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## Investigation of Effect of DC Glow Discharge On Intensity Distribution, Apparent Discharge and pH of Electrolytes

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### Abstract:

The glow discharge owes its name to the fact that plasma is luminous. We developed a new type of glow discharge system for the purpose of investigation of effect of dc glow discharge on intensity variation, apparent discharge and pH of electrolytes. We investigate the effect of concentration on the apparent discharge voltage and intensity of glow, effect of different pH of solutions on glow discharge, the effect of chlorine composition of the electrolyte on the metal line intensity and apparent discharge voltage. In order to confirm the presence of elements in the solutions we recorded line spectrum of the elements present in the glow discharge.

**Keywords:** Glow discharge, plasma, intensity, apparent, pH, elements

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### Introduction:

Glow discharge is a globally neutral, but contains regions of net positive and negative charges [1]. A new glow discharge emission source can be developed for the direct detection of metals in aqueous solutions and in drinking or wastewater by applying an atmospheric glow discharge in the air gap between solid and liquid interface. One interesting feature [2] of glow discharges is that gases such as C, O, N or H in metals can be analyzed directly. Usually these gases are present in the samples at extremely low levels so that they do not alter the discharge conditions. The technique first attracted attention as a method of carrying out electrolysis and realized that the chemical effects produced were far in excess quantitatively of those predicted by Faraday's laws. The dc glow discharges in dielectric liquids gave early considerations [3] in the form of breakdown. Luminescence is observed during the electrolysis of several organic electrolytes. The analysis of such phenomena is considered under chemi-luminescence [4]. Electrical breakdown in conducting aqueous solution has been attributed to the formation of a semi-non-conducting layer near the electrode surface [5]. Free radical formation and high yield of anodic oxidation have also been attributed to electrode glow phenomenon [6]. When a high potential gradient exists near the cathode, electrons are found to escape into the electrode/electrolyte interface [7].

Surface engineering [8] in solids has become an important field in materials science. Glow-discharge optical emission spectrometry (GD-OES) has proven to be powerful tool for the rapid analysis of elements in the surface of solids [8, 9]. Emission spectrometry [8] is a well-known technique for quantitatively analyzing an unknown material for the elements present. There are three common means of exciting the sample to produce the optical emission [8]. The first is to apply a high electrical voltage across the sample, which heats the sample in a spark discharge (arc/spark). The second is to dissolve the sample in acid, and "burn" the solution in an argon plasma (ICP). The third, glow discharge, sputters the sample surface with ionized argon atoms, and excites the sputtered surface atoms in argon plasma.

Glow discharges have attracted increasing interest in recent years [10, 11]. Both cause and result of this interest has been a broadening of samples that can be analyzed and an improvement in analytical performance. Gas-sampling discharges have permitted the analysis of flowing gases [10, 12]. Liquid samples present a greater challenge [10]. Although cathode sputtering introduces material from solid samples in to the bulk of discharge primarily as atoms, the relatively low gas temperatures are insufficient to desolvate liquid samples introduced into the bulk of discharge. Additionally, water-related species lower the metastable population in the negative glow. For these reasons, most techniques have focused [10] on drying a solution before introducing it into the glow discharge. Most commonly, this has been done by drying the sample onto a surface, which is then used as the glow discharge cathode. Cserfalvi and co-workers [13] used the type of glow discharge in which an electrolyte solution is the cathode, the anode is placed above this solution at a distance of a few millimeters and the discharge is generated between these electrodes in the gas phase, is known in electrochemistry [13-16]. This arrangement forms the basis for glow discharge electrolysis that was used to investigate the influence of the glow discharge

plasma on the oxidation process-taking place in the solution phase [13-16]. Under electrode glow condition, the Helmholtz electrical double layer acquires the characterizations of a reaction cage, and certain unusual chemical reactions become quite probable. The electrons escaping from the cathode into the electrode / electrolyte interface, known as hydrated electrons, give rise to many chemi-luminescent reactions, some such reactions activated by hydrated electrons, have been reported by Arnikar et al [17]. They have termed this phenomenon as *aqua luminescence*. Separation of metals from their halides and other plasma reactions, under electrical discharges, have also been reported [18]. This technique has been employed in liquid solutions by Heller et al. [7].

#### **Material and Method:**

The experimental arrangement used for the investigation of dc glow discharge is inexpensive arrangement and it is very much cost effective. It consists of tungsten electrode of length 40 mm and diameter 3mm fused in glass capillary tube and suspended axially in a hollow slotted stainless steel cylinder, of length 6 cm and internal diameter 2.54 cm. The stainless steel cylinder served as another electrode i.e. anode in the glow discharge. The suspended end of tungsten rod was carefully rounded. The tungsten electrode can be used as cathode by connecting it to the dc power supply of 700 V capacity having 1.5 A current capacity. In this arrangement the hollow cylinder was dipped in a electrolytic aqueous solution taken in a glass beaker. The depth of immersion of the tungsten electrode in electrolyte solution could be adjusted with the help of micrometer adjustable stand. By using this arrangement the tip of tungsten electrode could be just brought in touch with the upper surface of the solution or the distance between the solution surface and the electrode may be adjusted. In this way the solution itself acts as another electrode. The different electrolytic solutions have been taken for investigation using the glow discharge system. The system designed by us requires very less amount of electrolytic solution. The solid liquid junction is formed when current is passed through the junction. A plasma film is generated along the interfaces between solid and liquid. The plasma pressure is very near to the atmospheric pressure. When current is passed through the interface the atomic, ionic and molecular species are excited.

#### **Result and Discussion**

##### **The effect of concentration on the apparent discharge voltage and intensity of glow**

Using the same experimental arrangement the effect of concentration of aqueous solutions on the apparent discharge voltage which is required to just start the visible glow of colors and on the total intensity of emission were investigated by changing the concentration of aqueous solution of KOH. The concentrations of the solutions taken for the experiment are as 0.05 N, 0.1 N, 0.3 N, 0.5 N, 0.7 N and 1 N. When dc voltage was applied to the electrolyte cell, the behavior of corresponding apparent discharge voltage and apparent glow with the resultant intensity were observed. From this behavior as shown in figure 1 it can be seen that for concentrations 0.05 N to 1 N the apparent discharge voltage required just to start the glow decreased from 120 V to 35 V. The current passing through the discharge was almost constant (0.625 A). Figure 2 shows the intensity of the glow rises from 0 to 18 A.U. for discharge voltage of 120 V and current 0.375 A. Thus it is found that when concentration of aqueous solution of KOH increased the apparent discharge voltage decreased and intensity increased.

##### **Effect of different pH of solutions on Glow Discharge**

Atomic emission in case of tap water as cathode [1, 4], becomes stronger as pH of the solution is lowered by the addition of acid. Overall emission was found to grow in intensity for decreasing pH. The apparent discharge voltage was found to rise sharply with lowering of pH values [1, 4]. In present work a series of solutions adjusted to pH 1-6.5 with sulphuric acid and variation of intensity is recorded as a function of pH values of solutions. The discharge current was kept constant. For the experiment the solutions considered are i) 0.2N BaCl<sub>2</sub>, ii) 0.5N CdSO<sub>4</sub>.8H<sub>2</sub>O, iii) 0.1N CuSO<sub>4</sub> iv) 0.5 N KCl v) 0.2N MgSO<sub>4</sub> vi) 0.5N NaCl as the anode and cathode and one variations of intensities with pH are shown in figure 3. The intensity of emitted light was found to grow with decrease in acidity of different electrolytic solutions. Looking to the experimental results we can say that the intensities are proportional to the H<sup>+</sup> concentration of the solutions. Similarly variation of apparent discharge voltage as a function of pH of different electrolytic solutions were recorded by keeping discharge current at a constant value for i) Tap water ii) 0.1N ZnSO<sub>4</sub>.7H<sub>2</sub>O iii) 0.05N Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O iv) 0.05N MgSO<sub>4</sub> v) 0.05N NaOH as the anode and cathode and one displayed in figure 4. Overall discharge voltage depends slightly on pH value when pH was high. In the pH region of lower values a significant decrease of apparent discharge could be observed with decreasing pH. Thus in both the cases the acidification has great influence on the processes like ionization, recombination, electron temperature, electron impact excitation of energy levels etc in the discharge plasma.

##### **The effect of chlorine on the intensity of metal atomic lines and apparent discharge voltage during atmospheric glow discharge of aqueous solutions**

The influence of chlorine on the intensity of metal atomic lines emitted by an electrolyte cathode atmospheric glow discharge was investigated. In the present work this effect has been noticed by the

measurement of emitted intensity during dc glow discharge of the aqueous solutions. In this way it is also found that the applied discharge voltage, which is required just to start the glow gets decreased.

Comparatively the behavior of the dc glow discharge of the aqueous solutions of KOH and KCl, NaCl and NaOH, CuCl<sub>2</sub> and CuSO<sub>4</sub> was studied. During discharge, the significant increase in intensity and decrease in apparent discharge voltage was found for 0.5 N aqueous solution of KCl as compared to the 0.5 N aqueous solution of KOH. Thus for the same potassium metal element in aqueous solutions the intensity enhances with decrement in apparent discharge voltage by the presence of Cl as compared to OH. The similar observations are carried out for the solutions of NaOH and NaCl, and CuSO<sub>4</sub> and CuCl<sub>2</sub>. Thus the presence of chloride anions in the solutions helps to start the glow process during discharge as compared to other anions.

In the present work it was found that the intensity of emission of glow discharge increased and apparent discharge voltage gets decreased with the decreased pH of aqueous solutions. For the study of these effects the pH values of tap water is changed by using the acids HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The behavior of dc glow discharge of tap water under this operating condition for intensity was observed by keeping the discharge parameters at constant values (current: 150 mA, applied voltage: 100 V). It was found that intensity of discharge is found to be maximum when HCl is utilized for maintaining pH. This may be because of the physical environment experienced by H<sup>+</sup> ion in the solution. When HCl is utilized as absence of H<sup>+</sup> ion it may experience less resistance in the solution than when HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are utilized for the H<sup>+</sup> ion. Overall it is found that the presence of chlorine caused an enhancement of the metal line intensities and decrement in required apparent discharge voltage for glow. Thus the excitation mechanism of the elements in liquid gets affected by the presence of chlorine.

#### **Line spectrum of the elements present in the glow discharge**

In order to confirm the presence of elements in the solutions we recorded the line spectrum of the elements present in the glow discharge. Few of the spectra obtained in the experiment are displayed in figure 5 and 6. We also obtained the energy level diagram of the elements and obtained the wavelengths emitted by the elements. The comparison between the experimentally obtained lines with the spectrum obtained from energy level diagram shows very close agreement. This confirms the presence of the elements in the glow discharge. The reliability of the method of study of discharge glow for spectrochemical analysis increases.

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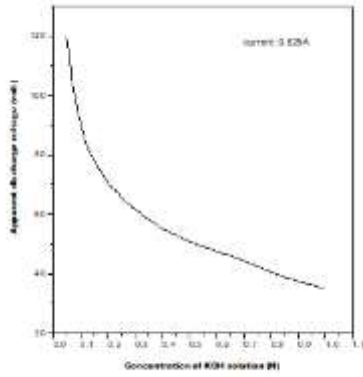


Figure 1: Variation of apparent discharge voltage as a function of concentration of aqueous solution of KOH

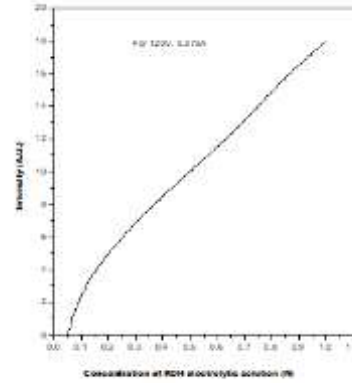


Figure 2: Variation of intensity as a function of concentration of aqueous solution of KOH

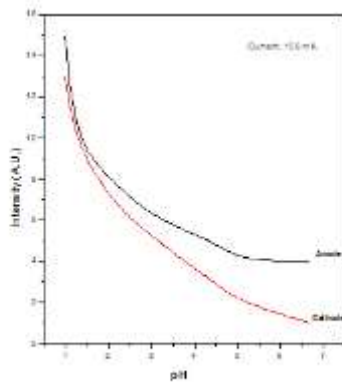


Figure 3: Variation of intensity of glow as a function of pH of 0.5N NaOH aqueous solution

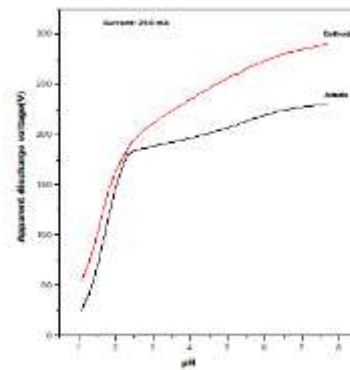


Figure 4: Variation of apparent discharge voltage as a function of pH of tap water

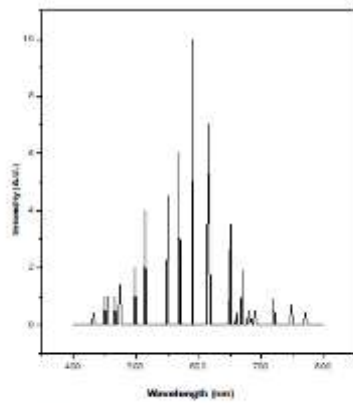


Figure 5: The spectrum record from the glow discharge of 0.5N NaOH electrolytic solution

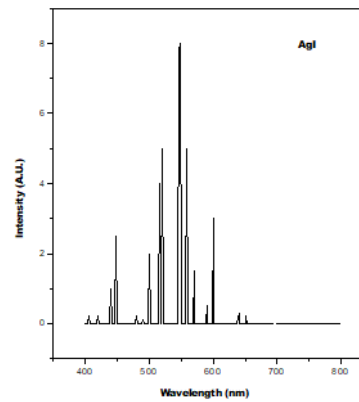


Figure 6: Line spectrum record from the glow discharge of 0.05N AgNO<sub>3</sub> aqueous solution