DETERMINATION OF IODIDE BY VOLUMETRIC TITRATION IN SUPPORT OF THE OIL ELETROLABELING WITH $^{123}$I

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ABSTRACT

The accuracy in measuring flow rate in pipelines is essential task to control various technical parameters in an industrial plant in oil industry and its derivatives. For this reason, it becomes increasingly widespread the uses of organic molecules labeled with radioactive isotopes mainly because of the wide possibility in use of different radioisotopes also due to the new labeling techniques.

This paper presents a study to develop an electrochemical technique for oil labeling with iodine -123 and to determine the yield of production by measuring the concentration of iodide (I$^-$) during this process. The volumetric titration technique was applied as a basis for quantitative and qualitative measures to monitor the labeling process. The results indicate the technical proposal as a viable alternative for monitoring electro labeling process of lubricating oils with iodine -123

Keywords: Radioactive tracers, Iodine -123, Electrochemistry, Iodine analysis.

1. INTRODUCTION

In the elements periodic table, iodine is a non-metal in the halogens group and it is represented by the symbol I. It has atomic number 53 and atomic mass of 126.9 uma. At room temperature, iodine is sublimated in the solid state and forming a violet gas. Its electronegativity is considerable and it has a certain facility in oxidize, mainly a in the presence of solutions with pH acid.

In aqueous solution, the iodine is presented in the form of ionic iodide (I$^-$) and iodate (IO$_3^-$). The iodine is sparingly soluble in water, although the solubility may be increased when it is in the form of iodide (I$^-$) because of the formation of triiodide (I$_3^-$). In addition, iodine has high solubility in organic substances.

The iodine has only one stable isotope, I-127 and 32 radioactive isotopes, among which the isotope I-123, focus of interest in this work. The half-life of I-123 is of thirteen hours with a typical gamma of 159 Kev.

The I-123 is an isotope produced in cyclotrons and is usually obtained by indirect reactions (1) or (2).

$$^{124}Xe(p,2n)^{123}Cs\rightarrow^{123}Xe\rightarrow^{123}I$$ (1)
\[^{124}\text{Xe}(p, pn)^{123}\text{Xe} \rightarrow^{123}\text{I}\]

A tracer is used to obtain information about the dynamic variations in an industrial plant and with its application is possible the study of physical, chemical and biological phenomena present in the industrial plant. For success in using a tracer, it is necessary that it present the same or similar characteristics the labeled material; however, one of its properties is that it should be possible to be detected. Moreover, it is essential that the tracer does not cause disturbances in the system during the injection steps, detection and sampling [1].

In oil industry and petrochemical plants the radiotracer methodology is one of the most appropriate techniques for analyzing the flows of organic compounds and for the identification of any fault in the plant’s operation. For this, radioisotopic labeling techniques of oil derivatives is important to guarantee an optimal radiotracer for troubleshooting inspection and process analysis.

In petrochemical industry one of the most widely used radiotracer is I-123 and it is used to label organic compounds using classical analytical methods such as extraction and separation techniques [2, 3]. This chemical processes are time consuming and require a direct action of the operator allows him to be exposed to high doses of gamma radiation.

### 2. ELECTROCHEMICAL METHOD

The labeling of organic compounds by the addition of iodine involves the production of elemental iodine (I\(_2\)). Among the existing methods for obtaining I\(_2\) from the sodium iodide (NaI) [4], the emphasis will be to electrochemical oxidation method. This technique involves the generation of the cation I\(^+\) from the electrochemical oxidation reaction (3).

\[
2I^- - 2e^- \rightarrow 2I^+ \rightarrow I_2
\]

The electrochemical oxidation technique has the advantage of determining the rate of formation of I\(_2\) and this operation can be monitored controlling the electric current supplied to the reaction cell. In addition, in procedures that require the application of radioactive iodine (I-123), the radiation exposure can be minimized, because the use of solutions with low iodine concentration is possible, this is crucial considering the limits of radiation exposure according the radiation protection laws.

For the practical, in application of electrochemical technique for labeling using iodine it is necessary to use an electrolytic cell and electrodes that are non-reactive with the medium in which the reaction proceeds. In this case, it is recommended the use of cells produced on glass and electrodes made of inert materials, such as platinum.

To measure and control the concentration of iodide during the lubricating oil labeling process, the volumetric titration method by precipitation as best suited to achieving the desired results. The precipitation method is employed to determine halides (Cl\(^-\), Br\(^-\) and I\(^-\)), cyanide (NC\(^-\)) and thiocyanate (SCN) from the formation of silver salts by use of standard silver nitrate solution (AgNO\(_3\)) [5].

In this study, the silver nitrate solution (AgNO\(_3\)) was standardization using as primary standard sodium chloride solution (NaCl) and potassium chromate as indicator (K\(_2\)CrO\(_7\)) [6]. For the determination of iodide in the samples will be used Fajans Method, in this technique the solution color-change is related to the absorption of the indicator on the surface of the precipitate [7]. In this case, the eosin (C\(_{20}\)H\(_6\)O\(_5\)Br\(_4\)Na\(_2\)) will be used as indicator.

### 3. MATERIALS AND METHODS
All stages of this work were carried out in Radiotracers Laboratory of Nuclear Engineering Institute (IEN/CNEN). At this early stage, it was decided to use sodium iodide salt (NaI) non-irradiated, in order to minimize exposure to ionizing radiation from the radioisotope I-123.

1.1 Equipments

The electrolytic cell used consists of a circular glass vase-shaped ø8cm x 10cm. This was entered three glass tubes with an opening at both ends. The tubes follow a triangular arrangement, the two diametrically opposite pipes is inserted a platinum electrode in a spiral shape. The third tube was used to extract the samples during the reaction. The reaction vessel was placed in the center of a plate with magnetic stirring, IKA brand, model C-Mag HS7, which allows mixing of the aqueous phase with the organic phase.

Because the non-spontaneous character of electrolysis reactions, the migration of chemical species is related to the supply of an electric current to system [8]. In this work, the electrodes were connected to an external voltage, HP brand, model 6227b. The operating voltage source was set at 0,6volts.

To analyze the concentration of iodide ion in the electrolyte solution was applied the precipitation volumetric titration using a silver nitrate solution (AgNO₃) 0.1 mol / L [9]. The titration system used sets a simple and user-friendly arrangement. It consists of a burette with a capacity of 50 mL, Erlenmeyer flask with 125mL capacity, a universal stand and a claw for fixing the burette support.

1.2 Sampling and Sample Preparation Procedure

The volume of sample (aqueous phase) corresponds to 0.5 mL. This volume was transferred to the Erlenmeyer flask which was added 1 mL of eosin solution (C₂₀H₆O₅Br₄Na₂) 0.1% m/v and 10 mL of deionized water. The sample was titrated with standard solution of silver nitrate (AgNO₃) 0.1 mol / L.

4. CONCLUSIONS

The chart one shows the calibration curve obtained in triplicate for analysis of solutions of sodium iodide (NaI) concentration of 2 mol /L; 1 mol /L; 0.5mol /L; 0.1 mol /L and 0,05mol /L.

The values were corrected based on the correction factor fc = 1,027; obtained after standardization of the solution of the silver nitrate solution (AgNO₃) 1 mol /L. The curve shows correlation coefficient of 0.994.

![Chart 1: Calibration curve for analysis iodide ions concentration (mol /L)](image_url)
To determine the yield of the reaction from the use of iodide ions in the aqueous phase, the system was stirred for one minute every five minutes for one hour so that the elemental iodine generated by the electrochemical process to be transferred to the organic phase.

After separation of the phases, samples were taken in triplicate of samples of the aqueous electrolyte phase. The temperature was maintained at 22 °C during the entire reaction time.

The results were expressed in the second chart obtained from the calibration curve (chart 1).

![Iodide Consumption Rate](image)

**Chart 2: Consumption rate of iodide ions during the electrochemical process.**

As noted in chart 2, in the initial stage of t = 0 to t = 10 minutes, the concentration corresponded 2.062mol/L of iodide. In this range, there is a sharp decrease in the curve which indicates a high rate of consumption of halide ions and hence the formation of elemental iodine.

Between t = 15 minutes to t = 40 minutes there is a slight decrease in consumption of iodide ions, being observed mean concentration of 0.493mol/L of this ion in aqueous solution. Finally, in the interval from t = 45 minutes to t = 60 minutes, there is stability of the system, with final concentration of 0.315mol/L iodide.

During the sampling procedure was seen that the system yields a satisfactory stirring mixture of the phases while allowing the transfer of elemental iodine into the organic phase. Moreover, the agitation favors the accumulation of the organic phase on the electrode surface, which may have reduced the efficiency of the electrochemical process in the later stages the interval t = 10 minutes.

Future studies will evaluate the influence of pH of the electrolyte solution and the change in system temperature to the income of the electrochemical reaction. It will be studied a methodology that allows the extraction of elemental iodine from the aqueous phase to organic without prejudice to the efficiency of the process by the adhesion of the organic layer on the electrode surface.

Looking more accurate measurements, a quantitative method will be studied for determination of the elemental iodine concentration in the organic phase. After, news tests will be performed using radioactive sodium iodide with I-123.

Stand out as benefits in applying the methodology proposed the low cost of the reactants involved, the simplicity of the application of the analysis technique by volumetric titration, the low complexity of the experimental arrangement proposed to carry out the electrochemical process and the versatility of application of radiotracer proposed.
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REFERENCES


