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CHARACTERIZATION OF ELECTROCHEMICAL CELL FOR PRODUCTION OF RADIOTRACER IN ORGANIC MEDIUM

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ABSTRACT

In a petrochemical plant, precise knowledge of the flow of the compounds that flow inside the pipelines that carry oil and these derivatives is crucial. To perform these controls a series of flow meters are installed inside ducts in direct contact with the fluid to be monitored. This invasive method presents a great limitation because the oil aggressive proprieties that require these measurement devices are subjected to frequent calibrations which, in turn, cause the stoppage of the plant and low productivity. In this sense, radiotracers has been used in conjunction with the time transient method, by configuring a precise and non-invasive measurement technique.

This work presents the study of the characterization of an electrolytic cell model for the production of petroleum derivatives labeled with Iodine-123 for use as radiotracer in the measurement of flow in ducts and the time transient method. Labelling of organic compounds usually a sequence of solvent separation and extraction steps which, when used for labeling oil and oil derivatives it causes high gamma exposition for the operator at considerable dose rates due to the need for direct interaction with the marking system.

The objective of this work is to develop a cell model that is part of a compact, automatically operated labelling system with physics and chemistry parameters defined to optimize the organic phase labelling processes of petroleum derivatives. The labelling cell is composed of a cylindrical reaction vessel where the aqueous medium containing the iodine-123 in the form of sodium iodide (NaI-I123) is inserted with about 2 mCi of activity and the organic medium. In the system are introduced, two Platinum electrodes where a voltage of 0. 8 V is applied. This system allows the production of radiotracer for a rapid pulse injection. The results show that there was no significant variation of the stability of the system in the temperature range of 25 °C to 40 °C and showed a labelling efficiency around 85%.

1. INTRODUCTION

The production of Petroleum and derivatives is of great economic importance and represents a subject of vital strategic interest for the producing countries of this commodity in the world.

The existence of petroleum reserves presupposes the presence of rocks of porous structure where the organic material is retained, where oil and natural gas coexist and their proportions depend on conditions of temperature, pressure and the geological structure of the forming rock. In order to extract the oil it is necessary to drill these rocky structures and the multiphase fluid extracted from the interior of these reserves has besides the crude oil the presence of natural gas, rock debris and water.

The transport of this material is carried out largely through ducts, since it is the most cost-effective mode for this type of transportation. However, this operation requires the precise

control of the volumes transferred inside the pipelines from a starting point of reserve to a certain destination point.

In the petrochemical industry, flow meters specific to each medium are used, installed inside the ducts and in direct contact with the multiphase medium present that has a highly abrasive characteristic. For this reason, these devices suffer damage and need to be calibrated periodically [1, 2]. This operation requires the paralysis of the operations of the plant, impacting on the industrial costs, maintenance costs of these devices, reduction of production and uncertainty of flow measurement. Another factor that can affect the flow measurement is the partial or total obstruction of the pipelines or the presence of leaks which, in turn, besides financial losses generate environmental impact.

Due to this economic-environmental demand, many oil-producing countries have invested in techniques capable of providing a reliable flow measurement that allows minimizing the impact mentioned previously. Thus, it is fundamental to use a non-invasive measurement technique that allows the acquisition of data in real-time for the correct monitoring of the flow measurement in oil and oil pipelines.

The use of radioactive tracer to flow measurement has been widely diffused in recent years due to the advantages for its use. However, it should be mentioned that in order to obtain a precise measurement the radiotracer used must have characteristics similar to those of the study medium [1, 2, 3].

One of the possibilities of radiotracer for organic fluids is the radioisotope iodine-123, one of the radioactive isotopes of the element iodine. It is a promising radiotracer due to its high degree of purity, which in turn inhibits the presence of contaminating elements in the final labeled product, besides being a gamma energy equal 159 KeV and half-life of 13.2 hours, which allows its use on the field [4]. In this work, the labelling of the organic fluid is obtained from iodine-123 in the chemical form of sodium iodide, connected to organic molecule of lubricating oil by an electrochemical reduction reaction so that the radiotracer presents characteristics similar to the medium to be monitored.

The objective of this work is to develop an electrochemical cell model that will be part of an automated, compact labelling system with physical and chemical parameters defined in order to optimize the organic phase marking processes of petroleum derivatives to be used as a radiotracer in the petrochemical industry.

2. THEORETICAL REFERENCE

The electrochemistry studies the oxidation and reduction reactions that produce or are produced by electric energy [5]. When we have the phenomenon of electron transfer in chemical reactions between different substances converting chemical energy into electrical energy, it is called a cell, if this phenomenon is characterized by the conversion to electric energy into chemical energy, it is called electrolysis [6]. These reactions occur inside electrochemical cells, which in the case of cells are called galvanic cells, and in electrolysis are called electrolytic cells. This study will be approached concepts related to electrolysis.

Since electrolysis is a chemical process opposed to cells, and the reversibility of a reaction is an unnatural process, it becomes necessary to apply an external voltage to promote the oxidation and reduction reactions inside the electrolytic cells [7]. The applied voltage value must be enough to obtain free ions from the dissociation or ionization of the chemical used as the reaction medium, called an electrolyte. The electrochemical labelling process of the petroleum and derivatives with iodine-123 occurs addition reaction in compounds that have instabilities in the carbon chain, such as oil-derived lubricating oils. Since iodine is a non-

metal, from the group of halogens, the addition reaction is called as a halogen process. In these reactions, a π (pi) type carbon bond is broken and then a halogen, in this case the iodine element, is inserted into the carbon chain. [8].

$$H_2C=CH_2+I_2 \longrightarrow \begin{matrix} H_2C-CH_2 \\ | \quad\quad | \\ I \quad\quad I \end{matrix}$$

The labelling of organic compounds by the addition of iodine occurs after the production of iodine (I_2). Among the methods to obtain I_2, the electrochemical oxidation method is the best [9]. This technique involves the generation of the cation (I^+) from the electrochemical oxidation reaction.

$$2I^- - 2e^- \longrightarrow 2I^+ \longrightarrow I_2$$

This technique has as an advantage over the conventional solvent extraction method since it requires the use of solutions of low iodine concentration that, from the point of view of radioprotection is fundamental since exposure to the radiation can be minimized. For the practical application of the electrochemical technique, the apparatus requires an electrolytic cell and electrodes that do not interact with the medium where the reaction is processed. In this case, it is necessary to use glass cells and electrodes made from inert materials such as platinum.

Figure 1 presents four conventional cell models with glass membrane synthesized for phase separation between cathode and anode and are generally used in electrochemical reactions. The models presented in figure 1 were used for the proposed synthesis, but it was observed that the glass membrane acted as an electrical insulator of the cell that made the aqueous phase marking reaction unviable.

Figure 1: Conventional cell models with synthesized glass membrane.

It was necessary to develop a cell model that would allow the passage of electric current to convert iodide (I^-) to free iodine (I_2). The proposed model is based upon the surface tension property observed in the interface between the aqueous and organic phases of the immiscible liquids [10]. In this system, the electrodes were isolated from the organic phase by two glass capillaries. A third capillary was introduced for insertion of a pH meter, thermometer and for withdrawal of samples from the aqueous phase. That is, the electrodes are in direct contact only with the aqueous phase that is denser than the organic phase. The organic phase is arranged directly on the aqueous phase. To promote mixing between phases during the electrolysis process the system is agitated. Samples are withdrawn after a period of rest where phase separation occurs again.

3. MATERIALS AND METHODS

The radionuclide iodine-123 ($E\gamma$ = 159 KeV and $T_{½}$ = 13.2 hours) used for this research was obtained from a solution of sodium iodide (NaI) was supplied by the Division of

Radiopharmaceuticals DIRA / IEN / CNEN. The radionuclide is produced in the cyclotron CV-28 via nuclear reaction (p, 2n) from the irradiation of Xenon gas (^{124}Xe), with purity equivalent to 99.9%, with proton beam in the energy range of 24 MeV.

The electrochemical reaction to produce the radiotracer in this study used a proposed electrolytic cell, without any physical barriers. The cell consists of a glass beaker with an internal diameter of 8 cm, with a capacity of 200 mL, where three glass tubes with internal diameter 2 cm each was inserted, two of which were used to isolate the electrodes from the organic phase and a third to withdrawal of samples and introduction pH meter and thermometer, according to figure 2a. The system for electrolabelling is shown in Figure 2b. The system was lead-shielded to minimize the effects of gamma rays from radioactive decay of iodine-123.

(a) (b)

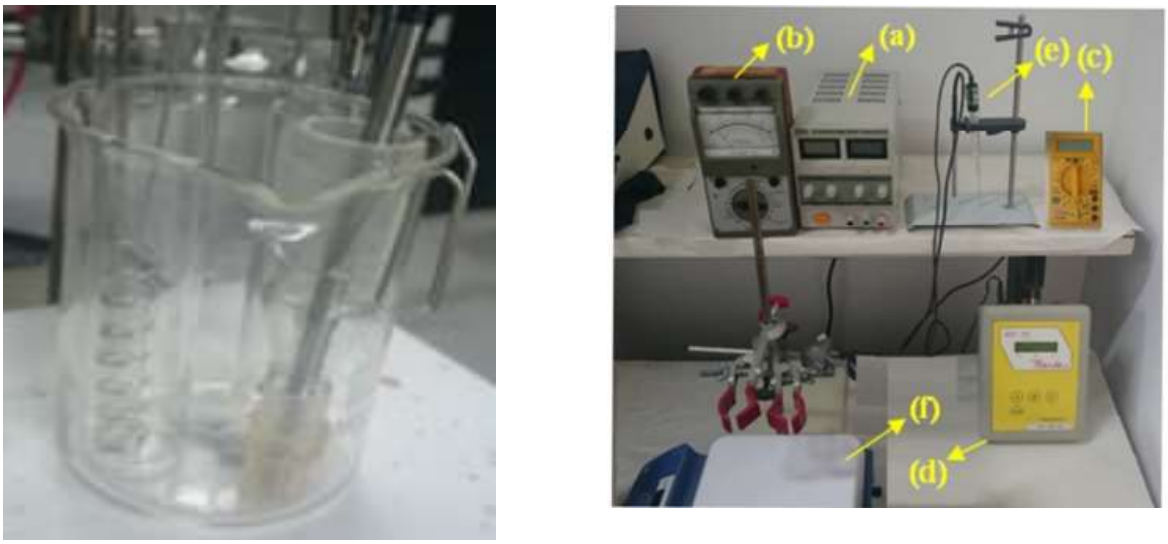

Figure 2- (a) cell used by the study; (b) Electrollabeling system. (A) voltage source, ICEL, model: PS-4000. (B) multimeter, UNIGOR, model: 4S; (C) Ammeter, UNI-T, model: DT830B; (D) Ph meter, MART, model: MB-10 with temperature sensor; (E) electrode, ANALYSER, model: 2A14 / PA. (F) magnetic stirrer with heating, IKA, model: C-MAG HS7

The electrolyte used was composed of 98% pure sulfuric acid, acetonitrile, 99.99% pure and deionized water 2: 2: 1 [11]. The stability of the system will be evaluated from the variation of the temperature in this work two groups were defined: Group I of the samples was subjected to a temperature of 25 ° C throughout the process while group II was subjected to a temperature of 40 ° C. The voltage applied to the cell was 0.8 volt during a period of 30 minutes, according to the existing methodology developed from the relation between the production of I_2 from the consumption of iodide ions during the labelling process [11]. As a method of evaluation of the marking process based upon the use of the proposed electrolytic cell, the technique of determination of the index of iodine in the oil samples labeled with iodine-123 was adopted. It is expected that during the reaction the double bonds will break so that the iodine generated in the electrolysis binds to the carbon chain by the halogen process [7]. With this, the number of double bonds in the oil tends to decrease as well as the number of the iodine number. The procedure of standard EN 14111 was used to measure the iodine content [12,13]

The mass equivalent to 0.015 g of the oil sample was weighed and transferred to a clean, dry beaker. The sample was dissolved in 20 mL of chloroform and 25 mL of the Wijs solution. After resting for one hour, together with a blank test that did not contain the

oil, 20 mL of the 10% potassium iodide solution and 150 mL deionized water were added. The system was shaken for 30 seconds. Then, the potentiometric titration with the standard solution of Sodium Thiosulphate in the concentration of 0,1 $mol.L^{-1}$ was carried out until reaching the point of equivalence, as verified by the potential change. In the blank, the absence of oil followed the same sequence of addition of the reagents until titration. In the blank sample there is no double bond to be broken, so the titration was done only for the removal of excess iodine. This data is important because it used to calculate the index of iodine. In order to evaluate the labelling process for the production of radiotracer in organic medium, the flow measurement was carried out in an experimental oil derivative transport line located at the Radiotracer Laboratory IEN / CNEN [14].

After the labelling, 10 mL of the labelled oil was injected into an oil pipeline with 2" diameter and where the oil flowrate is (4.0 ± 0.1) liters / minute. To measure the flow rate, the technique adopted was the Transient Time Method and to measure the tracer movement two NaI 1x1" scintillator detectors were positioned on the line. The first one, Position 1, was at two meters from the point of injection of the marked oil and the second, Position II, at three meters away from the first detector. Experimental data were acquired with the time interval between counts of 0.05 seconds.

4. RESULTS

The following results refer to two groups of samples, submitted to the same processing methodology, using the proposed electrolytic cell, but using different temperature. The variation of the temperature gradient was aimed at evaluating the stability of the process. Group I was subjected to a temperature of 25 ° C, while group II was processed at 40 ° C. In the determination the label process, the samples of oil labelled with iodine-123 were compared to a sample with any iodine called "white". Tables one and two shows the results by applying the potentiometric titration technique of the experiments performed at 25 ° C and 40 ° C, respectively.

Table 1: Determination of the iodine value at 25 °C with iodine-123

Sample	Vol(mL) $Na_2S_2O_3$ (Vb)	Vol(mL) $Na_2S_2O_3$ (Vt)	Sample Mass [g]	Iodine index
"white"	73,0	65,0	0,155	65,497
Experimental oil	73,0	72,0	0,147	8,633

Table 2: Determination of the iodine value at 40 °C with iodine-123

Sample	Vol(mL) $Na_2S_2O_3$ (Vb)	Vol(mL) $Na_2S_2O_3$ (Vt)	Sample Mass [g]	Iodine index
"white"	73,0	65,0	0,155	65,497
Experimental oil	73,0	72,0	0,151	8,404

When comparing the results obtained for the iodine value in the "white" sample and the labeled oil sample, a decrease in the iodine value is observed. The reduction of this value indicates that the halogen process occurred and, therefore, shows the efficiency of the electrolytic cell since it does not interfere in the migration of the chemical species involved.

Based on the results of the iodine number an efficiency of the labeling process is calculated around 85%.

After all steps of the electrolabelling process were completed, the lubricant oil already labeled with iodine-123 was tested in an experiment that evaluated the system response for determination of flow measurement by the technique of time transient measurement (RTD) in a Line of transport of experimental petroleum derivatives located in the laboratory of radiotracer of the IEN.

A sample of 10mL labelled oil was injected into the oil pipeline with a 2 "diameter and with flow rate adjusted to (4.0 ± 0.1) L / min. To obtain the data, two scintillator detectors were positioned on the line, two meters from the injection point and the second one at three meters from the first detector, being called, respectively, P1 and P2. Experimental data were acquired with the time interval between counts of 0.05 seconds. Figure 4 shows the recording of the trace cloud signal on scintillation detectors P1 and P2 and table 3, shows the mean residence time for each detectors, the transient time between the position P1 and P2 and the calculated flowrate Q.

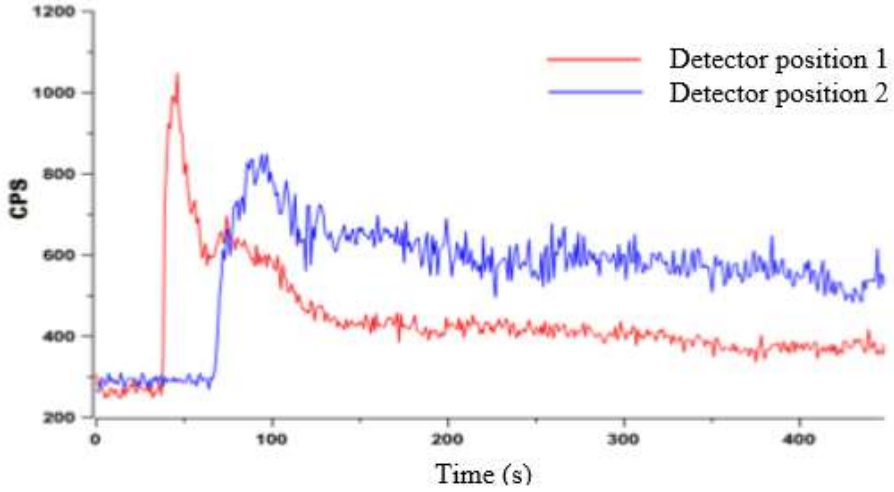

Figure 4: Record of the passage of the iodine-123 labeled radioactive oil cloud on the scintillation detectors D1 and D2 positioned on the 2 "transport line.

Table 3: Flow data calculated by the time transient technique.

D1 ($\tau_1 \pm \Delta\tau_1$) S	D2 ($\tau_2 \pm \Delta\tau_2$) S	Time Transient [s]	Experimental Flow [l/m]
49,91 ± 0,19	128,50 ± 0,34	86,66 ± 0,39	4,13 ± 0,21

Comparing the experimental value (4.13 ± 0.21) L/min with the theoretical value (4.00 ± 0.1) L/min given by the flow meter installed in the line we have a percentage error around 3%. In previous experiments, where the Au-192 [14], Au-198 nanoradiotracer directly injected in the medium (no labelling process) and the experimental error obtained was 10%. Comparing this result with the result with labelled oil (3%) is clear the improvement in Q measurements by the application of the label technique proposed in this work. This error can be improved in a new measurement by decreasing electronic noise and increasing the amount of tracer injected.

5. CONCLUSION

The experimental results allowed the initial objectives of the research to be achieved. As conclusions, we can highlight: The proposed electrolytic cell allows the application of the methodology for the marking of lubricating oil with iodine-123 using electrolytic technique with successfully yielding around 85%;

The proposed electrolytic cell layout allows the system to be automatically and properly shielded, allowing the operator to have a minimum exposure to gamma radiation in relation to the conventional solvent extraction method;

At the temperature range of 25 ° C to 40 ° C the technique is considered stable for use in the field, where the ambient temperature may suffer variation around the studied range.

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