

## Rapid Determination of Vanadium in Egyptian Crude Oils (Balayim) by Non-Destructive Activation Technique

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**ABSTRACT.** A nondestructive neutron activation analysis technique has been applied for rapid determination of vanadium as a trace element in Egyptian crude oils (marine and land of Balayim source), using a conventional as well as cyclic modes of irradiation. While the former one is carried out by pneumatic transfer rabbit system coupled with the 2 MW E RR-1, the latter mode is performed by rapid fluid transfer system in conjunction with 5 Ci Pu/Be isotopic neutron source. A Ge(Li) detection system was used for data collection.

Vanadium as a trace element in two samples of marine and land crude oils have been estimated and found to be  $44 \pm 4.4$  and  $80 \pm 8.0$  ppm respectively by cyclic activation analysis, which agree with the corresponding values of  $45 \pm 2.4$  and  $92 \pm 4.6$  ppm deduced by the conventional system. Both data are in fair agreement with previously reported values of chemical analysis.

### Introduction

Vanadium is one of the most abundant metallic elements in crude oils. It is introduced into oil during its formation as porphyrins and other high molecular weight complexes. During oil migration, these heavy molecules are retarded and vanadium concentrations decrease, along the course of migration. Accordingly, the concentration gradients of this element can be used in the study of the history concerning migration, accumulation and formation of the crude oil. In the mean time, it is considered as a catalytic poison in the cracking process and adversely affects the quality of the end products. The contamination of crude oil with such trace element, gives rise to corrosion of distilling facilities and internal combustion engines.

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So, due to the importance of the knowledge of trace-elements (especially vanadium) in crude oil, several methods are available for such analysis<sup>[1-9]</sup>. Emission spectroscopy, atomic absorption, X-ray fluorescence, polarography, calorimetry as well as the instrumental neutron activation analysis (INAA) techniques have been applied. All these methods suffer from limited sensitivity except the last technique (INAA) which was found to be well suited to the trace elements determination in crude oils<sup>[10-16]</sup>.

This work is devoted to the determination of vanadium as a trace element in one of the Egyptian crude oils (Balayim) using an activation technique. Two irradiation systems have been used for this purpose, the first is the Rabbit Pneumatic Transfer System (RPTS) using the Egyptian Research Reactor-1 (ET-RR-1) and the second is the Rapid Fluid Transfer System (RFTS), for cyclic activation using  $^{252}\text{Cf}$ -Pu/Be isotopic neutron source.

## Experimental Procedure

### Irradiation Facilities

Two irradiation facilities have been used to irradiate the samples under investigation:

#### a) A Rabbit Pneumatic Transfer System (RPTS)

It is installed at the gamma-ray spectroscopy laboratories of Inchass centre and is used for a series of irradiations in high thermal flux positions ( $\sim 2.45 \times 10^{13}$  n/cm<sup>2</sup>. sec.) near the core of the Egyptian Research Reactor-1 (ET-RR-1). A schematic diagram of the RPTS system is shown in Fig. (1). The figure shows also the irradiation place at position (A) and the counting station (low background chamber) in the measuring room.

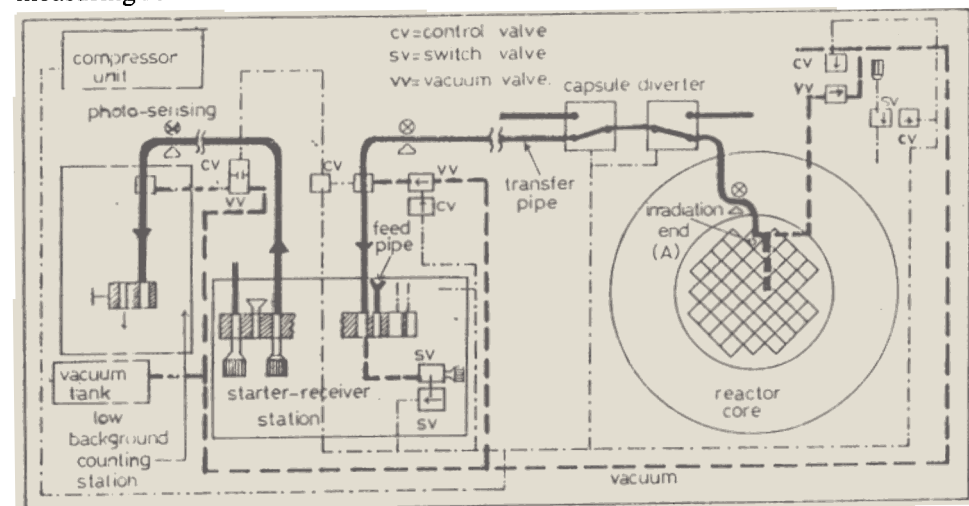


FIG. 1. Schematic diagram of the rabbit pneumatic transfer system (RPTS) at Reactor and Neutron Physics Department of the Nuclear Research Centre, Cairo, Egypt.

The system is operated under vacuum. A two-way air flow can be provided to the tubes. The direction of the air flow is controlled by means of the solenoid valve.

The starter-receiver station connects the radiation positions with the measuring points and serves for storing and repacking the sample carrier capsules. Its shielding consists of steel walls and lead glass windows.

The air flow necessary for moving the sample carrier capsule is ensured by the vacuum created by two high vacuum pumps, one for operation and the other serving as standby. They can be operated either automatically or manually. There is a vacuum tank of a capacity of 0.5 m<sup>3</sup> connected to the pump with an aerosol filter built-in between both pumps.

For venting the guide tubes and the starter-receiver station during operation, two low vacuum pumps are used, one for operation and the other for standby. The venting pipe system will discharge the air through a filter and is connected to the venting system of the reactor building.

A compressed-air supply device with a capacity of 24 m<sup>3</sup>/hr is connected to the rabbit system and used for operating the electro-pneumatic valve as well as the safety over pressure system.

The irradiation time is measured by a digital clock. The longest possible time of irradiation is about 10 hr.

The rabbit system is controlled from a keyboard built into a separate panel.

The dose rate is measured by a 3-channel system at 3 points: in the starter-receiver station, at the measuring point and in the rad-waste container. The system has its own power supply, evaluating and control logic, signalling and G-M detector.

#### **b) Rapid Fluid Transfer System (RFTS) for Cyclic Activation**

A rapid fluid transfer system with two directional flow capability has been constructed and tested. It has been used in developing on-line INAA analytical capabilities for in-situ application and industrial installations<sup>[17,18]</sup>. In typical laboratory systems, a pneumatic transfer system is used to move the sample from the neutron source place to the detection position. For a flowing liquid system, the tubing itself can be used as a transfer system with the neutron source placed at a convenient location and the detector placed at suitable distance.

It has been designed to provide a good geometry for irradiation and counting, variable flow rates and decay times. It could be easily disassembled for cleaning between experiments.

Figure (2) shows a sketch for the overall system. It consists mainly from, the sample feeder, a pump with reversible power motor, an irradiation chamber with an isotopic neutron source of (5 Ci, total activity) and with a Ge(Li) detector surrounded by the counting chamber to provide the maximum counting efficiency. The

average thermal neutron flux throughout the sample volume was  $\sim 9 \times 10^4$  n/cm<sup>2</sup>. sec., measured by means of foil technique. The transferring system is constructed from a rubber tubing of 4 m length and 5 mm diameter.

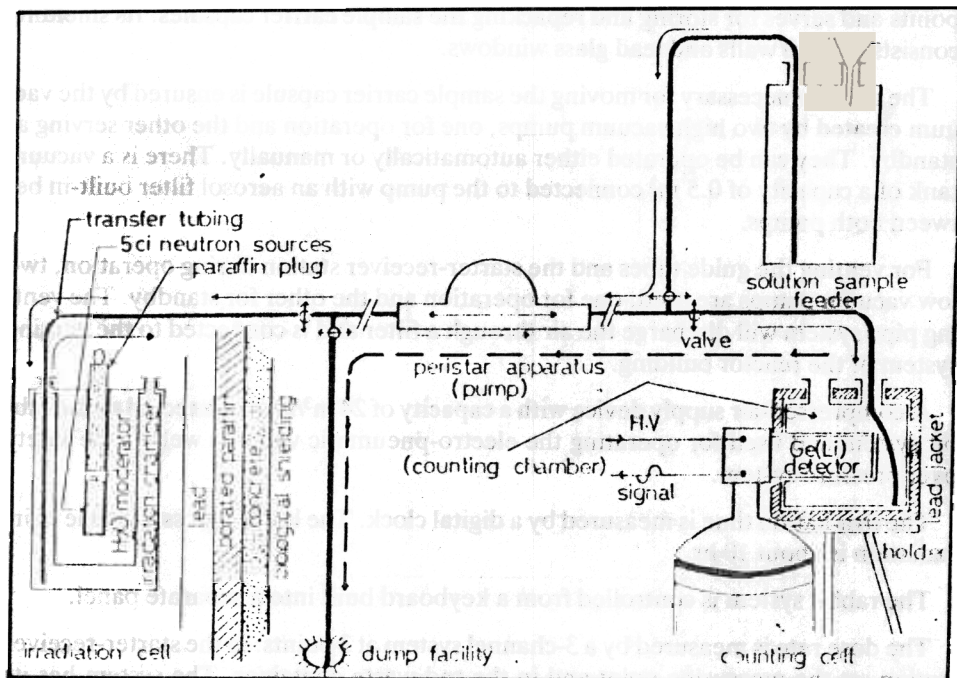


FIG. 2. Schematic Diagram for the Rapid Fluid Transfer System (RFTS).

## Sampling

Few litres of marine and land (Belayim) crude oil of Suez oil processing company have been used for analysis in this work. Standard samples of  $(\text{NH}_4\text{VO}_3 + \text{H}_2\text{O})$  and  $(\text{NH}_4\text{VO}_3 + \text{SiO}_2)$  with different concentration values of vanadium (from 0 up to about 500 ppm) have been used as well, to construct the calibration curves needed.

In order to determine the vanadium concentration values in both crude oils using the reactor neutrons, few milligrams were pipetted in small polyethelene container. The standard samples of  $(\text{NH}_4\text{VO}_3 + \text{SiO}_2)$  were prepared under the same conditions and send for irradiation by the (PRTS) to the same position of the oil samples for the same time. In case of using the (RPTS), one litre of  $(\text{NH}_4\text{VO}_3 + \text{H}_2\text{O})$  standard samples as well as one litre of each crude oil sample are used under the same conditions of irradiation and counting.

### **Irradiation and Activation Measurements**

Marine and land crude oil samples, and the standard samples of  $(\text{NH}_4\text{VO}_3 + \text{SiO}_2)$  and  $(\text{NH}_4\text{VO}_3 + \text{H}_2\text{O})$ , have been irradiated in the high thermal flux position ( $\sim 2.45 \times 10^{13}$  n/cm<sup>2</sup> sec.), near the core of the ET-RR-1 and by means of the 5 Ci Pu/Be isotopic neutron source ( $\sim 9 \times 10^4$  n/cm. sec.), using the RPTS and RFTS systems respectively.

$^{52}\text{V}$ (3.75 m), could be obtained by irradiating the natural vanadium, with thermal neutrons due to the nuclear reaction [ $^{51}\text{V}(\text{n}, \gamma) ^{52}\text{V}$ ], and few gamma-ray lines will be emitted. The most intense gamma-ray line at 1434.20 keV which has been used to identify vanadium in the samples under investigation.

The activity of  $^{52}\text{V}$  in crude oil samples as well as the corresponding standards were counted by means of single Ge(Li) spectrometer. A 4096-multi-channel analyzer coupled with Ge(Li) detector were used. The energy scale of the system was well calibrated using the appropriate gamma-ray standard sources in the interested region of work. A linear energy calibration of 1 keV/ch. has been obtained.

Each sample is irradiated for 5 sec in the high flux position at the (2 MW-ET-RR-1), then cooled for 5 min and counted for 5 min. The irradiation, cooling and counting times were chosen according to the different half lives of the radionuclides of the trace elements in the samples under investigation.

In case of using the (RFTS), each sample was recycled between the irradiation chamber and the counting chamber for 8 cycles with cycle time of 4 min.

### **Results and Discussion**

#### **a) Using the RPTS and the 2 MW-ET-RR-1**

The gamma-ray spectrum for each concentration value of vanadium of  $\text{NH}_4\text{VO}_3 + \text{SiO}_2$  standard samples has been recorded. The concentration values used were at: 51, 97, 106, 195 and 447 ppm (in addition to possible vanadium traces in matrix compound acting as B.G.).

The net peak areas of the  $^{52}\text{V}$  gamma-ray line for each concentration value are obtained. A portion of the decay gamma-ray spectra resulting from the thermal neutron irradiation of each sample showing the photo-line of  $^{52}\text{V}$  at 1434.20 keV was as plotted in Fig. (3). The calibration line of vanadium determination using the standard samples, could be plotted between the net peak area under the photoline 1434.20 keV and the concentration values of vanadium as shown in Fig. (4).

The gamma-ray spectrum for each crude oil sample (Marine and Land) could be measured under the same conditions. The concentration values of vanadium in both samples have been evaluated and corrected for background. The values were found at 45 and 92 ppm for marine and land respectively with an accuracy of  $\sim \pm 5\%$ .

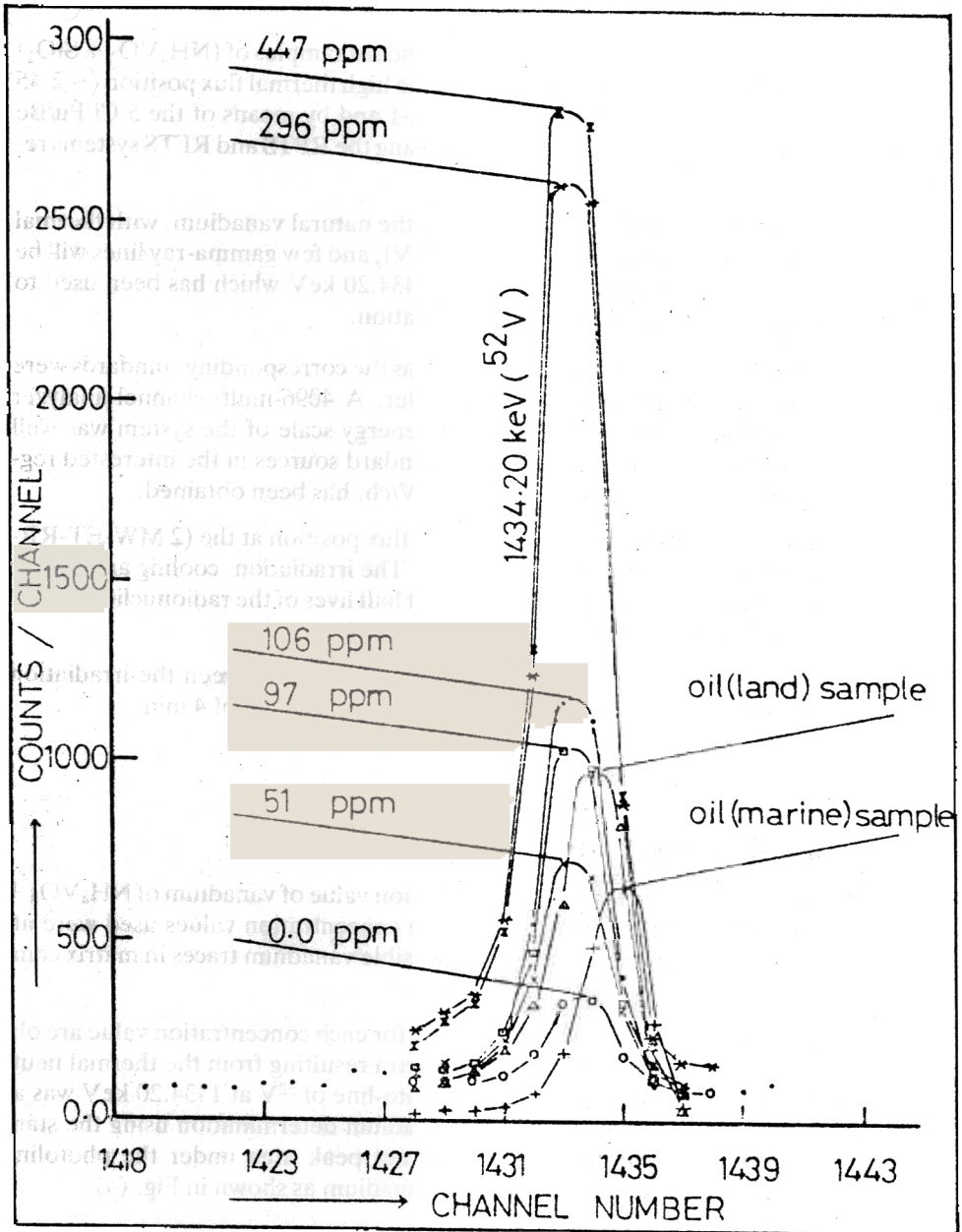


FIG. 3. The Decay Gamma-Ray Photopeaks Resulting From Thermal Neutron Irradiation of Both  $(\text{NH}_4\text{VO}_4 + \text{SiO}_2)$  Standard Powder Samples of Different Vanadium Concentration Values and Oil Samples Using the RPTS For Conventional Neutron Activation Analysis.

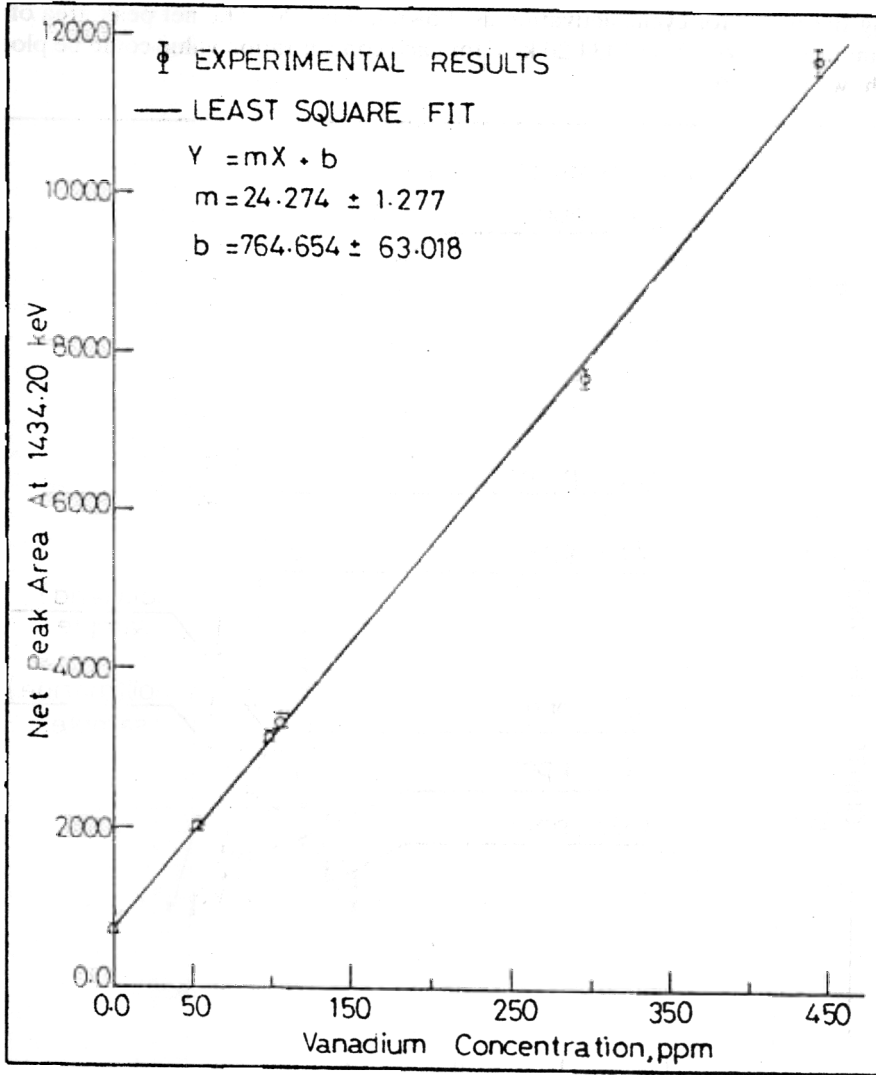


FIG. 4. Calibration Curve For Vanadium Determination in  $(\text{NH}_4\text{VO}_3 + \text{SiO}_2)$  Standard Samples Using the RPTS For Conventional Neutron Activation.

**b) Using the (RFTS) and the 5 Ci, Pu/Be Isotopic Neutron Source**

The gamma-ray spectra of six standard samples of  $(\text{NH}_4\text{VO}_3 + \text{H}_2\text{O})$  at vanadium concentration values of 32, 80, 128, 173, 225 and 276 ppm have been measured by using the RFTS for cyclic activation as shown in Fig. (5). The net peak area of the gamma-ray line of  $^{52}\text{V}$  at 1434.20 keV for each concentration value could be plotted as shown in Fig. 6.

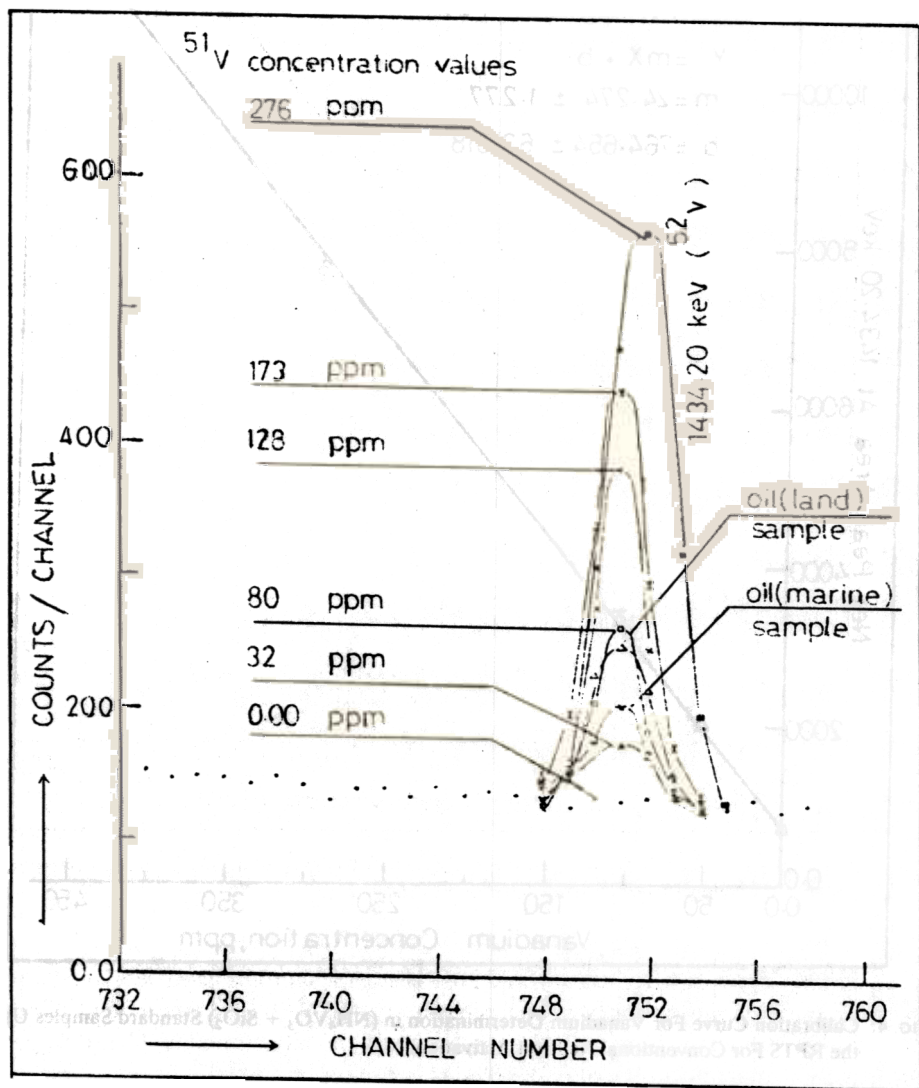


FIG. 5. The Decay Gamma-Ray Photopeaks Resulting From Thermal Neutron Irradiation of Standard Aqueous  $\text{NH}_4\text{VO}_3$  Solutions of Different Vanadium Concentration Values Using the RFTS For Cyclic Neutron Activation Mode.



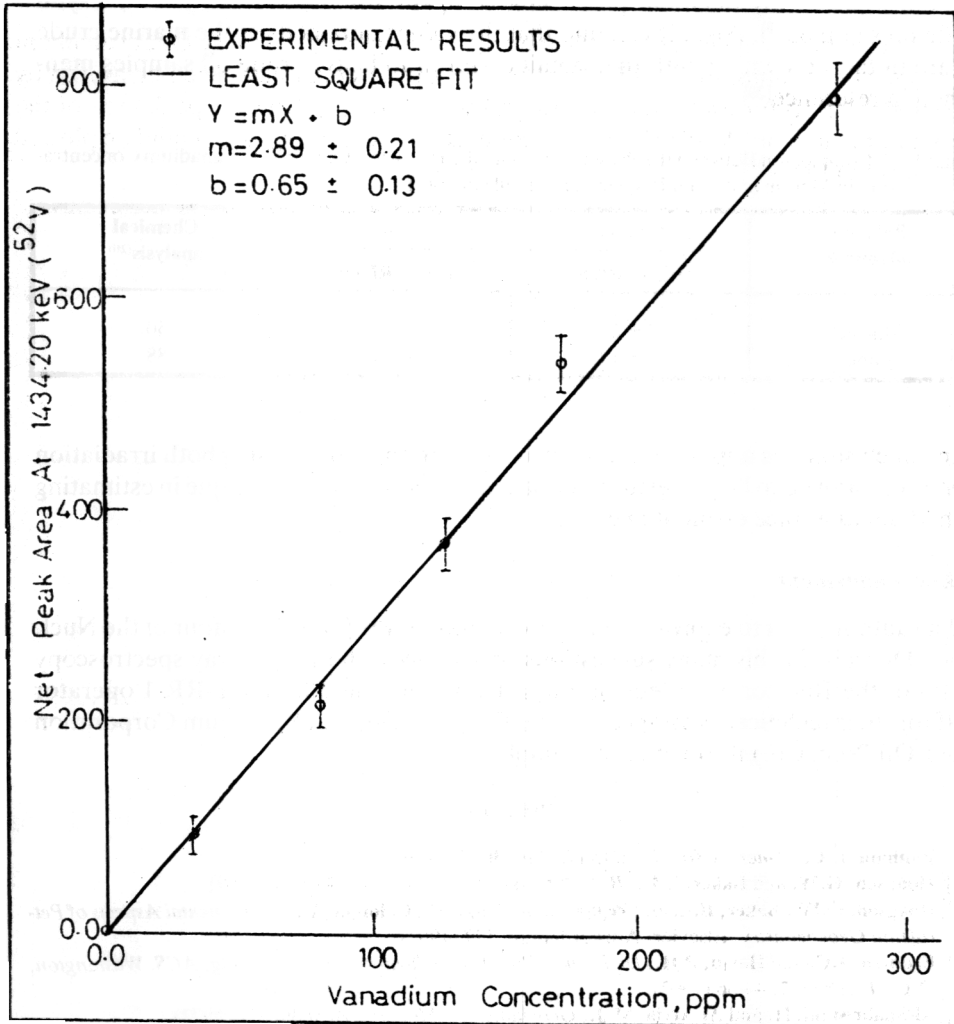


FIG. 6. Calibration Curve For V Determination in Aqueous  $\text{HN}_4\text{VO}_3$  Solutions (Standard Samples) Using the RFTS For Cyclic Neutron Activation Mode.

The gamma-ray spectra of marine and land crude oil samples have been measured under the same conditions and the net peak area at 1434.20 keV could be obtained. The vanadium concentration in both samples could be determined as 44 and 80 ppm respectively with an accuracy of  $\sim \pm 10\%$ .

Table (1) gives a comparison between the experimental data obtained in this work using the two systems RPTS and RFTS and that obtained by the chemical analysis

method reported by Suez Oil processing company for marine and land Balayim crude oil samples<sup>[19]</sup>. Also, it is found that the values obtained for the marine crude oil are in fair agreement with that obtained for arab heavy crude oil samples mentioned in reference<sup>[20]</sup>.

TABLE 1. A Comparison Between the Present Data and the Reported Values<sup>(20)</sup> of Vanadium Concentration in Marine and Land Balayim Crude Oil (in ppm).

Balayim oil source	Present	Work	Chemical analysis <sup>(20)</sup>
	Using (RPTS)	Using (RFTS)	
Marine	45 ± 2.4	44 ± 4.4	50
Land	92 ± 4.6	80 ± 8.0	88

In conclusion it is apparent that neutron activation analysis using both irradiation modes has proved to be powerful as a fast and nondestructive technique in estimating Vanadium as a trace element in crude oil.

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## التعيين السريع لعنصر الفاناديوم في خام زيوت بلاعيم المصري باستخدام نظام التنشيط الإشعاعي اللاتحريبي

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يعرض هذا البحث تقدير وفرة الفاناديوم كعنصر شحيح في خام زيوت بلاعيم المصري المنتج من الحقول البحرية والبرية باستخدام التحليل اللاتحريبي للعينات بتنشيطها إشعاعياً بالنيوترونات الحرارية ، وذلك بنظام التشعيع التقليدي بالمفاعل المصري الأول والمتضمن وحدة النقل السريع للعينات ، بالإضافة إلى استخدام نظام النقل الدوري للعينة فيما بين الكاشف ومصدر نيوتروني من خليط البلوتونيوم والبريليوم والبالغ شدته ٥ كوري .

وباستخدام مطياف الجرمانيوم الليثيوم يمكن تقدير وفرة الفاناديوم في كل من عينات الخام البحرية والأرضية وتبين أنها  $44 \pm 4$  ،  $80 \pm 8$  ، جزء من المليون على الترتيب باستخدام جهاز النقل الدوري والتي اتفقت مع النتائج التي استنتجت باستخدام المفاعل المصري الأول والتي كانت  $45 \pm 2$  ،  $92 \pm 4$  جزء من المليون ، وكلا النتيجةين توافقتا مع ما سبقتهما من نتائج معلنة باستخدام طرق التحليل الكيميائي .

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