3. The Data Set For Calibration Curve of Pd

STANDARD NUMBER	CONC GIVEN (mg/L)	CONCENTRATION FOUND, (mg/L)			
		No Buffer	1500 mg/L La	2500 mg/L La	5000 mg/L La
1	2.5	2.41	2.77	2.62	1.56
2	5	5.02	4.56	5.23	4.68
3	10	10.74	10.41	10.19	11.32
4	15	14.85	15.07	15.41	15.58
5	20	20.43	20.61	20.33	19.87
6	30	29.95	30.03	30.02	29.49

Table F.4.The Data Set of Pt, Pd and Rh for Calibration Curves

		No buffer	1500 mg/L La	2500 mg/L La	5000 mg/L La
Pt	Corr. Coeff. (r)	0.997	0.998	0.993	0.997
Pd		0.998	0.999	0.997	
Rh		0.993	0.997	0.994	
Pt	Slope (m)	2.0E-4	4.5E-4	3.6E-4	1.6E-2
Pd		8.6E-3	9.3E-3	8.9E-3	
Rh		1.7E-2	2.5E-2	2.6E-2	
Pt	Intercept (n)	3.5E-4	4.9E-3	5.3E-3	1.0E-2
Pd		3.3E-3	1.5E-3	1.1E-3	
Rh		2.3E-2	4.3E-2	5.4E-2	

CURRICULUM VITAE

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Schools:	İstanbul, Özel Kadıköy Kız Lisesi (1973 - 1976)
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	M.S. in Organic Chemistry, İstanbul Technical University (1985 - 1987)
	Ph.D. in Analytical Chemistry, Middle East Technical University (1987 -1994)
Present Working Adress:	Since December 1989: Chemistry Department, Erciyes University, Kayseri, Turkey