



## Convective Mass Transfer Coefficient Measurement Techniques

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### Keywords

Naphthalene,  
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Mass transfer,  
Electrochemical,  
Limiting current,  
Convective mass transfer coefficient.

### Abstract

Mass transfer is one of the most important processes in all engineering systems, especially in chemical processes. Mass transfer at the micro- and macroscales, resistances encountered during mass transfer, types of mass transfer, and the measurement of mass transfer rates are key topics. In this context, the methods used to measure the mass transfer coefficient play a key role in measuring mass transfer rates. Since the fluid flow occurs within closed channels and systems, especially in engineering contexts, understanding the mass transfer and determining its rate between a solid surface and a fluid are of primary importance. The most commonly used methods are the Electrochemical Limiting Diffusion Current Technique (ELDCT) and the Naphthalene Sublimation Technique (NST). This study reviews the advantages and disadvantages of both methods based on the literature. It is found that ELDCT is suitable for determining convective mass transfer coefficients in liquid fluid flow systems with strongly turbulent conditions. However, NST is more appropriate for gas fluid flow systems.

### 1. Introduction

Mass transfer is one of the most important processes in all engineering systems, especially in chemical processes. Mass transfer at micro- and macroscales, including the resistances encountered during it, its various types, and methods for measuring its rates, is among the key topics related to mass transfer. In this context, the techniques used to determine the convective mass transfer coefficient ( $k$ ) are crucial for determining the mass transfer rates. Since fluid flow occurs, especially within closed channels and systems in engineering, understanding the mass transfer phenomenon between a solid surface and a fluid, as well as accurately determining this transfer rate, is of primary importance.

There exist two main parameters affecting the mass transfer flux: firstly, the convective mass transfer coefficient at the wall-liquid interface, and secondly, the concentration difference between the wall and the fluid (as described in Eq.1). In a fluid flow system, the factors that affect the convective mass transfer coefficient ( $k$ ) are related to the properties of the fluid, the flow dynamics, and the system geometry. Additionally, the flow regime within a channel plays a significant role in determining the convective mass transfer coefficient, provided that the fluid and channel geometry remain constant [1].

$$N_A = k(C_{AS} - C_{A\infty}) \quad (1)$$

For over fifty years, researchers have studied mass and heat transfer processes, focusing on measuring mass transfer rates, with or without chemical reactions. Among the most well-known and widely used methods are the Electrochemical Limiting Diffusion Current Technique (ELDCT) and the Naphthalene Sublimation Technique (NST). Each of these methods has its own advantages and disadvantages.

Mass transfer coefficient measurement techniques offer several advantages compared to heat transfer coefficient measurement techniques, which can be summarized as follows: First, these techniques enable a more accessible and accurate study of relevant heat transfer processes. These techniques enable quicker modeling of different hardware configurations and allow for the early identification of thermal design issues, providing better control over thermal design. The ELDCT and the NST are particularly effective, as they can measure localized transfer coefficients at small points [2].

In the study, 43 papers were reviewed. Here, the advantages and disadvantages of these techniques, their relative superiority, their limitations, and practical implications were examined.

### 2. Measurement of mass transfer coefficient ( $k$ ) using the Electrochemical Limiting Diffusion Current Technique (ELDCT)

The ELDCT has been widely employed in various studies related to mass and heat transfer. This electrochemical reaction method operates under diffusion-controlled conditions and is particularly prevalent in chemical engineering applications involving liquids. ELDCT is effective for measuring both average and local mass transfer rates, as well as shear stress at the solid-liquid interface. By analyzing the limiting current density measured at the cathode, researchers can calculate the rates of mass and momentum transfer [3]. In scenarios governed by diffusion-controlled processes, measuring the limiting current provides a practical and precise method for determining mass and heat transfer rates, as well as for exploring specific hydrodynamic phenomena [4]. The primary objective of ELDCT is to evaluate mass transfer values within the

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electric field of an electrochemical flow system, considering specified flow conditions. This technique is particularly beneficial for determining wall fluxes in fluids with high Schmidt numbers and is favored for its ability to yield reliable results [5].

ELDCT has attracted researchers studying heat and mass transfer and has been widely used. The ELDCT is used in chemical engineering applications involving liquids. ELDCT is effective for measuring both average and local mass transfer rates, as well as shear stress at the solid-liquid interface. The rate of mass and momentum transfer can be calculated using the limiting current density measured at the cathode [3]. In diffusion-controlled processes, determining the limiting electrolysis current is a reliable and accurate technique for assessing mass and heat transfer rates, as well as for examining specific hydrodynamic phenomena [4]. The primary objective of ELDCT is to ascertain the mass transfer values within the electric field of an electrochemical flow system under specified flow conditions. This method has extensive applications in determining wall fluxes in fluids with high Schmidt numbers and is particularly appealing due to its ability to produce satisfactory results [5].

## 2.1. Literature review on measuring mass transfer coefficient (k) with ELDCT

The ELDCT has been utilized for measuring mass transfer rates between solid surfaces and fluids for over fifty years. Notable studies employing this technique include those by Mizushina (1971) [3], Wragg (1977) [6], Yapıcı et al. (1994) [7], Selman and Tobias (1978) [8], Arzutug and Yapıcı (2009) [9], Sara et al. (2009) [10], Arzutug (2025) [11], and Aydin et al. (2019) [12].

Quiroz and a few researchers have determined the  $k$  values in a parallel disk cell using ELDCT. They identified  $k$  as a critical parameter for understanding the electrochemical cell before initiating electrooxidation applications. Additionally, Quiroz et al. (2005) [13] demonstrated that the disk design has a significant influence on the mass transfer coefficient. Using rotating disk electrodes and ELDCT, Esenberg et al. (1954) [14] found a correlation that equally well demonstrates the dissolution rates of rotating solids and the rates of ionic mass transfer on rotating electrodes. This correlation aimed to determine the relationship between the physical and geometric properties of the system and the hydrodynamic conditions in the case of mass transfer from the rotating disk electrode to the electrolyte or from the electrolyte to the electrode. This study also aimed to demonstrate whether this general correlation is sufficient to determine the polarization curve and  $I_{LC}$  in an electrochemical cell operating under steady-state conditions.

A study conducted by Yapıcı et al. (2011) [15] utilized rotating disk electrodes and the ELDCT to determine the electrochemical diffusion coefficients of the ferri-ferrocyanide ion pair. This investigation was carried out in electrolytes containing ferri-ferrocyanide and  $K_2CO_3$  at various concentrations, across temperatures ranging from 288 to 388 K, and with viscosities between 1,060 and 145,000 Schmidt per square centimeter.

Szanto et al. (2008) [16] aimed to measure the diffusion coefficients by using the Levich equation (Eq.2) in their limiting current measurement experiments using ELDCT on a rotating disk electrode (RDE) and found a correlation for the limiting current:

$$I_L = 0.62zFAD^{0.667} \omega^{0.5} v^{-0.167} C_b \quad (2)$$

Where  $D$  is the diffusion coefficient,  $v$  is the kinematic viscosity ( $cm^2/s$ ),  $C_b$  is the analyte concentration ( $mol/cm^3$ ), and  $\omega$  is the rotation rate of the electrode ( $rad/s$ ). In this form of the equation, the constant with a value of 0.620 has units of  $rad^{1/2}$ . By measuring the limiting current at different rotation speeds, the diffusion coefficient can be calculated from the slope of a plot  $I_L$  vs.  $\omega^{0.5}$ . To determine convective mass transfer, researchers [16] identified the limiting current plateau region at steady state in the current-potential curve, as shown in Figure 1, which was obtained through linear sweep voltammetry. They explained that the current-potential curve consists of three distinct regions:

- Mixed Control Region: In this region, the primary reaction is influenced by both mass transport and electron transfer.
- Plateau Region: Here, the primary reaction is entirely under mass transport control.
- Final Region: In this region of the graph, a side reaction was observed, typically the decomposition of water, occurring alongside the primary reaction.

In a different study, the limiting current is attributed to the convective diffusion of the reactant toward the electrode. The presence of the plateau indicates that the transport of ions to the working electrode has reached its maximum speed, making it the determining step in the process. The researchers generated curves (a) and (b) in Fig.1, resulting from experiments performed on a rotating disk electrode (RDE). Both curves depict the conditions during the reduction of the  $Fe(CN)_6^{3-}$  ion on the same electrode and under identical experimental conditions. According to the researchers, the distinction between the two curves lies in their electrode surface conditions: curve "a" was derived from a polished and activated electrode. However, curve "b" originated from an electrode that was roughened under sunlight. This difference highlights the significant impact that the electrode surface condition has on the limiting current [16].

Additionally, ELDCT was applied to measure mixing time and assess the influence of various parameters [12]. This study represents the first use of ELDCT in the literature for evaluating the effects of the Reynolds number ( $3500 \leq Re \leq 10,000$ ), active ion concentration in the solution, Rushton turbine rotation speed, and solution kinematic viscosity on both global and local mixing times in a stirred tank system. The researchers concluded that ELDCT is a reliable, simple, and effective method for measuring mixing times.

Mahinpey and Trass (2005) [17] aimed to simulate atherosclerotic arterial blood flow and analyze the hydrodynamics of the system. They chose viscosity as a parameter and used glycerin as a viscosity modifier in the electrolyte. They examined mass transfer at high Sc numbers in both a straight pipe and a Y-forked pipe, using ferri-ferrocyanide electrolyte and ELDCT within a Y-forked flow model.

Volgin and Davydov (2008) [18] studied the  $I_{LC}$  for the electrochemical deposition of copper on a vertical electrode under stagnant electrolyte conditions. They aimed to quantitatively assess how the incomplete decomposition of copper sulfate and the supporting electrolyte, sulfuric acid, affects ionic transport and the limiting current density during copper electrochemical deposition. To achieve this, they compared the conditions of incomplete dissociation with those of nearly complete dissociation of both copper sulfate and sulfuric acid. Their analysis revealed that, in the presence of an excess of the supporting electrolyte, the incomplete dissociation of copper sulfate and sulfuric acid had only a minor impact on the  $I_{LC}$  [18].

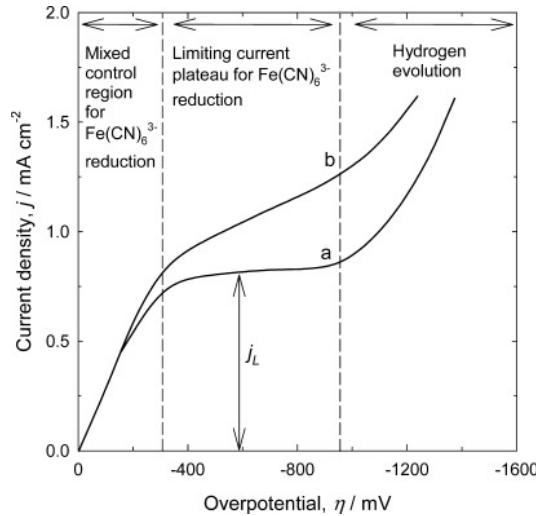


Figure 1. Current-potential curves obtained under different electrode surface conditions [17].

In another study, researchers examined the effect of the geometrical arrangement of ribs—both longitudinally and transversely—within a parallel-plate flow channel on the distribution of limiting current density. They found that the arrangement of these ribs significantly influenced the parabolic velocity profiles, resulting in regions of high, low, and zero mass transfer [19–20].

Sedahmet et al. (2001)[21] aimed to increase the electropolishing rate of vertical plates by employing mechanical stirring with an axial-flow impeller, specifically a 4-bladed, 45-inch inclined Rushton turbine, within a rectangular cell. They conducted experiments to electropolish copper using an  $H_3PO_4$  electrolyte. The simplicity of the experimental setup and the resulting polarization curves make the ELDCT a widely used method for investigating the influences of hydrodynamic conditions and workpiece geometry on the rates of electropolishing and electrochemical machining [21]. According to the researchers, their findings indicate that, for the 10 M and 12 M  $H_3PO_4$  solutions, a bright and smooth polish was achieved across the entire sample at all studied rotation speeds. However, with the less viscous 8M  $H_3PO_4$  solution, it was observed that the lower portion of the plate near the leading edge became abraded instead of polished when stirring speeds exceeded 1000rpm. These results suggest that high degrees of mixing could be avoided, particularly with low-viscosity solutions [21].

Harinaldi (2001) [22] studied the mass transfer rate in a flow channel with sudden expansion caused by a step at the inlet and flow separation from a slot jet produced by a layer above the step. The channel also functions as an electrochemical cell with electrodes at the bottom used to control flow, and assess turbulence intensity of the vortex and electrolyte flow from the slot jet. The researcher reported that the vortex and turbulence enhanced the electroplating mass transfer at the electrodes and performed experimental and computational studies to analyze how flow parameters affect the mass transfer rate between the electrodes. In this study, mass transfer coefficients were obtained by measuring the  $I_{LC}$  values (ELDCT) during the cathodic reduction of copper ions  $[Cu^{+2(aq)} + 2e^- \Rightarrow Cu_{(s)}]$  with mini cathodes at the bottom of the cell, using a 0.5 M  $CuSO_4$  solution as the electrolyte. The distribution of  $k$  values indicates that the wall-slotted jet alters the flow structure and turbulence intensity, which increases as the vortex region shrinks. For the flow channel, the mass transfer relationship is expressed as  $Sh=0.033Re^{0.6}Sc^{0.33}$  for  $Re$  numbers between 1500 and 4800 and velocity ratios of 0.7 to 2.6, where  $V_r$  is the ratio of the slot jet velocity to the main flow velocity [22].

Harinaldi (2011) [23] conducted extensive experimental studies to investigate the effects of flow separation and acoustic stimulation, which were created by a step and a speaker positioned at the channel inlet, on the mass transfer rate. In this research, the influence of fluid dynamics and acoustic stimulation parameters on the mass transfer rate between the electrodes was examined using ELDCT. As the electrolyte, a 0.5 (mol/L)  $CuSO_4$  solution was used. The speaker was used to apply acoustic excitation to the electrolyte flow, allowing for the control of turbulent intensity within the flow. The mass transfer rate was measured by recording the local  $I_{LC}$  at minicathodes located in the electrochemical cell. According to the researcher, acoustic excitation altered the mass transfer rate in the flow field and enhanced the rate of convective mass transfer during the electrochemical process. Some results indicate that as the  $Re$  number rises, the influence of acoustic excitation on the mass transfer rate becomes less significant, and the maximum mass transfer coefficients tend to converge to a single value. Additionally, there is an optimal Strouhal excitation number that supports the highest mass transfer rate, likely due to the existence of an ideal forcing frequency that promotes the formation of large-scale vertical structures and vortex coalescence in the shear layer during separation-reconnection flow [23].

## 2.2. Theory and application of the ELDCT

To measure convective mass transfer at a specific surface in a flow system, a cathode is placed on that surface, while an anode is positioned opposite it. If this electrode covers a larger surface area, it measures the average  $k$  values for that surface. Conversely, if it is a point electrode, it measures the local  $k$  values at that specific point. The method requires cathodic control of the system; therefore, when ELDCT is used for transport measurements, the cell is generally designed so that the anode area is larger than the cathode area. By selecting the electrode areas in this manner, the current density at the anode remains lower than that at the cathode, thereby ensuring that the system is cathodically controlled. As a result, the processes occurring at the anode do not influence the shape of the current-voltage curve. To maintain cathodic control during the process, the concentration of ferrocyanide is kept higher than that of ferricyanide. Additionally, the electrolyte temperature is stabilized at a constant level before measurements are taken. Before conducting experiments, the electroactive surface area of the cathode is determined experimentally.

In the literature, many electrochemical processes operate under  $I_{LC}$  conditions to maximize the lifespan of the electrolyte in the cell. Once all preparatory work is completed, the electrolyte flow is established at the desired rate, and a DC voltage is applied between the electrodes. A polarization curve is generated by passing DC through an electrochemical cell, typically consisting of a nickel anode and a nickel cathode containing a ferriferrocyanide pair (Fig. 2). In this curve, the section before the plateau indicates that the system is under chemical reaction control, while the portion above the plateau shows that it is under diffusion control. The increasing current value after the plateau reflects the

onset of a secondary reaction, specifically the decomposition of solvent water. In the context of the ELDCT, a polarization curve is first plotted to determine the  $I_{LC}$  value, either at rest or under flow conditions. To carry out these measurements, a voltage ranging from zero volts to 1.5 volts is applied between the electrodes in the electrochemical cell, while the corresponding current values are recorded. The polarization curve is useful in identifying the voltage at the midpoint of the plateau, which corresponds to the  $I_{LC}$  voltage. By applying this voltage to the electrochemical flow system being studied, the conditions for  $I_{LC}$  are met. Under the specified flow conditions, the  $I_{LC}$  passing through the cathode is measured, and the  $k$  value is subsequently calculated by substituting the  $I_{LC}$  value into Eq.18.

When using a ferri-ferrocyanide couple in this technique, firstly, the concentration of ferricyanide in the prepared electrolyte is typically set to be 4 to 10 times lower than that of ferrocyanide. This configuration ensures that the concentration of ferrocyanide at the anode remains sufficiently high so that the reaction at the anode is not limited by mass transfer. Secondly, the surface area of the cathode should be smaller than that of the anode. These arrangements ensure that the overall cell is cathodically-controlled. Additionally, in the ELDCT, a strong base (or strong acid) known as a supporting electrolyte is used. This supporting electrolyte disrupts the electromagnetic field between the electrodes, preventing ion migration. Generally, a 0.5 M NaOH solution is used with the ferri-ferrocyanide couple; however, other chemicals, such as KOH and Na<sub>2</sub>CO<sub>3</sub>, can also serve as supporting electrolytes. For a CuSO<sub>4</sub> solution, an H<sub>2</sub>SO<sub>4</sub> solution is used as the supporting electrolyte. The  $I_{LC}$  values vary depending on the flow rate under different flow conditions (see Fig. 3). The  $k$  value is calculated from the measured  $I_{LC}$  values using Eq.18. If needed, this  $k$  value can be substituted into Eq.17 to yield the mass transfer flux (kmol/m<sup>2</sup>s) for the selected electrode area on a solid surface where flow occurs. This value is then multiplied by the cathode area to determine the mass transfer rate. When a voltage is applied between two electrodes immersed in an electrolyte solution containing active ions, and this voltage is gradually increased over time, a voltage-current (polarization) curve is obtained that consists of three distinct regions. In this curve, the plateau representing the  $I_{LC}$  value is clearly visible (see Fig. 2).

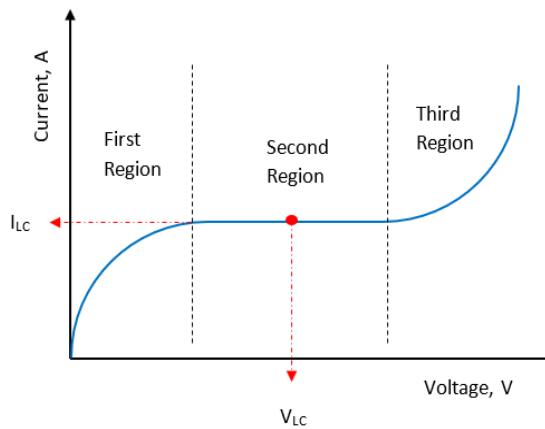


Figure 2. Polarization curve and limiting current [6-10]

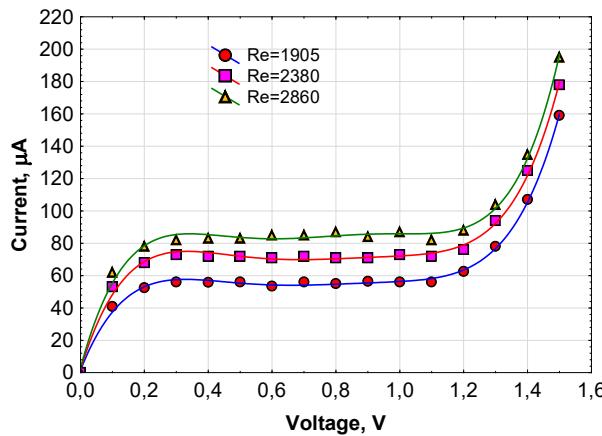
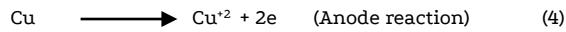
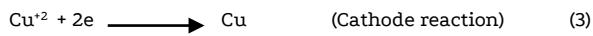


Figure 3. The polarization curves and the limiting current plateaus for the different Re flow [11]

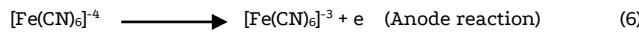
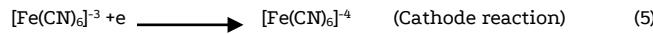
- REGION 1: When the applied voltage is low, the reaction rate at the electrode surface is either slower than or equal to the rate at which the reactant is transferred to the surface (this is determined by the diffusion of the reactant through the film).
- REGION 2: Once the voltage reaches a certain threshold, the reaction rate becomes faster than the rate of reactant transfer from the film to the electrode surface. This results in a plateau where the current remains constant. In this case, the reactant reaching the electrode surface is consumed immediately by the reaction, leading to a depletion of reactant concentration at the surface. Consequently, the process is controlled by the diffusion of ions through the film. The current generated in this region is known as the "Limiting Diffusion Current".
- REGION 3: A secondary reaction begins to occur in the system, resulting in solvent decomposition. This process leads to the formation of hydrogen gas (H<sub>2</sub>) at the cathode and oxygen gas (O<sub>2</sub>) at the anode.

The  $I_{LC}$  is a critical value for assessing the effectiveness of an electrochemical process. Accurately determining and maximizing this current is often essential for the success of such processes. The evaluation of the  $I_{LC}$  value has been a topic of considerable debate, and numerous methods have been proposed to ensure its precise measurement.

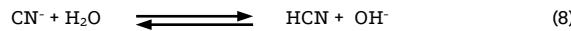
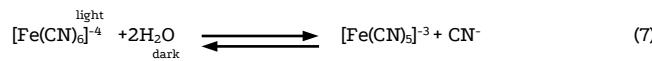
The first electrolyte system used in the ELDCT includes an aqueous solution of copper(II) sulfate ( $\text{CuSO}_4$ ) with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) as the inert electrolyte. This setup facilitates a cathodic copper deposition reaction. The reactions occurring at the anode and cathode can be summarized as follows (Eq.3 and Eq.4)



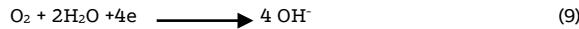
The most common electrolyte is a solution containing ferricyanide and ferrocyanide, containing  $\text{NaOH}$  or  $\text{KOH}$  as the inert electrolyte. In this solution, using  $\text{NaOH}$  as the supporting electrolyte, ferricyanide ions are cathodically reduced to ferrocyanide ions at the surface of an inert Ni or Ag cathode. At the anode surface, the formed ferrocyanide ions convert to ferricyanide. In the ferric-ferricyanide system, unlike the  $\text{CuSO}_4$  system, because there is no metal accumulation on the cathode surface, the mass transfer surface remains physically unchanged. Another advantage is that the solution composition is constant because the same reaction occurs in opposite directions at the cathode and anode [3]. The ferri-ferricyanide redox couple is the best electrolyte for experimental determination of the  $k$  values using ELDCT. Because it is stable in alkaline solutions and its chemical polarization at the cathode is so small that its critical flow velocity is very high. The electrochemical reaction occurring in the system is as follows (Eq.5 and Eq.6):



The disadvantage of using this electrolyte is the photochemical degradation of ferricyanide (Eq.7) and, more so, ferrocyanide, with the formation of HCN as follows (Eq.8):



The formation of HCN contaminates the electrolyte and poisons the electrode surface. To prevent this, the solution should never be exposed to light, and light-transmitting components of the system must be insulated by covering them with an opaque material. Especially, it is important to coat transparent measuring devices, such as flow meters and their connecting elements in the flow line, to avoid degradation of the electrolyte [4]. The effects of air exposure on the electrolyte and electrodes are complex, and there is significant uncertainty regarding how air impacts measurements. While oxygen is known to be a harmful component of air,  $\text{H}_2\text{S}$  gas can also be absorbed, likely due to the alkalinity of the solution. Thus,  $\text{H}_2\text{S}$  presents another potential poison for the electrodes. Additionally, a possible side reaction involving  $\text{O}_2$  at the cathode has been suggested by Aggerwaal et al. [24].



This reaction is unlikely to occur because the discharge potential for this process is significantly higher than the typical voltage range in which diffusion-controlled conditions are observed. Additionally, the presence of oxygen in the electrolyte may lead to the formation of an oxide film on the electrode surface, making oxidation of the ferrocyanide more probable. Therefore, it is essential to remove dissolved oxygen from the solution using an inert gas such as nitrogen ( $\text{N}_2$ ). Other components of air, present in smaller amounts, can also dissolve in the alkaline solution and act as contaminants or toxicants for the electrode. For instance, hydrogen sulfide ( $\text{H}_2\text{S}$ ) is thought to be absorbed by the electrode, contributing to its passivation. Electrode toxicants influence reactions in various ways. They may either accelerate competing reactions, which increases chemical polarization and prevents diffusion-controlled conditions from occurring, or they may block certain portions of the electrode surface, rendering the electrode ineffective for the intended reaction [3].

### 2.3. Mathematical calculation of convective mass transfer coefficient ( $k$ ) using ELDCT

In electrode reactions influenced by alternating concentration polarization and chemical polarization, ions are transported to the electrode surface, where both chemical and physical changes occur. When measuring mass transfer rates through electrochemical reactions, it is often more effective to neglect chemical polarization. This simplification assumes that the concentration at the liquid-solid interface is zero, making it easier to obtain mass transfer coefficients from the  $I_{\text{LC}}$ . Ions are generally transported from the bulk solution to the electrode surface through three main processes:

- Ion Migration: The movement of charged particles within the electric field generated by the electric potential gradient in the electrolysis cell.
- Diffusion: The movement of species driven by a concentration gradient or a chemical potential gradient.
- c. Convection: The mixing or hydrodynamic transport associated with fluid flow. Convection can occur in both laminar and turbulent flows, often characterized by the presence of stagnation zones. These fluid flows can arise from natural or forced convection [25].

The total electric current passing through the system is equal to the sum of the currents produced by diffusion, migration, and bulk flow.

$$I_{\text{Total}} = I_{\text{Difuzyon}} + I_{\text{Migration}} + I_{\text{Bulk}} \quad (10)$$

Assuming that the transfer event in an electrolysis cell occurs in a steady state and in a unidirectional direction perpendicular to the electrolyte surface, the one-dimensional mass transfer for an electrode is represented by the Nernst-Planck equation.

$$N_A = -D_{AB}(\partial C_A / \partial y) + (z_A F / RT) D_{AB} C_A (\partial \theta / \partial y) + C_A V_y \quad (11)$$

The three terms on the right-hand side of the equation represent the contributions of diffusion, ion migration, and convection. The convection term is not relevant in the redox process because the net bulk flow perpendicular to the electrode surface within the film layer is negligible. However, this term becomes significant during the metal deposition process on the electrode surface due to bulk flow, although its effect is minimal under normal conditions. To minimize ion migration, excess passive electrolyte can be added to the solution. Passive electrolytes do not react at the electrode surface and have relatively high concentrations and conductivities compared to the reacting species present. This additional electrolyte, due to its high conductivity, reduces the ohmic resistance of the solution to a negligible level, resulting in no significant potential gradient near the electrode, which can be assumed to be zero. Consequently, the system aims to be completely diffusion-controlled, eliminating the impact of ion migration. Additionally, the contribution from bulk flow within the boundary layer is also negligible compared to the diffusion rate.

$$I_{\text{Total}} = I_{\text{Diffusion}} \quad (12)$$

If ion migration is assumed to be zero, all electric current arises from the reaction of ions at the electrode surface. Thus, the equation is as follows:

$$N_A = -D_{AB}(\partial C_A / \partial y) \quad (13)$$

Integrating the equation in the general case gives the following expression for the mass transfer rate:

$$(-D_{AB} / \partial y) = k \quad \text{and} \quad \partial C = C_{\infty} - C_s \quad (14)$$

$$N_A = k(C_{\infty} - C_s) \quad (15)$$

The reaction occurring at the electrode surface is very rapid, so the reaction immediately consumes the ions arriving at the electrode surface. Since the system is diffusion-controlled within the film in the limiting current state, the concentration at the electrode surface will be  $C_s = 0$ , and Eq.15 becomes:

$$N_A = k C_{\infty} \quad (16)$$

According to Faraday's Law, the transfer of reacting ions to the surface is directly proportional to the  $I_{LC}$  and is given as follows:

$$N_A = I_L / zFA \quad (17)$$

When Eq.16 and Eq.17 are combined, the following Eq.18 is obtained:

$$k = I_{LC} / zFAC_{\infty} \quad (18)$$

In this context,  $I_{LC}$  refers to the limiting current (Amper),  $A$  represents the active electrode surface area of the local cathodes ( $m^2$ ),  $z$  indicates the number of electrons transferred in the electrochemical reaction—where  $z$  is equal to 1 for ferri-ferrocyanide redox reactions— $F$  is the Faraday constant (approximately  $96487 \text{ C mol}^{-1}$ ),  $C_{\infty}$  is the concentration of ferricyanide in the electrolyte ( $\text{mol} \cdot \text{m}^{-3}$ ). After steady-state conditions are established in the flow system, the  $I_{LC}$  values are measured under these flow conditions using a PC-controlled data acquisition system. By substituting the measured  $I_{LC}$  values into Eq.18, local  $k$  values can be calculated. This process allows for the determination of the  $k$  distribution throughout the testing region in the flow system [25].

### 3. Measurement of $k$ using the Naphthalene Sublimation Technique

The convective heat transfer coefficient is typically determined through complicated experiments that require sophisticated equipment and challenging measurements. However, an alternative method for obtaining the convective transfer coefficient to ELDCT is through mass transfer experiments, which offer high accuracy and are easier to conduct. One of the most effective methods for measuring  $k$  is the NST, developed in the 1950s and still in use today, also [26].

The NST is reliable for measuring both average and local mass (heat) transfer coefficients at surfaces, applicable in various scenarios. Nonetheless, it does have certain limitations. This technique is particularly valuable in complex flows and geometries, as well as in situations with large gradients in wall transport velocity. Mass transfer boundary conditions, which are similar to those for isothermal and adiabatic walls, can be effectively implemented in convective heat transfer. Additionally, the nature of mass transfer allows for the application of these boundary conditions in a way that avoids errors similar to those caused by conduction losses in a wall.

Local transfer coefficients can be measured with high accuracy and detail using automated measurement systems. These systems help eliminate most human errors during the measurement process and reduce external sublimation losses. Often, the desired heat transfer coefficient can be confidently derived from the measured mass transfer results using the heat/mass transfer analogies.

However, this method is generally not suitable for certain flow conditions, particularly high-speed flows. This is due to natural convection and recovery temperature effects that arise from the thermal lift effect of latent heat during sublimation. While the NST is relatively easy to implement and yields quite accurate measurements, it is crucial to consider its limitations and disadvantages, especially regarding the recovery effect in high-speed flow scenarios.

#### 3.1. Literature studies on the measurement of $k$ using the Naphthalene Sublimation Technique

NST was utilized to measure local or average heat and mass transfer coefficients in studies related to heat and mass transfer within flow systems that have various geometries and flow conditions, transitioning from laminar to turbulent flow. The researchers concluded that convective heat transfer coefficients could be determined more easily and accurately than through traditional heat transfer measurement methods. A review of the literature shows that NST has been effectively applied in heat transfer studies. However, given the limitations associated with the NST method, it has been used for heat transfer problems under specific conditions, as noted in the examples below.

In heat transfer experiments, it is often difficult to measure local heat transfer coefficients in detail when the temperature changes rapidly over a small region. Such measurements include large-wall conduction errors due to steep gradients in transfer rates across the region. However, mass transfer techniques ensure easier measurement of mass transfer coefficients even in similar situations, such as near a corner

or edge, where there is a large gradient in the convective coefficient. Mass transfer results can be translated into heat transfer results using a heat/mass transfer analogy. Although the analogy requires the Sc and Pr numbers to be equal [27].

The sublimation of spherical naphthalene samples in air at 1 atm, without recycling, was investigated by Curteanu et al. (2014)[28]. The researchers collected experimental data by measuring the sample weight over time under various airflow conditions. This data was then used to calculate the mass transfer rate, degree of sublimation, and sublimation propensity. An artificial neural network combined with a genetic algorithm was employed to identify the optimal process conditions for naphthalene sublimation. This approach linked the effects of airflow characteristics to the minimum or maximum sublimation rates and determined the optimal operating conditions [28].

Kwoon et al. (2011) [29] examined the local and average heat and mass transfer characteristics in a pit using the NST. In their study, the researchers considered pit depth and flow Re number, which ranged from laminar to turbulent, as key parameters. They observed that velocity fluctuations in the turbulent layer above the pit increased with both pit depth and Re number. The interaction of the turbulent layer and the resulting secondary flows was found to enhance the Sh number around the trailing edge of the trough and in the trailing plateau region, respectively. The authors concluded that NST effectively captures the convective component of heat transfer in systems with significant convection coefficient gradients, such as a trough cavity, because it minimizes errors caused by wall conduction and radiation.

Conjugate modeling was employed to analyze the convective heat and mass transfer coefficients in the airflow and the porous material during the convective drying of a partially saturated porous flat sheet. While the benefits of conjugate modeling were highlighted in this study, Defraeye et al. (2012) [30] pointed out the necessity for detailed modeling of the convective boundary conditions. These conditions are highly dependent on the drying behavior of the porous material and may not always be essential.

Liu et al. (2001) [31] utilized NST measurements on the horizontal roof of a building to assess the convective heat transfer coefficient (CHTC) at the external surface. They aimed to accurately calculate the heat transfer from the roof to the surrounding air and correlate it with the airflow around the building. They placed test specimens with glazed surfaces, cast from molten naphthalene, at twenty different points on the roof. The researchers found that the temperature changes at the naphthalene surface had minimal impact on the experimental results. Consequently, the CHTC derived from this study was compared to reference values using the heat balance method. The CHTC obtained was shown to be higher than values reported in the literature, particularly across a wide range of wind speeds. This discrepancy was attributed to variations in the dimensions of the target building, the representative wind speed height, and wind turbulence.

In a review by Çelik and Eren (2002) [26], the properties, advantages, disadvantages, and application techniques of NST were explored, which is frequently used in heat transfer applications. They stated that this technique can effectively measure even the most complex geometries, such as the inner surface of a pipe or the edge of a hole.

In a heat transfer study employed by Schmidt (2001) [34], NST was used to obtain heat transfer coefficients for electronic modules mounted on laboratory equipment, naphthalene castings, and printed circuit boards. Some researchers who applied NST in cooling electronic equipment reported that the mass transfer process could be established with cleaner boundary conditions, and that heat transfer coefficients could be determined more easily and accurately than through traditional measurement methods [31-34].

Schmidt (2001) [31] described the NST, which is used to capture convective heat transfer from the surfaces of electronic modules mounted on printed circuit boards. He reported that this technique was successfully applied to determine average and local CHTCs for finned heat sinks mounted on an electronic board. Schmidt stated that using NST facilitated a more accurate analysis of the heat transfer processes under investigation and enabled faster modeling of various hardware configurations. Additionally, he mentioned that NST helped in the early detection of thermal design problems.

Because it is a fundamental element in heat and mass transfer studies, the effect of the boundary layer on a flat surface under laminar and turbulent flow conditions was investigated by Park and Yoo using NST. The experimental  $k$  values obtained were converted into heat transfer coefficients using an appropriate analogy. These transfer numbers were then converted to dimensionless parameters such as the Sh, Nu, and Colburn J-factors. The dimensionless numbers were then compared with those obtained from correlations of heat and mass transfer from flat surfaces under laminar and turbulent conditions. The researchers reported that the experimental results obtained were in better agreement with turbulent correlations than with laminar ones, based on local Sh numbers and local St numbers. The researchers reported that the analogy between heat, mass, and momentum is more appropriate for a turbulent boundary layer [35].

Heat transfer in channel flows is known to increase with the interruption of boundary layer development, the increase of the turbulent intensity, and the formation of swirling and/or secondary flows. In a heat transfer study conducted in a channel by Kwon et al., the local/average heat transfer coefficients for a unit cavity and its surroundings at shallow or moderate depths were experimentally investigated. To this end, local  $k$  values obtained in detail using NST were measured by Kwon et al. and converted to the heat transfer coefficients using a heat/mass transfer analogy. In this study, the flow conditions for compact heat transfer devices range from laminar to low-speed turbulent flow regimes. The literature has identified the need for further studies on flow conditions to design an energy-efficient system in hollow channels, determine an effective regime and design parameters, and develop a flow/heat transfer regime map. Therefore, this study was conducted to obtain local convective heat/mass transfer coefficients on a hollow surface using NST [36]. The researchers stated that the NST was more suitable for measuring CHTCs in a system with a large convective coefficient gradient, such as a dimple cavity, because it eliminates wall conduction and radiation errors.

Schmidt employed laboratory equipment, naphthalene casting, and NST to measure the transfer coefficients for electronic modules installed on printed circuit cards. The Molki and Faghri have noted that standard thermal techniques can be used to obtain CHCTs, but both radiation and conduction losses have to be considered in the measurements [31,37]. The researchers using NST pointed out that radiation and conduction losses are not present in the NST [31,37].

### 3.2. Application and mathematical calculation of the Naphthalene Sublimation Technique

The test sample can be easily prepared using various methods, including dipping, machining, spraying, and casting. The experimental procedure, as summarized by Schmidt [31], is as follows:

- First, create a sufficiently smooth naphthalene surface of the desired shape, which is necessary for simulating heat and mass transfer. This can be achieved through casting or machining.

- Since naphthalene's vapor pressure is sensitive to temperature, bring the sample temperature into thermal equilibrium with the laboratory air temperature.
- Before each measurement, hold the naphthalene sample under test conditions for approximately ten minutes to achieve thermal equilibrium with the laboratory environment. This step also ensures the pneumatic removal of free naphthalene particles from the test surface.
- To determine the total mass transfer from the naphthalene-coated surface, weigh the resulting naphthalene test piece on a precision balance (to the nearest 0.00001 grams) before beginning the run.
- Select the measurement period so that the average change in surface elevation is between 0.001 and 0.003 inches. Use a very accurate stopwatch capable of measuring to the nearest millisecond; a typical measurement lasts between 20 and 30 minutes.
- To determine the total or local mass lost, take measurements before and after the start-up. Repeat these measurements for accuracy.
- Apply a correction to the pre- and post-run measurements to account for sublimation due to natural convection during the actual measurements. This correction is determined from an auxiliary run that replicates all aspects of the actual data run, but without forced airflow.

### 3.2.1 Measurements

There are two main methods for measuring mass transfer rates:

- Weighing the test sample before and after a run to obtain the average mass transfer coefficients on a surface,
- Measuring the local mass transfer coefficient by assessing the thickness of the naphthalene coating with a thickness gauge.

### 3.2.2. Weighing method

The average transfer coefficient can be determined by weighing the test sample before and after a run. This method requires a high-resolution balance. Compared to thickness measurements, the weighing method experiences fewer natural convection losses during measurement due to the shorter measurement time, which is approximately 5 minutes. The weight capacity of high-resolution balances is generally limited. Commonly, an analytical balance with a resolution of 0.1 mg and a maximum capacity of 200 g is utilized. In some cases, local measurements can be conducted using samples composed of several small pieces, which allows approximately 10 mg of naphthalene to sublimate. Typically, the average Sherwood numbers (Sh) obtained from weighing measurements align closely (within 3%) with the numerically integrated values derived from independent local measurements [27]. This method has been developed to determine local mass transfer coefficients. Generally, there are five steps involved in determining the mass transfer coefficients, which are expressed as the dimensionless convective mass transfer coefficient known as the Sherwood number [26-27].

- Coat test samples with naphthalene.
- Measure the profile or weight of the initial naphthalene-coated surface.
- Experiment by passing fluid over the naphthalene-coated sample under the specified conditions.
- Re-measure the profile or weight of the naphthalene-coated surface.
- Calculate the mass transfer coefficient or Sherwood number from the weight loss of the sublimated naphthalene. Then, calculate the heat transfer coefficient and Nu number using a suitable mass/heat analogy.

### 3.2.3. Local mass transfer coefficient measurements

The local measurement method is well-developed and can be applied to various surfaces, including flat surfaces, circular cylinders, simple curved contours, and bores. For local measurements, the non-sublimated edges (metal parts) surrounding the naphthalene casting sample serve as a reference surface. These edges should be highly polished and feature a small circular indentation that corresponds to the original point used to locate the sample on the measuring table. Detailed local values can be obtained by averaging several points across the measured surface area. A computer-controlled automated surface measurement system has been developed to scan the profile of the naphthalene surface. To obtain accurate local sublimation depths of the naphthalene surface, several factors must be considered: (a) precise positioning of the samples before and after exposure to airflow, (b) accurate depth measurements, and (c) rapid data collection to minimize natural convection losses [38-40].

Mass transfer coefficients, represented by Sh numbers, are determined by measuring the sublimation depth before and after a wind tunnel experiment. The total sublimation depth is calculated by finding the difference in surface elevation before and after the experiment. To obtain the net sublimation depth, external sublimation caused by natural convection is subtracted from the total sublimation depth. The heat transfer coefficient is defined using Eq.19:

$$k = \frac{N_A}{\rho_{v,w} - \rho_{v,\infty}} \quad (19)$$

Here,  $N_A$  is the molar flux of naphthalene ( $A$  represents naphthalene) ( $\text{kmol}/\text{m}^2\text{s}$ ),  $\rho_{v,w}$  is the vapor density of naphthalene at the wall, and  $\rho_{v,\infty}$  is the vapor density of naphthalene in the free fluid stream. Generally, the density of naphthalene in the bulk fluid is taken as  $\rho_{v,\infty}=0$ , and when substituted into Eq.19 above, then Eq.21 is obtained.

$$\rho_{v,w} = \frac{P_{v,w}}{RT_w} \quad (20)$$

$$k = \frac{N_A T_w}{P_{v,w} - P_{v,\infty}} = \frac{N_A}{P_{v,w}} \quad (21)$$

Here,  $P_{v,w}$  is the vapor pressure of naphthalene at the wall, and  $P_{v,\infty}$  is the vapor pressure within the fluid stream. A simpler equation (Eq-22) is obtained by reforming the vapor pressure within the fluid stream by setting  $P_{v,\infty} = 0$  as follows:

$$Sh = \frac{kL}{D_{AB}} \quad (22)$$

#### 4. Comparison of both methods: Advantages and disadvantages

One of the primary advantages of the ELDCT is that redox reactions occur at both the anode and cathode. This allows the concentration of ferricyanide to remain constant in the electrolyte [41,42]. Additionally, the ELDCT is suitable for both localized and regional measurements and does not experience the naphthalene losses associated with NST. The ELDCT is an appropriate technique for measuring both stagnant fluid conditions and fluid flows at various speeds, including low, medium, or high speeds (such as in impinging jets). The challenges that arise with the NST do not affect this technique. Nevertheless, the challenges of ELDCT can be listed as follows: When performing local mass transfer coefficient ( $k$ ) measurements using the ELDCT, it is crucial to avoid creating any protrusions or pits on the surface of the local cathode, which can be placed on either a metal or non-metallic surface. Before testing, the electrode surface must be thoroughly sanded and polished. Following this preparation, the electroactive surface area of each local cathode should be determined experimentally. This step is essential and hard because the electroactive area of the nickel (Ni) or copper (Cu) electrodes, after sanding and polishing, may differ from their geometric area.

In heat transfer experiments, measurements often include conduction and radiation losses. As a result, isothermal and adiabatic boundary conditions are only approximate. However, these boundary conditions can be applied with minimal error using the NST. A naphthalene-coated surface acts as an isothermal boundary condition for heat transfer, while a non-sublimating (inert) surface is equivalent to an adiabatic wall. Additionally, it is possible to switch abruptly from an isothermal to an adiabatic boundary condition on a mass transfer surface; this transition is not feasible in heat transfer due to conduction and radiation effects [26]. Because conduction and radiation losses are typically present in heat transfer experiments, the boundary conditions are approximate. Nonetheless, when NST is used, experiments can be conducted with very little error, effectively resolving this boundary condition issue [26,38].

The NST method easily separates pure convection from conduction in coupled heat transfer situations, looking like needle-fin arrays or packed beds. This allows mass transfer experiments to focus on the convective part of heat transfer since errors from wall conduction and radiation are removed. When the test surface is kept at constant temperature and pressure, the vapor pressure and concentration of naphthalene at the surface stay uniform. This boundary condition is similar to an isothermal surface in a related heat transfer problem. On a surface covered with naphthalene, mass loss occurs continuously due to diffusion and convection. In this case, concentration gradients and mass flux mirror temperature gradients and heat flux. By measuring sublimation depths, time-averaged local mass transfer rates can be determined. Although the heat/mass transfer coefficient is measured under isothermal conditions, it can also be used under other boundary conditions because, in turbulent flows, the heat/mass transfer coefficient is only weakly affected by the wall temperature distribution. A mass transfer test section can be easily built and processed with NST. It doesn't require complex heating or measurement systems, like insulation or thermocouple connections. NST only needs a naphthalene-coated sample, which can be simply made by casting. Also, by ensuring the proper boundary conditions,  $k$  can be measured with NST even in complex geometries with moving parts [26-27].

The NST can be effectively applied to large surfaces. However, this method requires extended measurement times in low-velocity flows. During these long measurement periods, it becomes challenging to control surface temperature fluctuations. This can lead to increased naphthalene loss due to natural convection, resulting in inaccurate measurements. To mitigate this issue, the size of the test surface is sometimes reduced [26-27, 38]. NST also has limitations at high speeds due to aerodynamic viscous heating. The temperature rise caused by the recirculation effect is critical in high-velocity flows, as the vapor pressure of saturated naphthalene on the test surface is highly sensitive to temperature changes, leading to measurement errors.

In scenarios involving wall jet or impinging jet flows on a naphthalene-coated surface, the shear stress at the surface is significant. In these cases, loss can occur due to evaporation or abrasion from mechanical erosion of the naphthalene surface, further compromising measurement accuracy. During the NST measurement period, the shape of the naphthalene-coated test surface gradually deteriorates due to sublimation. This deterioration ultimately leads to inaccurate assessments of the sublimation depth. The results obtained with the NST are time-averaged and cannot be used under rapidly changing conditions. Thus, ELDCT is suitable for situations, such as impinging jet flows, powered swirl flow, and powered turbulent flows.

Due to the challenges associated with casting naphthalene or manufacturing cast naphthalene in complex geometries, NST cannot be used to determine the  $k$  values. While average measurements are possible, localized measurements are feasible because of the surface roughness of complex geometries. If a naphthalene-coated test sample is placed in the upstream region of a turbine providing airflow in an air-supplying tunnel used for measuring  $k$  with the NST, the naphthalene vapor temperature at the surface of the test sample—aligned with the tunnel wall—will differ from the temperature of the free air stream carrying the naphthalene vapor within the channel. This temperature difference will cause inaccurate measurements. The NST can be used under isothermal and adiabatic wall boundary conditions, but it cannot operate under constant heat flux conditions. Results can only be obtained when the Schmidt number ( $Sc$ ) is 2.28. The NST can be applied under constant temperature conditions, where the test surface temperature is uniform. However, the temperatures of different points under the constant heat flux conditions are not constant. If the test surface is held at a constant (uniform) temperature and pressure, the sublimation rate on the surface is constant. This surface boundary condition corresponds to the isothermal surface boundary condition for heat transfer. Therefore, on a surface under constant heat flux conditions, the naphthalene vapor pressure varies at each point on the test surface because each different point on the surface does not have a uniform temperature. In other words, the sublimation rate at each point will vary. Therefore, NST cannot be used under constant heat flux conditions.

While the NST could be applied to the gas flow systems, it can also be applied to liquid systems when using specific solvents. It is important to note that the mass transfer of naphthalene in gases occurs by sublimation, whereas in some organic solvents, it takes place by dissolution.

## 5. Results

The NST or ELDCT are applicable in mass transfer processes as well as in heat transfer problems. These methods are used to determine mass (or heat) transfer rates and to analyze the distribution of transfer coefficients across different dimensions. In the literature, numerous research studies have been conducted on thin-walled structures, focusing on various geometric properties and types of loads.

While ELDCT is appropriate for determining convective mass transfer coefficients in liquid fluid flow systems, NST is more suitable for gas fluid flow systems. Because NST suffers from sublimation erosion losses, ELDCT is more reliable for determining  $k$  in turbulent flow systems.

NST cannot be used to determine the  $k$  values in fluid flow systems with complex geometries. Additionally, there exist measurement errors associated with determining  $k$  values due to sublimation losses in NST. However, these types of measurement errors are impossible in ELDCT. Furthermore, if using 0.1 mm diameter nickel electrodes and a data card with a sliding average feature at each electrode to take measurements at the microampere or nanoampere level, one can achieve greater accuracy in measurements compared to those of NST. This is because ELDCT allows for repeated measurements at a single point, thereby improving accuracy, but it is not possible to take repeated measurements at a single point using NST. For this reason, these measurements provide more accurate local and average measurements compared to NST.

The basis of NST's usage is based on the analogy between heat and mass transfer processes. A dimensional analysis of the equations governing heat and mass transfer reveals that for geometrically similar configurations and similar boundary conditions, equations in the same form can be derived. As a result, a simple relationship exists between the Sherwood number, which describes the mass transfer process, and the Nusselt number, which describes the heat transfer process. In mass transfer experiments, the boundary condition corresponds to an isothermal surface, similar to the scenario in the analogous heat transfer problem.

## Nomenclature

ELDCT : The length of the specimen in horizontal direction

NST : The length of the specimen in vertical direction

RDE: Rotating disk electrode.

LC: Limiting current, (A)

DC: Direct current, (A)

CHTC: Convective heat transfer coefficient (W/m<sup>2</sup>K)

$k$ : Convective mass transfer coefficient (m/s)

$z$ : The number of electrons transferred in the electrochemical reaction

F: Faraday's constant (96487 Cmol<sup>-1</sup>)

A: Electrode active surface area (m<sup>2</sup>)

C: Coulomb

I: Current (A)

$I_{Lc}$ : limiting current, (A)

i: Current density (A.dm<sup>-2</sup>)

Sh: Sherwood number

Sc: Schmidtn number

Nu: Nusselt number

Pr: Prandtl number

St: Stanton number

$C_{\infty}$ : the concentration of ferricyanide in the electrolyte (kmol/m<sup>3</sup>),

$C_s$ : the concentration at the electrode surface (kmol/m<sup>3</sup>),

## Declaration of Conflict of Interests

The author declares that there is no conflict of interest. They have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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