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Homemade Hazardous Inorganic Mercury Quick Screener Using Arduino Analysis of Mercury Ion Concentration in Love River(Kaohsiung, Taiwan) and Running Water

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Abstract

In this research, nano-gold solution was synthesized first, and thiols with different carbon numbers (3, 11, 12) were changed to combine with nano-gold. And then carboxylate was used to capture inorganic mercury in water. We observed the changes of the color of the solution, and used the self-made Arduino quick sieve to detect the mercury ion concentration in the water.

In this research, we used the nano-gold solution to connect with 3-thiol propionic acid (MPA), and prepared the standard mercury ion solution at 0, 2, 4, 6, and 8 ppm and 2 6-pyridine dipyridine, which had a strong effect on other metal ions. Formic acid (PDCA) reagent improves the sensitivity of the quick screener. The relationship between the absorbance and the concentration calibration line (=0.99) measured by the spectrophotometer is compared with the result of self-made quick sieve (=0.96±0.01), which reveals that our measurement was reliable and could be actually applied to the rapid inspection of running water. The mercury ion detection method in this research had special selectivity.

Combined with the technology of the Internet of Things, the concentration of natural water can be quickly obtained. Greatly reduces the cost of traditional testing.

Keywords: nano-gold solution, metal mercury, fast sieve, drain water, Arduino

Introduction

1.1 Research motivation

Taiwan has always been a prosperous area for heavy industry development. A few years ago, Director Zeppelin shot the tragic situation of Houjin Stream polluted by waste water in Taiwan.

Those toxic chemicals would be absorbed by other organisms. Through bioaccumulation, we could ultimately ingest them.This may cause irreversible damage to our health. In recent years, although the government has complied with international conventions to detect the content of heavy metals in water, the detection required a lot of money to purchase expensive instruments, and consumed a lot of manpower and time. Therefore, in order to prevent the hazards of releasing water. We developed a simple device by Arduino, using color sensors to distinguish the corresponding color changes of particles of different sizes. It is a fast and cheap device to measure mercury irons in the water, which allows more people to check the safety of the water quality around them.

1.2 Research Purpose

1. We connected gold nanoparticles to thiol groups and carboxylate groups. Find the optimal **carbon chain length** and **solution composition ratio**, in order to capture mercury ions in water selectively.
2. We used the concept of IoT (Internet of Things) to develop a cheap and small device, which can quickly detect whether the mercury ions in the water exceeded the standard.

1.3 Literature Review

Aggregation effect on the surface of nano-gold particles

The nano-gold particles have different color changes in different sizes. The reason is that when the particle size is less than or equal to the wavelength of light, the particles will absorb the incident light. This absorption is due to the fact that when the electromagnetic radiation of different wavelengths collides with the nanoparticles, the electromagnetic radiation will oscillate and resonate with the conducting particles. The energy of electromagnetic radiation is transferred to the nanoparticle, and the energy is absorbed. This absorption can also be said to be the displacement of the plasmonic band. When the distance between nanoparticles is small and the particles are larger, they will absorb red light with a longer wavelength band. On the other hand, when the particle size is small, they will absorb blue light with a shorter wavelength band.

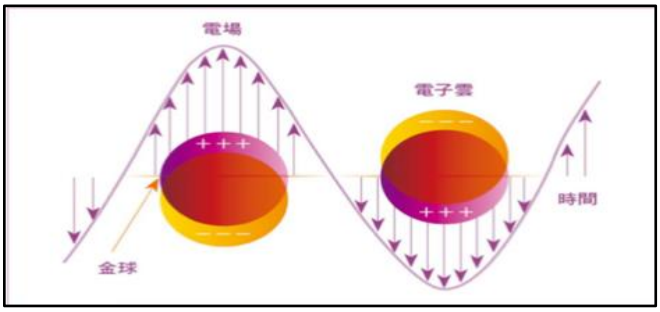


Figure (1) Surface effect of gold nanoparticles. Image source: Science and Technology Grand View Garden

Research methods

2.1 Equipment

A. nano-gold particles synthesis

   a. test tube
   b. electromagnetic heating stirrer
   c. Ultrasonic cleaning machine

   d. electromagnetic stirrer

   e. Micropipette

f. Snaking condenser tube
g. double neck bottle
h. Spectrophotometer
i. Microcentrifuge tubes

B. homemade sensor

a. Arduino Mega2560

b. TFT LCD Display Module

c. TCS34725 Color sensor

d. resistance (220 Ω)

e. Dupont Line

f. red laser

g. green laser

C. Pharmaceuticals and Running Waters

a. $HAuCl_4$ (1M)

b. sodium citrate

c. 3-mercaptopropionic(MPA)

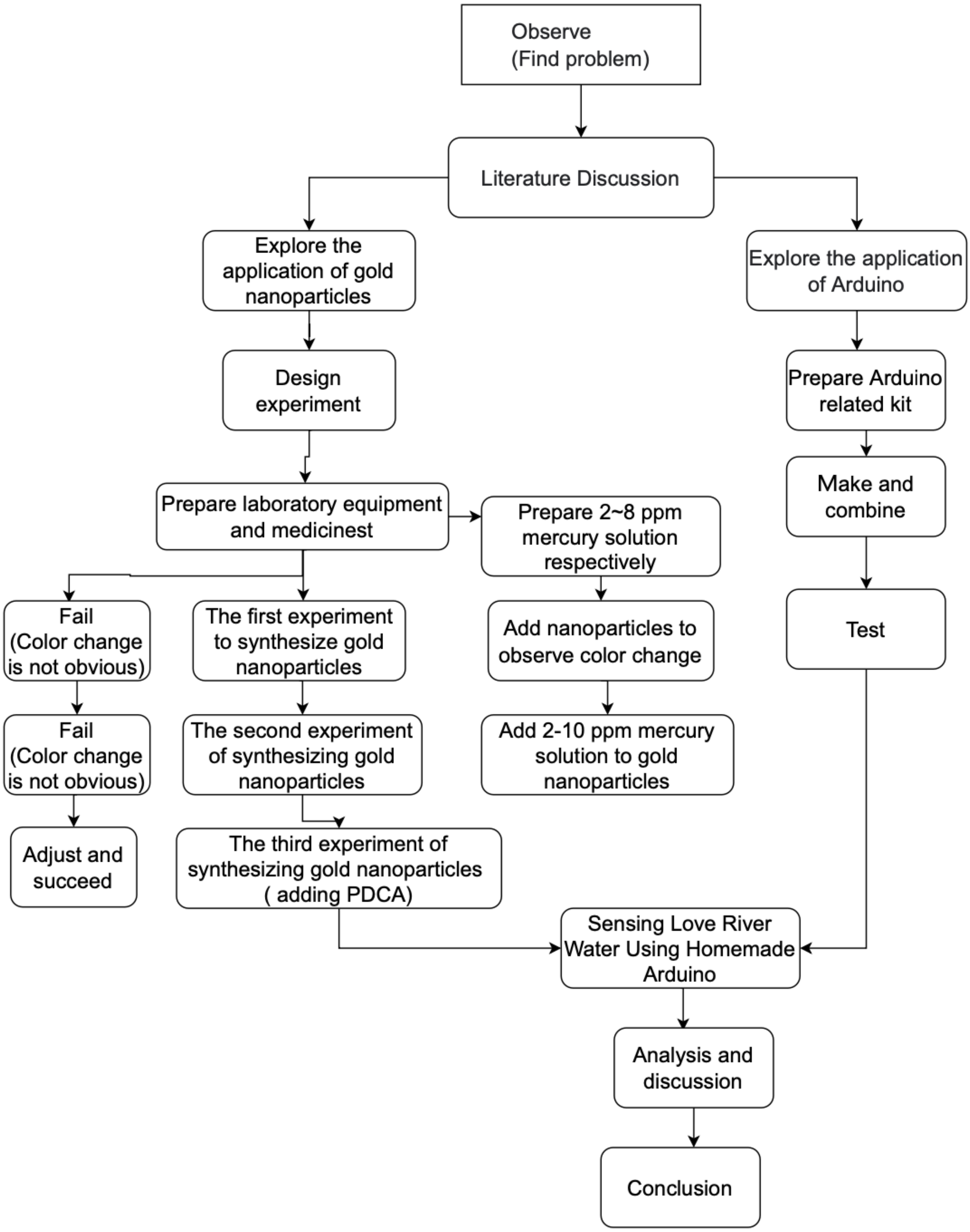
d. $HgCl_2$

e. 2,6-Pyridinedicarboxylic acid(PDCA)

f. Running water from Love River and Houjing Steam

2.2 Process and methods

A. Structure of the research



B. Write programs and tests

We integrated and modified the sample program, and wrote the program for the self-made quick filter.

```
buttons[0] = Button(40, 175, 110, 50, true);
buttons[0].BorderColor = ILI9341_DARKGREEN;
buttons[0].Color = ILI9341_GREEN;
buttons[0].SetFontSize(2);
buttons[0].SetTextPos(40, 17);
buttons[0].SetTextColor(ILI9341_DARKGREEN);
buttons[0].SetText(F("Yes"));

buttons[1] = Button(170, 175, 110, 50, true);
buttons[1].BorderColor = ILI9341_BLACK;
buttons[1].Color = ILI9341_RED;
buttons[1].SetFontSize(2);
buttons[1].SetTextPos(40, 17);
buttons[1].SetTextColor(ILI9341_BLACK);
buttons[1].SetText(F("No"));

SetNumLabels(2);

labels[0] = Label(12, 30, 2);
labels[0].TextColor = ILI9341_BLACK;
labels[0].SetText(F("These are the results of\n the calibration.\n\n Would you like to save\n them?"));

double m = model.getSlope(), b = model.getIntercept(), rSquared = model.getDetermination();
m = round(m*100.0) / 100.0;
b = round(b*100.0) / 100.0;
rSquared = round(rSquared*1000.0) / 1000.0;

labels[1] = Label(12, 120, 2);
labels[1].TextColor = ILI9341_BLUE;
labels[1].SetText("C = " + String(m, '\002') + " x F + " + String(b, '\002') + "\n\n R2 = " + String(rSquared, '\003'));
```

Figure (2) Calibration partial code

Purpose: To calculate the new regression line and value, we need to define the button position on the touch screen in Calibration and let the machine press the calibration again to calibrate and receive the value.

```
colorview
#include <Wire.h>
#include "Adafruit_TCS34725.h"

// Pick analog outputs, for the UNO these three work well
// use ~560  ohm resistor between Red & Blue, ~1K for green (its brighter)
#define redpin 3
#define greenpin 5
#define bluepin 6
// for a common anode LED, connect the common pin to +5V
// for common cathode, connect the common to ground

// set to false if using a common cathode LED
#define commonAnode true

// our RGB -> eye-recognized gamma color
byte gammatable[256];


Adafruit_TCS34725 tcs = Adafruit_TCS34725(TCS34725_INTEGRATIONTIME_50MS, TCS34725_GAIN_4X);
```

Figure (3) color sensor partial code

Purpose: Modify and improve the built-in code from the machine where the problem occurs and to confirm the sensitivity of the color sensor.

```
graphicstest

#include "SPI.h"
#include "Adafruit_GFX.h"
#include "Adafruit_ILI9341.h"

// For the Adafruit shield, these are the default.
#define TFT_DC 9
#define TFT_CS 10

// Use hardware SPI (on Uno, #13, #12, #11) and the above for CS/DC
Adafruit_ILI9341 tft = Adafruit_ILI9341(TFT_CS, TFT_DC);
// If using the breakout, change pins as desired
//Adafruit_ILI9341 tft = Adafruit_ILI9341(TFT_CS, TFT_DC, TFT_MOSI, TFT_CLK, TFT_RST, TFT_MISO);

void setup() {
  Serial.begin(9600);
  Serial.println("ILI9341 Test!");

  tft.begin();
```

Figure (4) Touching screen partial code

Purpose: Using the built-in code to confirm the pins of the touch screen and Arduino.Then confirmed whether the touch was normal or not, wondering whether it would be delayed or deviated from the position.

C. Assemble homemade machines

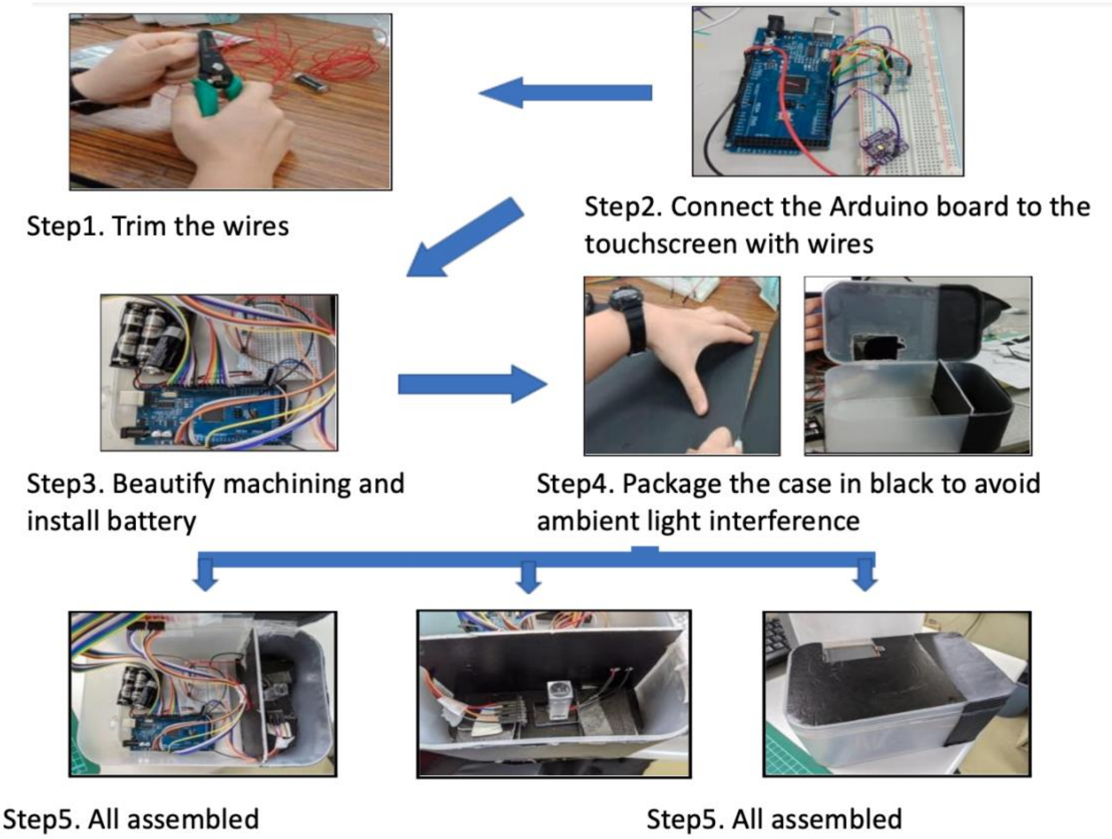


Figure (5) Assembly steps flow chart

D. Screen display and operation steps

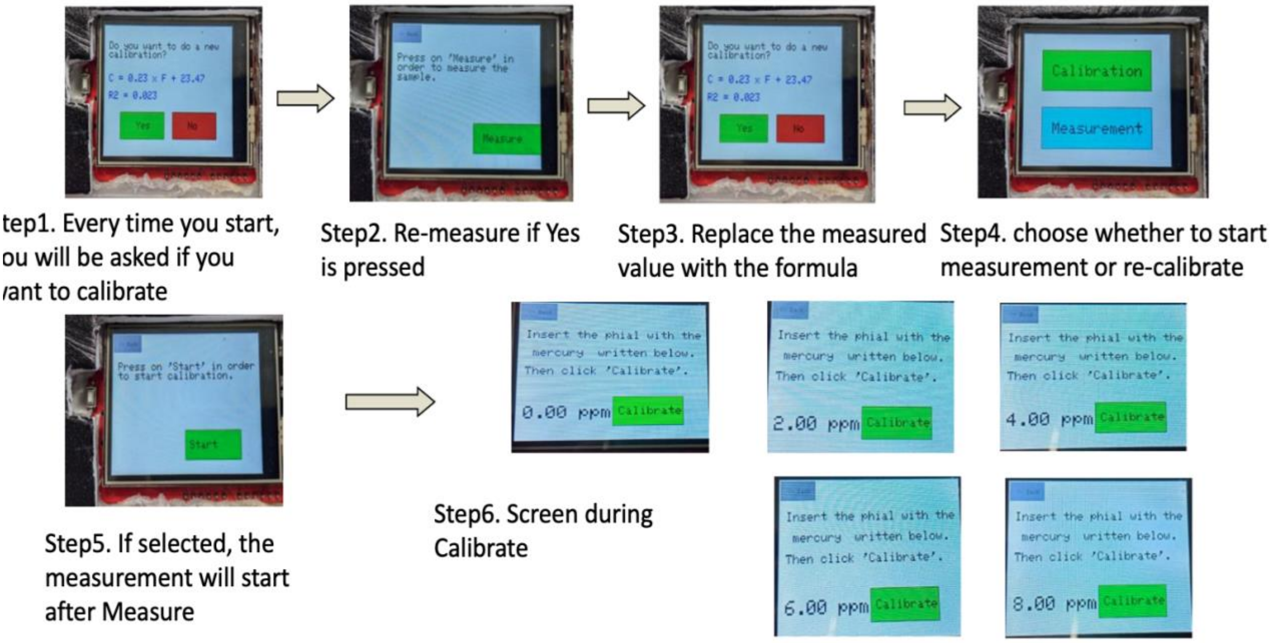


Figure (6) Flow chart of operation steps

E. Design drawing of quick sieve

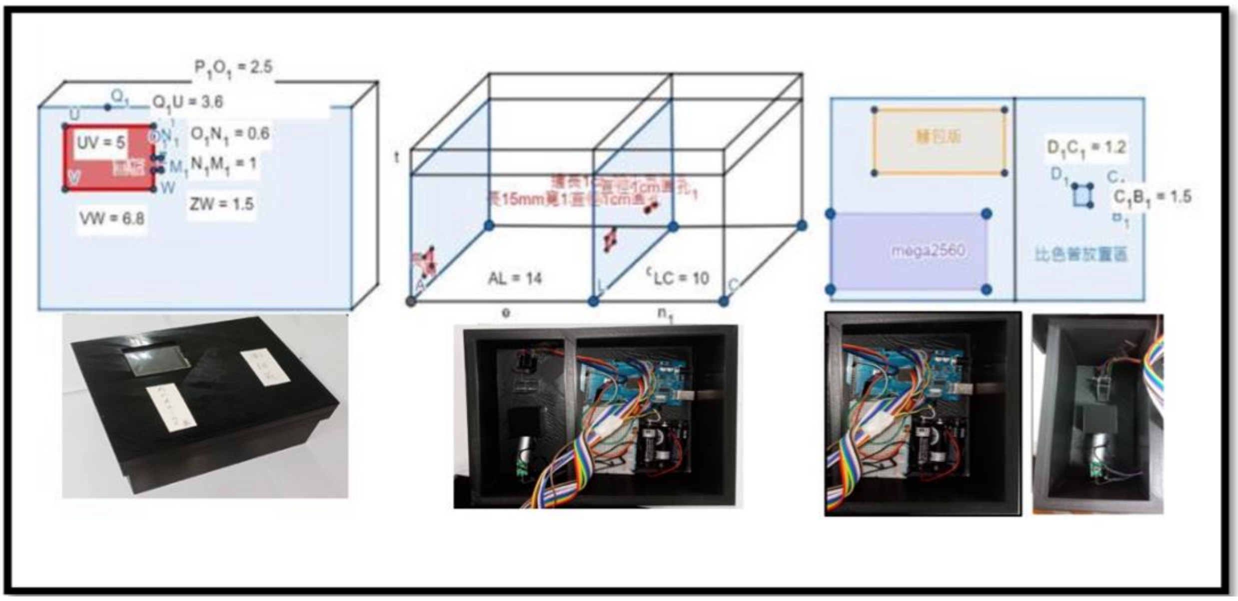


Figure (7) Design drawing and actual finished product drawing of quick screen (by GeoGebra)

2.3 **Synthesis of gold nanoparticles solution**

	Method for formulating gold nanoparticles	Thiol and combine it with nanogold
The first experiment to synthesize gold nanoparticles	20 µl of tetrachloroauric acid + 10 ml of deionized water was heated to boiling, and after boiling, 1% sodium citrate aqueous solution was added (0.0228 g of sodium citrate was added to 2 ml of deionized water).	1 ml of 10-3M 12-mercapto 12-alkanoic acid (MDA) aqueous solution (dissolved in isopropanol) was added to the gold nanoparticles and stirred for 24 hours.
The second experiment of synthesizing gold nanoparticles	Heat 20 microliters of tetrachloroauric acid + 20 ml of deionized water to boiling, add 1% sodium citrate aqueous solution after boiling (0.0228 g of sodium citrate is added to 2 ml of deionized water), and boil for 8 minutes.	Pipette 900 microliters of tetrachloroauric acid solution, add 100 microliters of 10-3M 11-thioundecanoic acid (MUA) aqueous solution (dissolved in alcohol), and stir for 24 hours.
The third experiment of synthesizing gold nanoparticles	Heat 20 µl of tetrachloroauric acid + 10 ml of deionized water to boiling, add 38.8mM sodium citrate aqueous solution after boiling (0.02 g of sodium citrate is added to 2 ml of deionized water), and boil for 8 minutes.	Aspirate 1 ml of nanogold and add 10 µl 10^{-4}M of 3-thiolpropionic acid (MPA) and placed in a refrigerator at 4 degrees for 2 hours.

Eventually we chose 3-Mercaptopropionic acid (3-thiol propionic acid)third experiment to synthesize gold nanoparticles because it has higher solubility (lower carbon number) and obvious discoloration which were more suitable to modify gold nanoparticles.

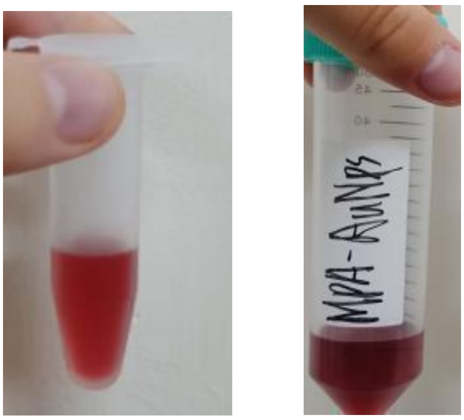


Figure (8)The nano-gold synthesis successfully (bright red)

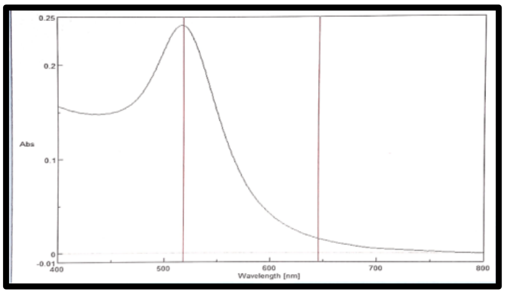


Figure (9) Spectrum after preparation of gold nanoparticles

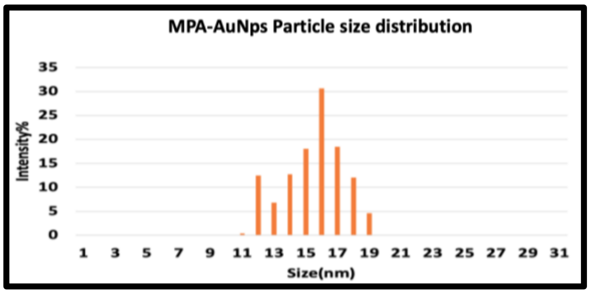


Figure (10) The particle size distribution of gold nanoparticles added with MPA

2.4 Preparation of mercury ion solution (standard addition method)

A. Experimental premise:

The preset standard of mercury pollution in drinking water in Taiwan is 2 ppb (Parts Per Billion, 1 part per billion). However, the concentration of mercury ions in this study is too low to observe the aggregation of gold nano-particles, and it wasn't easy to prepare ppb solution, either.

Therefore, we selected the mercury solution of $HgCl_2$ with a concentration of 10-4M. Then we added the nano-gold solution, the buffer solution respectively, and measure the in the range of 2~10 ppm (Parts Per Million).

B. Experimental method:

a. Add 10-4M HgCl2 solution to pH 9 buffer according to the amount to 2700μl (colorimetric tube 3/4 height)

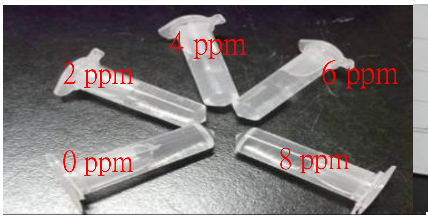
b. Add 300μl of Au NPs (gold nanoparticles, Au NPs) according to the amount

c. The preparation form (1) is as follows:

type	Deionized water (ul)	MPA-Au NPs (ul)	10-4M Mercury solution (ul)	PDCA(10-3M) (ul)	Tris-buffer(pH9.0) (ul)
0 ppm	400	100	0	250	250
2 ppm	300	100	100	250	250
4 ppm	200	100	200	250	250
6 ppm	100	100	300	250	250
8 ppm	0	100	400	250	250

Form(1) HgAu NPs(μl)+ Ph9 buffer(ul)formulation ratio table

The prepared mercury solution and the color change after adding gold nanoparticles are shown in the following figures (11) and (12):



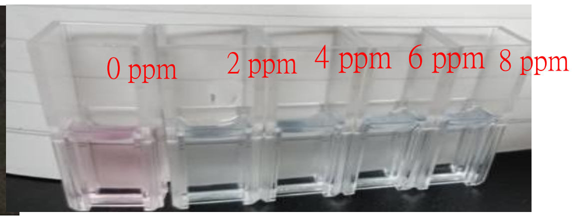


Figure (11) The diluted mercury after solution Figure

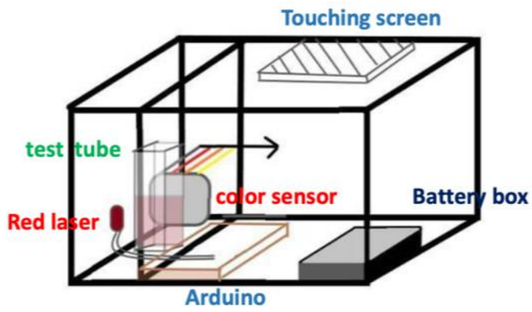
Figure (12) The mercury solution adding gold nanoparticles

Results and Discussion

3.1 Using the self-made quick sieve to measure the mercury content in the solution

A. Perspective view and principle of self-made quick screener:

Principle: After the nano-gold captured the mercury, the aggregation made the particles different in size. Therefore, under the illumination of the red LED, the light data detected by the machine was different, and the concentration of the mercury solution could be judged accordingly.



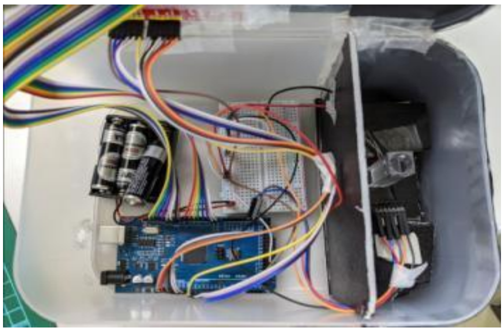
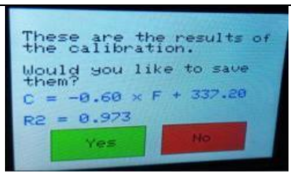


Figure (13) Instrument Design and Internal Devices

Pour the solution into the colorimetric tube, and press the Measure button. The gold nanoparticles would combine with mercury ions, then the particles would become larger and absorb more light. Irradiate with red LED, the color sensor could receive the R.G.B. colors through the solution, and transmits the data back to the touch screen (recalibration is required). Eventually, the concentration of mercury in the solution can be calculated.

B. Measurement results

<table>
<tr>
<td>
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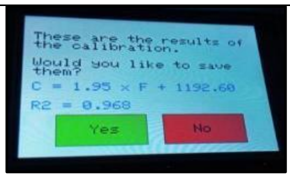
<td>
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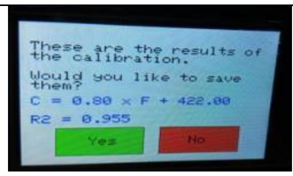
<td>
</td>
</tr>
<tr>
<td>The first quick sieve measurement correction =0.97</td>
<td>The scend quick sieve measurement correction =0.96</td>
<td>The third quick sieve measurement correction =0.95</td>
</tr>
</table>

Form (2) Quick sieve measurement correction range

3.2 Actual detection of mercury concentration in discharge water

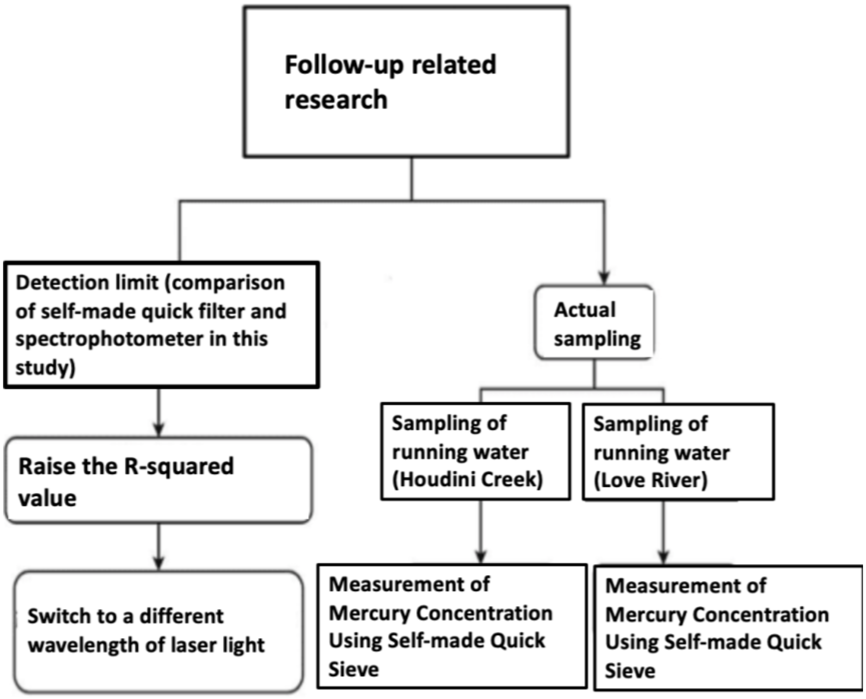


Figure (14) Measurement results of self-made quick sieve

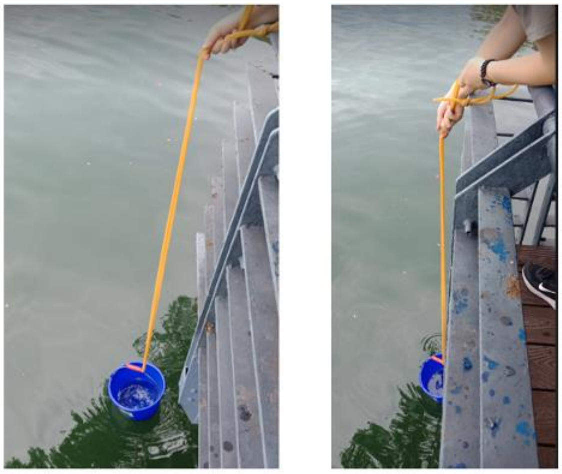
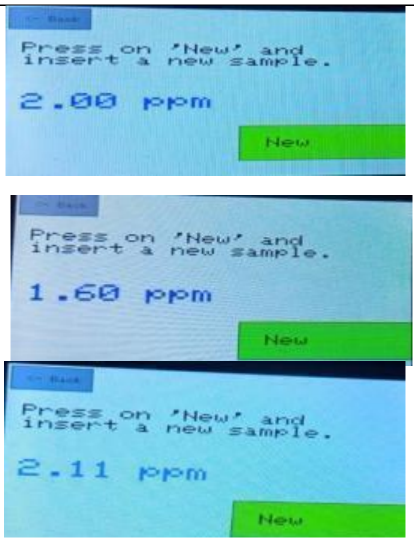
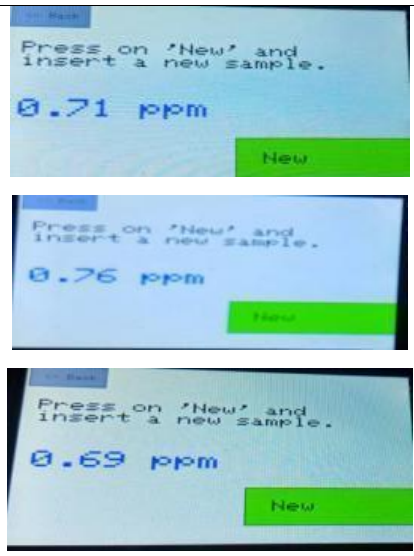
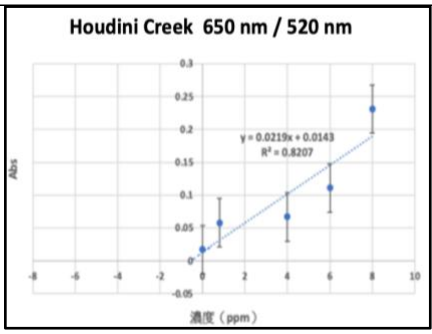
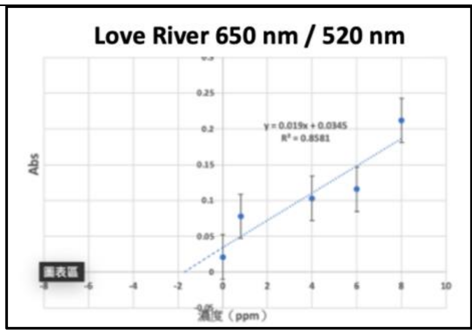


Figure (15) The process of taking water from the Love River

Figure (16) Add MPA-Au NPs to running water (Love River and Houjing Steam)

		
Linear regression		
Calibration line	Remaining stream water (release water) Y=0.0219 X +0.0143 =0.82	Love river water (release water) Y=0.019 X +0.0345 =0.85
	Standard addition method (squeeze stream): When Y (absorbance) = 0 (using extrapolation) X(concentration)=0.65 (ppm)	Standard addition method (love river water): When Y (absorbance) = 0 (extrapolation method) X(concentration)=1.81 (ppm)

3.3 Improvement of fast screen

A. **Purpose**: Using the division of the light intensity of the two wavelengths to remove the interference factors of the external light source, so that the measurement results were more accurate and lower concentrations of mercury pollution could be measured.

B. Change the way:

a. Sensing value: RGB sum 650nm (red light) / 520 nm (green light).

b. Light source: red LED light □ red and green laser pointer.

C. Perspective view of the improved self-made quick sieve

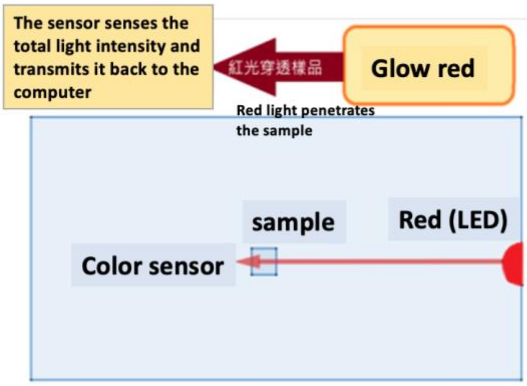


Figure (17) Perspective view of self-made quick screener before improvement

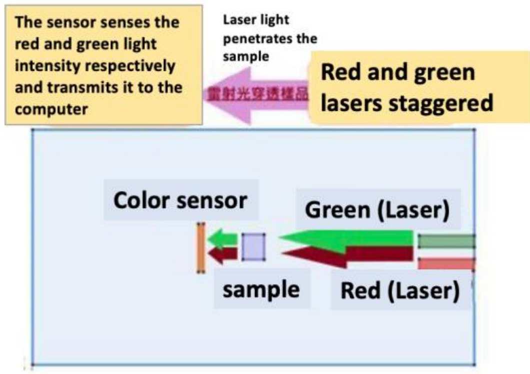


Figure (18) Perspective view of self-made quick screener after modification

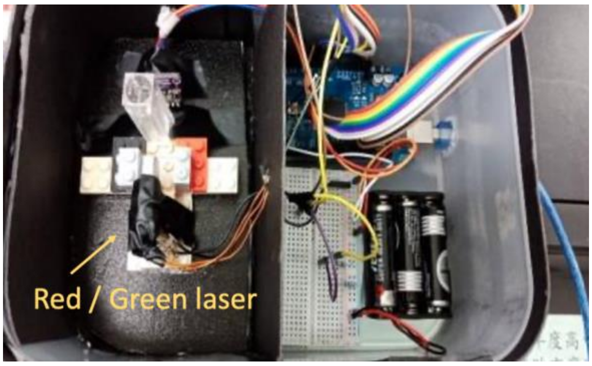


Figure (19) The actual device after improvement

3.4 Improvement principle

From the Uv-Vis spectrum, it could be known that the nano-gold solution and mercury ions in this study had obvious absorbance at 520 nm (unaggregated)/650 nm (aggregated) respectively. However, the different colors of LEDs were determined by the chips with different wavelengths, and the red chip generally had a wavelength of 620~630nm. Moreover, the wavelength range was relatively scattered. Therefore, we chose a single frequency red (650nm) and green (520 nm) laser pointer (high intensity))to use black thick cardboard around the colorimetric tube, in order to prevent light leakage, absorb unnecessary reflections. Foremost, the direction of the laser light source was more fixed than that of the LED, which should increase the sensitivity of the instrument.

3.5 Color change of mercury and nanogold solutions with different concentrations

Inquiring about relevant information, it was found that if PDCA (chelating ligand) is added to the solution first, it is easy to combine with mercury. Because the pore size of PDCA is very similar to that of mercury ions. Therefore, the specificity of the combination of MPA-Au NPs and mercury ions was improved, and the accuracy of the measurement of inorganic mercury concentration was, too. However, the combination of MPA-Au NPs and mercury ions made the particles larger, so the absorption peak shifted red. Finally, the solution color became blue.

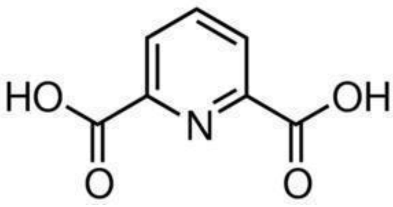


Figure (20) PDCA structure diagram 2,6-pyridinedicarboxylic acid (PDCA)

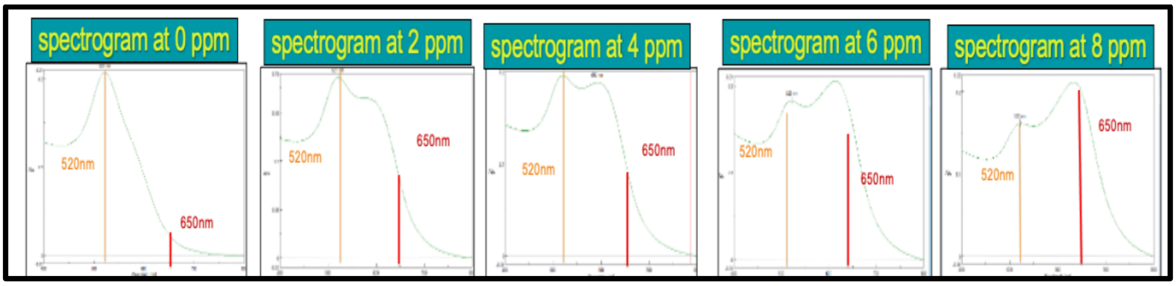


Figure (21) Absorbance-wave peak changes at different mercury ion concentrations (ppm)

We wandered that if PDCA (chelating ligand) was a necessary element for this experiment, formulating it at the above concentration and used the Uv-Vis spectrum 520 nm/650 nm to make a regression line with the mercury ion concentration, and its value was 0.99.

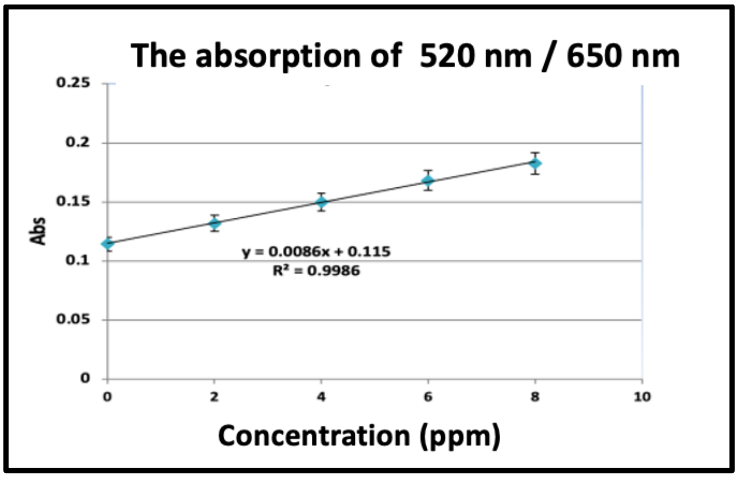


Figure (22) Regression line with PDCA measurement added,=0.99

Finally, we chose to modify gold nanoparticles with 3-thiopropionic acid (MPA). One end of MPA had a thiol group, which could be connected to gold nanoparticles; while the other end had a carboxylate group, which could form coordination with mercury metal ions. Having opposite charges to each other, we reduced the negative charge on the surface, so that the aggregated particles became larger and the color deepens.

3.6 **The self-made mercury ion quick sieve in this study**

We prepared 0 ppm, 2 ppm, 4 ppm, 6 ppm, 8 ppm inorganic mercury nano-gold solution, confirm its concentration by atomic fluorescence spectroscopy, and finally measured the relationship between absorbance and concentration and perform linear regression (R2=0.99). In this study, we made a quick sieve, repeated the above steps and calibrated the test, and obtained=0.96±0.01 compared with the spectrophotometer Uv-Vis, which had certain reliability.

A. **Tyndall effect in colloidal solutions**

For agglomerated solute particles, different color changes could be observed due to the scattering effect around them. The larger the aggregation, the red-shift of the absorption wavelength, and the color of the solution turns blue. On the contrary, the smaller the aggregated particles, the blue-shift of the absorption peak, and the color of the solution turns red.

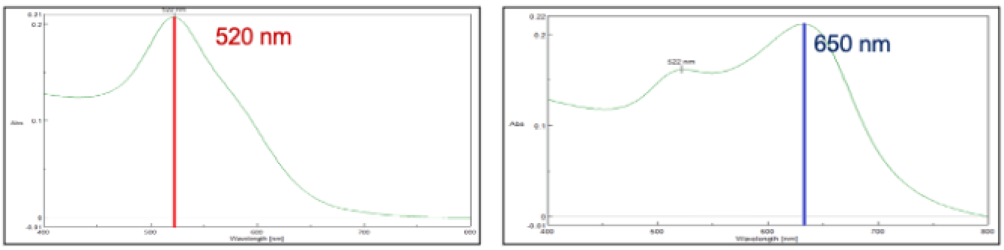


Figure (23) Unaggregated (520 nm) and aggregated (650 nm) wavelength changes

B. **Spectral wavelength selection and background processing**

When the gold nanoparticles were not aggregated, a distinct wave front appeared around 520 nm in the visible wavelengths. When the aggregated particles were larger, a wave front would slowly appear near 650 nm in the visible light wavelength, and the wave front near 520 nm would become smaller and smaller at this time. So we used 650/520 nm because these two values were the most representative when changing, and dividing the two lights could remove the interference caused by the environment.

Form (3) Spectral processing method

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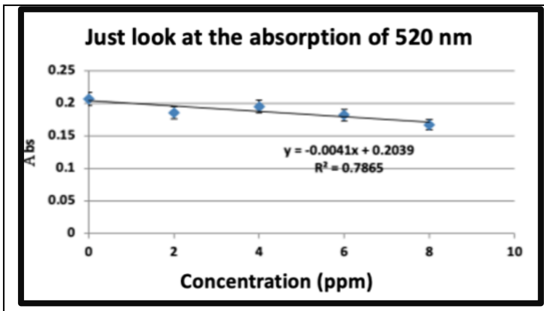
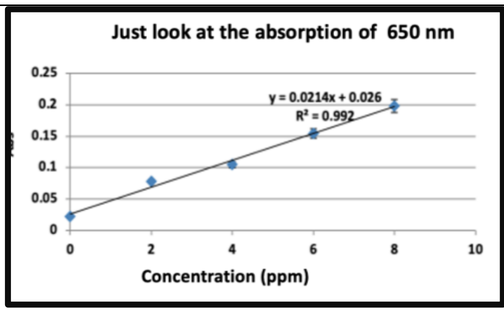
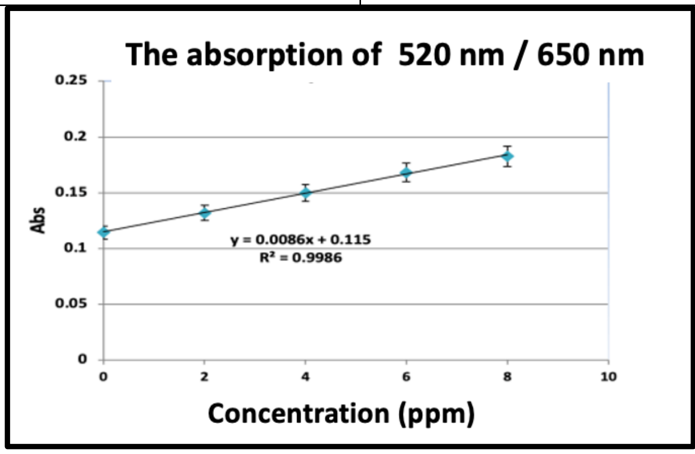
<tr><td>
</td><td>
</td></tr>
<tr><td>= 0.79</td><td>= 0.99</td></tr>
<tr><td colspan="2">
</td></tr>
<tr><td colspan="2">= 0.99</td></tr>
</table>

C. Can change the carbon chain length of thiol or different functional groups (groups) to detect different ionic solutions respectively.

Thiol molecules with different carbon numbers were modified on the nanoparticles, one end of the nanoparticle was attached to SH; the other end was connected with organic functional groups (groups) such as COOH, NO_2, NH_2, OH, etc.We could add different ionic solutions (Mn2+) to compete for the binding sites between gold particles, resulting in the effect of gold particles polymerizing and changing color. For example, carboxylic acid groups (-COOH) and heavy metals (lead, cadmium, mercury ions) had good bonding ability. In order to increase the selectivity of a certain metal ion, appropriate experimental procedures and the proportion of added solvent were designed.

With this mode, the interference of other ions or substrates was removed, and the specific detection of target metal ions was achieved. In this study, in addition to selecting carboxylic acid groups to capture mercury ions, PDCA was added externally (check related literature, the binding constant with mercury ions is as high as 1020.8), thereby removing the interference of other ions and improving the accuracy of the experimental results.

CONCLUSIONS AND RECOMMENDATIONS

4.1 Self-synthesize gold nanoparticles and connect thiol groups and carboxylate groups to find the optimal carbon chain length and solution composition, so that the solution is selective and captures mercury ions in water.

A. According to the experiments (1), (2) and (3), we found that the mercaptan with less carbon number: 3-thiol propionic acid (MPA), has better mercury capture ability and water solubility, which is used to increase the speed filter sensitivity.

B. The preparation method of gold nanoparticles in this study:

We added 20 microliters of tetrachloroauric acid to 10 ml of deionized water and heat to boiling, then added 38.8 mM sodium citrate aqueous solution (0.02 g of sodium citrate is added to 2 ml of deionized water), and boil for 8 minutes.

	Deionized water	MPA-AuNps (ul)	10^{-4}M Hg solution	PDCA (10^{-3}M) (ul)	Tris-buffer(pH9.0) (ul)
0ppm	400	100	0	100	400
2ppm	300	100	100	100	400
4ppm	200	100	200	100	400
6ppm	100	100	300	100	400
8ppm	0	100	400	100	400

C. The configuration method of mercury solution in this study:

Pipette 1 ml of nanogold, add 10 μl of 10-4M 3-thiopropionic acid (MPA), and then place in a refrigerator at 4 degrees for 2 hours.

4.2 Combining the concept of IoT (Internet of Things): Develop a low-cost and small-sized device to quickly detect whether the mercury content in running water exceeds the standard.

A. Combined with the Arduino color sensor and calibrated with five standard solutions, the linear relationship between different concentrations and absorbance was obtained, thereby identifying the degree of mercury ion pollution.

B. Change the red LED to a single frequency red and green laser light, which could reduce the error caused by the interference between the light source itself and the external environment.

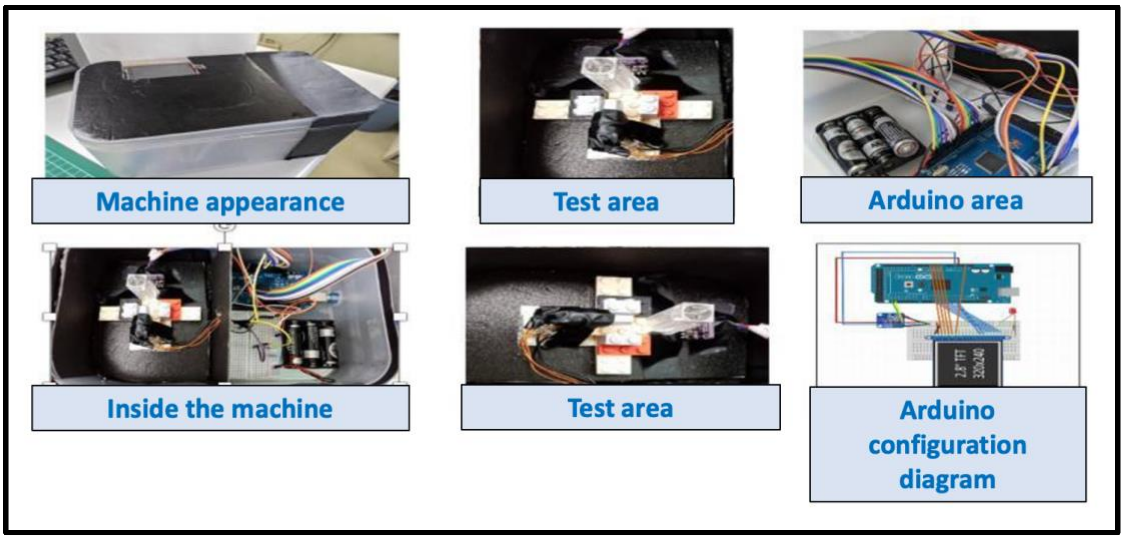


Figure (24) The actual installation drawing inside the machine

4.3 This instrument was used to quickly screen mercury pollution, inexpensive and efficient (measured for about 5 minutes at a time), the material cost was about 865 NT dollars.

Equippment	Price (NT dollars)
1.Arduino MEGA2560	250
2.TFT touching screen	370
3.TCS34723 color sensor	132
4. bread board	50
5. resistance	45
6. resistance	8
7. red LED	10
Total price	865

Figure (24) Machine total cost chart

Thanks

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Citation

A. GitHub code

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b. https://github.com/adafruit/Adafruit_ILI9341
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d. https://github.com/adafruit/Adafruit-GFX-Library
e. https://github.com/adafruit/Adafruit_BusIO

B. Journal

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