

## Separation and Spectrophotometric Determination of Platinum (IV) in Natural Waters, Simulated Samples and Prepared Solid Complexes using 1- Phenyl-4-Ethylthiosemicarbazide.

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### Abstract

A very simple, highly sensitive and selective spectrophotometric procedure was developed for the determination of platinum(IV). It is based on the reaction at pH  $\approx$  3 between the synthesized 1-phenyl-4-ethyl thiosemicarbazide (HPETS) and Pt(IV) forming a green complex, Pt(IV): PETS (1:2), that floats quantitatively with oleic acid (HOL) surfactant. It exhibits higher absorbance at  $\approx$  715 nm in both aqueous and surfactant layers. Beer's law is obeyed up to the concentration  $0.39 \text{ mg L}^{-1}$  for a standard aqueous solution of Pt(IV). The molar absorptivities in aqueous and surfactant are  $0.14 \times 10^5$  and  $0.5 \times 10^5 \text{ mol L}^{-1} \text{ cm}^{-1}$ , respectively. It is observed that the molar absorptivity in surfactant layer is higher than that in aqueous. The different analytical parameters affecting the floatation and determination processes were examined. The proposed procedure has been successfully applied to the analysis of Pt(IV) in natural waters, prepared solid complexes and simulated samples. The results obtained agree well with those samples analyzed by atomic absorption spectrophotometry (AAS). Moreover the floatation mechanism is suggested based on some physical and chemical studies on the solid complexes isolated from aqueous and surfactant layers.

**Keywords:** Flotation; Platinum complexes; Spectrophotometric determination

### Introduction

Many industrial waste water streams contain heavy metals, which are of great environmental concern and must be removed prior to water discharge or water recycling<sup>[1,2]</sup>. Froth flotation is a separation method used for the beneficiation of a considerable portion of the world's mineral ores. Flotation is routinely used for the beneficiation of platinum for which the bulk of world production is from South Africa. Most South African platinum concentrators use mechanically agitated flotation cells. This is due to the general philosophy in the platinum industry that increasing power intensity increases the rate of flotation<sup>[3]</sup>. Numerous techniques exist for the separation and concentration of metal ions including evaporation of solvents, electrode position, liquid- liquid extraction, surface adsorption, precipitation and ion exchange.

Impregnated materials, immobilized reagents, electron- osmosis and flotation have been reported<sup>[4]</sup>. Although some of these techniques may be tedious, having

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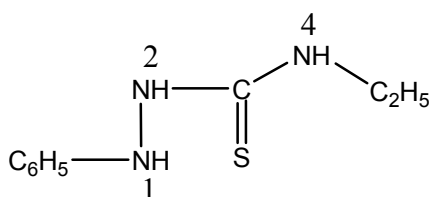
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limited concentration factors, lengthy and rigid conditions for the separation of solid adsorbents <sup>[5]</sup>, the flotation technique has many advantages that overcome these drawbacks. It has recently received considerable interest owing to its simplicity, rapidity, economy, good separation yields ( $R > 95\%$ ) for small impurity agent concentrations ( $10^{-6}$ - $10^{-2}$  mol L<sup>-1</sup>). A good prospect of application for species having different nature and structure, flexibility, friability of equipment and processing for recovery purpose <sup>[6]</sup> is established. It is believed that this process will soon be incorporated as a clean technology to treat water and waste water <sup>[7]</sup>. Moreover, flotation is suggested as a method for elimination of interferences <sup>[8]</sup>. Spectrophotometry still represents an attractive technique for the determination of metal ions in aqueous media because of its simplicity, being inexpensive and is readily available <sup>[9]</sup>. Therefore, spectrophotometry after selective flotation was chosen for this investigation. This paper is concerned with the investigation for the best conditions of Pt(IV) separation of by flotation technique followed by its spectrophotometric determination through a proposed procedure.

## Experimental

### *Material and reagents*

Unless otherwise stated, all chemicals used were of analytical reagent grade. Deionized water was used for preparing aqueous solutions. 1- Phenyl-4- ethyl thiosemicarbazide (structure 1) was synthesized as has been described elsewhere <sup>[10]</sup>. The purity was checked by elemental analysis and spectral studies. The product is easily soluble in ethanol; hence its stock solution ( $1.0 \times 10^{-5}$  mol L<sup>-1</sup>) was prepared. Oleic acid (HOL) stock solution ( $6.36 \times 10^{-2}$  mol L<sup>-1</sup>) was prepared by dispersing 20 ml of HOL (food grade with sp. gr. 0.895, provided by J.T. Baker Chemical Co.) in 1L of Kerosene. Platinum stock solution was prepared by dissolving the requisite amount of H<sub>2</sub>PtCl<sub>6</sub> in deionized water.



Structure 1

### *Sample collection and pretreatment*

One liter of tap or Seawater sample was filtered, the pH adjusted to  $\approx 1$  with concentrated HCl to prevent losses by sorption or coprecipitation, and preserved in high quality clean plastic containers.

### *Prepared solid complexes*

This procedure was applied on two synthetic complexes <sup>[11]</sup> after its elucidation by determining the metal ion by using standard methods <sup>[12]</sup> as well as AAS procedure and comparing with the proposed procedure.

#### *Simulated sample*

Four simulated samples were prepared as EAg<sub>5</sub>, EG<sub>2</sub>, EAg1000 and EG<sub>5</sub> <sup>[13,14]</sup>. These samples containing platinum at different concentrations after adjusting the pH of the sample solutions and Pt(IV) was floated and spectrophotometrically determined by the recommended procedure.

#### *Apparatus*

The flotation cell (a cylindrical tube with a 15 mm inner diameter and 290 mm length, a stopcock at the bottom and a stopper at the top) was the same type as previously described <sup>[15]</sup>. The spectral data were recorded on a UV/Vis-1601 Shimadzu spectrophotometer with personal spectroscopy software version 3.7, using 1 cm path length stopper quartz cuvettes. The pH was adjusted with HCl and / or NaOH and measured with a Metrohm 744 pH meter (Metrohm, Herisau, Switzerland).

#### *Separation Procedure*

All samples used in this investigation were in the form of aqueous solutions after suitable treatment. Therefore, the following procedure was applied to all samples. A suitable aliquot containing a known amount of Pt(IV), specified for each investigation, was mixed with a suitable amount of HPETS followed by the addition of 3 ml of deionized water. After adjusting with HCl and/or NaOH to the required pH, the solution was transferred to the flotation cell and the total volume was made up to 10 ml with an ethanol- water mixture to ensure a final ethanol volume fraction of 30 %.

The cell was shaken well for a few seconds to ensure complexation. To this, 3 ml of HOL (of known concentration) was added. The cell was then inverted upside down twenty times by hand. Bubbles were created inside the cell. Mean while, the stopper of the cell was removed to permit air movement, after that allowing it to stand for 5 min. After complete flotation of the colored complex, the concentration of Pt(IV) in the surfactant layer was determined spectrophotometrically.

#### *Measurement*

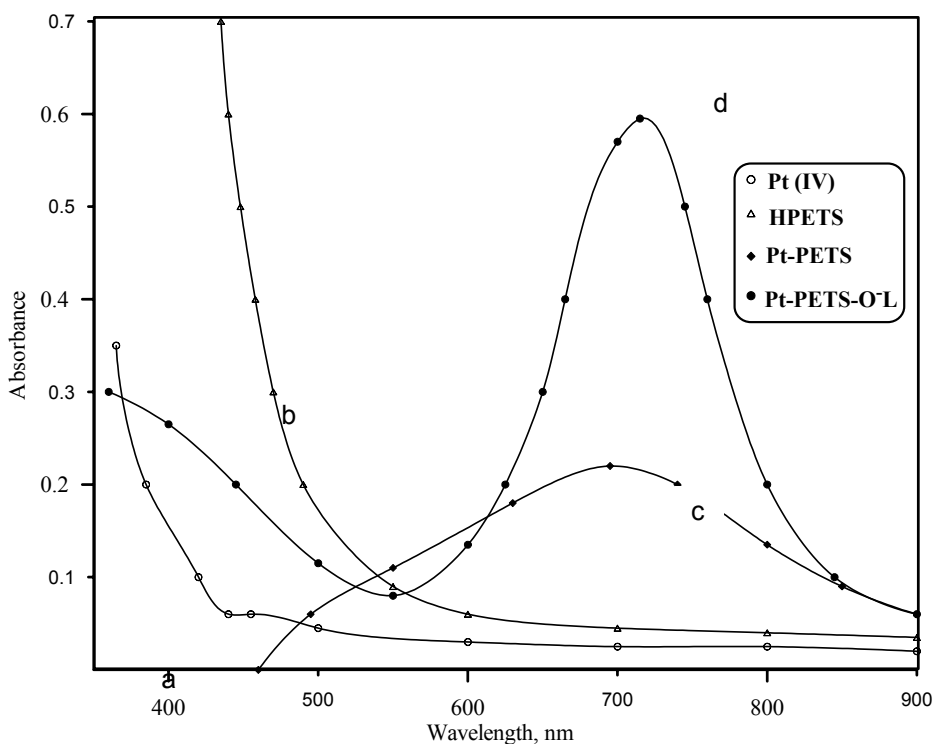
The concentration of Pt(IV) in the floated layer was determined spectrophotometrically by transferring a suitable volume to the quartz cell and measuring the absorbance at 715 nm against the reagent blank (HPETS). The analyte concentration was calculated from a calibration curve constructed by taking different concentrations of Pt(IV). The flotation efficiency (%F) was calculated from the relation: % F =  $C_s / C_i \times 100$ , where  $C_i$  and  $C_s$  denote the initial Pt(IV) concentration and its concentration in the surfactant layer, respectively. All the experiments were carried out at room temperature, (~ 25°C).

## Results and discussion

In order to obtain the optimum conditions for the maximum flotation efficiency of Pt(IV) with the HOL surfactant, the different factors affecting this process have been studied. It should be noted that maximum absorbance of the complex Pt-PETS corresponds to its maximum flotation efficiency. So, the maximum absorbance can be expressed by the maximum floatability of the analyte and the inverse is true, as well <sup>[9,16]</sup>.

### Absorption Spectra

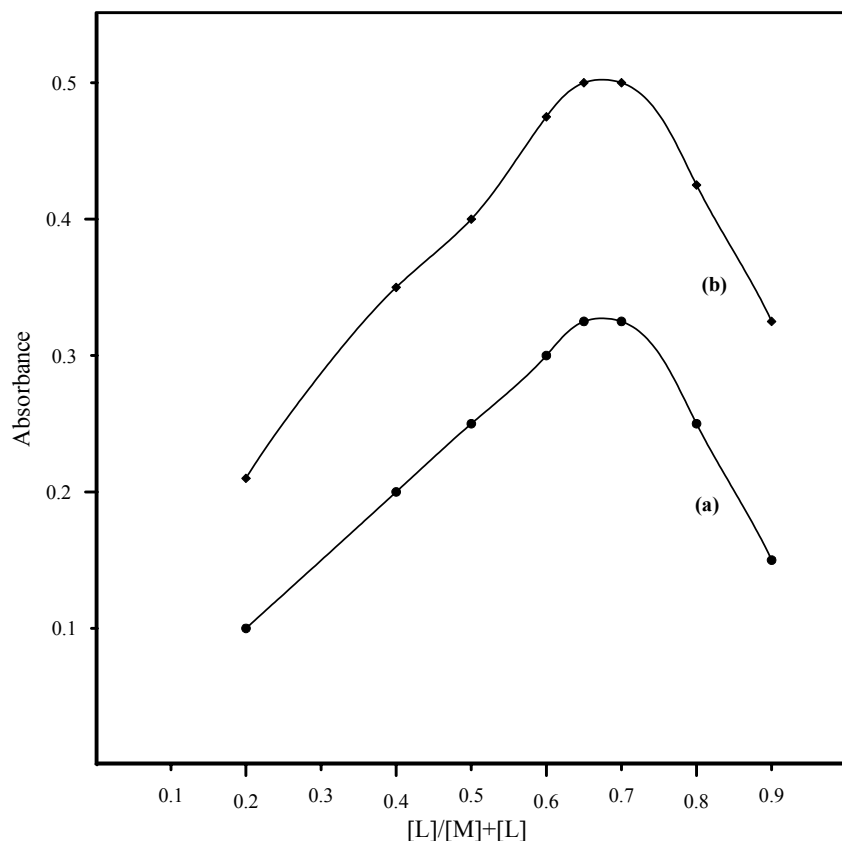
The absorption spectra of Pt(IV), HPETS reagent and of Pt-PETS complex formed in aqueous ethanol solution (30% v/v) and that floated into the HOL layer are given in figure 1. Notice that the absorption spectra of the analyte and the ligand (curve a and b) have no absorption bands in the region that corresponds to that of the complexes Pt- PETS and Pt- PETS-HOL( curves c and d, having their maximum absorbance at 715 nm). Moreover, it is interesting to note that the floated complex has a higher absorbance value in comparison with that formed in the aqueous solution resulting in an enhancement in the sensitivity of the spectrophotometric determination of Pt(IV) after flotation. The higher absorbance in the floated layer is due to the preconcentration factor in the extraction. Hence, subsequent analysis of the colored complex was carried out at 715 nm after flotation.



**Figure 1.** Absorption spectra of (a) Pt(IV),  $1.3 \times 10^{-5} \text{ molL}^{-1}$ , (b) HPETS,  $3 \times 10^{-5} \text{ molL}^{-1}$ , (c) Pt-PETS and (d) Pt-PETS-OL- solutions

### Composition of the complex

The composition of the platinum complex was studied by the continuous variation method. A typical graph obtained (figure 2) by the former method showed that 1:2 (Pt: PETS) complex is formed in the surfactant and aqueous solutions (curves a and b). The same molar ratio observed for the complex structure in the aqueous and floated layers may reflect the absence of HOL interaction with the complex coordination sphere. Moreover, it must be noted from the data in figure 2 that the HOL surfactant intensifies the color of the complex (higher absorbance than in the aqueous solution) which confirms the determination of Pt(IV) after floatation of its complex<sup>[17]</sup>.



**Figure 2.** Continuous variation method for. (a) Pt-PETS system at 710nm  
(b) Pt-PETS-OL- system at 715nm

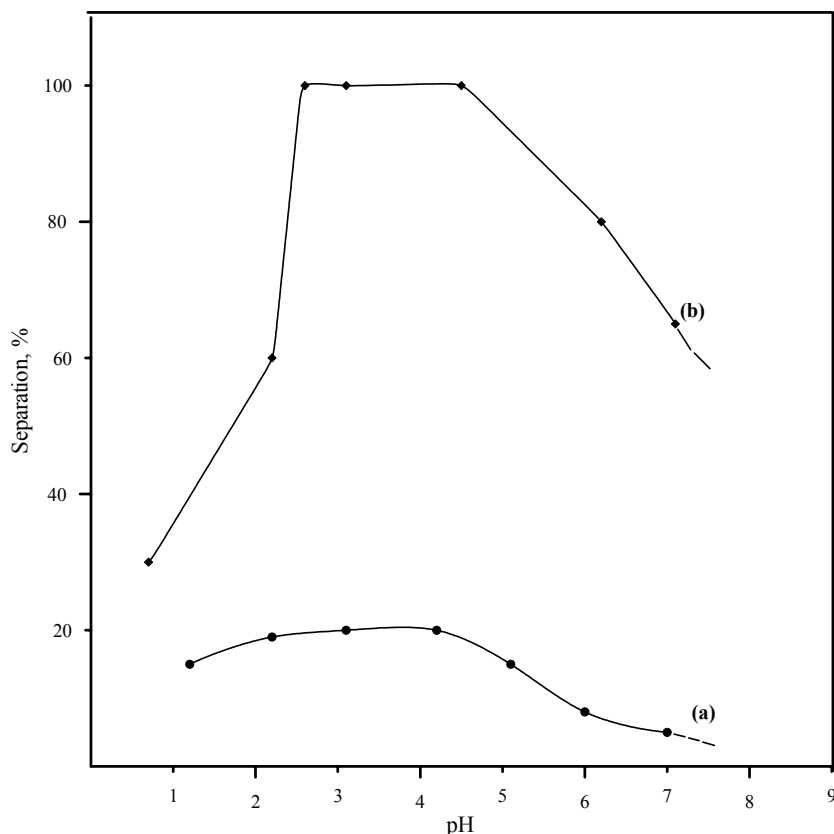
### Effect of pH

Since the pH of the medium is a highly significant factor in the flotation processes, pH was the first variable to be optimized. A series of experiments was carried out to study the effect of pH on the flotation efficiency of  $10^{-5}$  mol L<sup>-1</sup> Pt(IV) with  $5 \times 10^{-4}$  mol L<sup>-1</sup> HOL in the presence of  $2 \times 10^{-5}$  mol L<sup>-1</sup> HPETS. The results presented in Fig. 3. show that, the floatability of the Pt-PETS complex increases with increasing pH, reaching its maximum value (maximum and nearly constant absorbance) in the pH range 2.5-4.5, in which a dark green complex is obtained. The optimal pH used was pH  $\approx$  3 for all experiments.

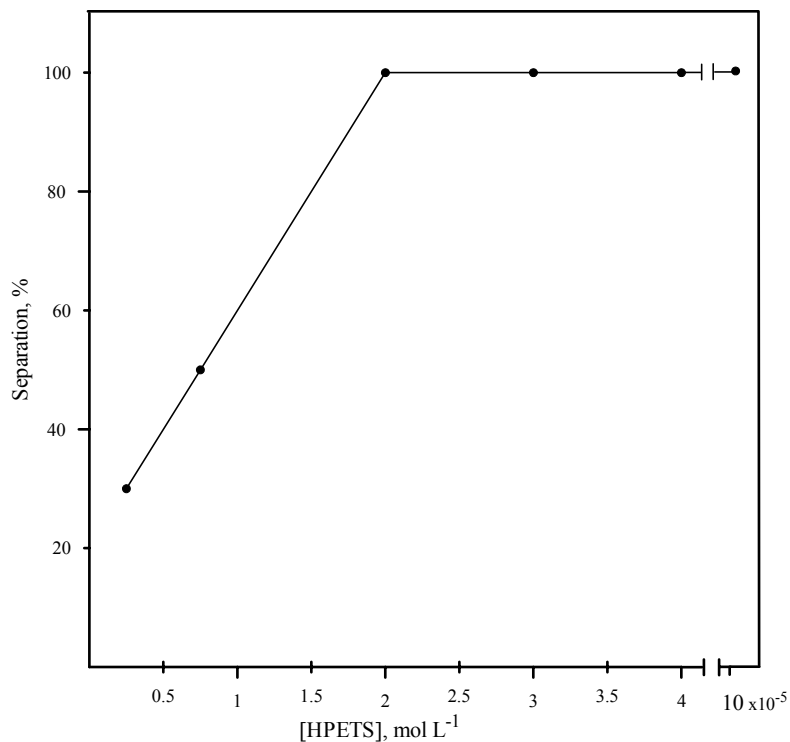
### Effect of ligand concentration

Initial experiments were performed to float Pt(IV) with HOL surfactant alone. However, the flotation efficiency did not exceed 20%. Therefore, a trial was made to improve this process using different reagents. It was found that the use of some thiosemicarbazide derivatives as collecting agents in this regard, especially 1- Phenyl-4- ethylthiosemicarbazide (HPETS), gave optimistic results. The floatability of a series of solutions containing  $10^{-5}$  mol L<sup>-1</sup> Pt(IV),  $5 \times 10^{-4}$  mol L<sup>-1</sup> HOL and various amounts of HPETS at pH  $\approx$  3 was investigated.

The results are shown in figure 4. As can be seen, the flotation efficiency (equivalent to the maximum absorbance) increases with increasing concentration of the ligand, reaching its maximum value (ca. 100%) at a 1:2 (Pt: HPETS) ratio. These results agree well with those obtained in figure 2. Moreover, the excess of ligands has no adverse effect on the flotation process and so the procedure be applied to real samples containing Pt(IV). Accordingly, a concentration of HPETS which equal to twice that of Pt(IV) was used in the recommended procedure.



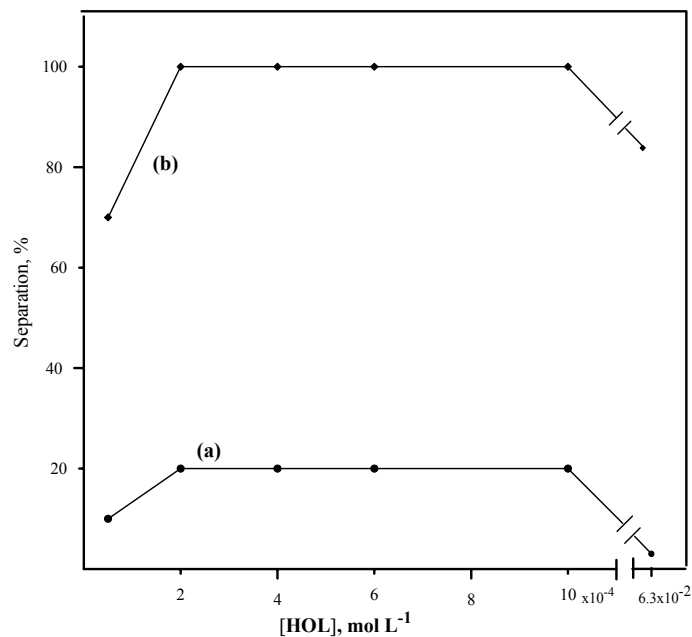
**Figure 3.** Effect of hydrogen ion concentration on the separation efficiency of  $10^{-5}$  mol L<sup>-1</sup> Pt(IV) using  $5 \times 10^{-4}$  mol L<sup>-1</sup> HOL.  
(a) without HPETS (b) with  $2 \times 10^{-5}$  mol L<sup>-1</sup> HPETS



**Figure 4.** Effect of [HPETS] on the separation efficiency of  $10^{-5} \text{ mol L}^{-1}$  Pt(IV) at  $\text{pH} \approx 3$  using  $5 \times 10^{-4} \text{ mol L}^{-1}$  HOL.

#### *Effect of surfactant concentration*

Samples of floated Pt(IV) were tested with different concentrations of HOL without ligand (figure 5, curve a). The floatability of Pt(IV) was tried in the presence of HPETS using various concentrations of HOL. The results, graphically presented in ( Fig.5, curve b), show that the maximum floatability of Pt(IV), obtained over a wide concentration range may be due to the formation of a stable envelope of surfactant on the surface of air bubbles or a hydrated micelle coating on the surface of analyte-ligand system <sup>[18]</sup>. As a result, the hydrophobicity of the resulting surface was not satisfactory for flotation. Accordingly,  $5 \times 10^{-4} \text{ mol L}^{-1}$  HOL was used throughout the measurements for Pt(IV) determination.

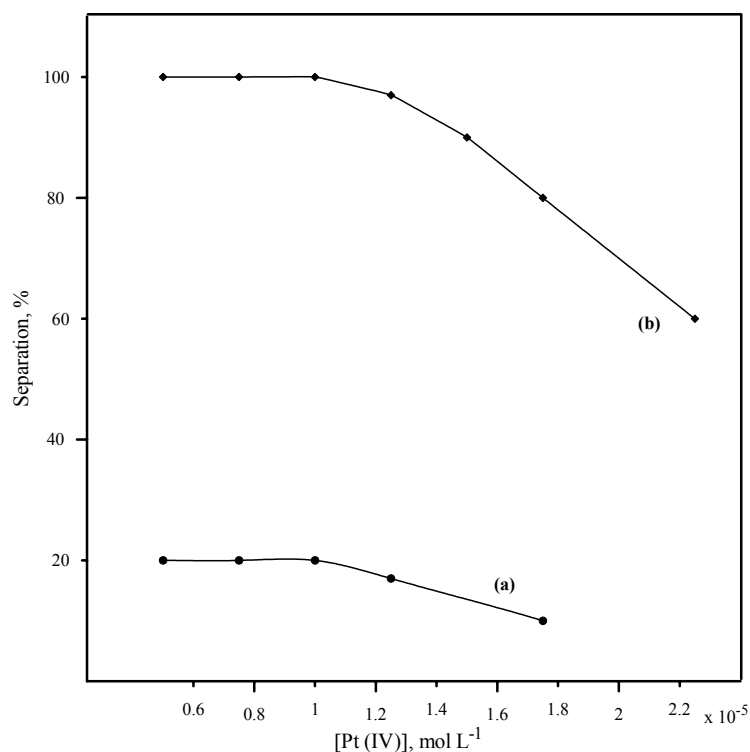


**Figure 5.** Influence of [HOL] on the the separation efficiency of  $10^{-5} \text{ mol L}^{-1}$  Pt(IV) at  $\text{pH} \approx$  : (a) in absence of HPETS and (b) in presence of  $2 \times 10^{-5} \text{ mol L}^{-1}$  HPETS

#### *Effect of Pt(IV) concentration*

To confirm the data obtained in figure 4, another series of experiment were carried out to float various amounts of Pt(IV) ions in the presence of  $2 \times 10^{-5} \text{ mol L}^{-1}$  HPETS using  $5 \times 10^{-4} \text{ mol L}^{-1}$  HOL at  $\text{pH} \approx 3$  (figure 6). As can be seen, the floatability reaches 100% at a Pt(IV) concentration  $10^{-5} \text{ mol L}^{-1}$ , corresponding to 1:2 molar ratio (Pt : HPETS), which agrees well with the data obtained in figure 4. At higher concentrations of the analyte, the flotation efficiency decreases. This may be attributed to the fact that the amount of HPETS is insufficient to bind all Pt(IV) ions that exist in the solution. Consequently, in the analysis of Pt(IV) in its natural unknown samples, excess ligand can be safely used.





**Figure 6.** Separation efficiency of different Pt(IV) concentrations at pH  $\approx$  3 in absence of HPETS (curve,a) and presence of  $2 \times 10^{-5}$  mol L<sup>-1</sup> HPETS (curve,b) using  $5 \times 10^{-4}$  mol L<sup>-1</sup> HOL

#### *Effect of temperature*

To study the effect of temperature on the flotation efficiency of Pt(IV), the solution containing Pt(IV), HPETS and HOL as surfactant were either heated or cooled to the same temperature. The solution of HOL was quickly poured into the Pt(IV) solution. The mixture was introduced into the flotation cell jacketed with 1cm thick fiberglass insulation.

The flotation and determination procedure was then followed. Since the floatability and absorbance of the complex Pt-HPETS were not markedly affected by raising the temperature from 5 to 80°C, measurements were carried out at room temperature  $\approx$ 25°C. However, given that most industrial influents are usually hot, the simple procedure presented here may find its application in the analysis of Pt(IV) ions directly in industrial waste waters.

#### *Effect of time*

The minimum time required for the color development of the Pt-HPETS complex was found to be  $\approx$ 2 min at room temperature. The absorbance of the floated complex, measured at 715 nm, was constant for 20 min, after which the color begins to fade. The total time required for one determination was 6-8 min. Therefore, the use of this simple procedure for analysis of Pt(IV) may be considered as time saving compared to some another techniques.

### 3.9 Effect of foreign ions

Under the optimized conditions determined as above, analysis of Pt(IV) ions ( $10^{-5}$  mol L<sup>-1</sup>) using ( $2 \times 10^{-5}$  mol L<sup>-1</sup>) HPETS as the ligand and oleic acid ( $5 \times 10^{-4}$  mol L<sup>-1</sup>) as the surfactant was studied in the presence of high concentrations of various cations as a separate and combined states. The data displayed in table 1, referring to the ions behave safely towards the separation process under the optimized conditions ( $2 \times 10^{-5}$  mol L<sup>-1</sup> HPETS,  $5 \times 10^{-4}$  mol L<sup>-1</sup> HOL at pH ≈ 3). Table 2 is concerned with concomitant ions having a significant role, Cu(II), Au(III) and Ni(II) have a hazard effect on the complexation process of the analyte. The effects are completely overcome by using a sufficient ligand amount ( $2 \times 10^{-3}$  mol L<sup>-1</sup>) covering the analyte and interferents. Fortunately, such interfering complex does not affect completely on the determination process.

**Table1.** Effect of some ions on the separation and spectrophotometric determination of  $10^{-5}$  molL<sup>-1</sup> Pt (IV) in the presence of  $2 \times 10^{-5}$  molL<sup>-1</sup> HPETS, using  $5 \times 10^{-4}$  molL<sup>-1</sup> HOL surfactant at pH ≈ 3.

Interfering ion (s)	[Interferent ] each (ppm),	Separation, %
Na (I)	1000	100
K (I)	1000	100
Mg (II)	500	100
Ca (II)	1000	100
Zr (IV)	500	100
Co (II)	1000	100
Fe (II)	500	100
Ag (I)	500	100
Na (I) + K (I)	500	100
Mg (II) + Ca (II)	500	100
Zr (IV) + Co (II)	500	100
Mg (II) + Ca (II)	500	100
Na (I) + K (I) + Mg (II) + Ca (II)	1000	100
Na (I) + K (I) + Zr (IV) + Co (II)	1000	100

**Table 2.** Effect of some foreign ion (s) individually or in combination on the separation and determination of  $10^{-5} \text{ mol L}^{-1}$  Pt (IV) at  $\text{pH} \approx 3$  in the presence of HPETS, using  $5 \times 10^{-4} \text{ mol L}^{-1}$  HOL surfactant.

Interfering ion (s)	[Interferant] (ppm), each	Separation, %	
		Using $2 \times 10^{-5} \text{ mol L}^{-1}$ HPETS	Using $2 \times 10^{-3} \text{ mol L}^{-1}$ HPETS + $0.01 \text{ mol L}^{-1}$ DMG + $0.01 \text{ mol L}^{-1}$ KF
Au(III)	500	80	100
Pd (II)	500	20	100
Ni (II)	500	100	100
Cu (II)	500	20	100
Fe (III)	500	20	100
Cu (II)+ Co (II)	500	20	100
Cu (II)+ Ni (II)	500	20	100
Cu (II)+ Ag (I)	1000	20	100
Cu (II)+Fe (III)	500	40	100
Co(II)+ Ni (II)	500	70	100
Pd (II)+ Ag(I)	200	20	100
Pd (II)+ Cu (II)	500	20	100
Pd (II)+ Co(II)	200	20	100
Au(III) +Ag (I)	500	100	100
Pd(II) +Ni(II)	100	20	100
Cu(II)+ Co(II)+ Ni(II)	300	10	100
Ag(I)+ Au(III)+ Pd(II)	500	10	100
Ni(II)+ Co(II)+ Ag(I)	500	100	100
Ni(II)+ Co(II)+ Au(III)	100	100	100
Pd(II)+ Cu(II)+ Co(II)	100	10	100

An observable interfering effect is represented with the effect of Pd(II) and Fe(III) on the separation and determination of Pt(IV). This behavior is expected from Pd(II) due to the high affinity with the analyte properties. Increasing the complexing agent concentration did not offer an acceptable solution, Dimethylglyoxime reagent removes the Pd(II) interference from the Pt(IV) determination. This may be due to the formation of more stable Pd-DMG complex than Pd-HPETS. The Fe(III) interference is completely overcome by the use of HF which is characterized by the formation of highly stable nonfloatable complex with Fe(III). Accordingly,  $2 \times 10^{-3} \text{ mol L}^{-1}$  HPETS +  $10^{-2} \text{ mol L}^{-1}$  DMG and  $10^{-2} \text{ mol L}^{-1}$  HF are successfully used during the application of the proposed procedure without interfering effect.

#### *Effect of ionic strength*

Table 3 summarizes the effect of varying the ionic strength of different salts on the flotation efficiency of  $10^{-5} \text{ mol L}^{-1}$  Pt(IV) with  $5 \times 10^{-4} \text{ mol L}^{-1}$  HOL in the presence of  $2 \times 10^{-5} \text{ mol L}^{-1}$  HPETS at  $\text{pH} \approx 3$ . The salts used in adjusting the ionic strength generally resemble those present in natural water samples. As can be seen, the ionic strength of the medium has not markedly affected the flotation process nor the determination of Pt(IV).

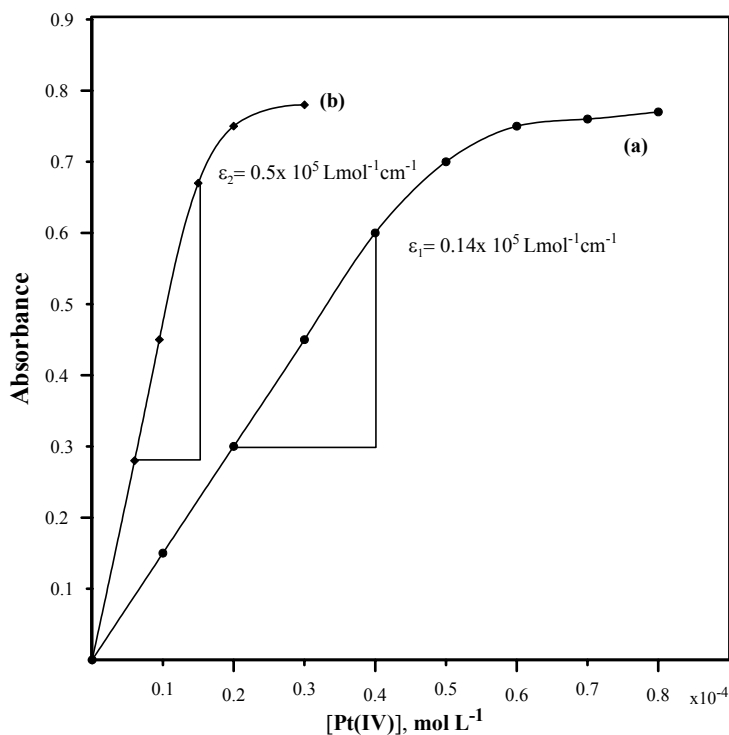
**Table 3.** Spectrophotometric determination of Pt(IV) added to some natural water samples delivered from different locations after separation – flotation using  $2 \times 10^{-3}$  molL<sup>-1</sup> of HPETS and  $5 \times 10^{-4}$  molL<sup>-1</sup> HOL at pH  $\approx$  3.

Type of water (Location)	Analyte added ( ppm)	Mean recovery*, %
Tap water	1.00	100 $\pm$ 0.01
(Jeddah)	1.95	100 $\pm$ 0.01
Sea water	1.00	100 $\pm$ 0.01
( Jeddah)	1.95	100 $\pm$ 0.02
Sea water	1.00	100 $\pm$ 0.02
(Dammam)	1.95	100 $\pm$ 0.03
Sea water	1.00	100 $\pm$ 0.01
(Al-Khobar)	1.95	100 $\pm$ 0.03
Sea water	1.00	100 $\pm$ 0.02
(Yanbu )	1.95	100 $\pm$ 0.03
Sea water	1.00	100 $\pm$ 0.01
(Jazan)	1.95	100 $\pm$ 0.02

\* Average of three readings

#### Calibration curve and sensitivity

Under the optimum conditions described in the recommended procedure, the calibration curves (figure 7, curves a and b) show good linearity up to  $5 \times 10^{-5}$  mol L<sup>-1</sup> of Pt(IV). The molar absorptivities are  $0.5 \times 10^5$  and  $0.14 \times 10^5$  L mol<sup>-1</sup>cm<sup>-1</sup> for the colored complex in the aqueous and scum layers, respectively. The analytical detection limit of a standard aqueous solution, calculated on the basis of  $3\sigma$  [17], was found to have  $10^{-5}$  mol L<sup>-1</sup> Pt(IV). Moreover, close inspection of the calibration curves reveals that the determination of the analyte after flotation enhances the sensitivity of the spectrophotometric procedure [17].



**Figure 7.** Beer- Lambert s law for the systems Pt-PETS in aqueous solution (curve a) and Pt-PETS –O-L in scum layer (curve b).

### Flotation mechanism

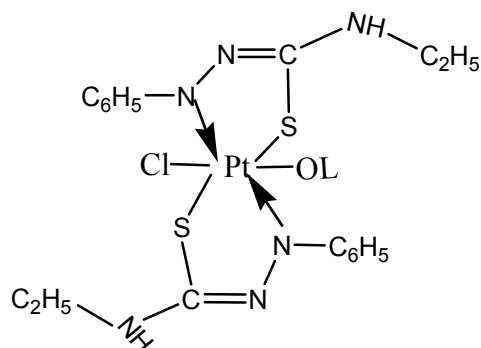
The flotation mechanism of Pt(IV) may be suggested based on some points such as, the same molar ratio (1:2) of the two purely isolated complexes in aqueous and surfactant layers as well as their similar color, this may support the absence of surfactant chemical interaction with the complex structure. But to establish a careful view about the separation mechanism additive studies must be considered as, (a) The elemental analysis for C, H and N which introduces  $[\text{Pt}(\text{PETS})_2\text{Cl OL}]$  as the proposed formula for the surfactant complex. On the other hand the  $[\text{Pt}(\text{PETS})_2\text{Cl}_2]$  is the proposed structure for the aqueous complex. (b).

A comparison between the ligand IR and its isolated complexes in aqueous and surfactant layers reveals that the ligand behaves as a mononegative bidentate in the two complexes. The binding sites are suggested based on the following evidence: i) the disappearance of  $\nu_{\text{IV}}(\text{C}=\text{S})$  at  $776\text{ cm}^{-1}$  followed by the appearance of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{S})$  bands at  $1580$  and  $640\text{ cm}^{-1}$ , ii) the appearance of bands at  $\approx 320, 360$  and  $450$  assigned to  $\nu(\text{Pt}-\text{Cl})$ ,  $\nu(\text{Pt}-\text{S})$  and  $\nu(\text{Pt}-\text{N})$  bands.

The appearance of new bands in the floated complex at  $1700\text{ cm}^{-1}$  assigned to  $\nu(\text{C}=\text{O})$  band and the absence of any band in the range from  $1300-1400\text{ cm}^{-1}$  which is characteristic for  $\delta(\text{OH})$  band, this may indicate the presence of  $^-\text{OL}$  molecule covalently attached with the surfactant complex instead of chloride ion in covalent with the complex.

Moreover, the electronic spectra of the complexes exhibit a band at  $\approx 14,140\text{ cm}^{-1}$  which assigned for the octahedral geometry for  $d^6$  complexes.

Thermogravimetric analysis for the complex isolated in scum shows a sharp decomposition step at  $196-250\text{ }^\circ\text{C}$  temperature range. This step is corresponding to the removal of one OL ion. This supports the presence of OL molecule attached with the complex structure. Also, the non conducting behavior of  $10^{-3}\text{ mol L}^{-1}$  of the complex in DMF offers an assertion for the presence of surfactant molecule inside the coordination sphere although the use of relative acidic,  $\text{pH}(\approx 3)$ .



**Structure 2:** The complex in scum layer

## Application

To investigate the applicability of the recommended procedure to natural water samples (taken from different locations), the recoveries of known amounts of Pt(IV) added to these samples were examined after adjusting the pH at  $\approx 3$ . The Pt(IV) concentration was determined spectrophotometrically in the surfactant layer at 715 nm or by atomic absorption spectrophotometry (AAS) in the mother liquor for some samples under investigation.

Spectrophotometric determination of Pt(IV) after flotation gives satisfactory results compared to those obtained by AAS. Thus the proposed procedure of Pt(IV) determination after flotation makes the procedure highly selective and sensitive. Simulated samples as well as solid complexes were investigated. The results of the application of the proposed procedure to the recovery and determination of the analyte in all types of samples (table 4,5, and 6). The sensitivity of the proposed procedure for the separation and analysis of Pt(IV) was investigated by calculating the relative standard deviation for the different samples, which reflects that, the procedure is highly sensitive and precise.

**Table 4.** Application on the separation and spectrophotometric determination of Pt(IV), in presence of  $2 \times 10^{-3} \text{ mol L}^{-1}$  HPETS using  $5 \times 10^{-4} \text{ mol L}^{-1}$  HOL, from synthetic mixtures of foreign ions.

Synthetic mixtures, 100 ppm of each.	Pt(IV), ppm		A.E.	R.E.	S	$\delta$	Mean recovery
	Added	Found					
Pd(II)+ Co(II)+ Cu(II)	1.95	1.96	0.01	+0.513	0.013	0.66	100 $\pm$ 0.01
Ni(II) + Co(II) + Cu(II)	1.95	1.95	0.0	0.0	0.0082	0.418	100 $\pm$ 0.02
Ru (III)+ Rh (III)+ Ni(II)	1.95	1.94	-0.01	-0.513	0.016	0.811	100 $\pm$ 0.01
Ru(III)+ Rh(III)+ Pd(II)	1.95	1.95	0.0	0.0	0.016	0.811	100 $\pm$ 0.01

**Table 5.** Analysis of Pt(IV) in various complexes after applying the proposed separation- spectrophotometric procedure under the recommended conditions.

Complex	Pt (IV), %		A.E.	R. E.	S	$\delta$
	Cal.	Found				
[Pt (HCPTS) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	36.6	36.5	-0.10	0.270	0.089	0.242
[Pt (G <sub>T</sub> PTS) (H <sub>2</sub> O) Cl <sub>2</sub> ]	24.6	24.8	+0.20	0.813	0.114	0.463

**Table 6.** Comparative results for the determination of Pt(IV) in some simulated Silver and Gold samples using the recommended procedure.

Sample	Pt(IV) , ppm		A.E.	R.E.	S	$\delta$
	certified	separated				
E Ag <sub>5</sub>	5.00	5.005	+0.005	0.1	0.024	0.476
EG <sub>2</sub>	92.0	92.08	+0.08	0.0869	0.114	0.124
E Ag 1000	1080	1080.32	+0.32	0.029	0.3449	0.032
EG <sub>5</sub>	11.0	11.1	+0.1	0.909	0.139	1.27

## Conclusion

This paper is concerned with a new procedure for the separation of platinum ion by flotation technique. Also, proposed a spectrophotometric procedure for its determination after preconcentration. This is depending on the formation of stable green color for the analyte with an organic reagent. The optimum conditions for the separation of the green complex were examined. The proposed procedure was successfully applied in different areas.

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