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Design and development of novel reagents for rapid and Selective extraction and separation of selected precious metals

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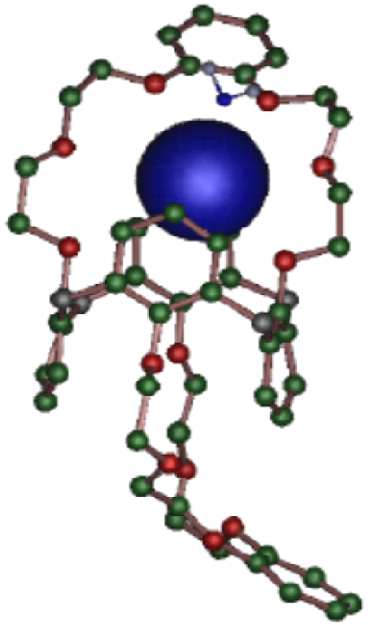
Prof. of Chemistry
University of Hail- Saudi Arabia

What is the main requirements for perfect extractant..?

Design of new extractants : main criteria

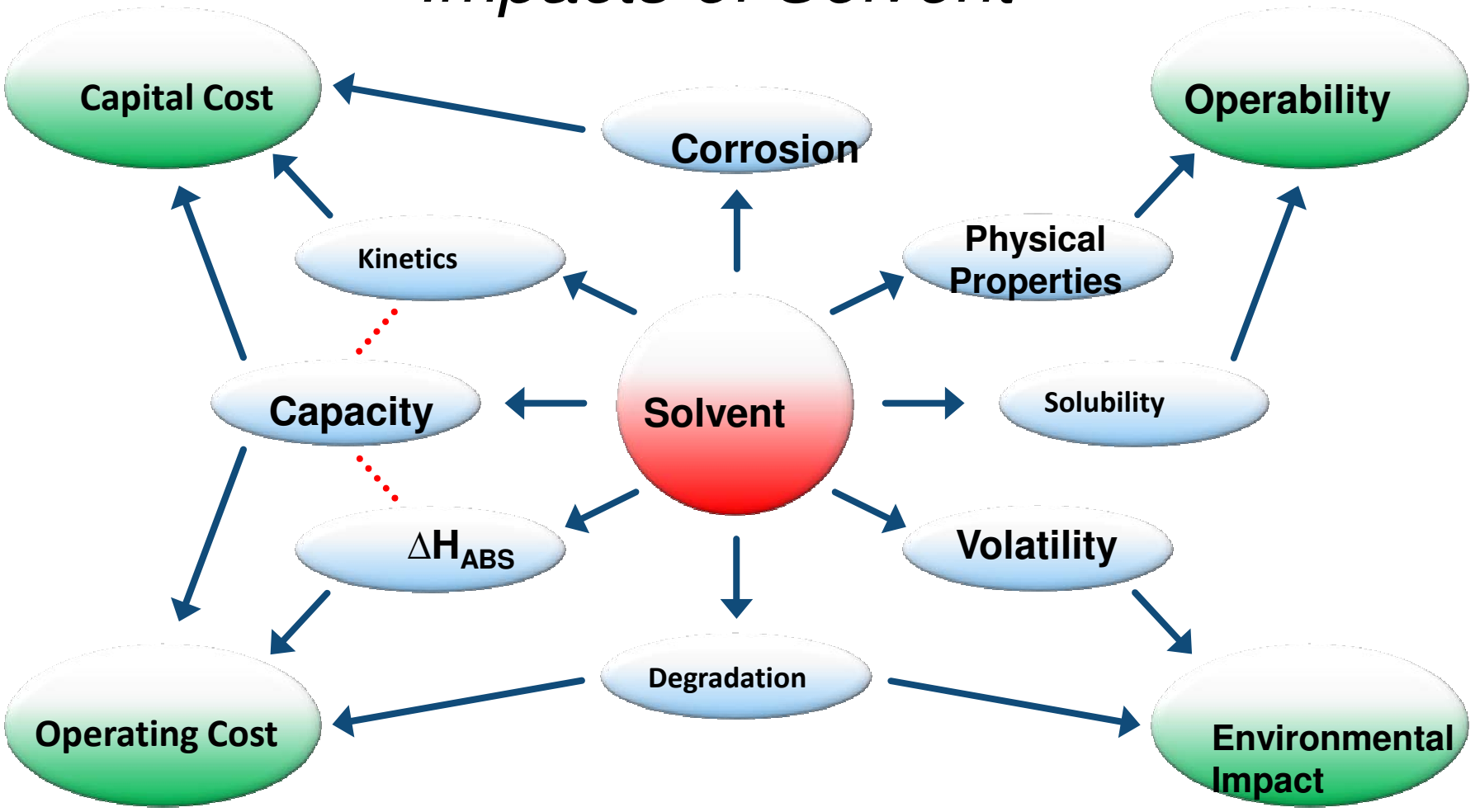
- Ability to separate
  - Affinity
  - Selectivity
  - Reversibility
- Medium effects
  - Solubility
  - Stability / hydrolysis, radiolysis
- Industrialization
  - Kinetics
  - Physical properties
  - Ability to regeneration
- Secondary waste minimization
  - Incinerability (C, H, O, N)



Design of new extractants : main criteria

Atomic Energy Authority

Impacts of Solvent



APPLICATION OF SOLVENT EXTRACTION IN METALS

PRECIOUS METALS

- Solvent extraction is generally used for the separation and purification of the PGM in hydrometallurgical processes.
- Different extractants have been developed and employed as solvent extraction reagents for precious metals for both commercial and analytical purposes including

such as;

- ✓ hydroxy oximes,
- ✓ alkyl derivative of 8- hydroxyquinoline,
- ✓ neutral organophosphorus compounds,
- ✓ amines and esters and so on.

In general, these extractants have some limitations; such as ;

- ***slow kinetics of extraction,***
- ***poor solubility in aliphatic diluents***
- ***Used efficiency only at low acid concentration***

i.e.(instability in acidic medium).

To overcome these problems:

There is a need for development of novel ligands which have high selectivity and efficiency for precious metals.

Amides have come to play an important role in this subject.

The principle advantages of amides as new extracrants

- ✓ Easy synthesis to obtain inexpensive product,
- ✓ Total incineration to limit secondary wastes
- ✓ Resistant to irradiation with formation of harmless radiolytic product compounds (e.g.; carboxylic acid and amines)
- ✓ Good separation factor in highly acidic medium,
- ✓ Easy re-extraction (Stripping)

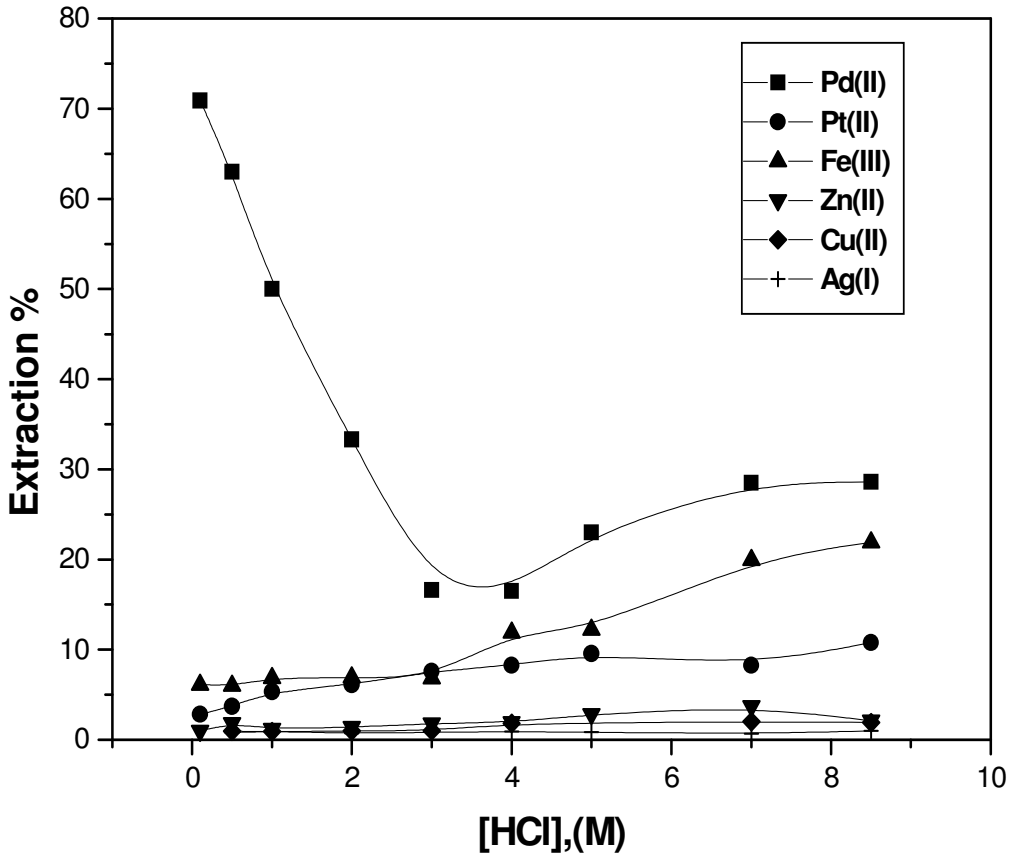
What are amides?

Amides are classified based on the total number of alkyl or aryl group bonded to the nitrogen atom.

$R\text{-}CO\text{-}NH_2$ $R\text{-}CO\text{-}NHR'$ $R\text{-}CO\text{-}NR'R''$

Some Examples
for Mono-amides/Di-amides As Extractants

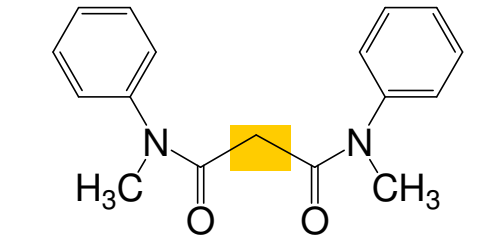
Example for monoamides extractants -Extraction of PGM and base metals



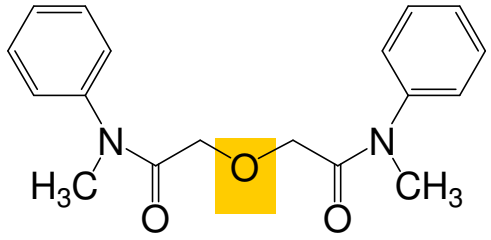
Extraction of Pd(II), Fe(III), Pt(III), Zn(II), Cu(II) and Ag(I) from hydrochloric acid solution with DOCY in toluene.

Diamides as effective extractants for Lanthanides / actinides

Modify Diamide structure



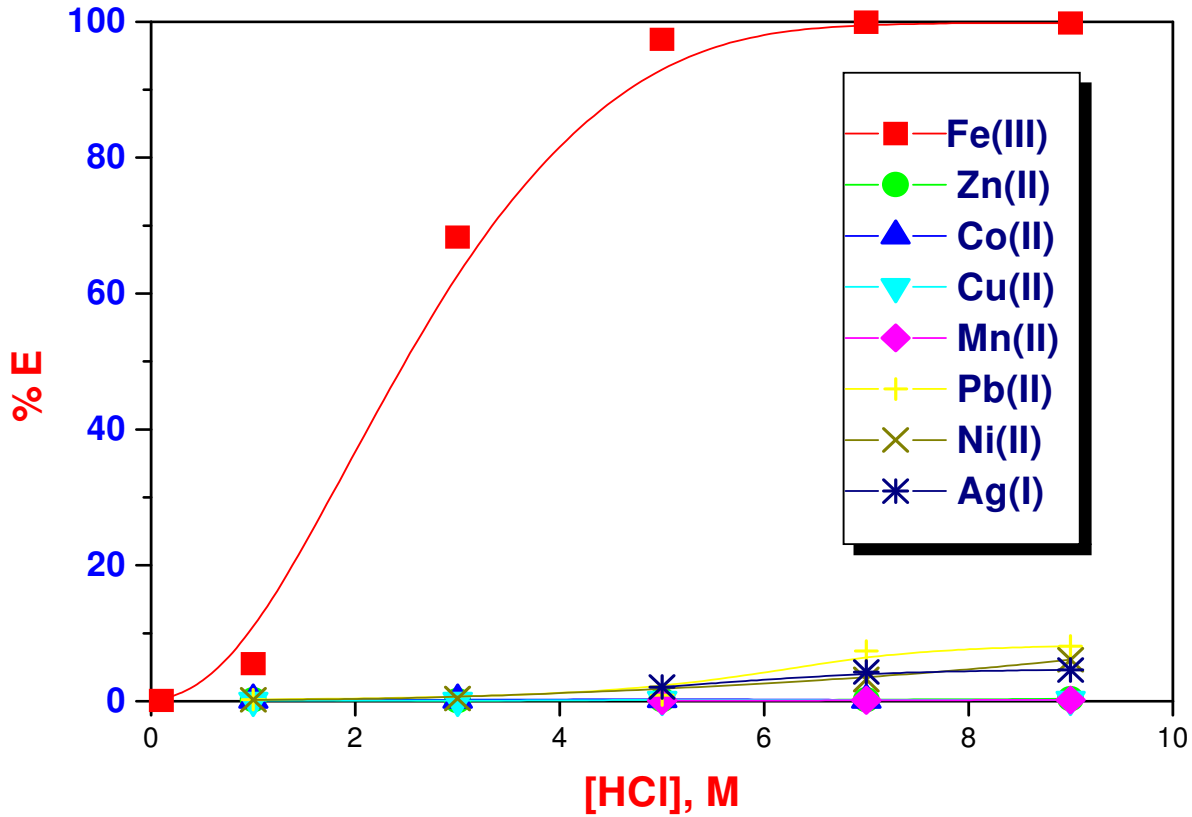
***N*,*N*'-dimethyl-*N*,*N*'-diphenyl-malonamide (MA)**



***N*,*N*'-dimethyl-*N*,*N*'-diphenyl-diglycolamide (DGA)**

(DGA) shown Stronger Affinity toward Ans(III) than (MA)

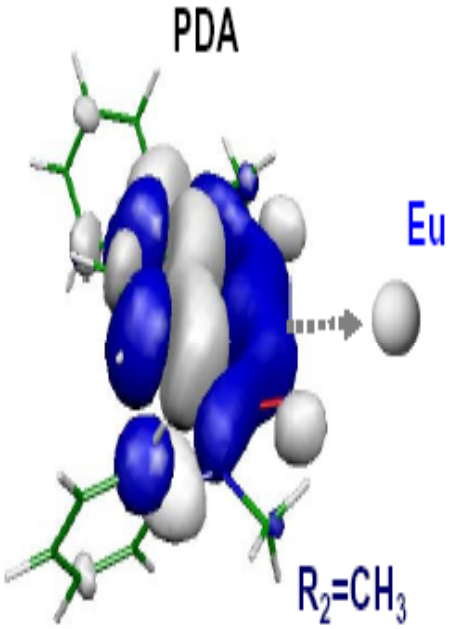
Example for damides (Malonamides)--Extraction of PGM and base metals



Selective extraction of Fe(III) from (multicomponent mixtures) of each of Zn(II), Co(II), Cu(II), Mn(II), Pb(II), Ni(II) and Ag(I) by DMDPhCITDMA from different HCl concentrations

Heteo-amides(Nitrogen-Oxygen/Pyridine amides)

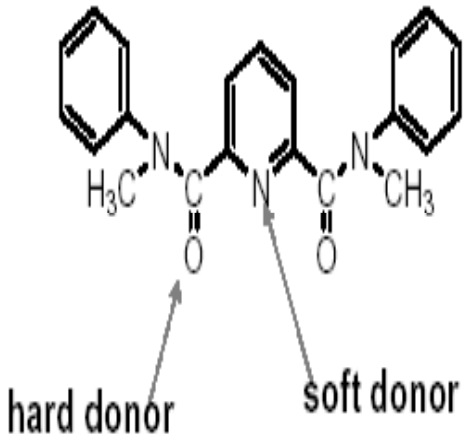
NO-type hybrid donor extractant for An(III)/RE(III) separation



R_1=Ph

Electronic structure of PDA molecule (calculated by Gaussian98)

NO-donor type extractant
Pyridine amide



Molecular design is required to improve the SF(Am/Lns)

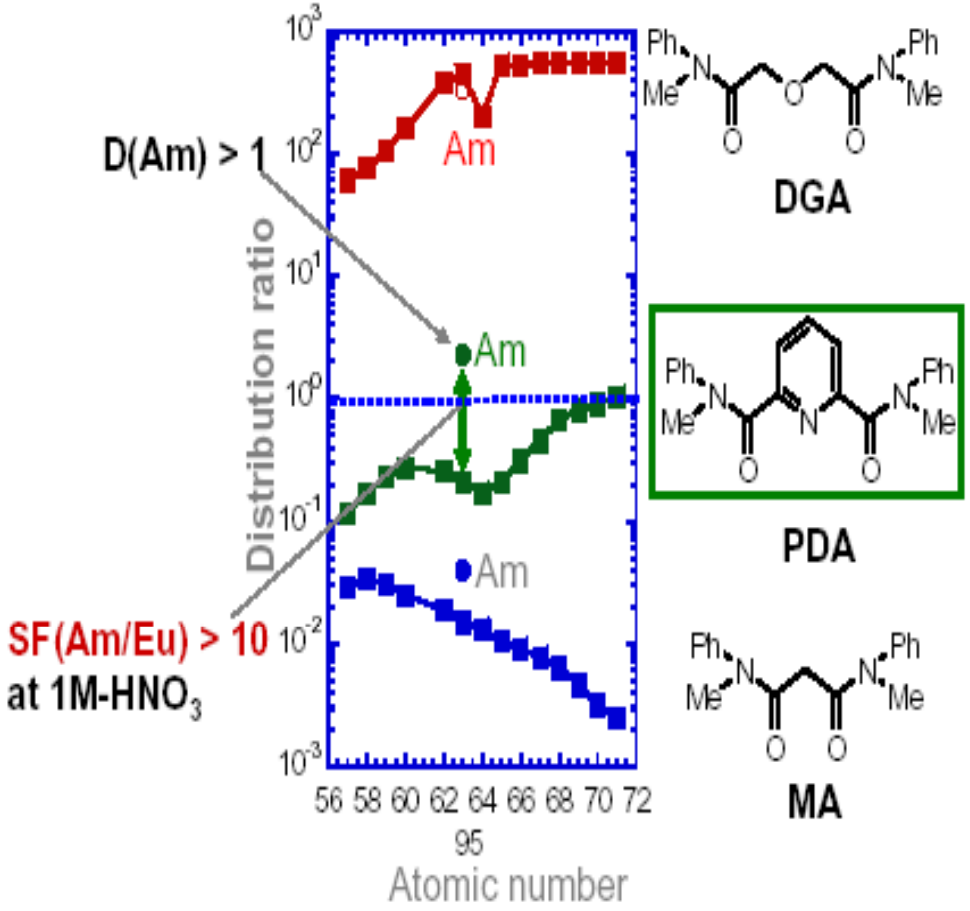
A series of py- amides

(mono- and diamides)

have been synthesized

and tested for effective and selective of minor actinides from In(III).

Am/Ln separation from 1M-HNO_3

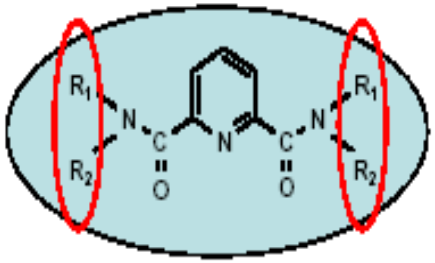


DGA

PDA

MA

- Effective and selective MA(III) separation from rare earths using PDA is in progress by modifying its alkyl groups attached to amidic nitrogen atoms.



e.g., R_1=Ph, R_2=CH_3

⇩

R_1=Ph, R_2=C_nH_{2n+1} (n=4, 8, …)

Organic phase:
0.1M PDA + Chloroform

As shown ,hetro-amides(py-amides) gives best separation of Am(III) / Lanthanides compared with other extractants MA or DGA.

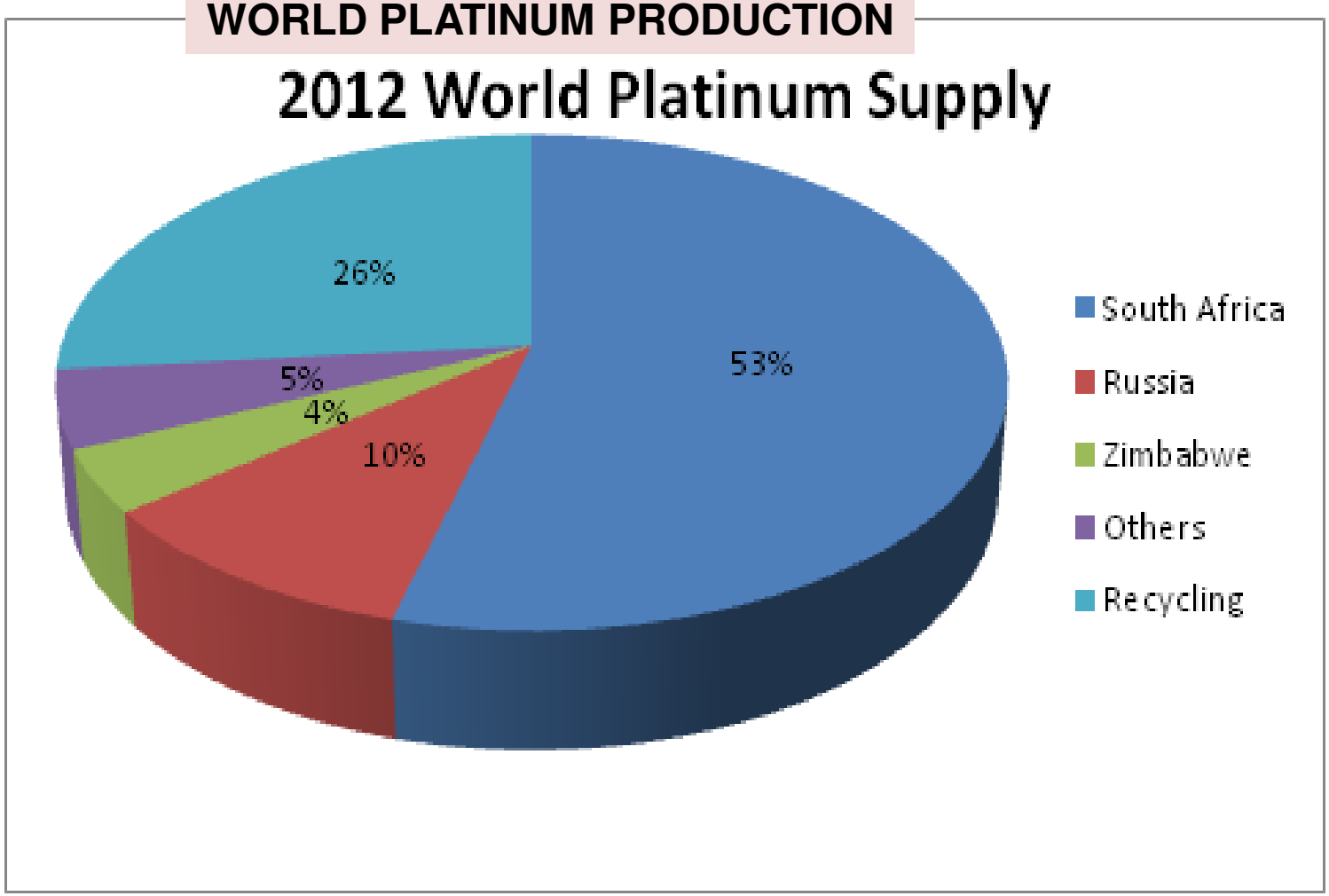
It was hoped that these compounds, owing to the presence of a ***soft donor nitrogen atom*** and an ***amide function***, would be able to coextract all actinides (III, IV, VI) but reject lanthanides(III). ***(We are still on the way)***

Our experiments progress depending on modifying the PDA alkyl groups attached to amidic nitrogen atoms to obtain effective and selective separation of minor actinides(III) from rare earths

PRECIOUS METALS

Solvent extraction is generally used for the separation and purification of the PGM in hydrometallurgical processes.

WORLD PLATINUM PRODUCTION



As shown in figure,
Due to the limitation in world platinum supply.
Recycling of secondary waste is very important.

World Supply of Platinum, including recycling (2012)

The relationship between production and consumption of PGM:

Example spent- catalytic converters

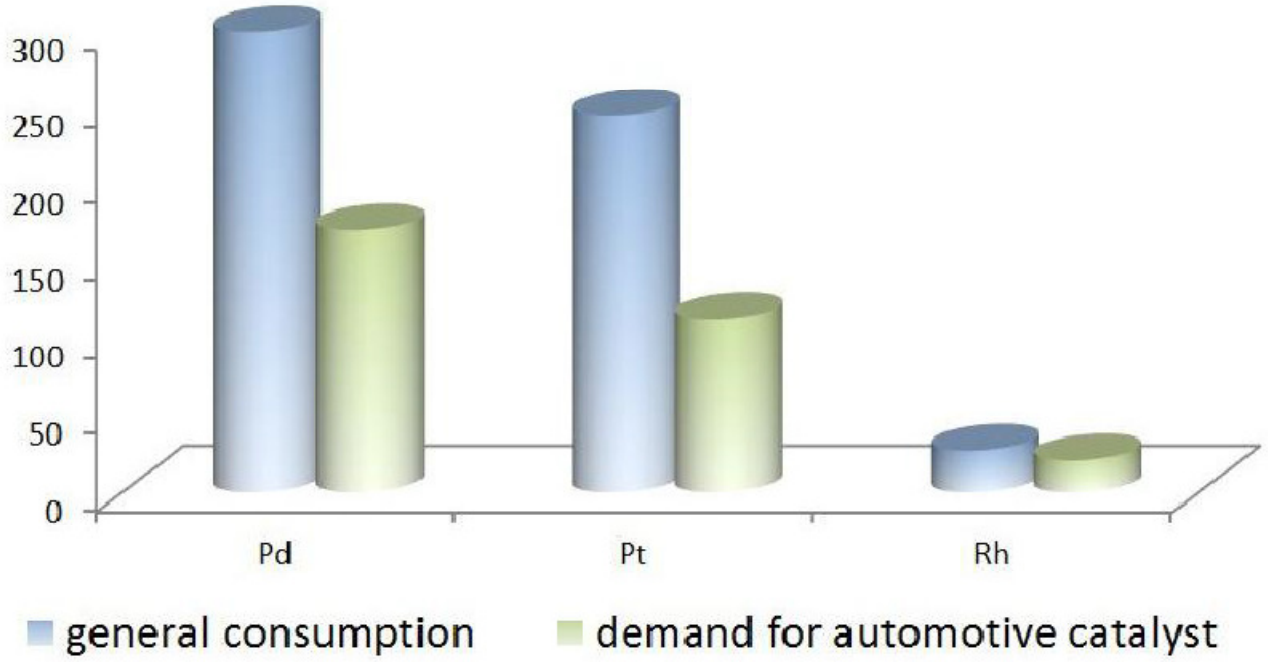
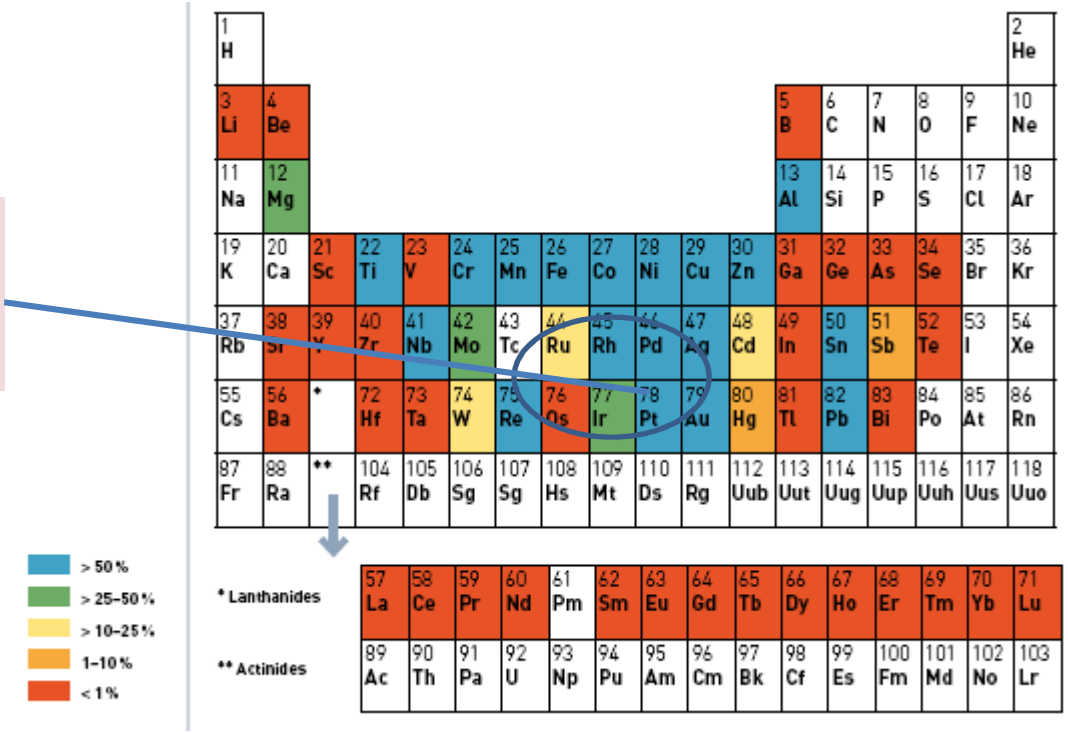


Figure shown the general consumption of PGMs, together with the demand for automotive catalyst applications

Nowadays no cheaper materials are available that offer similar properties for these kinds of catalytic reactions. Taking into account that catalytic converter contain approximately up to 15 g of PGMs, it could easily supposed that this field represents the main application for platinum, palladium, and rhodium. Furthermore, the spent catalytic converters represent a high-grade raw material in comparison to primary sources.

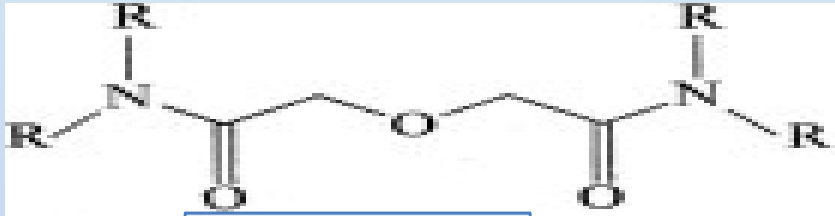
Recycling of most technology metals still lags way behind …

precious metal recycling rates less than 15%

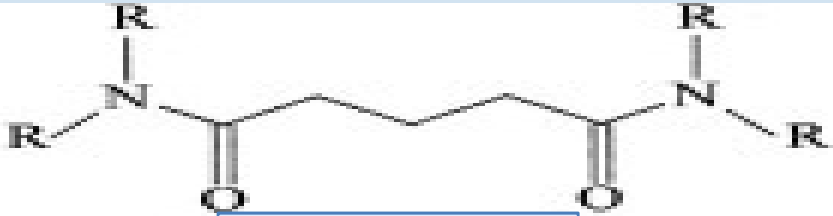


New report (April 2013):
Metal Recycling: Opportunities, Limits, Infrastructure
http://www.unep.org/resourcepanel/Publications/MetalRecycling/tabid/106143/Default.aspx

- On search of new reagents, **thiodiglycolamides(TDGA)** was recently introduced due to its good acid resistance and high extraction efficiency of PGMs.



Diglycolamide



Glutaramide

Thio-diglycolamides (TDGA)

- **Sulfur** and **oxygen** atoms are classified as different types, such as "soft" and "hard" bases, respectively.
- Therefore, it is expected that a new extractant with both **sulfur** and **oxygen** as coordinating atoms can be expected to show high selectivity for metal ions.

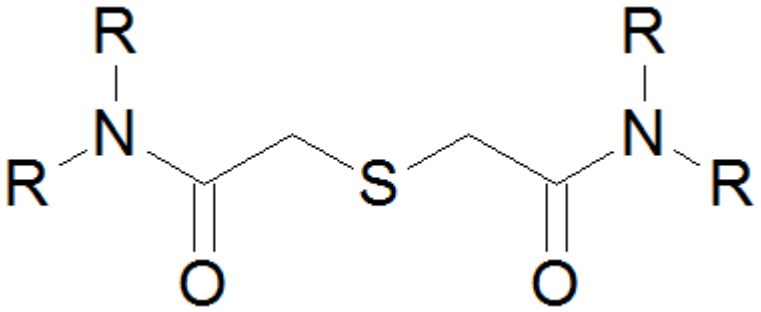
A new three structurally related thiodiglycolamides (TDGA)-with different substitution- namely:

***N,N,N′,N′*-tetra-n-hexyl-thiodiglycolamide (THTDGA),**

***N,N,N′,N′*-tetra-2-ethylhexyl-thiodiglycolamide (TEHTDGA), and**

***N,N,N′,N′*-tetra-n-octyl-thiodiglycolamide (TOTDGA)**

have been synthesized and studied for its extraction behavior towards Pd(III), Pt(IV), Rh(III), Cu(II), Ni(II) and Fe(III) from nitric acid medium.



R = hexyl group (C_6H_{13})

= octyl group (C_8H_{17})

= ethylhexyl group ($C_2H_5C_6H_{12}$)

Structure of thiodiglycolamides (TDGA).

The effect of TDGA structure

Influence of alkyl group (R) on the extraction % of Pd(II), Pt(IV), Rh(III), Cu(II),Ni(II) and Fe(III) from nitric acid solution with the different synthesized TDGA.

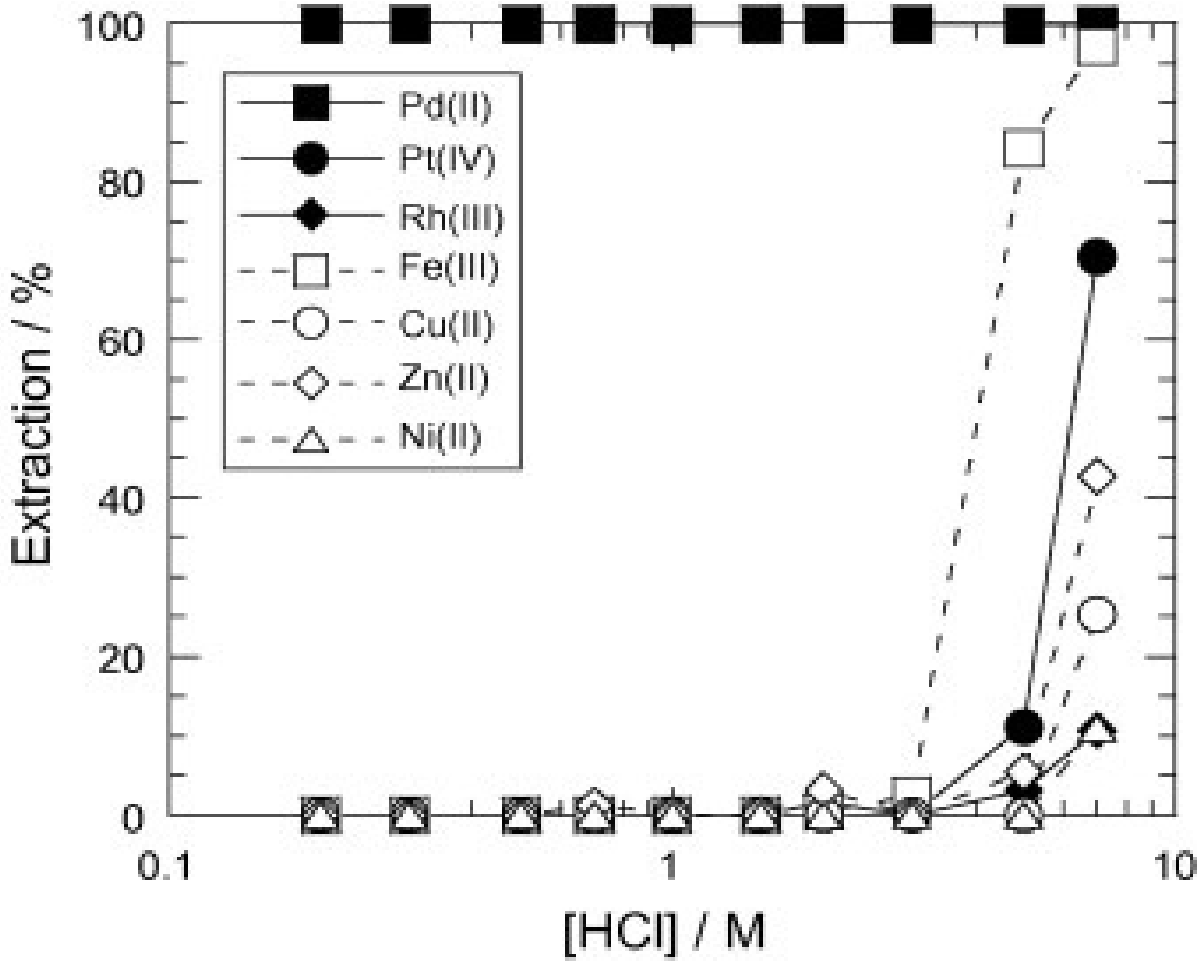
$RRNC(O)CH_2SCH_2C(O)NRR$								
Name	Alkyl group (R)	No. of C atoms	Extraction (%)					
			Pd(II)	Pt(IV)	Rh(III)	Cu(II)	Ni(II)	Fe(III)
THDGA	n-C_6H_{13}	28	99.00	<0.10	<0.10	<0.10	<0.10	~0.10
TEHDGA	$CH_2CH(C_2H_5)C_4H_9$	36	99.70	<0.10	NE	NE	<0.05	~0.10
TOTDGA	n-C_8H_{17}	36	98.10	<0.10	NE	<0.001	NE	~0.10

The synthesized TDGA showed great extractability and selectivity for palladium than other investgated metal ions.

The branched alkyl group, (ethyl-hexyl), was found to enhance the extraction of Pd compared to the long chain (octyl group) or (hexyl group).

Extraction of PGMs from HCl solutions by using TDGA

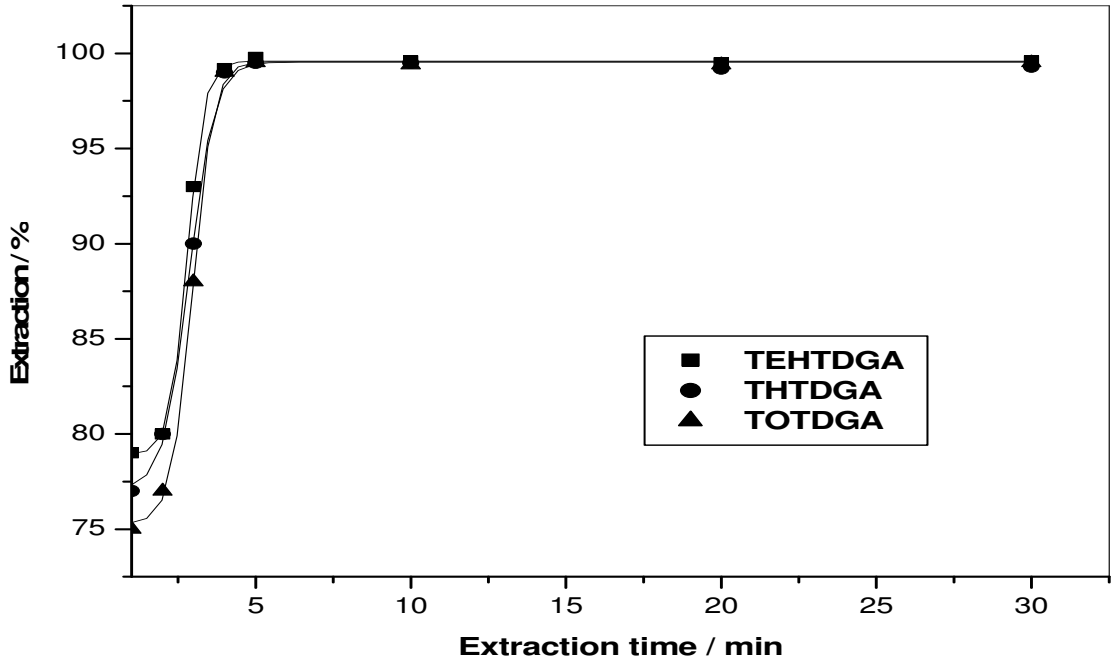
Extraction behavior of PGM and base metal from different molarities of HCl solutions



It was found that, the E % of Pd is almost 100% at all HCl concentrations

Effect of Shaking time (kinetics) on the extraction of Pd by using TDGA:

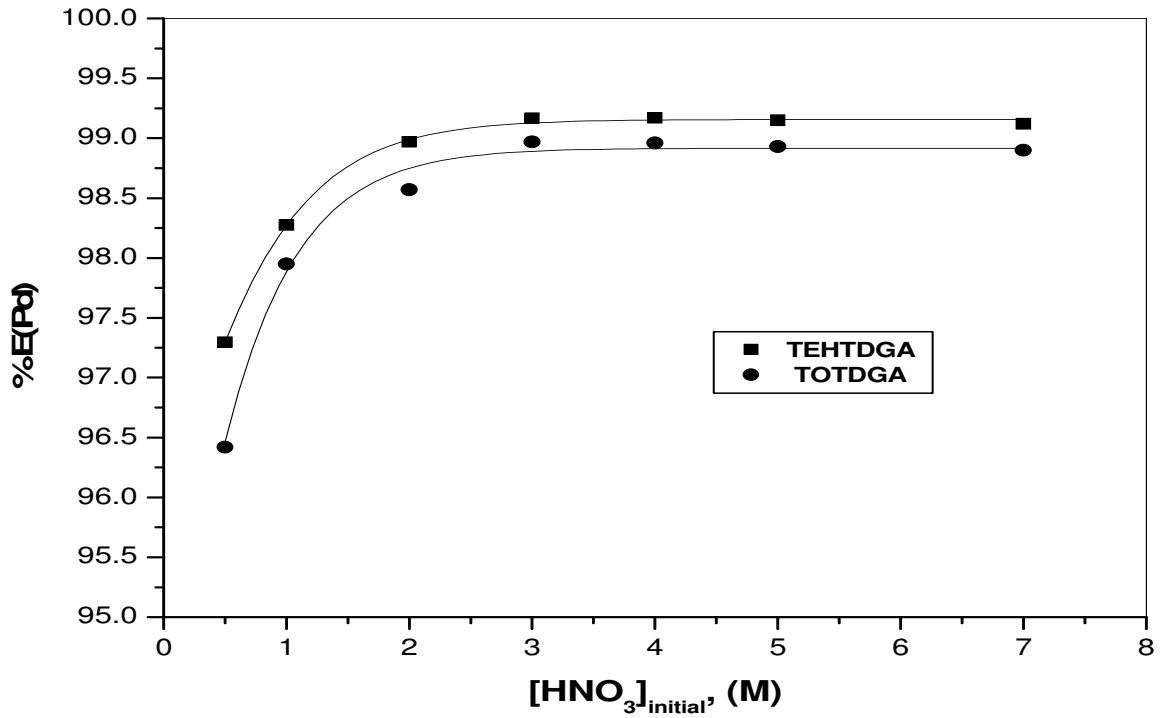
Extraction percentage of Pd in nitric acid with TDGA in toluene as a function of the contact time.



It was found that the %E for pd has a maximum vales at about 4 minutes, while, all the other investigated metal ions are not extracted under these conditions.

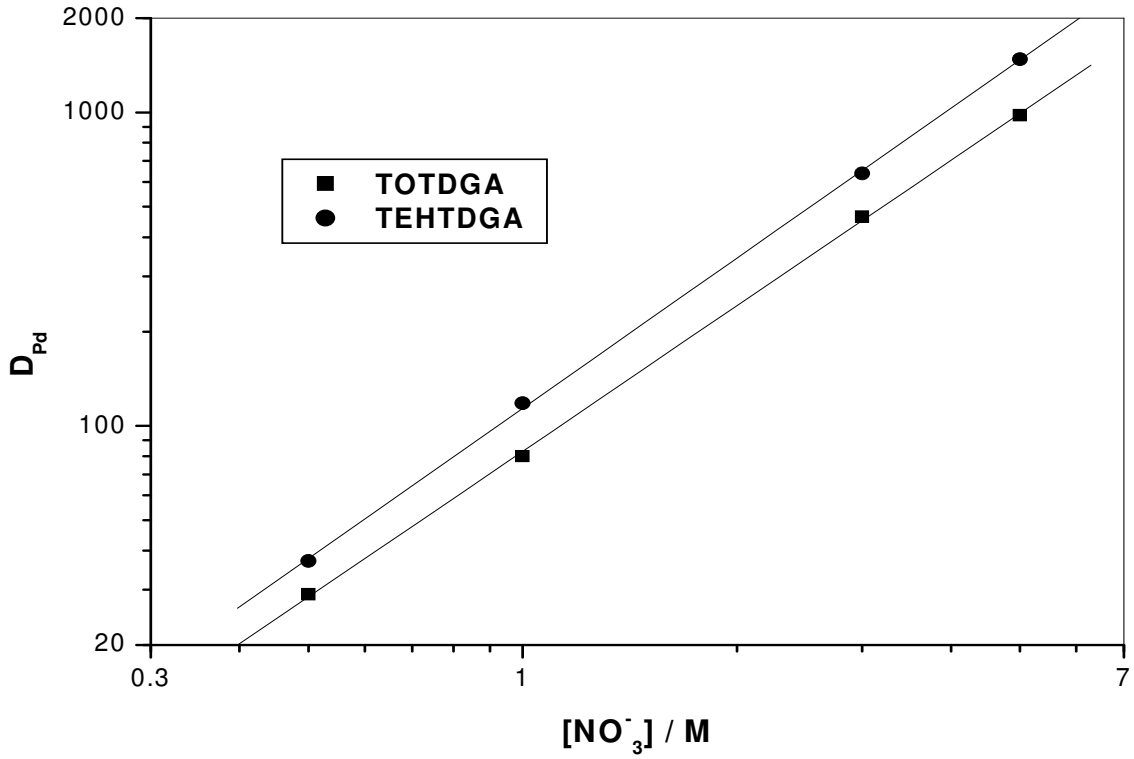
Extraction of Pd from HNO_3 solutions by using TDGA:

Extraction behavior of Pd(II) from different concentrations of nitric acid solutions with TDGA in toluene.



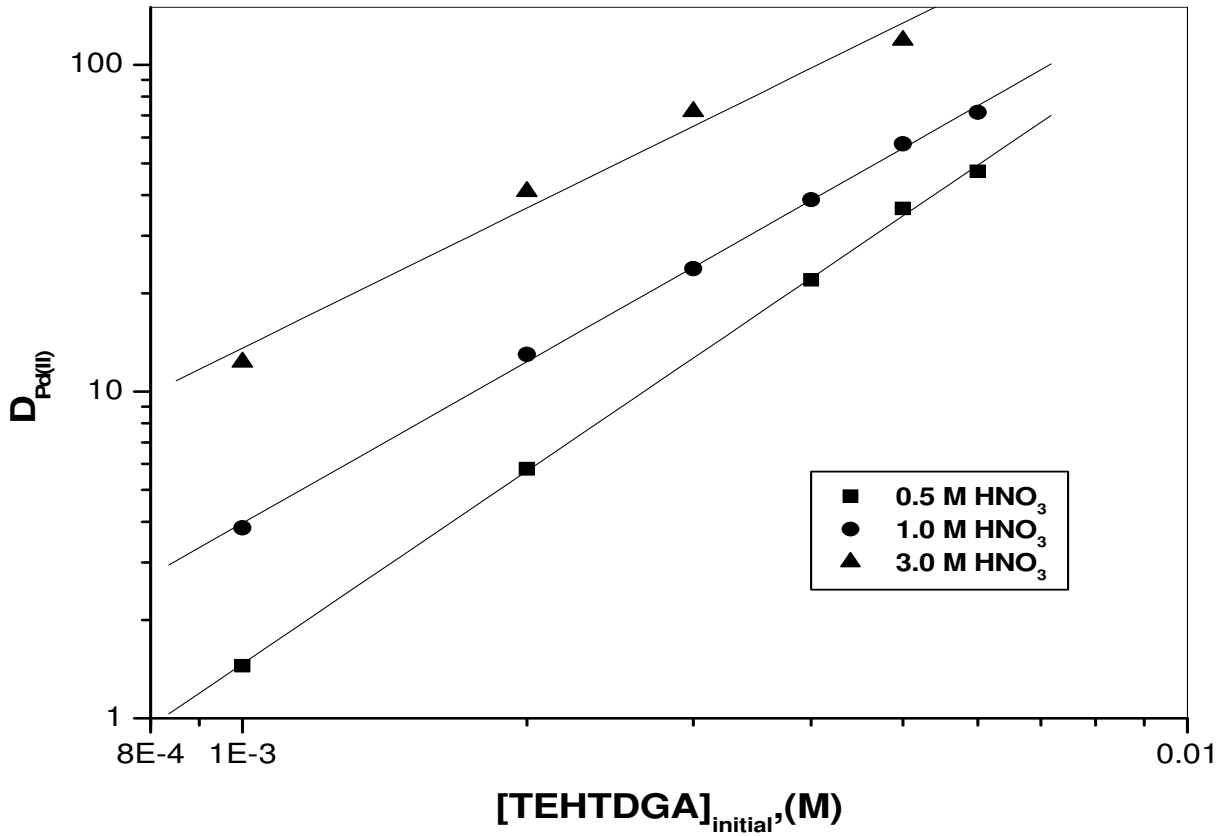
The extraction of Pd with TDGA sharp increase with increase the concentration of nitric acid to reach a maximum extraction value at about 3.0 M nitric acid .

Effect of nitrate ion concentrations (salting-out effect)on the extraction of Pd(II) by using TDGA:



The relation between the distribution ratios of pd, D_{pd}, and NO_3^- ion concentration is a straight line relationship with slope equal to ~2 for TDGA

Effect of TDGA concentrations on the extraction of Pd(II) at different HNO_3 concentrations:



The relation between the distribution ratios of pd, D_{pd}, and TDGA concentration is a straight line relationship with slope equal to ~2 for TDGA.

Composition of Pd(III) extracted species

Slopes analysis values of Pd(II) extracted with TDGA in toluene or n-dodecane at different nitric acid concentrations.

TDGA	Toluene			n-dodecane		
	HNO_3, (M)			HNO_3, (M)		
	0.5	1	3	0.5	1	3
TOTDGA	2.23	2.10	1.97	2.1	2.12	1.90
TEHTDGA	2.15	1.9	1.96	2.20	2.0	1.87

The slope analysis values closed to 2.

Indicated that, the extracted species of Pd with TDGA is

$$Pd^{+2}_{(aq)} + 2\,NO^{-}_{3(aq)} + 2\,TDGA_{(o)} \rightleftharpoons Pd(NO_3)_2.2TDGA_{(o)}$$

Extraction behavior of Pt(IV), Rh(III), Fe(III), Cu(II), and Ni(II)

from different nitric acid concentrations solutions by using TETDGA .

HNO_3, (M)	Extraction %				
	Pt(IV)	Rh(III)	Fe(III)	Cu(II)	Ni(II)
0.5	NE	NE	NE	NE	NE
1.0	<0.01	<0.01	0.01	<0.01	<0.001
2.0	<0.01	<0.01	0.01	<0.01	<0.05
3.0	<0.01	<0.01	<0.1	<0.10	<0.08
4.0	0.10	<0.01	0.20	<0.10	0.20
5.0	~0.15	<0.03	0.30	0.2	0.20

As shown in Table , Pt(IV), Rh(III), Fe(III) Cu(II), and Ni(II) are poorly extracted by TDGA at all nitric acid concentrations.

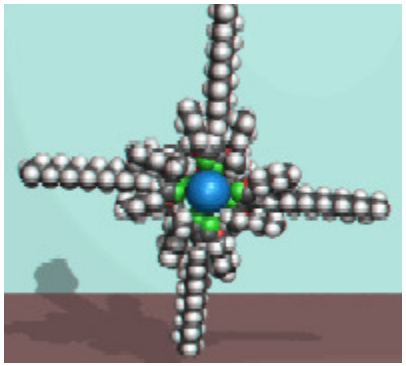
The general extraction ability of TDGA is in order;

Pd(II) >> Fe(III) > Pt(IV) > Cu(II) > Ni(II) > Rh(III).

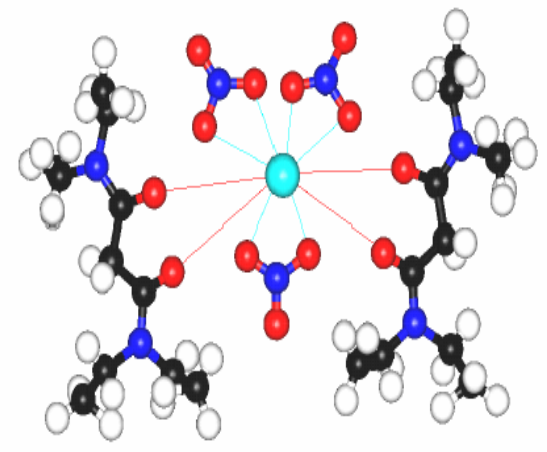
Based on the obtained data, ***a very effective separation of palladium from the other investigated platinum -group or base metal ions can be obtained in nitric acid medium using TDGA.***

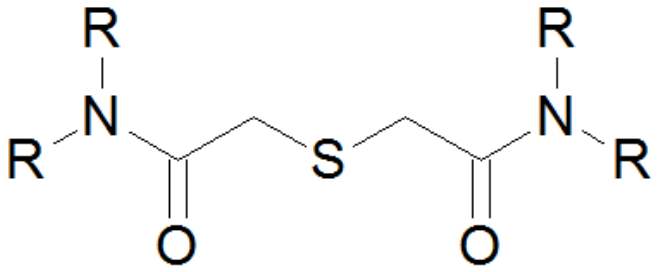
CONCLUSIONS

- We synthesized a number of sulfur-containing diamides (TDGA) as new extractants for PGM.
- The results showed a good selectivity for pd.
- TDGA; Fast kinetic (< 5 min), 100% Pd(II)extraction .
- The nature of N- substituted in TDGA is of importance for metal ion extractions.
- TDGAcould be a potential candidate for selective separation of Pd(II) from other PGMs and base metal ions .



ON GOING AND FUTURE WORK





The novel synthesized ligands (TDGA) will be evaluated for separation and recovery of palladium and other PGM from spent catalyst solution (we are still on the way).

A vision without action is a dream,

ACTION WITHOUT VISION IS A NIGHTMARE

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