

## Electrothermal Atomic Absorption Spectrophotometric Determination of Vanadium, Nickel And Lead In Hydrocarbon Polluted Soils

Dr.Mahmood M. Barbooti\*, Mais A. Mohammed\*  
& Bashar H. Qasim\*

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### Abstract

The present work is a part of a project on the environmental site assessment of a local petroleum refinery to evaluate the extent of pollution of the site with focus on selected places of potential pollution. Soil samples were collected at various depths from almost all locations including: production units, storage tanks, the landfill lagoons at the outside boarder of the refinery and the residence location. The analyses of vanadium, nickel and lead were carried out on extracts of the soil samples made by five different dilute solutions of acetic acid, nitric acid, calcium chloride, EDTA. The nature of the solvent is a determining factor in the efficiency of transport of heavy metals from the soil into the solution. All of the measurements were conducted by graphite furnace atomic absorption spectrophotometry.

It was concluded that heavy metals are available even for the weakest extracting solvent. This was an indication on the nature of the V, Ni and Pb, where they are in inorganic forms due to the degradation by the microorganisms of the soil and aided by dozens of raining seasons and severe hot summers of Iraq. However the soil keeps some of the heavy metals in the original organo-metallic nature which resulted in only partial extraction of these metals with the solutions employed. Thus, the danger from these metals is limited due to their insolubility in water. The range of vanadium detected in the various extracts is ; for nickel, the range was and for lead the concentration range was . The V contents were in the range of 0.01 – 0.37 mg/Kg. The Ni content ranged between 0.06 and 4.5 mg/Kg. The range of Pb contents obtained was in the range of 0.025 – 22.5 mg/Kg. The V and Ni concentrations at the deep soil samples were less than that of the surface samples in most locations. Meanwhile, the penetration of lead contamination seems easier than V and Ni.

**Keywords:** Polluted Soil Analysis, Vanadium, Nickel, Lead,  
Electrothermal Atomic Absorption.

تقدير الفناديوم والنيكل والرصاص في عينات تربة ملوثة بالمواد  
الهيدروكاربونية بواسطة الامتصاص الطيفي الذري الكهروحراري

الخلاصة

تم في البحث الحالي دراسة وتقييم الاثار البيئية لعمليات التصفية على التربة في موقع مصفى الدورة. تم جمع عينات تربة على أعماق مختلفة ومن أغلب اماكن الوحدات الانتاجية والخزانات ومواقع ردم المخلفات خارج سور المصفى. تم اجراء تحاليل مختبرية تفصيلية لتقدير الفناديوم، النيكل والرصاص في مستخلصات التربة باستخدام عدة مذيبات مائية تمثلت في محاليل مخففة

من حامض الخليك، حامض النتريك، كلوريد الكالسيوم، و EDTA. سحقت عينات التربة المجففة بصورة طبيعية وأخذت عينة وزنها ١٠ غرام ووضعت في بيكر مع كمية من المذيب وتم تحريكها مغناطيسياً لفترات زمنية تعتمد على نوع المذيب. ففي حالة حامض الخليك المخفف تطلب الاستخلاص ١٦ ساعة. رشحت محتويات البيكر الى دورق حجمي وغسلت التربة المتبقية واكمل الحجم الى ١٠٠ مل. استخدمت تقنية الامتصاص الطيفي الذري بواسطة التذير الكهروحراري بالفرن الغرافيتي لتقدير تراكيز الفلزات في المستخلصات. لقد تبين من الدراسة بأن مستوى التلوث بالفناديوم يقع ضمن نطاق 0.01 – 0.37 ملغم/كغم. أما تركيز النيكل فنراحت 0.06 و 4.5 ملغم/كغم. كما أن تراكيز العناصر عند السطح أعلى منها في العينات المأخوذة على اعماق معينة. أما الرصاص فكانت أعلى مستوياته عند خزان رباعي أثيل الرصاص المتروك 0.025 ملغم/كغم وأقلها في تربة المنطقة المحيطة بالشعلة 22.5 ملغم/كغم وهي أبعد نقطة في المصفاة عن وحدة تدعيم الغازولين بالرصاص. دلت النتائج على تحول واضح لنسبة كبيرة من المركبات العضوية الفلزية من النفط الخام بفعل الكائنات المجهرية في التربة يساعدها تعدد مواسم الامطار المتعاقبة لمدة تزيد على العقدين والتي يتبعها مواسم الصيف شديدة الحرارة في العراق. ويذكر بأن الطبيعة العضوية للفلزات الثقيلة المدروسة قد تم الاحتفاظ بها جزئياً من خلال وجود فقط تحول جزئي لها في التربة.

### Introduction

Metals play an integral role in the processes of microorganisms. Some are essential to, serve as micronutrients, and to use for redox-processes; to stabilize molecules through electrostatic interactions; as components of various enzymes; and for regulation of osmotic pressure [1]. Many other metals have no biological role are nonessential [1] and potentially toxic to microorganisms. Toxicity of nonessential metals occurs through the displacement of essential metals from their native binding sites or through ligand interactions [1, 2]. In addition, at high levels, both essential and nonessential metals can damage cell membranes; alter enzyme specificity; disrupt cellular functions; and damage the structure of DNA [1]. Petroleum refining is among the most important industries utilizing the crude oils and contributes very much

to the production of large number of essential materials in the modern life. Refining uses so many technologies to extract the light fractions and reforming of some cuts into more valuable products. Catalytic cracking and vacuum distillation are involved to reduce the required operating temperature of the petroleum processing. One of the major costs of the refining industry is the emission of various pollutants to the environment, represented by air water and soil. In Japan, petroleum industry produces more than 250 million tons of wastewater with 140 tons of COD; a final disposal volume of waste materials of 3 thousand tons after recycling more than 22 thousand tons in addition to hundreds of tons of volatile organic compounds, VOC, CO<sub>2</sub>: 7.0 million tons; SO<sub>x</sub>: 2,700 tons; NO<sub>x</sub>: 3,300 tons; soot and dust: 130 tons [3]. Petroleum refining in Iraq back dates to the 1950's when Daura refinery

was first constructed to the south of Baghdad. Daura refinery receives crude oil from various oilfields in Iraq and the production conditions are modified in accordance with the specifications of the blend. Many of the refinery operations and activities are classified among the examples of land uses likely to generate hazardous materials [4].

Heavy metals like vanadium and nickel are among the most naturally abundant organo-metallic compounds in crude oils [5] and hence their existence in soil can be an indicator for petroleum pollution. Lead on the other hand is an essential element in the refining industry as it is incorporated in the well known, but internationally abandoned, anti-knock additive for gasoline. Vanadium and nickel are characteristics of the crude oils and usually occur as porphyrinic complexes and nonporphyrinic compounds [6]. Palmroth et al [7] studied the metal contamination of hydrocarbon soil and the action of phytoremediation processes on the residual levels of heavy metals in soils. The heavy metal determination studies are important for the assessment of mobility and bioavailability of metals in soils. For lead the significance of the determination comes from the fact that it can pose significant groundwater or ecological risks in the environment. In lead contaminated soils, biota and vegetation influence the transformations of lead together with environmental parameters such as soil pH and organic matter content

[8]. Further, heavy metals cannot be biodegraded, but persist indefinitely, complicating the remediation of contaminated soils. Vanadium and nickel in dust fall can be used as indicators of power plant pollution [9].

The purpose of the present work is to study the distribution of V, Ni and Pb and the possibility of penetration through the soil of Daura Refinery. The graphite furnace atomic absorption spectrophotometry will be utilized for the determination of the metal concentrations in the soil of Daura refinery site. Various solvent systems were employed to recover these metals from soil samples.

### Experimental

#### Apparatus

All AAS measurements were carried out using a Shimadzu AA 640 flameless atomic absorption spectrophotometer (Shimadzu Scientific Instruments, Kyoto, Japan) equipped with a graphite furnace atomizer. The experimental conditions of the ETA AAS for V, Ni and Pb are given in Table 1.

#### Materials and Chemicals

The atomic absorption standard solutions were supplied from Merck, Germany). The  $\text{CaCl}_2$  and acetic acid were analytical grade reagents from BDH, England). Nitric acid and ethylenediaminetetraacetic acid disodium salt ( $\text{Na}_2\text{-EDTA}$ ) were supplied from Reidel-Dehaene, Germany. All dilutions and working solution were done with deionized distilled water.

Four solutions were prepared for the extraction of metals from soil, namely: 0.01 M  $\text{CaCl}_2$ ; 0.11 M acetic

acid; 0.5 M nitric acid and 0.02 M ethylenediaminetetraacetic acid disodium salt (Na<sub>2</sub>-EDTA) [11]. Acetic acid extraction took the longest time interval (16 hr). After the extraction, the soil solvent mixture is allowed to cool and stand for 15-30 min and filtered and transferred quantitatively into 100-ml volumetric flask and completed with distilled water.

#### Sampling Plan

Soil samples were collected from various locations of the site. The most acceptable practices [10] were applied during the sampling process to ensure that the sample is representative and undergo the least contamination in an area of soil. Surface and deep soil samples were collected from specific locations of potential pollution. The distribution of the soil sample locations is schematically shown in Fig. 1.

#### Results And Discussion

##### Optimization of Atomic Absorption (AA) Conditions:

The composition of the various extracts, however, differs from the composition of the standard solutions and hence some experiments were carried out to assess the effect of the matrix on the AA signals of V, Ni and Pb. Vanadium requires relatively high atomization temperatures and hence any expected interference from the matrix is inferior. This is in agreement with the results of Barbooti and Jasim [12]. For the Pb atomization, where the relatively high volatility of the element does not necessitate the application of high temperatures, no serious interferences could be obtained from either of acetic acid or

EDTA solutions. Meanwhile, considerable interference from CaCl<sub>2</sub> was expected and hence matrix modifier addition [13] was necessary to overcome the simultaneous volatilization of the salt with the Pb atoms.

##### Major Contamination Sources:

The contamination of soil with hydrocarbons and heavy metals are the results of many operations in the refinery. Firstly, the periodical cleaning of storage tank bottoms and the spread of the cleaning products on soil is another contributor in the pollution. Secondly, the water mixed with oils from many leaks in the piping and pumps of the steam were noticed on the floor of the kerosene improvement unit. Thirdly, the periodical cleaning of heat bundles to remove accumulations of scales leads to sludge and heavy oily residues. The oily wastewater is also generated during heat exchanger cleaning. Further, some temporary solutions for the loading or addition of additives have environmental drawbacks as they leak and the fluids are directed to the main steams and channels in their way to the wastewater treatment system.

Over an area of more than 1500 sq m there located the TEL addition unit. The area is characterized by the smell of apple juice which is indicative of TEL pollution in the air and soil. The whole area is abandoned currently and negotiations are continued with the authorities of the Ministry of Environment to agree on a regular dumping site to move away an old TEL tank in the location. The tank has some defects and holes and

frequently repaired locally with wood pieces. Soil sample around this abandoned tank was taken at surface and down to a depth of 30 cm.

The four extraction media employed represent various leaching power and avoid destruction of the soil structure by acting on the added heavy metals and not on the compositional heavy metals. The trace metal concentrations of the soil samples are listed in Figs 2 -4 for comparison.

#### Heavy metal Pollution

In recent years, the trend has been to express heavy-metal levels in soils as plant- or potentially plant-available metal levels [14-16] rather than "total" concentrations. This implies that "weaker" extractants or chelating agents be used in heavy-metal studies. The EDTA, in either the disodium or di-ammonium salt form, has been used extensively in a host of studies as an extractant of potentially plant-available heavy metals. In some trials, EDTA was found to give a very good indication of the pollution hazard of heavy metals in soils as well as being a reliable test for predicting plant-available metals [16, 17]. Neutral salt extractants are generally weaker extractants than EDTA and give an indication of the immediately exchangeable (therefore immediately plant-available) metals. Examples of such extractants are  $\text{BaCl}_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4$ -Acetate buffered at pH 7, and more. van der Waals et al [18] reported an increase in metal extractability after liming of sacrificial sewage sludge disposal soils. Panichev et al [19] used 0.1  $\text{Na}_2\text{CO}_3$  solution for the extraction of V from soil and got a limit of

detection  $0.2 \mu\text{g g}^{-1}$ . They concluded that considerable amount of vanadium (about 50%) in soils and plants is present as V(V) species.

The vanadium contents of refinery soil were ranging between 0.01 mg/Kg at a depth of 30 cm between the API tank and the cooling tower and 0.37 mg/Kg near the slope tanks. For Ni, the range was between 0.06 mg/Kg under the pipes, i. e., partially protected from deposition and fall outs and 4.5 mg/Kg (near the flare) surface sample. For Pb, the range of concentration was 0.025 mg/Kg near the cooling towers which is almost the farthest point from the TEL feeding unit to 22.5 mg/Kg in the surface soil by the TEL tank (the center of Pb in the refinery).

It is clear that the EDTA extracts gave the highest metal concentrations for a single sample. This reflects the high extraction capacity of EDTA in comparison with the other three solutions and hence the high complexing power of EDTA. For vanadium and nickel, and although their origin is mostly the organometallic (porphyrinic and nonporphyrinic) [5, 6], they exhibited concentrations that are close to each other regardless the nature of the extractant. The high extracting ability of EDTA did not improve the measured concentrations significantly indicating their availability and in the same time the low levels. However, the soil contains metabolically diverse bacteria and viable hydrocarbon-degrading microbiota [7, 20] that could degrade hydrocarbons supported by the long time exposure

to sun shine and raining seasons over decades. Thus, vanadium and nickel are present mostly as simple inorganic species that avail themselves to extraction even for the weak extractants [8].

It is clear that the vanadium contents of surface soil are always greater than the deep soil indicating very slow migration of vanadium through the soil layers. With the exception of location 4, it is clear that the nickel contents of surface soil are always greater than the deep soil indicating very slow migration of nickel through the soil layers. However, organometallic V and Ni are insoluble in water [5] and hence the migration into deep soil will be a property of inorganic forms of these metals to be able to be transported with water. Meanwhile, the penetration of lead contamination seems easier than V and Ni as some of the surface samples has greater Pb contents than the surface soil. This can also be attributed to the use of other anti-knock compounds in the Daura refinery since 2002, i.e., no new emission of tetraethyl-lead from the gasoline improvement unit.

The overall conclusion from the relatively low metal contents determined by these analyses can best be represented by the partial extraction of these metals and that the organometallic nature is partially retained. Purely inorganic extractants like  $\text{CaCl}_2$  and  $\text{HNO}_3$  at the dilution employed, only partially attack the organometallic bonds and hence the heavy metal levels determined stands far behind the petroleum hydrocarbon content of the

soils studied. In conclusion, the heavy metal pollution is not a significant case in the Daura site.

### Conclusions

From the above practical study, it can be concluded that heavy metals are available even for the weakest extracting solvent. This was an indication on the nature of the V, Ni and Pb, where they are in inorganic forms due to the degradation by the microorganisms of the soil and aided by dozens of raining seasons and severe hot summers of Iraq. However the soil keeps some of the heavy metals in the original organo-metallic nature which resulted in only partial extraction of these metals with the solutions employed. Thus, the danger from these metals is limited due to their insolubility in water. The V and Ni concentrations at the deep soil samples were less than that of the surface samples in most locations. Meanwhile, the penetration of lead contamination seems easier than V and Ni.

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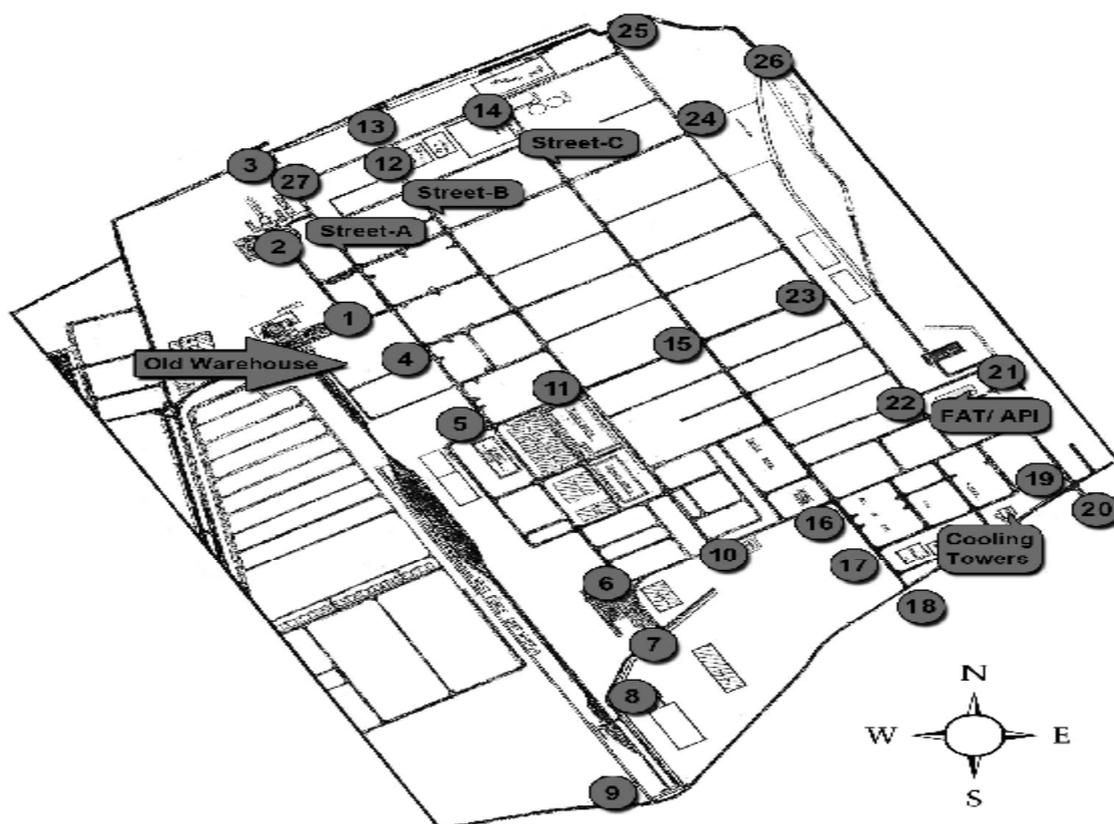
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**Table (1) The Experimental Conditions Of The Eta Aas For V, Ni And Pb.**

Parameter	V	Ni	Pb
Wavelength, nm	318.5	232.0	217.0
Lamp Current, mA	8	6	5
Drying Time, s	40	40	50
Drying Temperature, °C	105	105	105
Ashing Time, s	25	30	30
Ashing Temperature, °C	1100	750	450
Atomize Time, s	5	4	5
Atomize Temperature, °C	2550	2300	1900
Range of Standard Solutions, mg/L	0.5 - 5	0.2 - 2	0.1 – 0.6

Table (2) Heavy Metal Contents of Soil Samples

No.	Description	Metal Contents, mg/kg		
		V	Ni	Pb
1	Center of Waste accumulation lagoons	0.1	0.16;	0.2
2	Center of Waste accumulation lagoons	0.1	0.14	0.32
3	Center of Waste accumulation lagoons	0.1	0.175	0.28
4	Center of Waste accumulation lagoons	0.1	0.65	0.275
5	New project	0.14	1.480	0.96
6	Between slop tanks and the CT	0.37	0.14,	0.025
7	R.O Chlorine pumps, chamber	0.55	0.21	1.5
8	R.O Chlorine pumps, chamber, 3 m far from surface sample	0.05	2.1	17.5
9	Near the flare,	0.1	4.5	2.5
10	Near the flare,	0.1	0.33	0.25
11	By the burnt tank, naphtha 2113	0.06	1.06	0.085
12	fire residue around Tank 2113	0.04	0.72;	0.045
13	25 m distant from burnt tank 2113	0.11	0.48	0.6
14	area between tanks and warehouses	0.31	0.23	0.12
15	Near strategic tank 2101, crude oil	0.17	0.58	0.65
16	3m distant from Tank 2100 crude oil	0.21	0.35;	0.07
17	tank 2110	0.09	0.11	0.08
18	Pipeline between new project and main street (Storage tanks side)	0.05	0.06	0.11
19	Between sub-surface room and CT	0.05	0.15	0.385
20	Near furfural tank	0.58	0.21	1.67;
21	Tank 2114, depth	0.14	0.55	1.70
22	Tank 2114	0.21	1.75	1.70
23	Near discarded TEL tank	0.17	0.36;	22.5
24	Between API tanks and the CT	0.12	0.4	1.4
25	Between tanks and the slop CT	0.1	0.29;	9.5
26	Between API tank and and CT	0.01	0.03	0.053
27	Main street between ENGECCO and CT	0.07	0.75	2.75
28	Main street between ENGECCO and CT	0.05	0.47	1.245
29	Area near the rectangular basin and (CT)	0.1	0.34	14.25
30	Area near the rectangular basin and (CT)	0.14	0.335	1.86
31	Subsurface RO pumps chamber, Near outer fence by the river	0.05	0.65	6.5
32	Subsurface RO pumps chamber, Near outer fence by the river	0.02	0.08	0.35
33	Grasses,	0.01	0.02	0.04
34	Soil around the Guard Room by the Flare	0.2	0.43	0.06
35	By the MEK Barrels	0.05	10.1	0.61
36	By the MEK Tank	0.13	0.05	0.04



**Figure (1) The distribution of the soil sample locations is schematically**  
 1. Gate, 2 The Garden near the head quarter ; 3 Outer gate near fence ; 4 Near old warehouse ; 5 Lube 1, opposite new boiler, 6 Opposite to asphalt loading ; 7 Opposite Wax plant ; 8 Near railways ; 9 Near railway gate ; 10 Lube 2, ; 11 Opposite to TEL unit ; 12 Near the new project ; 13 Rear of main building of light oils ; 14 Opposite the gasoline improvement furnaces ; 15 Opposite to Tank 2148 ; 16 Opposite to vacuum distillation, Lube 3 ; 17 Lube 3, Furfural Unit ; 18 Energy Dept. 2, opposite boiler 10 ; 19 MEK Dept ; 20 Gate door near Japanese unit ; 21 Eastern fence, near API basin of Lube ; 22 North, Opposite to API basins ; 23 Opposite warehouse of safety and fire Dept. ; 24 Wastewater dept near sludge incinerator ; 25 Gate 6 by the flare ; 26 North east of flare ; 27 Chemicals area ; 28 Above ground storage tanks

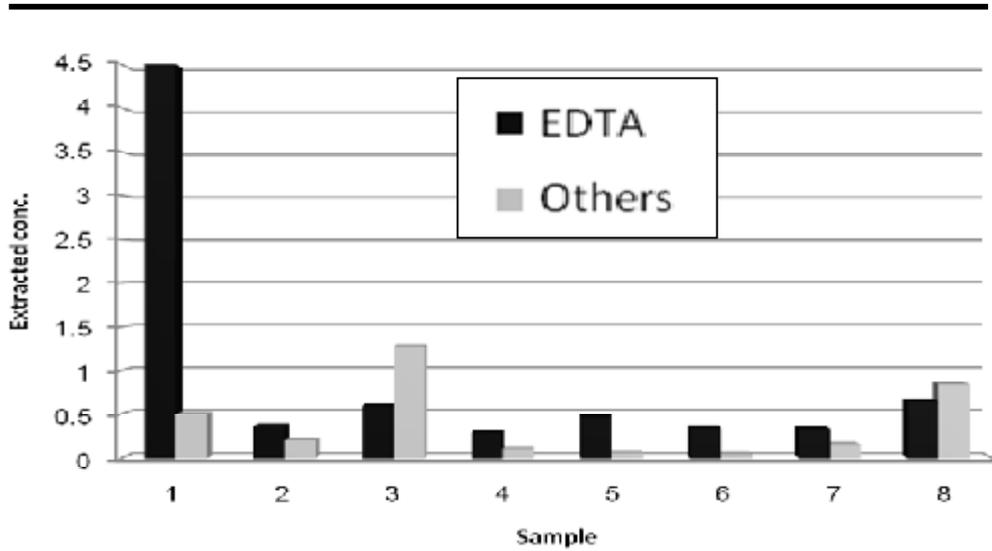


Figure (2) Comparison between the Nickel extraction by EDTA and other solvents. Black shed refers to EDTA and Grey to other extractants.

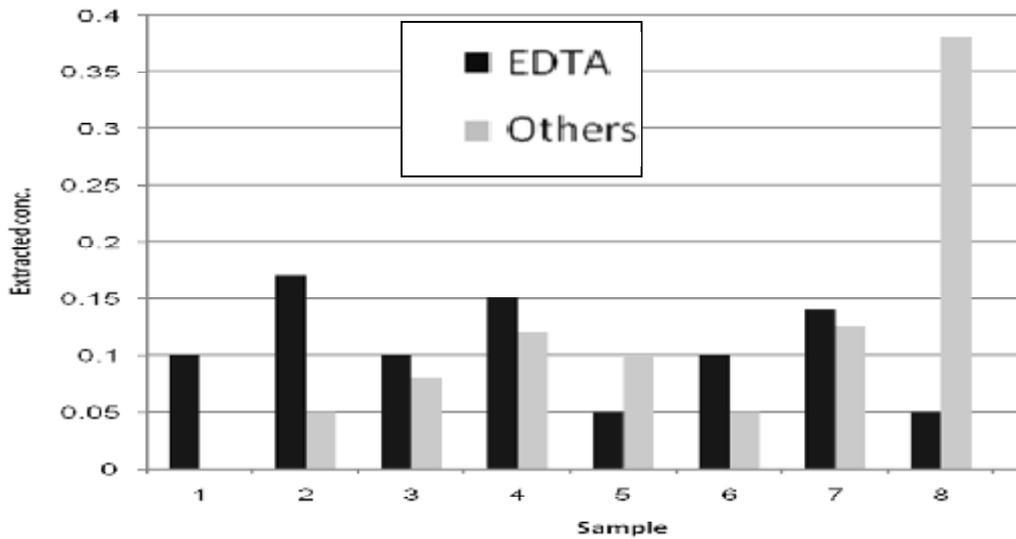


Figure (3) Comparison between the vanadium extraction by EDTA and other solvents, Black shed refers to EDTA and Grey to other extractants.

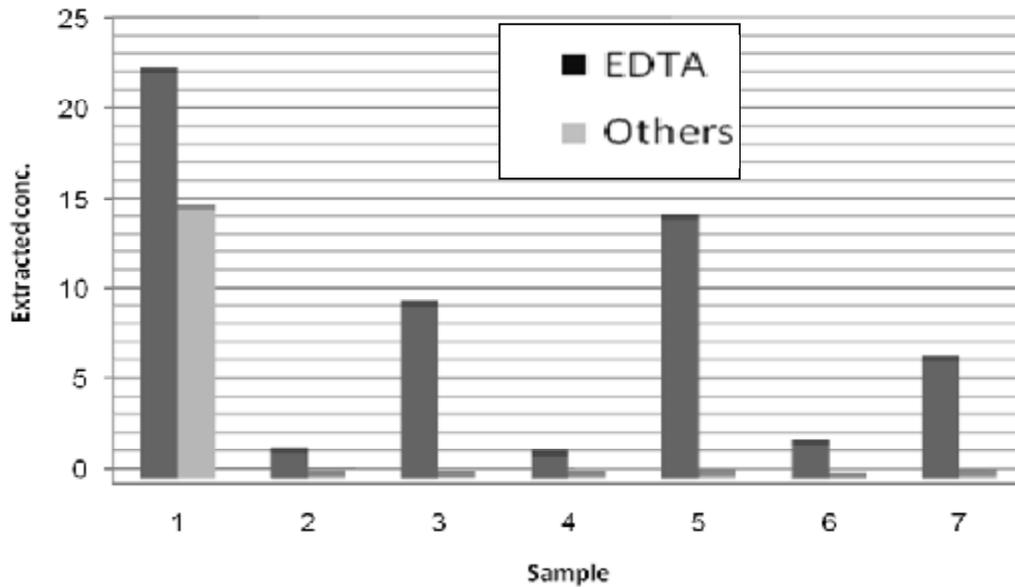


Figure (4) Comparison between the lead extraction by EDTA and other solvents. black shed refers to EDTA and Grey to other extractants.