



**UNIVERSITI PUTRA MALAYSIA**

**DEVELOPMENT OF CHEMICAL SENSOR BASED ON FATTY  
HYDROXAMIC ACID FOR THE DETERMINATION OF VANADIUM (V)  
AND IRON (III) IONS**

**AZIZUL BIN ISHA.**

**FS 2005 23**

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IRON(III) IONS**

**By**

**AZIZUL BIN ISHA**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfilment of the Requirements for the Degree of Master of Science**

**April 2005**



*To my beloved mom and dad, for their understanding and  
patience with this thesis  
To my sister and brother in law;  
to my nephew, Nur Hanis Qistina; and to all the others.*

*azizul*



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in  
fulfilment of the requirement for the degree of Master of Science

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**Chairman: Nor Azah binti Yusof, PhD**

**Faculty: Science**

Chemical sensor based on the use of uv-visible spectrophotometer and optical fibre reflectance spectrometer (OFRS) for the determination of Fe(III) and V(V) ions have been developed in this study. Fatty hydroxamic acid (FHA) was used as a reagent for both metals and shows good properties after characterization using manual batch method. FHA immobilized on poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) as sensing membranes were successfully applied for determination of V(V). However, both immobilization processes were not showing any measurable signal in determination of Fe(III).

PMMA membrane immobilized FHA was characterized using uv-visible spectrophotometer. The sensing membrane changed from colorless to dark purple in the presence of V(V) with response time of five minutes. The relative standard deviation (RSD) of the reproducibility were found to be 9.29% and 7.09% for V(V) at concentration of 50 ppm and 200 ppm, respectively.



Interference from foreign ions were studied at 1:1 mole ratio of V(V) to interfering ion. The interference faced by Fe(III) was the greatest when it was compared with other cations, whereas phosphate ion gave the highest anion interferences. The limit of detection of the PMMA membrane immobilized FHA was calculated to be 8.4 ppm.

PVC membrane immobilized FHA was characterized using optical fibre reflectance spectrometer. The sensing membrane changed its color from colorless to purple in the presence of V(V) and with response time of five minutes. The RSD of the reproducibility were found to be 3.91% and 3.85% for V(V) at concentration of 1 ppm and 20 ppm, respectively. Interference from foreign ions were studied at 1:1 mole ratio of V(V) to interfering ion. Fe(III) was found to interfere most compared to other cations, whereas citrate gave the highest anion interferences. The limit of detection of the PVC membrane immobilized FHA was calculated to be 0.1 ppm.

The results obtained from both instruments which have been developed in this study were compared with the well established method of inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The comparison results show an excellent agreement between the developed method and ICP-AES method. This indicates that the results obtained from both methods are comparable.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia  
sebagai memenuhi keperluan untuk ijazah Master Sains

**PEMBINAAN PENDERIA KIMIA BERASASKAN ASID LEMAK  
HIDROKSAMIK BAGI PENENTUAN ION VANADIUM(V) DAN  
FERUM(III)**

Oleh

**AZIZUL BIN ISHA**

**April 2005**

**Pengerusi: Nor Azah binti Yusof, PhD**

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Penderia kimia berasaskan penggunaan spektrofotometer ul-nampak dan spektrofotometer gentian optik pantulan (OFRS) bagi penentuan Fe(III) dan V(V) telah dibina dalam kajian ini. Asid lemak hidroksamik (FHA) telah digunakan sebagai reagen bagi kedua-dua jenis logam dan menunjukkan ciri-ciri yang baik dalam penciriannya menggunakan kaedah bayaan manual. FHA dipegunkan di dalam poli(vinil klorida) (PVC) dan poli(metil metakrilat) (PMMA) sebagai membran penderia telah berjaya di gunakan dalam penentuan V(V). Walaubagaimanapun, kedua-dua kaedah pemegunan tersebut tidak menunjukkan sebarang isyarat yang boleh diukur dalam penentuan Fe(III).

Membran PMMA terpegun FHA telah dicirikan dengan menggunakan spektrofotometer ul-nampak. Membran penderia tersebut telah berubah warna daripada lutsinar kepada ungu gelap dengan kehadiran V(V) dengan masa tindak balas selama lima minit. Sisihan piawai relatif (RSD) bagi

kebolehulangan adalah 9.29% dan 7.09% bagi V(V) pada kepekatan 50 ppm dan 200 ppm, masing-masing.

Gangguan daripada ion luar telah dikaji pada nisbah mol 1:1 bagi V(V) terhadap ion pengganggu. Fe(III) telah menunjukkan gangguan yang paling tinggi berbanding kation lain, manakala fosfat menunjukkan kesan gangguan anion yang paling tinggi. Had pengesanan bagi membran PMMA terpegun FHA yang telah dihitung adalah 8.4 ppm.

Membran PVC terpegun FHA telah dicirikan menggunakan OFRS. Membran penderia tersebut telah berubah warna daripada lutsinar kepada ungu gelap dengan kehadiran V(V) dengan masa tindak balas adalah selama lima minit. RSD bagi kebolehulangan adalah 3.91% dan 3.85% bagi V(V) pada kepekatan 1 ppm dan 20 ppm, masing-masing. Gangguan daripada ion luar telah dikaji pada nisbah mol 1:1 bagi V(V) terhadap ion gangguan. Fe(III) telah menunjukkan kesan gangguan yang paling tinggi berbanding kation lain, manakala sitrat menunjukkan gangguan anion paling tinggi. Had pengesanan membran PVC terpegun FHA yang telah dihitung adalah 0.1 ppm.

Keputusan yang diperoleh daripada kedua-dua penderia yang dibina dalam kajian ini telah dibandingkan dengan kaedah yang telah diiktiraf iaitu spektroskopi plasma gandingan aruhan - pancaran atom (ICP-AES). Keputusan menunjukkan terdapat persetujuan yang sangat baik antara kaedah yang dibina

dan kaedah ICP-AES. Ini menunjukkan keputusan yang didapati daripada kedua-dua kaedah ini adalah sebanding.



## **ACKNOWLEDGEMENTS**

Thanks to Allah the Almighty and the Merciful, who had given me strength and guidance along the way of life. I would like to thank all of the people that have assisted in the fulfillment of this work. I can only hope that I remember everyone who has some way; shape or form facilitated my achievement.

I owe my parents and family much gratitude for their love and support, which has made this possible. I would like to take this opportunity to express my deepest appreciation to my supervisor, Dr Nor Azah binti Yusof, Associate Professor Dr Musa bin Ahmad and Professor Dr Zulkarnain bin Zainal for their invaluable advice, guidance and constructive criticism. Their enthusiastic supports are always in my deepest memory.

The faculty and students in chemistry department (Dedy Suhendra and Kwa Pei Yeen) is by far the most brilliant, demanding and rewarding individuals I've ever had the pleasure of working with. I would like to give a huge thank you to my friends' abang Sanusi, Sufi, Anuar, Shaari, Sheikh, Thahira, kak Salina, Fiona, Teng Jin, Eddy, kak Mazu and Ace for all the moral support.

Finally, I would like to thank all lecturers and the laboratory staff in Universiti Putra Malaysia and Universiti Kebangsaan Malaysia for their help and assistance. The past and present students of the sensor group in UKM (UKMCHEBS) have been great and deserve a thank you as well. I would like to acknowledge the Ministry of Environmental and Science of Malaysia for funding this research through IRPA research grant IRPA 09-02-04-0818-EA001.



I certify that an Examination Committee met on 5<sup>th</sup> April 2005 to conduct the final examination of Azizul bin Isha on his Master of Science thesis entitled “Development of Chemical Sensor Based on Fatty Hydroxamic Acid for the Determination of Vanadium (V) and Iron (III) Ions” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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## DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



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**AZIZUL BIN ISHA**

Date: 6/7/2005

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## LIST OF ABBREVIATIONS

A	absorbance
FHA	fatty hydroxamic acid
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
PMMA	poly(methyl methacrylate)
PVC	poly(vinyl chloride)
RSD	relative standard deviation
UV-visible	ultra violet-visible



## **CHAPTER I**

### **INTRODUCTION**

#### **Heavy Metals**

Metals are defined chemically as elements which conduct electricity, have a metallic luster, are malleable and ductile, form cations and have basic oxides (Atkins and Jones, 1997). Metals have been used widely for thousands of years. Most of the metals has influenced on the quality of life seriously and also caused environmental problem.

Heavy metal is defined as a group name for metals and semimetals (metalloid) that have been associated with contamination and potential toxicity or ecotoxicity. However, there is no precise definition of heavy metals term in the relevant literature, which reflects inconsistency use even by authoritative body such as IUPAC (Duffus, 2002).

Before 1936, the term of heavy metals was described as “guns or shot of large size” or great ability (Ogilvie, 1884; Williams, 1930). Later, the definition of heavy metals terms is based upon the density of elemental form of the metal (Bjerrum, 1936; Grant and Grant, 1987; Parker, 1989; Lozet and Mathiew, 1991; Morris, 1992; Streit, 1994; Thornton, 1995; Falbe and Regitz, 1996). However, it has been realized that density is not of great of significance in relation to the reactivity of a metal (Duffus, 2002).



Another definition is based on atomic weight or mass, but the mass criterion is still confusing (Bennet, 1986; Lewis, 1993; Rand *et al.*, 1995). Soon, the definition is referred on atomic number which provides a good agreement by several authors (Lyman, 1995; Burrel, 1974).

Other term of the definition is based on other chemical properties such as density for radiation screening, density of crystals and reaction with dithizone. This definition shows that, the term of heavy metals is based vaguely on toxicity (Hodgson *et al.*, 1988).

McIntyre and Mills (1975) described that, toxicology is the scientific discipline which studies toxic or poisonous substances which cause alteration or disturbances in the function of the organism leading to harmful effects of which the most serious is, the death of the organism in question. Toxicity is the property or properties of a material that produces a harmful effect upon a biological system, whereas toxicant is a material that produces this biological effect (Landis and Yu, 1995).

Beside mercury, lead and cadmium, iron and vanadium has been reported as toxic elements that exist in our environment. The sensitive determination of these metal ions is of particular significance in environmental analysis. One of the more promising methods for determination of vanadium is spectrophotometric based chemical sensor, which is presented in this study.



## **Vanadium: The Existence in Nature and Toxicity.**

Vanadium is a common element in lithosphere. It is important for living organism. Its role in physiological systems includes insulin like effect, inhibitory effect on some enzymes and cholesterol synthesis, catalytic effect in oxidation of various amines (Waldron, 1980).

Vanadium is a grayish-silver metal in group V of the periodic table. It is malleable and ductile. Vanadium can exist in oxidation states of +2, +3, +4 and +5, those in the +5 and +4 states being the most stable (Clark, 1968).

Vanadium is found in soil and rocks as minerals such as patronite ( $V_2S_5 + nS$ ), carnotite ( $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$ ), roscoelite ( $2K_2O \cdot 2Al_2O_3 \cdot (Mg, Fe)O \cdot 3V_2O_5 \cdot 10SiO_2 \cdot 4H_2O$ ), descloizite ( $4(Pb, Zn)O \cdot V_2O_5 \cdot H_2O$ ), cupro-descloizite ( $4(Cu, Pb)O \cdot (V, As)_2 \cdot 5H_2O$ ) and vanadinite ( $Pb_5(VO_4)_3Cl$ ) (Vinogradov, 1959; Waldron, 1980). Crude oil also contains vanadium, which is present as an organometallic complex. The vanadium concentration in crude oils varies greatly, depending on their origin. During the burning of fuel oils, the vanadium is left behind as vanadium pentoxide in the solid residue, soot, boiler scale and fly ash (Merian *et al.*, 1991).

Vanadium is widely used in metallurgical and chemical industries. A major commercial use of vanadium has been in steel production. Ferrovandium is one of the most common forms in which vanadium is added during steel-



making to give tough, strong and heat resistant. Beside that, it is also a major alloying element in high-strength titanium alloys (Waldron, 1980).

Another important use of vanadium is as a catalyst in the production of chemicals. Vanadium pentoxide is the principal catalyst used in oxidation of sulphur dioxide to sulphur trioxide in the production of sulfuric acid. Vanadium oxychloride, tetrachloride and triacetylacetonate are used as polymerization catalysts for soluble copolymer of ethylene and propylene. In dye manufacture and dyeing, vanadium compounds are used as mordants. Ammonium metavanadate has been used as a catalyst in the dyeing of leather and fur (Merian *et al.*, 1991).

In the recent years, the growth of metallurgical and chemical industries had caused health and environmental problems. Vanadium at ppb level is necessary to normal cell growth but is toxic for living organism at ppm level. Gavasov *et al.* (2000) has reported that, the tolerable level of vanadium in drinking water in Bulgaria is 100 ppb.

Human exposure to vanadium has severe effects on the cell growth, the cardiac muscle, the diuretic kidney function (Gavasov *et al.*, 2000) and the symptoms such as nervous depression, coughing, vomiting, anemia and increased risk of lung cancer, that are sometimes fatal (Ahmed and Banoo, 1999). The neurotoxicity of vanadium can cause somnolence, convulsions, respiratory failure and gastrointestinal irritation with diarrhea (Faulkner-Hudson, 1964).





Acute poisoning of vanadium causes nervous disturbance, paralysis of hind legs, breathing difficulties, convulsion, hemorrhagic enteritis and finally death. Inhalation of toxic doses causes nasal bleeding and acute bronchitis. The symptoms of toxicity from inhalation include severe conjunctivitis with a purulent eye discharge, rhinitis, soreness of the pharynx, bronchitis and a green-coated tongue (Venugopal and Luckey, 1978). Barceloux (1999) reported that, the toxicity of vanadium compounds increases as the valence increases.

Vanadium can enter the aquatic system through leaching of parent rocks and soil and the transport of water (Hilton and Bettger, 1988). Burning of fossil fuels such as crude petroleum, fuel, oils, some coals and lignite had released vanadium into the environment (Ahmed and Banoo, 1999).

#### **Iron: The Existence in Nature and Toxicity.**

Iron is the most abundant element in the core of the earth and one of the most abundant in the earth's crust. It plays an essential role in photosynthesis (Merian *et al.*, 1991) and is limiting growth nutrient for phytoplanktons in some parts of the open oceans (Strickland *et al.*, 1965; Hudson and Morel, 1989). Beside that, in the biosphere it acts as an active center of a wide range of proteins such as oxidases, reductases and dehydrases (Cotton and Wilkinson, 1972).