國立臺灣大學工學院化學工程學系

學士班學生論文

Department of Chemical Engineering
College of Engineering
National Taiwan University
Bachelor’s Thesis

利用電漿光譜長時間即時監測溶液中重金屬之網頁平台開發

Development of a Long-Term, Real-Time, and Web-based Heavy Metal Water Monitoring System Using Plasma Spectroscopy

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中華民國 112 年 4 月

April, 2023

國立臺灣大學學士班學生論文
口試委員會審定書

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本論文係張宗旻君（B09504007）在國立臺灣大學化學工程學系完成之學士班學生論文，於民國 112 年 04 月 11 日承下列考試委員審查通過及口試及格，特此證明

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Acknowledgment

First and foremost, I would like to thank my advisor, Prof. Hsu, for offering me the freedom to learn and explore in things that I am interested of, such as how to operate a Linux computer using the command line, or a chance to become familiar with different programming languages, or how to set up a server. I especially want to thank him for giving me a platform to materialize those intellectual knowledge into real-world application, so I can gain a sense of achievement and contribute back to society in a way that is not possible in a lecture course. I also want to mention how much I enjoy our weekly meetings. Not only I learned how to conduct scientific research in a professional and rational manner, I enjoy our endless debate over a number of things such as course selection, future career plans, etc. I consider myself a very fortunate person to know him from the Computer Programming course he opened in my freshman year and be given the opportunity to enter his lab in the sophomore year. It is definitely my honor and pleasure to be a part of his plasma lab. Secondly, I would like to thank my friend, Ching-Yuan Wang, for being present in all the experiments I have conducted in this work, for our system is rather complicated and dangerous in terms of personal safety. I would like to thank him for always double-checking the high-voltage circuit for me and offering kind words and emotional support in the darkest of times. I could not have finished this work without him. Lastly, I would like to thank my second friend, Tang, for setting such a good example for me, for I would not have developed such a passion for programming if it was not for him. It is so rare to meet someone who works with such intense passion nowadays, so I want to especially thank him for inspiring me, on top of all the professional programming knowledge he provided me throughout this work.

中文摘要

長久以來，水污染一直是公眾關注的議題。然而，既有量化溶液中金屬元素的分析工具，包括：電化學、金屬比色法、及感應式耦合電漿等技術，皆存在著不同程度的缺陷，導致無法進行長期、即時、與遠端水質監控系統的建立。因此，本研究採用電漿光譜技術，建立一個具有長期、即時、及遠端的水質監控系統。本研究透過水溶液電漿光譜技術，分析溶液中的金屬元素，並將 Linux 微型電腦樹莓派（Raspberry Pi）導入實驗裝置中，進而進行長期、即時、及遠端的水質監控。透過施與浸泡於水溶液中的電極一個高壓脈衝波，可以在水溶液中產生電漿。再透過分析生成的電漿光譜，進而可以檢驗出溶液中的金屬元素。本研究使用一個直徑為 0.3 毫米的白金電極產生電漿，並以水下光學元件獲取電漿放光，最後透過光譜儀紀錄這些光學資訊。樹莓派同時調控了 500 伏高壓脈衝波的寬度、點燃電漿、觸發光譜儀並且紀錄光譜。如此多功能的設計允許了電壓脈衝波和光譜儀的精確同步。另外，樹莓派在本實驗裝置亦擔任一個 HTTP 的網路伺服器，以提供客戶端友善的操作界面及更安全的連線。光譜儀和電壓脈衝波的精確同步，顯著提高了光譜數據的品質。本研究中的實驗數據可以清楚地識別出濃度為 10ppm 的鎂、10ppm 的鉛和 10ppm 的銅。本研究進行了一個長達數十小時的遠端監控實驗。更長時間的監控測試，透過編碼，在本系統中可以被容易達成。關於測試溶液的資訊可以透過電子郵件、Line 通訊軟體等等途徑，即時通知用戶。因為在每次電漿生成前，樹莓派都會自動選擇並設置適當的高壓脈衝波寬度，因此本系統可以被廣泛地應用於不同的 pH 值和導電度條件，如此可以證明本檢測系統的可靠性。透過選取最佳脈衝波的寬度，本系統可有效免除樣品預處理的人為步驟。樹莓派取代了傳統工業控制設備，成功降低了實驗裝置的成本和尺寸。透過在樹莓派上進行編碼可設計出不同的檢測模式，使得本研究之水質檢測系統更加靈活，以及更具有實際應用價值。

關鍵字：水溶液電漿、放射光譜、重金屬檢測、樹莓派、長期檢測、即時檢測、網頁平台

ABSTRACT

Water pollution has been a severe public concern for decades, however, existing analytical tools that can quantify metallic elements such as electrochemistry, metal colorimetry, inductively coupled plasma, etc., have certain drawbacks that prevented the establishment of a long-term, remote water monitoring system. Therefore, such a system is ever in need and will be introduced in this work. In this work, plasma spectroscopy is used to analyze metallic elements in solution, and the imposture of Raspberry Pi, an open-source Linux mini-computer, allows for long-term, real-time, and remote control of the system in a flexible and low-cost manner. By applying a high pulsed voltage to the electrode immersed in the solution, plasma can be ignited. Metallic elements, namely Mg, Pb, and Cu, are tested using the optical emission of the plasma. The detection probe used in this work comprises a platinum electrode 0.3 mm in diameter surrounded by a glass tube and underwater optical components to acquire the emission. Raspberry Pi is used to simultaneously modulate the width of 500-V high voltage pulses, ignite plasma, trigger the spectrometer, and acquire spectra. Such an arrangement allows for precise synchronization of voltage pulses and spectra acquisition with the spectrometer. Raspberry Pi also acts as an HTTP web server in this setup to provide a friendly user interface and a more secure connection. Precise synchronization of spectrometer and voltage pulses significantly improves the overall quality of spectroscopic data. Metallic elements Mg, Pb, and Cu with concentrations of 10ppm, 10ppm, and 10ppm are clearly identified. A long-term monitoring session lasting up to tens of hours is tested remotely, and extension to a longer time duration is straightforward. Warning messages can be sent out instantly via multiple pathways such as E-mail and Line APP. It is shown that this detection system is reliable since proper high voltage pulse width is selected and set prior to every detection, this guarantees the choosing of an optimal pulse width for each solution with a wide range of pH and conductivity. As an optimal pulse on-time is chosen according to the conductivity of each solution, the need for sample pre-treatment is eliminated. The use of Raspberry Pi replaces the conventional industrial control equipment with the benefits of reduction in cost and system size. With the flexibility of programming on Raspberry Pi, the detection process can be designed such that different detection frequencies can be imposed on demand.

Keywords: Solution Plasma, Optical Emission Spectroscopy, Heavy Metal Detection, Raspberry Pi, Long-term, Real-time, Web-based

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Chapter 1 Introduction

1.1 Preface

Solution plasma is a term that refers to various plasma systems that operate under aqueous conditions. In these systems, plasma is generated within the solution or within the environment in contact with the solution. When using the spectroscopy technique with solution plasma, existing heavy metals can be recognized as certain characteristic wavelengths are inspected, the intensities of those metallic wavelengths can then be used for quantitative analysis after proper processing. Moreover, solution plasma spectroscopy technique is capable of analyzing multiple heavy metals rapidly and simultaneously while having little to no interference between each element.

In this work, a Raspberry Pi board is integrated into the plasma generation unit to control the spectrometer for spectrum acquisition, while simultaneously modulate the pulse on-time for plasma ignition. By constantly modulating the applied on-time, this innovative system overcomes the requirement for sample pretreatment. Raspberry Pi also acts as an HTTP web server in this setup to provide friendly user interface and a more secure connection. This way, a long-term, remote water monitoring system that is capable of providing real-time information about real-world solution is introduced. With the flexibility of programming on Raspberry Pi, the detection process can be designed such that different detection frequencies can be imposed on demand. Warning messages can be sent out instantly via multiple pathways such as E-mail and Line APP. The use of

Raspberry Pi replaces the conventional industrial control equipment with the benefits of reduction in cost and system size.

1.2 Research Motivation and Goal

Water pollution with heavy metallic ions has been a severe public concern for decades for it directly impacts the environment and can cause tragic health problems. Analytical tools allowing for in-line and real-time monitoring of metallic elements are therefore highly desired. Techniques such as electrochemical sensors, fluorescence spectroscopy, and ion-specific electrodes are widely used. These techniques, however, mostly is incapable of detecting multiple elements simultaneously. It mostly requires the water solution to be under designated conductivity and pH values for precise measurement. The use of these techniques is therefore very limited. Lab-scale techniques such as ICP-OES (inductively coupled plasma optical emission spectrometry) and ICP-MS (mass spectrometry) allow for analyzing test solutions with a wider range of variety. They, however, are bulky and expensive. They also require rather tedious sample pretreatment. Operating in a long-term and continuous manner is therefore challenging.

Therefore, a long-term water monitoring system that is capable of providing real-time information about real-world solutions is desired and will later be introduced in this work.

Chapter 2 Literature Review

2.1 Heavy Metal Contamination

2.1.1 Sources of Heavy Metal Pollution and Regulations

There are a number of inspection criteria regarding water quality, such as water temperature, pH value, electrical conductivity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), etc. Among them, electrical conductivity is a measure of the saltiness of water and is measured in micro-siemens per centimeter (μS/cm). Electrical conductivity is of extreme importance when it comes to heavy metal contamination, for conductivity is an index of how easy it is for electricity to flow in water, and metallic ions conduct electricity by simply moving in solution. Freshwater is usually between 0 and 1,500 μS/cm and typical seawater has a conductivity value of about 50,000 μS/cm. Table 1 listed the conductivity of various types of water [1]. Irrigation water in Taiwan should have a conductivity lesser than 750 μS/cm according to the Taiwanese government [2].

Table 1. Conductivity of Various Water Types

Water Type	Conductivity (μS/cm)
Distilled Water	0.5 - 3
Melted Snow	2 - 42
Irrigation Water (R.O.C.)	<750
Tap Water	50 - 800
Potable Water (U.S.)	30 – 1,500
Freshwater Streams	100 – 2,000
Industrial Wastewater	10,000
Seawater	55,000

Taiwan is a densely populated area with well-developed industries. However, improper land usage and farmland pollution are frequently reported. Factories are commonly seen in agricultural districts and industrial wastewater and waste product are often, directly or indirectly, discharged into nearby water channels without being treated. Heavy metal is one of the most common and severe issues regarding water pollution, for heavy metal can easily form complex with inorganic and organic substances in soil, and are difficult to remove after formation. Nor can they be biodegraded like volatile organic compounds. Therefore, once the soil is polluted with heavy metals, nearby crops will absorb those toxic pollutants and accumulate in human body through the inter-related food chain. To prevent the above scenario, the Environmental Protection Administration of Executive Yuan, R.O.C. (Taiwan) has established "Soil Pollution Monitoring Standards" in terms of soil pollution. Another regulation, "Soil Pollution Regulatory Standards", is established specially to prevent the deterioration of soil pollution. The concentration limits of pollutants are summarized in Table 2 [3].

Table 2. Concentration Limit of Metallic Pollutants in Taiwan (unit: ppm)

Heavy Metal		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Regulatory Standard	Soil	60	20	250	400	20	200	2000	2000
	Agricultural Farmland		5		200	5		500	600
Monitoring Standard	Soil	30	10	175	220	10	130	1000	1000
	Agricultural Farmland		2.5		120	2		300	260

2.1.2 Current Water Monitoring Techniques and Limitations

(1) Metal Colorimetry [4, 5]

Colorimetric technique is one of the easiest ways to detect heavy metals in solution, for color change occurs when certain oxidation-reduction reaction or coordination reaction takes place. After applying organic chromogen to the solution, quantification of the metallic element can be performed according to the product's color as stable chelate is formed. Appropriately selected chromogenic agents can achieve in high selectivity, high sensitivity, and stable product composition. However, this technique is not capable of simultaneously detecting multiple elements, for each metal requires a specific chromogen. Also, its performance is easily affected by impurities, meaning pre-treatment of tested samples is always mandatory.

Figure 1. Metal Colorimetry Detector [6]

(2) Electrochemical Measurement [7, 8]

The electrochemical measurement technique operates by measuring the current change on the electrode as various voltages are applied. This way, the quantification of specific metal ions can be achieved. Anodic Stripping Voltammetry is one of the most common examples of this technique, it operates by measuring the induced current on the working electrode during electrochemical stripping. This technique is capable of achieving excellent selectivity and sensitivity for specific metals. However, it relies heavily on the electrochemical reaction taking place on the electrode's surface, meaning the state of the electrode's surface and the composition of the electrolyte are extremely critical. Therefore, this technique might fail to operate under challenging conditions, such as low pH solution or solution containing organic pollutants. The electrodes also need to be replaced rather frequently, making it difficult to operate in a long-term and continuous manner.

Figure 2. Anodic Stripping Voltammetry Instrument [9]

(3) Inductively Coupled Plasma (ICP)

The ICP system operates by first vaporizing the liquid solution into gas form, then all the gaseous analytes are atomized, ionized, and thermally excited due to the extremely high temperature of the system. By analyzing the plasma spectrum with a spectrometer (ICP-OES) [10] or analyzing the created atoms or molecules with a mass spectrometer (ICP-MS) [11], the qualification and quantification of target elements can be achieved. ICP has the lowest detection limit of all the techniques being introduced in this work, reaching a single-digit ppb level, and is capable of simultaneously detecting multiple elements in one operation. ICP is currently the most used heavy metal detection technique in laboratories world-wide, for it has extremely high versatility and sensitivity and an extremely low detection limit. However, it is bulky and expansive, and require rather tedious sample pre-treatments with a warm-up stage. This means remote operation and real-time feedbacks are not possible with this technique.

Figure 3. Inductively Coupled Plasma Instrument [12]

In summary, existing analytical tools still contain certain drawbacks that prevented the establishment of a long-term, remote water monitoring system, such as:

(1) The need for sample pretreatment.

(2) The need for consumables replacement.

(3) Cannot be operated remotely or automatically, and require on-site labor.

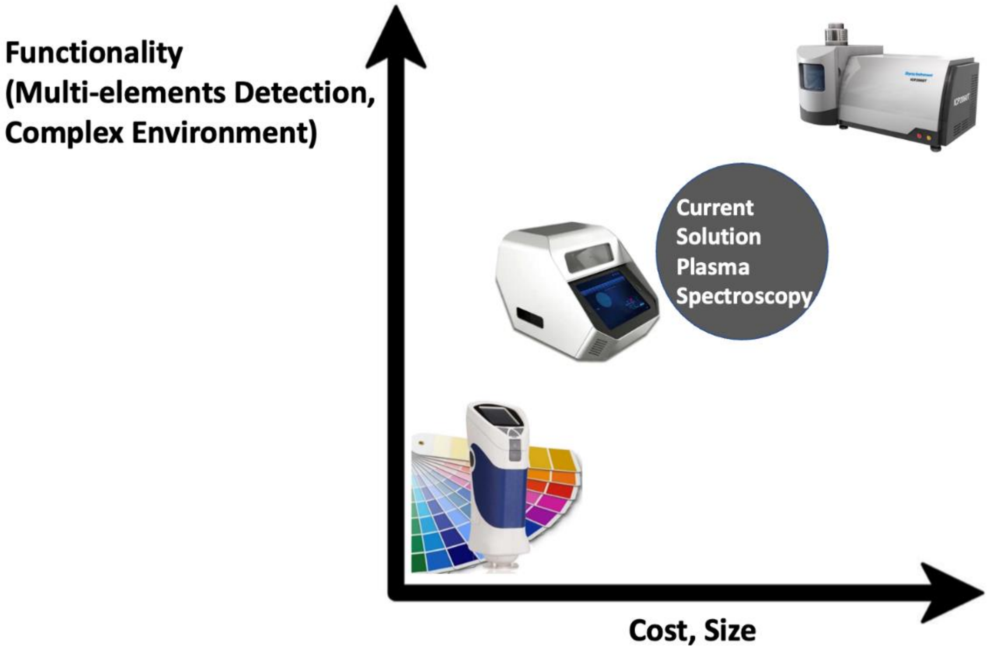


Figure 4. Overall comparison of various techniques

2.2 Plasma

Plasma is a partially or wholly dissociated gas that is mainly composed of neutral gas, ion, electron, atom, molecule in the excited state, and gas cluster with free radicals. It is electrically neutral and is often recognized as the fourth state of matter.

2.2.1 Reaction Mechanism

When external electric field is applied to gas, electrons are transformed into high-energy particles. As these high-energy particles collide with one another, they undergo a series of complex chemical and physical reactions [13]. As high-energy electron collides with atom, the outer electron of the atom dissociates, generating free electron. These newly generated electrons then collide with other atoms to generate more electrons, until a complete breakdown is reached. Ionization is the most important reaction regarding the stability of plasma. As high-energy electron collides with a gas molecule, it destroys the chemical bonding between particles and generates free radicals. Since free radical carries unpaired electron and have high reactivity, dissociation is the most important reaction regarding the reactivity of plasma. As high-energy electron collides with a gas molecule or atom, the electron on the molecule or atom is excited from ground state to excited state. As the molecule or atom relaxes back to a lower energy state, energy is released in the form of electromagnetic waves. Since different wavelengths of light can be emitted due to different energy gaps, excitation-relaxation is the essence of plasma spectroscopy. The reactions introduced above are listed in Table 3.

Table 3. Plasma Generation Mechanism

Reaction	Mechanism
Ionization	$e^- + A \rightarrow A^+ + 2e^-$
Dissociation	$e^- + AB \rightarrow A + B + e^-$
Excitation	$e^- + A \rightarrow A^* + e^-$
Relaxation	$A^* \rightarrow A + hv$

2.2.2 Empirical Formula and Observation

Paschen's Law is an empirical formula that describes the relationship between the breakdown voltage and the product of pressure and electrode gap.

$$V_b = \frac{B(p \cdot d)}{\ln[A(p \cdot d)] - \ln\,[\ln\,(1 + {}^{1}/_{\gamma_{se}})]}$$

Where V_b is the breakdown voltage, d the electrode distance, p the gas pressure, γ_{se} the secondary dissociation coefficient, A and B are constants. The breakdown voltage of plasma is defined as the minimum voltage required to successfully generate plasma. Figure 5 shows the Paschen curve of various gases [14]. The right side of the curve is the case where gas pressure is high, or the electrode distance is large. In this case, collision happens frequently and electrons are quickly deprived of their kinetic energy for gas pressure is high, and the effectiveness of the applied electric field is insignificant for the electrode distance is large. The left side of the curve shows the case where gas pressure is low, or the electrode distance is small. In this case, the collision with gas molecules is difficult for gas pressure is low, and the electron acceleration is not effective for the distance is short. These scenarios account for the upward concave of the curves.

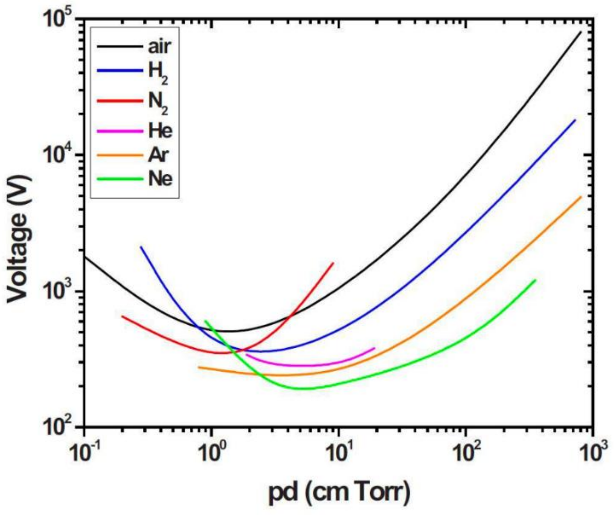


Figure 5. Paschen curve of various gas [14]

2.2.3 Classification

Plasma can be roughly categorized into low-pressure plasma and atmospheric pressure plasma according to its operating pressure. Low-pressure plasma usually operates at a pressure of less than 0.001 atm. This means electron has longer mean free path, and it barely collides with neutral gas nor loses energy during the acceleration process. Therefore, the electron temperature is higher than that of the neutral gas ($T_e > T_g$), implying this is a non-thermal-equilibrium system [15], as shown in the left half of Figure 6. Conversely, when the pressure increases, the mean free path decreases, and the high-energy electrons are more likely to collide with neutral gas. In this case, the gas temperature and the electron temperature reach equilibrium ($T_e = T_g$), implying this is a thermal-equilibrium system. The former is easier to generate plasma due to the fact electron energy is hardly lost in collision, while the latter often requires an external electric field to successfully generate plasma.

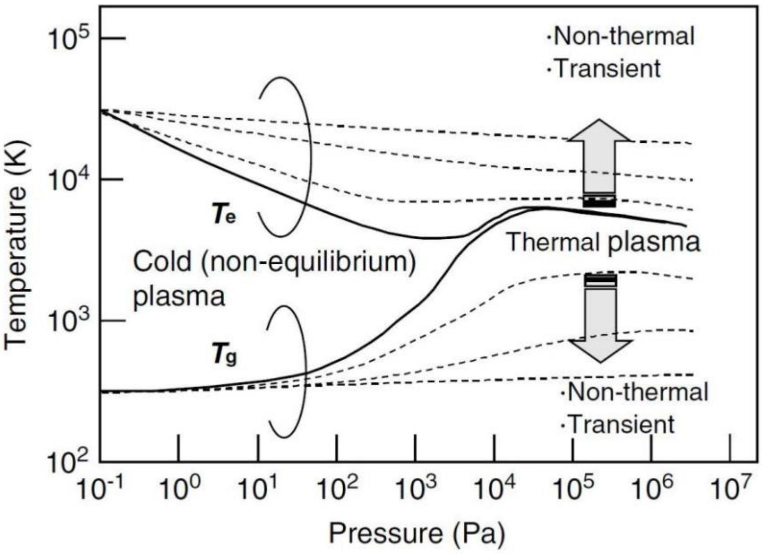


Figure 6. Electron and gas temperature under different operating pressures [15]

2.3 Solution Plasma

2.3.1 Principles

Solution plasma [16-20] is a term that refers to various plasma systems which operate under aqueous conditions. There are a variety of classification methods regarding solution plasma, among them, the method proposed by Bruggman and Leys [21-23] is the most commonly used. Bruggman and Leys divided solution plasma into three categories (1. Direct liquid phase discharge, 2. Discharge in the gas phase with liquid electrode, 3. Discharge in bubble in liquid) according to the type of electrode being utilized and the way it contacts with aqueous solution. In these systems, plasma is generated within the solution or the environment in contact with the solution, such that ultraviolet rays, high shock waves, and large quantities of highly reactive substances [24], such as hydroxyl radicals (OH·), oxygen atoms (O), ozone (O3), hydrogen peroxide (H2O2) [25], etc. are released, as shown in Figure 7.

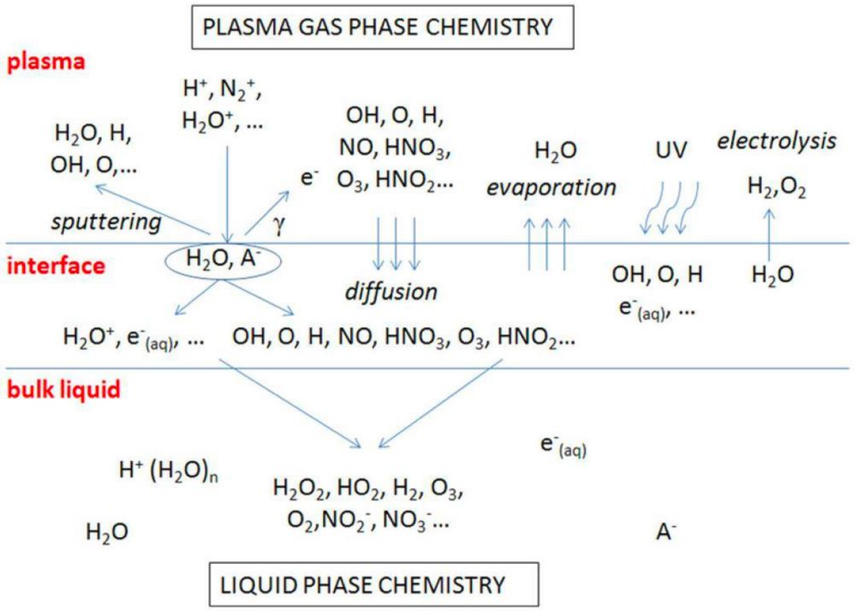


Figure 7. Reaction mechanism and existing substances in solution plasma [25]

2.3.2 Difficulties in Solution Plasma Studies

Although solution plasma has been widely employed in various fields, however, the mechanism of its physical and chemical reactions had not yet been fully understood due to its complicated nature. The reasons are listed as follows:

(1) Plasma is generated on a three-phase interface [26], namely, solid phase (metal electrode), liquid phase (aqueous solution), and gas phase (bubble or gas film). This makes the mass and heat transfers in between phases difficult to predict. As shown in Figure 8.

(2) Compared to the generation of plasma in the gas phase, the density of liquid is 1000 times higher than that of gas, resulting in a higher frequency of ionization. This makes the multi-particles-collision difficult to understand.

(3) Solution plasma contains reactions with responses in different time scales (ps~s) [27], indicating complex coupling relationships among particles.

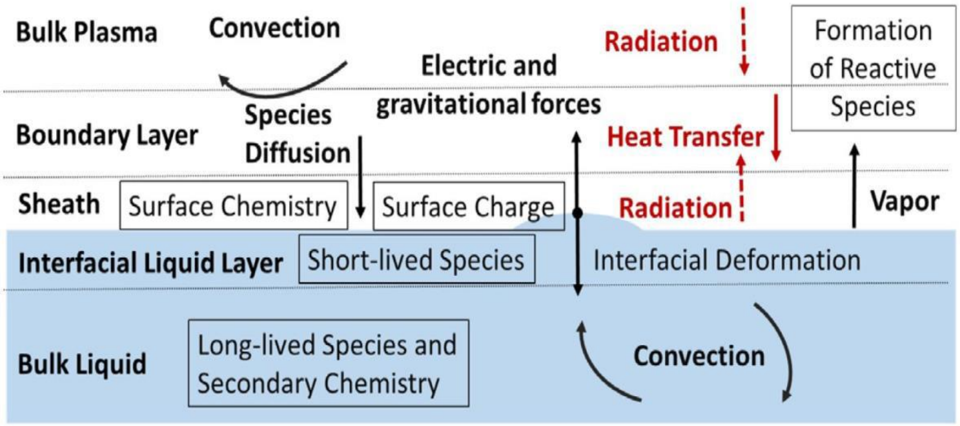


Figure 8. Mass transfer and heat transfer of solution plasma

2.3.3 Solution Plasma Spectroscopy and Its Challenges

The solution plasma spectroscopy technique [28-31] operates by inspecting the characteristic wavelengths of each metallic element on the plasma spectrum, in order to determine the existence of those elements. The intensities of those wavelengths can later be used for quantitative analysis after proper processing. Solution plasma spectroscopy technique can simultaneously detect multiple heavy metals while having little to no interference between each element. This is because the electron transfer energy gaps of different metals are distinguishable on the plasma spectrum, therefore, each element has its own one or two characteristic wavelengths. Solution plasma spectroscopy is often utilized to achieve degradation of organic matter [32], material synthesis [33] [34], and analytical analysis [35] . Figure 9 shows a plasma spectrum with various metal emissions.

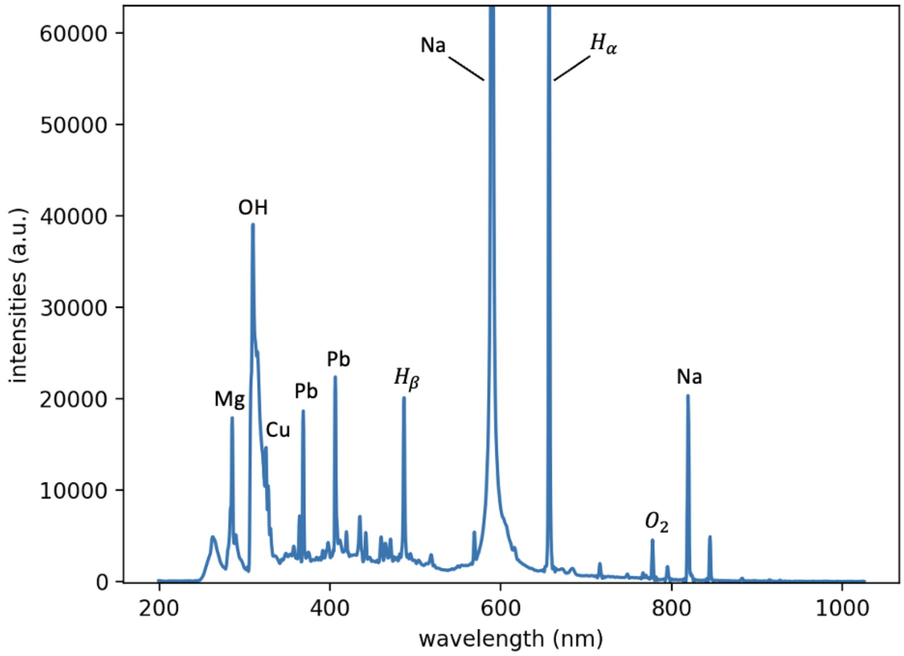


Figure 9. Plasma spectrum with various metal emissions

Solution plasma spectroscopy is a powerful and robust technique that is capable of detecting multiple metallic elements with little to no interference between each element. However, there are still many difficulties when it comes to practical application.

(1) In addition to metallic ions, spectrum also includes the emission of other existing atoms or molecules within the system. This makes it difficult to extract quantitative information concerning metallic elements.

(2) The formation of plasma in solution is affected by factors such as pH value, conductivity, etc. If the operating conditions are not strictly managed [23, 36], plasma might fail to exist, or the generated plasma might exist in an unstable state. Sample pretreatment such as adding acids or salts [37], or sample pre-evaporation[38] is frequently required. This means both qualitative and quantitative analysis are rather tedious, or difficult, when it comes to unknown solutions.

(3) Since plasma generates electric current and heat as it exists, long-term monitoring is challenging due to its natural decay. For example, mild damage might occur to the working electrode as time proceeds. This makes it difficult to monitor and perform metal detection over a long period of time.

All in all, these limitation makes it challenging to accomplish in-line and real-time analysis of metallic elements with the solution plasma spectroscopy technique.

2.4 Raspberry Pi

Raspberry Pi is a low-cost and miniaturized sized (85mm x 56mm) single-board computer that is designed to support students in low-income areas to engage with computing. This mini-Linux computer has 2 micro-HDMI displays and 4 USB ports. It also has 40 GPIO pins that are capable of inputting or outputting digital signals, which makes the control of any compatible electronics rather simple and straightforward. Raspberry Pi has been utilized in multiple scientific fields and analytical applications, such as microfluidic biosensors [39] [40] [41], electrochemical analysis [42], optical spectroscopy or imaging systems [43] [44], etc. An actual image of Raspberry Pi is shown in Figure 10.

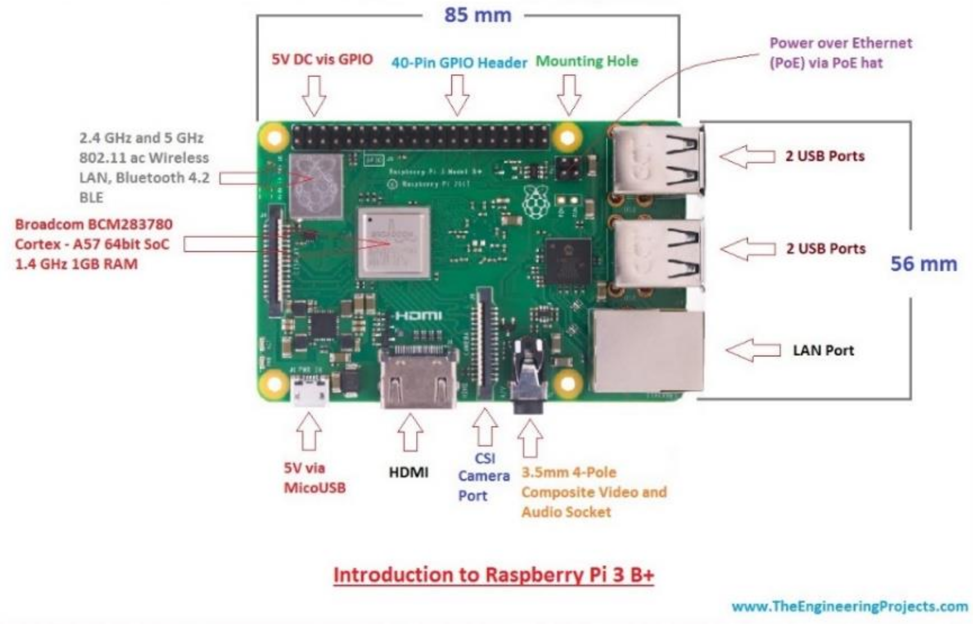


Figure 10. Raspberry Pi [45]

Chapter 3 Experiment Apparatus and Methods

3.1 Experiment Apparatus

3.1.1 Plasma Generation Unit

A detection probe with a dimension of 150mmx20mmx20mm is created as the plasma generation unit. It has a center pinhole of 7mm in diameter. This is where the working electrode is placed. The working electrode is a glass tube 7mm in diameter with a 0.3mm diameter platinum wire in the middle. The grounding electrode is a platinum wire 0.5 mm in diameter and 10 cm in length.

3.1.2 Power and Pulser

A 500V DC power supply (GPR-100H15, GW Instek) is used as the high-voltage source. A switching device is imposed to control the passage of this high-voltage source and will be addressed as “pulser” throughout this work.

Pulser is composed of an insulated gate bipolar transistor (IGBT, IXYP20N120C3), an operational amplifier, a 9V battery, and a Raspberry Pi board. As Raspberry Pi sends out a digital signal of 3.3V through its GPIO pin, IGBT’s G gate opens, and high voltage is allowed to pass through the C gate. Since IGBT requires at least 6V of input signal to function, an amplifier is employed within the setup to boost the signal from 3.3V to 8V. The 9V battery is used to provide the additional power supply requested by the amplifier.

3.1.3 OES Acquisition Unit

The underwater lens has a 10mm focal length and a 90 degrees reflective angle, this design structure helps guide the optical emission of plasma into the optical fiber (600 µm diameter) with little to no loss of emission intensity. A spectrometer (OES-2030-010-FUV2, Li-ion Ltd, Taiwan) is positioned at the other end of the optical fiber to record the emission.

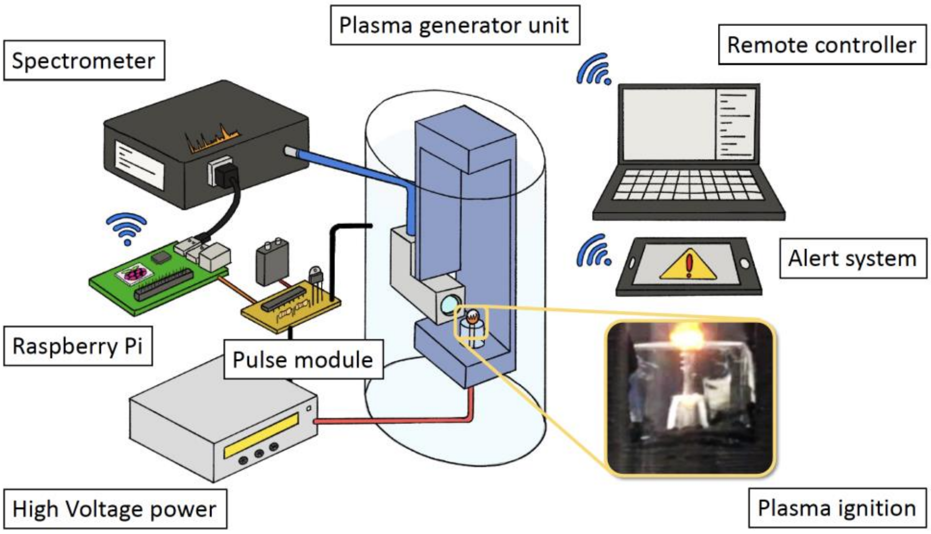


Figure 11. Device Setup

3.2 Experiment Methods

3.2.1 Chemicals/Solution Preparation

In this work, six metallic elements, namely Mg, Cu, Pb, Mn, Sr, and Zn are tested. Nitrate salts are used. $Mg(NO_3)_2$ (Alfa Aesar, 98.0-102.0%), $Cu(NO_3)_2$ (J.T. Baker, -), $Pb(NO_3)_2$ (Sigma-Aldrich, ≥99.0%), $Mn(NO_3)_2$ (Alfa Aesar, 98%), $Sr(NO_3)_2$ (Alfa Aesar, 99.0%), and $Zn(NO_3)_2$ (J.T. Baker, 99.0-101.0%) are used without further purification. Solutions of different concentrations and conductivities are prepared. Calculated amount of metal solution, deionized water, and Sodium Nitrate are separately added to determine the concentration and conductivity of each solution. The concentration of heavy metals ranges from 10mg/L to 200mg/L, and solution conductivities are controlled to be within the range of 3000 to 18000μS/cm, which is the typical conductivity range of industrial wastewater. All solutions have a pH value of around 5.

3.2.2 Remote Operation of Raspberry Pi

Raspberry Pi can be operated remotely, which offers users the benefit of mobility. In this system, there are two remote ways to connect to the Raspberry Pi, they are:

(1) Secure Shell Protocol (SSH)

SSH is a TCP application protocol used to make secure connections to a remote device in order to perform file-sharing or host configuration tasks. One may navigate Raspberry Pi's file system with the SSH protocol using the Linux command line. However, the operating interface on one's computer is the terminal for Mac OS (or MobaXterm, an online free app, for Windows OS), not exactly the most user-friendly interface, so this method is recommended for system managers inside the lab only, and not common users. Also, since users may gain full access to the entire operating system, meaning all the files and directories, inside the minicomputer, it is also not wise to permit this full access to common users.

(2) Hypertext Transfer Protocol (HTTP)

Even though SSH has proven to be a simple and secure way of connection for people such as the system admin, however, it has some drawbacks that prevent the water monitoring system being developed from becoming a user-friendly and secure product for common users. For instance, SSH uses terminal as its operating interface, which requires a certain degree of programming knowledge upon operation, and, SSH allows full access of the entire operating system to authorized user in a manner that is not wise nor recommended in terms of system security. Therefore, a new connecting method and interface are desired and shall be introduced.

In this system, Raspberry Pi is programmed to function as an HTTP web server with Nginx, a web server software program that serves web applications to clients over the internet. With this web-based transfer protocol, users can easily submit their experimental parameters (ex: pulse on-time, spectrometer integration time, mode resting time, monitoring duration, frame per detection, etc.) through the self-developed website on their browser without the risk of exposing the entire Raspberry Pi's operating system. A "Security Check" stage is designed to appear prior to the actual "Parameters Setting" stage so that those who do not know the correct passcode will be rejected and those who do may proceed. After submitting a number of parameters with one's cellphone or computer, plasma is ignited accordingly. A compressed file containing numerous plasma spectrums will then be delivered to the user's Download folder after the entire server-side operation is completed. The website interface is written in HTML, CSS, and JavaScript, while the server-side code is written purely in JavaScript. Plasma ignition and spectrum acquisition is written purely in Python.

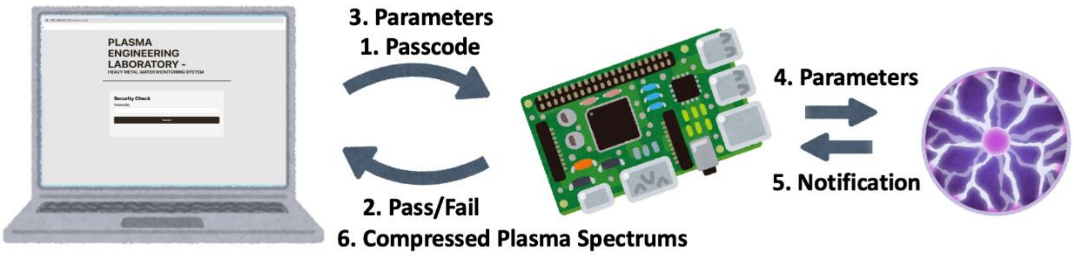


Figure 12. Web-based Plasma Ignition Illustration

3.2.3 Plasma Ignition by Raspberry Pi

By integrating Raspberry Pi into the solution plasma system, the mini-Linux computer will be performing two tasks simultaneously to generate plasma.

Raspberry Pi is connected to the spectrometer via a USB port, and with the help of the programming scripts provided by the vendor, direct manipulation of the OES device can be achieved. This way, Raspberry Pi can replace the conventional, large-size personal computer as the spectrometer reader. Data is delivered to and saved within the Raspberry Pi operating system folder. One of the GPIO pins on Raspberry Pi is connected to IGBT's G gate. As the pin outputs a digital signal of 3.3V for some time interval, the G gate opens for that amount of time and the high voltage of 500V provided by the DC power supply flows through the C gate. Plasma is then ignited on the end of the working electrode that is immersed in the liquid solution. This way, the Raspberry Pi board will be replacing the industrial, high-cost pulsing machine as pulser.

The two tasks mentioned above, spectrometer reading (data acquisition) and pulsing (data creation), are exactly synchronized by using Python. This means the two tasks start simultaneously and the spectrometer only functions when plasma is being generated.

Chapter 4 Results and Discussion

4.1 Solution Plasma System Overview

In this system, both working and ground electrodes are immersed in the aqueous solution, however, their contact areas are different. This causes the current density of the two electrodes to differ as well. The current density of the working electrode is higher than that of the ground electrode, therefore, the working electrode is in charge of heating the aqueous solution and producing bubbles. As a sealed gaseous layer, or bubble, is formed between the aqueous solution and the working electrode due to sudden heating and electrolysis, plasma can be generated within this confined layer when the breakdown voltage is reached. Multiple reactions occur simultaneously, such as electron ionization, dissociation, and excitation. The microscopic result is that water and salts within the solution are heated and vaporized, resulting in a centimeter-sized bubble mostly consisting of H_2, O_2, and water vapor. Also, when plasma is generated, electrons of metallic ions have a large chance of being excited and therefore migrating to a higher energy level. Optical emission corresponding to the metallic element can be observed as the electron drops back to a lower energy state. Each metallic element has its own unique position on the plasma spectrum, which can be used as an identifier of the metal.

Figure 13 shows three spectrums in the metal emission range (250nm-550nm) that differ in applied On Time. Six metals (Mg, Cu, Pb, Mn, Sr, Zn) are added to the solution, and the emissions of Mg, OH, Cu, Pb, and H_β are labeled within the figure. Mg is observed at 285.58nm and Cu is observed at 324.82nm on the plasma spectrum. Pb shows emission at both 368.34nm and 405.78nm. Metals Mn, Sr, Zn are out of the current detecting zone for they overlap with N_2 emission. When testing the solution, the emission intensities increase with the pulser's On Time, indicating a positive correlation between spectrum intensities and the length of pulser's On Time.

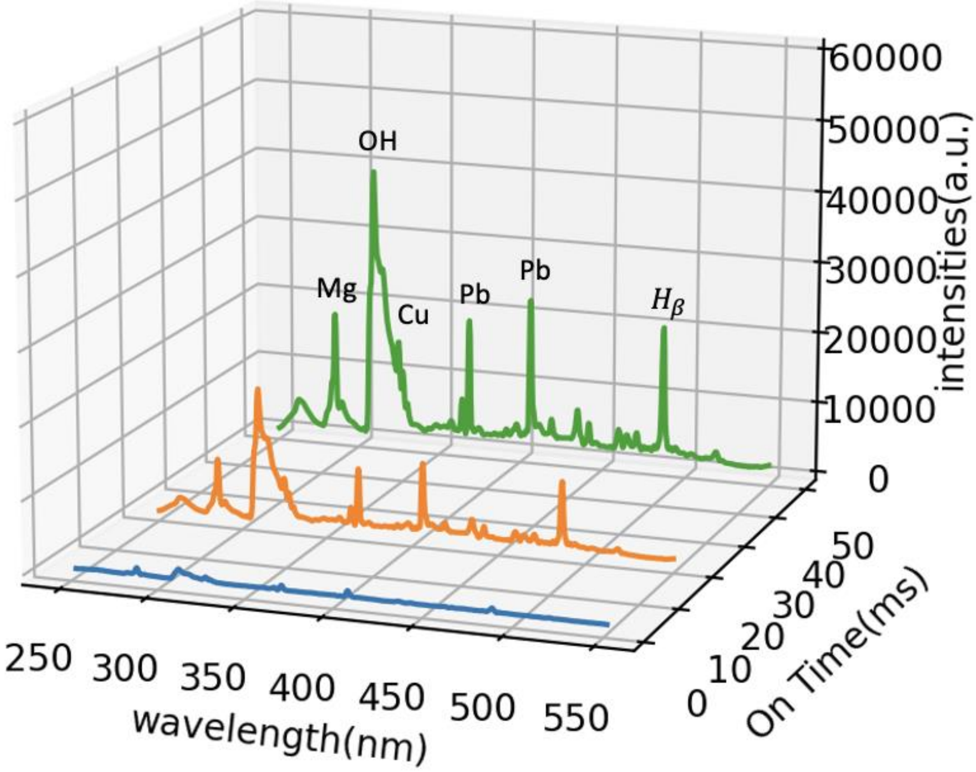


Figure 13. Low Conductivity Solution Spectrums

Solution properties/experiment parameters: Conductivity 8510 μS/cm. pH 4.78. Metal concentration (Mg, Cu, Pb, Mn, Sr, Zn) 100ppm. Integration time 200ms. Voltage 500V. On Time 1ms (blue line), 20ms (orange line), 50ms (green line).

4.2 Importance of Pulse Selection

Plasma in solution has been recognized as a promising technique concerning heavy metal detection. However, it has the drawback of being highly restricted to solution conductivity. This means sample pretreatment is required, and real-time analysis cannot be achieved. To overcome the predicament, an experiment is conducted and thoroughly discussed within this section.

To simulate real-world situations, two solutions that differ greatly in conductivity (EC:8510 μS/cm, EC:17240 μS/cm) but of the same pH value and metal concentration are prepared. Various On Time (1ms, 20ms, 50ms) are applied to both solutions. Figure 13 shows three spectrums of the low conductivity solution in the metal emission range (250nm-550nm), while Figure 14 shows those of the high conductivity solution also in the metal emission range. From Figure 13 and Figure 14, as 1ms is applied to both solutions, barely any optical emission regarding the metallic peaks can be observed. 1ms is therefore concluded as an unsuitable choice for both solutions. From Figure 13 and Figure 14, when 50ms is applied to both solutions, even though the spectrum looks rather reasonable for the low conductivity solution, however, this is obviously not a suitable choice for the high conductivity solution, for the spectrum is too saturated and the board-bend underneath is too large in height. Figure 14 shows that there exists an optimal On Time for every solution depending on their conductivity. If an unsuitably large On Time is applied, a completely saturated spectrum might be obtained at one point, and permanent damage of the working electrode might occur. Therefore, a selection process should take place prior to the actual heavy metal detection to guarantee an optimal performance.

With the system being proposed in this work, Raspberry Pi can actively and automatically modulate the applied On Time until the optimal value is found. This way, real-world solutions with a wide range of conductivity and pH values can be tested.

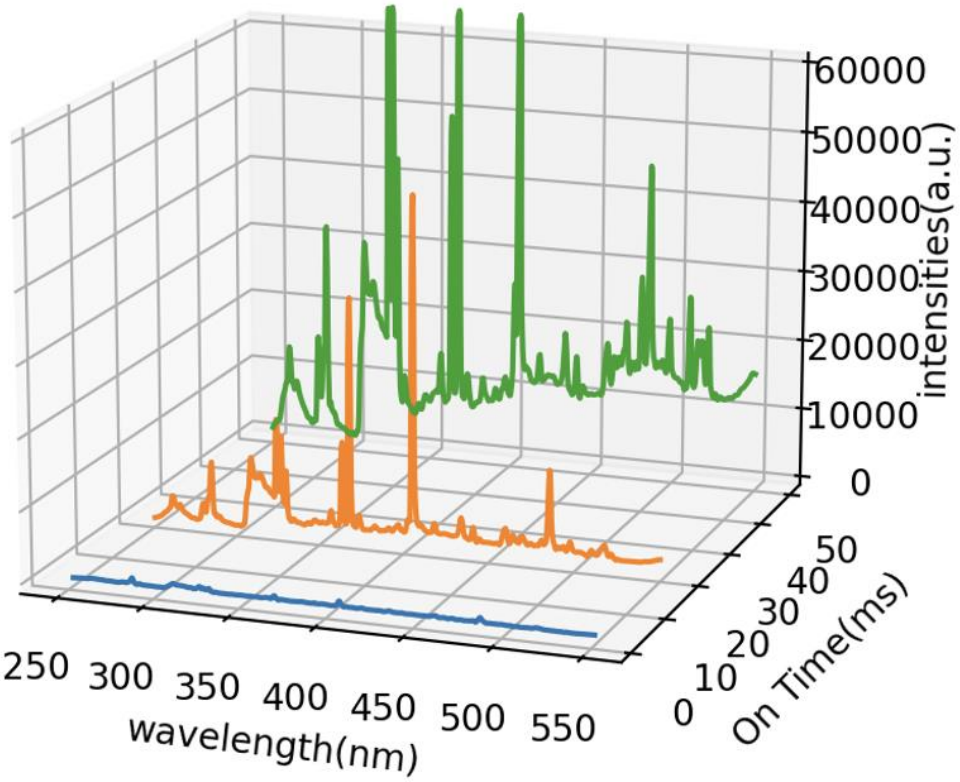


Figure 14. High Conductivity Solution Spectrums

Solution properties/experiment parameters: Conductivity 17240 μS/cm. pH 4.78. Metal concentration (Mg, Cu, Pb, Mn, Sr, Zn) 100ppm. Integration time 200ms. Voltage 500V. On Time 1ms (blue line), 20ms (orange line), 50ms (green line).

4.3 Two-Tasks-Synchronization

To illustrate the importance of tasks synchronization, namely spectrometer reading and pulsing. A brief go-through with the use of the previous, asynchronized setup shall be addressed. After the DC power supply is turned on, the pulsing device will function with some programmed duty time, each plasma emission is then recorded by the spectrometer. The two tasks run on two separate timelines, which leads to poor data quality of huge variance, as shown in Figure 15a, due to the fact the spectrometer might record plasma emission of different time intervals, as shown in Figure 15b. Also, throughout the process, the pulsing device works non-stop, meaning plasma is continually being generated on the working electrode, as shown in Figure 15b. This shows the working electrode lifetime is somewhat wasted, for not every emission is recorded by the spectrometer.

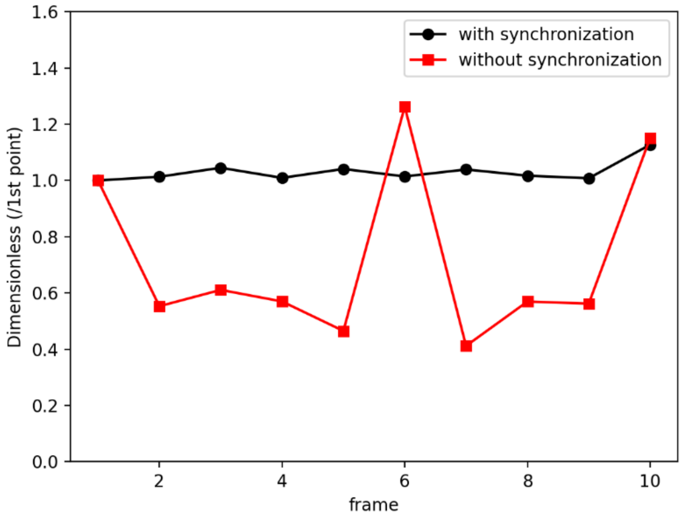
With the synchronization method being employed, one can be confident of how long the optical emission is recorded, achieving a decrease in data variance, as shown in Figure 15a, and the working electrode lifetime may be maximized for its usage is kept to a bare minimum, as shown in Figure 15c. This is very crucial when it comes to long-term operation since electrode's condition directly impacts data quality. In this work, a Raspberry Pi is integrated into the system to perform this tasks-synchronization using Python.

In Figure 15a, ten black dots are the OH intensity from ten consecutively acquired spectrums using the synchronization method, while the ten red squares are the OH intensity from ten consecutively acquired spectrums using the asynchronization method.

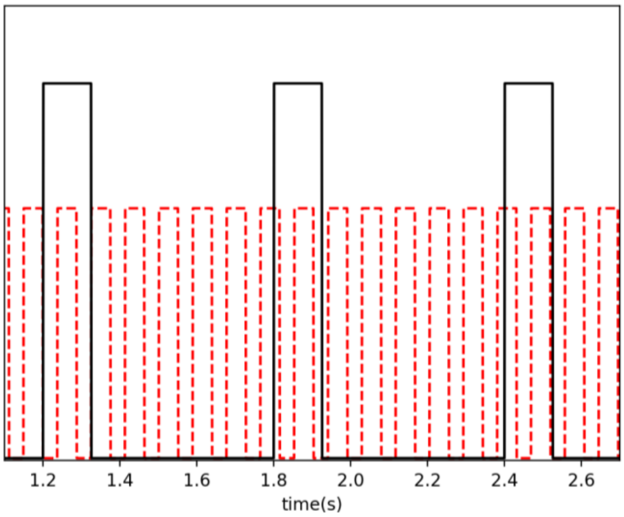
All ten OH intensities are normalized to the first OH intensity for each method.

In Figure 15b and c, black solid line indicates the spectrometer's integration time, which is 125ms, while the red dashed line indicates the pulser's On Time, which is 50ms. The overlapping of the two lines illustrates the performance of the asynchronization method in Figure 15b, and that of the synchronization method in Figure 15c.

(a)



(b)



(c)

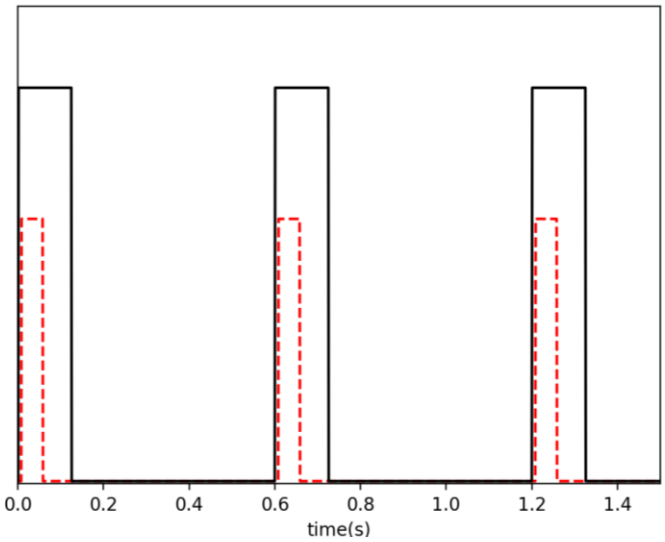


Figure 15. The Importance of Two-Tasks-Synchronization

4.4 Long-Term Water Monitoring Process

Prior to every plasma ignition, an On Time selection takes place to choose the optimal value for each solution. The selection process is written in a python script which shall now be introduced. At the beginning of the script, two variables, Counter and On Time, is set as 0 and 10, respectively. Plasma is then ignited with On Time duration equaling 10ms. If the integration area of the spectrum exceeds a value of 2,000,000, this stage ends with the optimal On Time determined as 10ms. If not, the Counter variable will increase by 1 and the unknown solution will be tested again with On Time equals 10ms. The Counter variable may only go up to 3, then the program automatically resets Counter to 0 and increase On Time variable by 10. The previous procedure is repeated until the optimal On Time is found. On Time value can only go up to 50ms, due to the fact working electrode may be permanently damaged if plasma is ignited for a time duration longer than 50ms. 10ms is chosen as the initial starting point because its H-alpha emission intensity divided by its OH emission intensity is how the conductivity of any unknown solution will be determined.

With the optimal On Time being determined, the system proceeds to the metal detection stage, and plasma is ignited using the selected On Time. If traces of metal are detected, event-based mode will be activated, and 10 spectrums will be acquired consecutively in a high frequency manner. If not, regular mode will be employed, and the solution will be inspected periodically. The resting time between each ignition may be customized for both detection modes, such as 1 minute or 10 minutes for event-based mode, and 1 hour or 1 day for regular detection mode. 10 min and 1 hour are arbitrary set as examples in Figure 16. This operation shows the versatility of the water monitoring system being proposed.

Every time the event-based mode is activated during the monitoring period, data analysis of the 10 spectrums will be performed in a real-time manner locally on Raspberry Pi. This way, an immediate message alert concerning heavy metal contamination can be sent out to users, in the form of E-mail or Line text, so that preventive measurements can be implemented correspondingly.

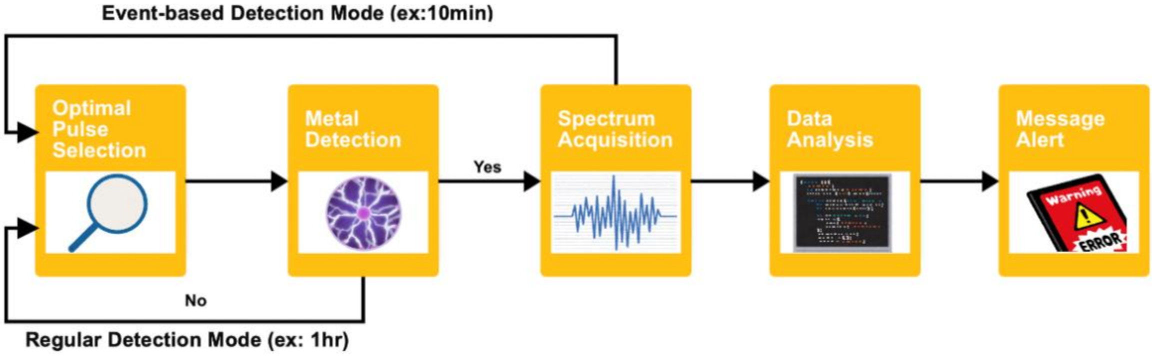


Figure 16. Long-Term Monitoring Process Flowchart

4.5 Real-time Data Acquisition and Analysis Event

An overnight water-monitoring experiment was conducted with 50ms as the optimal On Time chosen for the tested solution. By default, the solution is monitored every 30 minutes to examine the existence of heavy metals. When the solution is tested positive, such as at time 1.5, 3.5, and 24.5 hour, the system automatically switches to event-based mode and monitors the change in metal concentration while sending out warning message via E-mail every 10 minutes. The system returns to the regular mode when no trace of metal is observed, such as at time 2 and 4 hour.

The system is capable of correctly identifying heavy metallic element with the presence of interferons, such as methyl blue which was added at the very end of the experiment. The system is also capable of identifying multiple metallic elements simultaneously with little to no cross-species interference. Regarding the detection of Pb, it has been observed repeatedly that the first point is often abnormally high in intensity, therefore would be excluded when performing further data analysis.

Figure 17 shows the working concept of the long-term water-monitoring experiment. Each pulse-like signal indicates 1 metal detection with 10 spectrums being acquired. This stage takes exactly 6 seconds. Resting time in between each metal detection varies with the detection mode being employed, which is 30 and 10 minutes for regular and event-based mode, respectively. All data points are normalized to the OH intensity of each spectrum.

During the long-term monitoring session, different scenarios are tested and various types of spectrums are acquired. At time 3.5-hour, Mg and Pb are detected simultaneously. This is a feat that cannot be accomplished by most electrochemistry techniques, but is achievable with the plasma spectroscopy technique. At time 24.5-hour, methyl blue is added to test the performance of metal detection with the presence of organic interferon. Pb can still be clearly identified. This shows the stability of the system.

Immediate alerts can be sent to users via E-mail or Line APP by Raspberry Pi when metals are detected, using the SMTP Python module and LINE Notify, respectively. An actual spectrum may be attached when using E-mail, while only characters and strings may be sent out with Line APP.

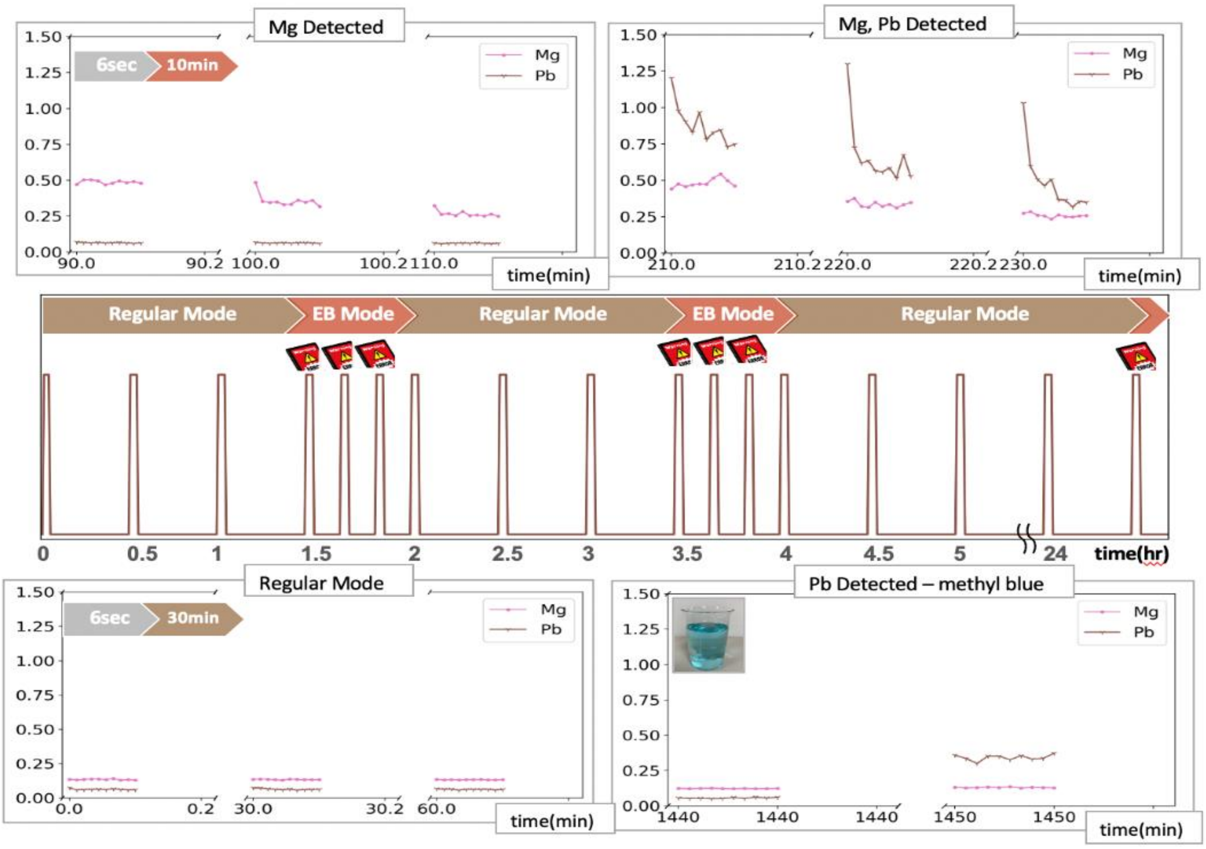


Figure 17. Long-Term Monitoring Event Timeline

Figure 18 shows four spectrums in the metal emission range (275nm-475nm) from the previous long-term monitoring experiment. All spectrums are normalized to their OH intensity. The fourth spectrum shows the emission of blank (no metal) solution, while the remaining three contain either Mg, Pb, or both elements. E-mails are sent to users for the upper three spectrums, while none were sent out for the blank solution.

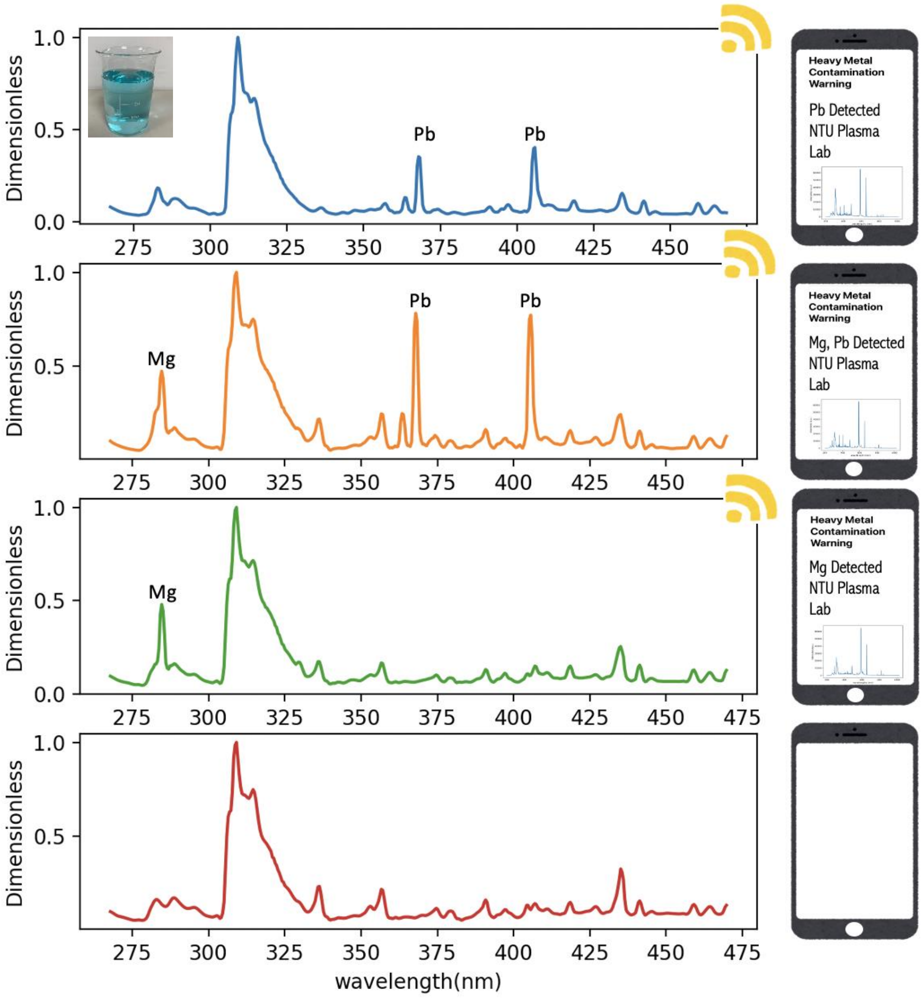


Figure 18. Long-Term Monitoring Event Spectrums

Chapter 5 Conclusions and Future Work

In this work, a Raspberry Pi board is integrated into the solution plasma system. This makes the water monitoring system reliable since proper high voltage pulse width is selected and set prior to every detection, guaranteeing the optimal performance of every plasma emission. This pulse on-time selection also eliminates the need for sample-pretreatment. The Raspberry Pi board is also used as a spectrometer reading device within the setup. This two-tasks synchronization is very crucial for long-term operations since keeping electrode's usage to a minimum maximizes its lifetime. Significant improvement in the quality of the overall spectroscopic data is observed. A long-term monitoring session lasting up to tens of hours is tested remotely and different detection frequencies can be imposed on demand. Warning messages can be sent out to users instantly via multiple pathways when heavy metal is detected. The use of Raspberry Pi replaces the conventional industrial equipment with the benefits of reduction in cost and system size. Raspberry Pi also acts as an HTTP web server in this setup to provide a friendly user interface and a more secure connection. All in all, a web-based water monitoring system that describes novelty in both device and application is offered.

In this system, due to the system’s complicated nature such as complex spectrum, electrode decay, etc., the quantification of metallic elements in low concentration is still a challenge. Using the built-in computational power of Raspberry Pi, machine learning algorithms can potentially be utilized to improve the accuracy of the spectroscopic analysis. This way, detection limit and quantification of metal concentrations have a high chance of being improved in the future.

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Curriculum Vitae

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Conference Presentation

1. **Tsung-Min Chang**, Ching-Yuan Wang, and Cheng-Che Hsu, "Development of a Long-Term, Real-Time, and Remote Heavy Metal Monitoring System in Solution by Plasmas Modulated Using Raspberry Pi", The 15th International Symposium on Advanced Plasma Science and its Applications for Nitrides and Nanomaterials / The 16th International Conference on Plasma-Nano Technology & Science, Gifu, Japan, March 2023.