



Convenient flow injection analyzer for each element monitoring system in tannery sewage

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Abstract

A low-cost detection device based on a flow injection pump and a spectrophotometer was developed for the automatic spectrophotometric detection of leather sewage in various sections of a tannery water plant. The equipment was computer controlled by a program written in Qt. The effects of reagent concentration, sample salinity, and foreign ion interference on the samples were investigated. The national standard method was used to judge the accuracy of the test, select the standard solution test method arbitration, and calculate the spiked recovery. A positive hexagonal carousel was set up in the device to place the standard liquid pool, into which the test liquid and standard color developer were pumped by peristaltic pump respectively, and the cuvette used a 1 cm quartz channel pool, which was pumped into the test after the sample finished color development. This device can be used for tanning production staff to quickly judge the effect of each chemical in the process and improve production efficiency.

Keywords: flow injection analyzer; automatic spectrophotometric detection; tannery sewage





1. Introduction

The leather processing industry is generally considered a highly polluting industry^[1]. However, from the perspective of the livestock industry, the leather industry holds significant importance^[2]. The core value of this industry lies in the conversion of potential biological pollution into resources, making full use of animal hair and leather, thereby avoiding environmental issues resulting from their disposal^[3-5]. Since animal fur is typically unsuitable for food production, it is often discarded during the processing of animals such as rabbits, cattle, and sheep, potentially leading to decomposition and environmental issues^[6-8]. From an economic perspective, processing these waste materials into leather or fur gives them added value^[9]. Therefore, the leather processing industry not only reduces waste generation but also offers sustainable pathways for resource recovery and reuse^[9].

The variation in trivalent chromium concentration in chrome tanning solution is crucial in the leather-making process. With an increasing recycling cycle, the concentration of trivalent chromium may undergo changes, directly impacting the performance and yield of leather production^[10]. Therefore, continuous monitoring and analysis are necessary to ensure the stability and appropriate concentration of trivalent chromium during leather production^[11]. Managing chromium-tanned wastewater is a critical issue in leather processing. During wastewater treatment, transferring trivalent chromium into chromium-containing sludge requires a detailed understanding of the concentration of trivalent chromium in the wastewater and other relevant parameters^[12]. These data are crucial for effective wastewater treatment and environmental protection. Given the significance of chromium in the leather industry, the development of trivalent chromium detection instruments applicable to leather processing and wastewater treatment is essential. Such instruments can assist leather factories in real-time monitoring of trivalent chromium concentration in chrome tanning solution, providing data to support decision-making and compliance^[13].

In routine laboratory measurements, the volumetric analysis method is often used, where trivalent chromium is first oxidized to hexavalent chromium using an oxidizing agent, followed by titration with a reducing agent^[14-16]. The main drawbacks of these methods are the intricate and time-consuming procedures, which are not suitable for rapid, continuous testing of large sample quantities. Additionally, they rely entirely on manual operations, leading to data instability and analytical errors. Among the aforementioned methods for testing chromium content, it is found that using diphenylcarbazide with citrate salt for colorimetric detection, coupled with a handheld spectrophotometer, provides a relatively simple and convenient way to rapidly determine chromium (VI) in water^[17]. However, since trivalent chromium is the predominant form in chromium tanning wastewater, using this method still requires an oxidation step and consideration of interference from other factors^[18-20]. Therefore, this paper will focus on the feasible scheme of the existing technology center to use spectrophotometry to quickly detect trivalent chromium to explore and create^[21].

The primary aim of this paper is to establish both a method and an instrument for the rapid and quantitative determination of trivalent chromium content in chrome tanning wastewater. This method aims to equip leather producers with the capability to continuously monitor chromium content, thereby contributing to the enhancement of intelligent water management systems and the improvement of environmental monitoring systems^[22-24]. We employed the following approach in this paper: In order to simulate chrome tanning wastewater, we prepared a solution using HLS-C chrome tanning agent as the source of chromium and sodium chloride, along with formic acid, as the sources of interference. We assessed the accuracy of trivalent chromium determination and adopted the widely accepted sodium chromate colorimetric method as the reference method. We also determined the maximum absorption wavelength in the simulated chrome tanning wastewater and constructed absorbance-concentration relationship curves at varying salt concentrations and organic acid contents. Furthermore, we developed an automated testing system and collected multiple samples of chrome tanning wastewater to compare the measurement results obtained through both the direct colorimetric method and the sodium chromate colorimetric method.





2.2. Material and Methods

2.1. Reagents and solutions

The chrome tanning waste simulated solutions was prepared based on the HLS-C chrome tanning agent (Brother Technology Co., Ltd.) as the chromium source, sodium chloride (AR, Sinopharm Chemical Reagent Co.) and formic acid (AR, Shanghai Lianxiang Chemical Reagent Co.) as the interference source^[12].

In the arbitration experiments, the stock solution of Cr(VI) (4.00 mM) was prepared by dissolving the above $\text{Cr}_2\text{Cr}_2\text{O}_7$ solid. Working standards of Cr(VI) were prepared daily by stepwise dilution of stock solution^[13].

2.2 Preparation for maximum absorption wavelength measurement

The maximum absorption wavelength of the test trivalent chromium solution used for the automatic test system was determined by adjusting different salt concentrations and organic acid contents in the trivalent chromium simulation solution to plot the absorbance-concentration relationship curve in the visible section. Firstly, 7.31 g of HLS-C chromium tanning agent (whose Cr_2O_3 content is 23.5%) was accurately weighed, dissolved, transferred and fixed in a 250 mL volumetric flask, and this solution was the chromium standard stock solution with a Cr^{3+} concentration of 4.70 g/L. Secondly, the composition of the specific mock solution is shown in Table 1, and a double-beam UV-vis spectrophotometer (TU-1901, Persee, China) to plot the visible scanning spectra. Finally, the colorimetry was then performed by spectrophotometer (722s, Yidian, China) using the maximum absorption peak in the scanning spectrogram as the emission light intensity with a 1 cm cuvette. The blank solution without chromium solution was used as zero adjustment and the standard curve was plotted with the measured absorbance as the vertical coordinate and the corresponding chromium content as the horizontal coordinate.

Table 1. Solution composition parameters of simulated chrome tanning waste liquor

Categ	Impact Factor	1	2	3	4	5	6	7
A	HLS-C concentrations (g/L)	0.545	0.545	0.545	0.545	0.545	0.545	0.545
	NaCl concentrations (g/L)	20	30	40	45	50	55	60
	HCOOH (mL)	-	-	-	-	-	-	-
B	HLS-C concentrations (g/L)	0.545	0.545	0.545	0.545	0.545	0.545	0.545
	NaCl concentrations (g/L)	-	-	-	-	-	-	-
	HCOOH (mL)	0.2	0.5	0.8	1	1.5	2	2.5

2.3. Description of the apparatus

The schematic diagram for the determination of Cr(III) is depicted in Fig. 1-A. The schematic diagram of the test set is shown in Fig. 1-B, and the specific structure and function can be found in our published content. Briefly, the set consists of an analytical control module, a detection module and a pumping module^[25,26]. The Raspberry Pi 3b+ (Yahboom, China) is used as the core of the analysis control module, and the external Raspberry Pi 3-way relay expansion board (Junroc, China) is used to control the peristaltic pump (KCP-C-S04B, Kamoer, China) in the pumping module to start and shut down, and to accomplish the pumping of samples and ultra-pure water for cleaning into the inlet of the check valve (2.5mm o.d.) at the inlet end. The detection module consists of a spectrophotometer (722s, Yidian Analytical, China) as the main device to modify the detector and transfer the absorbance data into the Raspberry Pi via a USB to serial data cable (DT-5003A, DTECH, China). In addition, the laboratory-made "top and bottom feed-through" cuvette (1 cm×1 cm×3 cm) was connected to the outlet of the tee fitting (2.5 mm o.d.) through silicone tubing (2 mm i.d.), and the two inlet ends of the tee fitting (2.5 mm o.d.) were connected to the outlet of the check valve (2.5 mm o.d.). All components of the instrument were housed in a closed cabinet (30 cm×60 cm×30 cm) with light insulation. A touch screen (1024*600 dpi, wiki, China) is embedded in the cabinet to display the software visualization interface of the system and to keep the circuit board for displaying the absorbance data of the spectrophotometer^[27-29].



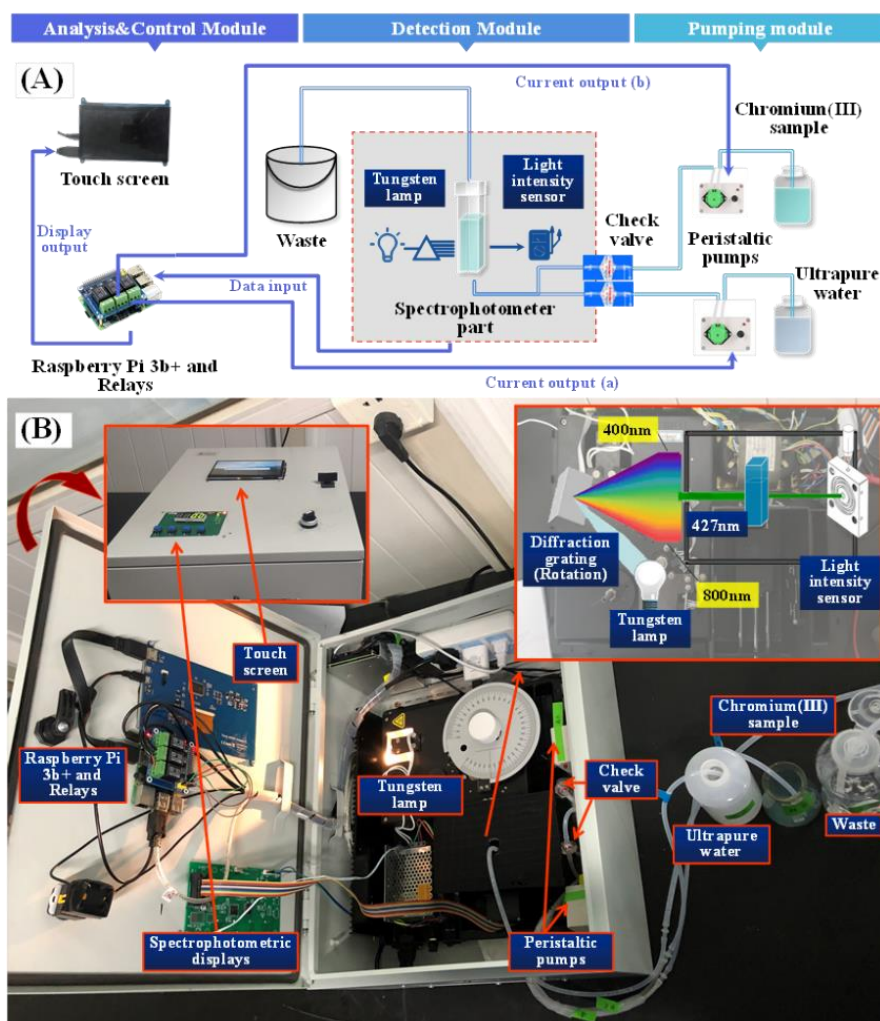


Fig. 1. Schematic diagram of the device used for rapid determination of trivalent chromium and the internal connection path (A). Photograph of the trivalent chromium rapid determination device in operation (B).

2.4. Measurement and analysis procedures

The simple flow of the detection device is shown in Fig. 2A, and the visualization interface of the self-programmed program is given in Fig. 2B. The program runs on a Linux system and is written in C++ based on the Qt programming platform, which reads the absorbance value in the spectrophotometer through the RS232 data transmission cable and calculates the output chromium concentration value through the built-in functions of the program^[30,31]. The simple operating procedure is described as follows. First, click and preparation button on the control program, through the Raspberries PI peristaltic pump control relay start a, such as 1 m hydrochloric acid and ethanol volume of pipeline cleaning fluid pumping line and color dish 20 s and then pumped into ultrapure water, and set the spectrophotometer fixed light intensity of 427 nm, treat the monitor screen of a spectrophotometer absorbance to zero, close the peristaltic pump a. Click the start detection button on the control program, start the peristaltic pump B through the raspberry PI control relay, pump the chrome solution to be measured into the colorimeter, stop pumping until the absorbance on the spectrophotometer screen is stable, and then the trivalent chromium concentration and absorbance value are displayed on the screen. After the final confirmation, click the end button to repeat the cleaning process of the first step^[32].



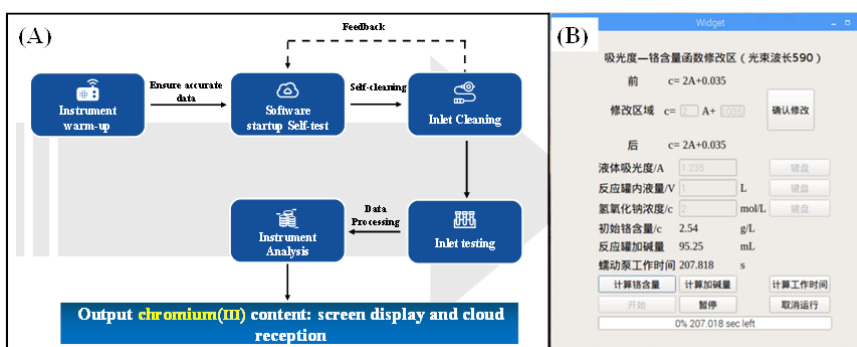


Fig. 2. Simplified process for the operation of detection system devices (A). Interactive program with Chinese interface (B)

2.5. Sample collection and comparison of methods

The following five chrome tanning solutions were used to evaluate the accuracy of the trivalent chromium test: sample No. 1 was obtained from the chrome tanned sheepskin of student A in the light and chemical engineering leather laboratory of Jiaying University, with a blue-green transparent state; sample No. 2 was obtained from the chrome tanned yakskin of student B in the light and chemical engineering leather laboratory of Jiaying University, with a blue-green transparent state; sample No. 3 was obtained from the sheepskin of Wenzhou Ruihua Leather Co. The sample No. 4 was taken from the non-fur chrome tanning solution recycled by Zhejiang Zhonghui Fur Co. The sample is dark green and can transmit light, but there are more hair fibers, so the sample will be filtered and treated as sample No. 7.

The sample solution was first tested using a homemade chromium detection device following the process and the chromium content was read after the data was stabilized. Since the method of detecting chromium content in the samples was based on the chromium tanning sample solution, but the impurities in it interfered with the determination of chromium content, so an interference analysis was required. Since the impurity content is not easily expressed, the HACA 2100N turbidimeter was used to express it by measuring the turbidity in the chromium tanning sample solution. Further, sodium chromate colorimetric method was used as the arbitration method for chromium content determination, and the chromium concentration measured by it was used as the standard concentration to determine the accuracy of the chromium detection device measurement results. Finally, in order to verify the accuracy of the above method, the chromium tanning sample solution was also processed and verified using the spiked recovery method^[33].

3. Results and discussion

3.1. Considerations of the apparatus design

The maximum absorption peak of visible light absorption curve of chromium tanning waste liquid was simulated by chromium powder solution under different salt content and different pH conditions, and the maximum absorption wavelength was determined as a basis^[13]. The maximum absorption in this experiment was consistent with previous studies, so it can be confirmed that this wavelength can be used for rapid detection of the instrument, and then programming.

3.2. Measurement results of absorption wavelength

The visible absorption curves of chromium tanning waste solution simulated with Cr^{3+} concentration of 0.55g/L chromium powder solution at different salt levels and different pH conditions are shown in Fig. 3. From Fig. 3-A, it can be seen that the visible light absorption curves at different salt concentration levels are close to overlapping, and all are smooth curves with consistent and not sharp peaks at the maximum absorption wavelength. From Fig. 3-B, it can be seen that the visible absorption curves of chromium powder solutions at different levels of formic acid content, i.e., different pH, almost coincide exactly with the spectrogram situation at the level of changing salt concentration. And the results of three experiments conducted under the premise of excluding machine and human errors are in agreement.



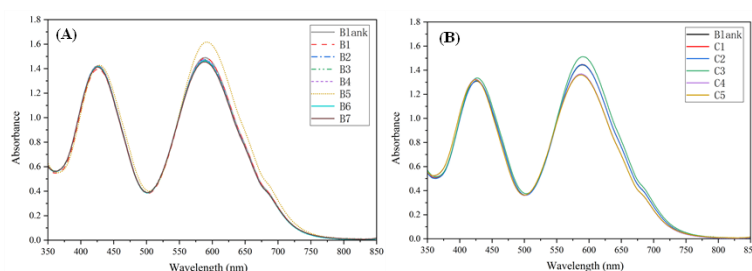


Fig. 3. Spectrogram of the experiment on the effect of salt concentration on absorbance interference (A). Spectrogram of the experimental effect of pH on absorbance interference (B)

This study explores the transformation of a standard curve as a function of detection procedure regarding chromium concentration. The specific application scenarios are divided into two categories, one is to monitor the absorption of chromium in tanning liquids by collagen during the tanning process, and the other is to detect chromium in chrome tanning waste liquids to provide data support for the addition of chemical treatment drugs. Since both of them are large production situations, the requirements for concentration accuracy are not very high, so this study will not go deeper into the influence of the standard curve based on the emission wavelength corresponding to each salt concentration or pH within the double wave peak on the chromium concentration detection errors. Finally, the two maximum absorption peak lengths of chromium powder solution with Cr^{3+} concentration of 0.55g/L were selected as 427nm and 591nm, respectively, to determine the emission light intensity of the instrument.

3.3 Comparison of Chromium Content Measured by Direct Colorimetric Method and Sodium Chromate Colorimetric Method

Based on Fig.3 , Table 1, and Table 2, the final selection of Cr^{3+} concentration for the chromium powder solution is 0.3 g/L, with two maximum absorption peaks at 427 nm and 591 nm. Further steps will be taken to establish a standard curve for the ultimate data analysis.

Table 2. Maximum Absorption Wavelengths of 0.545 g/L Chromium Powder Solution with Cr^{3+} Concentration at Different Salt Contents

NaCl(g/L)	0	20	30g/L	40g/L	50g/L	60g/L
Wavelength	426	427	426	427	425	428
h (nm)	589	590	590	589	590	592

Table 3. Maximum Absorption Wavelengths of 0.545 g/L Chromium Powder Solution with Cr^{3+} Concentration at Different Formic Acid Contents

HCOOH(g/L)	0g/L	1.5g/L	2.0g/L	2.5g/L	3.0g/L
Wavelength	426	427	426	427	427
(nm)	591	591	591	591	590

The reason for adding sodium chloride and formic acid to adjust different salt contents and pH values to consider their impact on the maximum absorption wavelength of the chromium powder solution is because in conventional chrome tanning processes, a large amount of sodium chloride must be added to suppress acid swelling. Chromium ions easily form complexes in aqueous solutions, and different pH conditions will induce the formation of different chromium complexes. Formic acid is a commonly used organic acid in the chrome tanning process, which has a significant impact on the formation of chromium complexes. Therefore, the method of adjusting different sodium chloride and formic acid contents is used to verify whether it will cause a significant shift in the maximum absorption wavelength of the chromium powder solution. Obviously, salt content and formic acid content have no significant impact on the maximum absorption wavelength.

3.4 Working Curve Based on HLS-C Chromium Tanning Agent as the Standard Sample

Based on Fig. 4, it can be concluded that the working curve made with HLS-C chromium tanning agent as the standard sample shows good linearity. The standard equation measured at a wavelength of 427 nm is: $y = 0.5807x - 0.0017$, $R^2 = 0.9997$; the standard equation measured at the maximum absorption wavelength of 591 nm is: $y = 0.5667x - 0.0028$, $R^2 = 0.9996$.



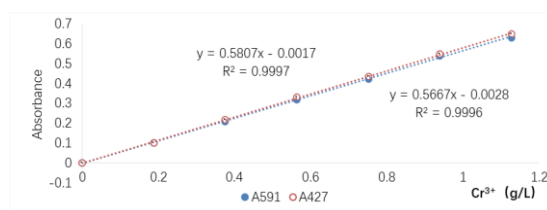


Fig. 4. Cr^{3+} concentration working curve with HLS-C chromium tanning agent as the standard sample

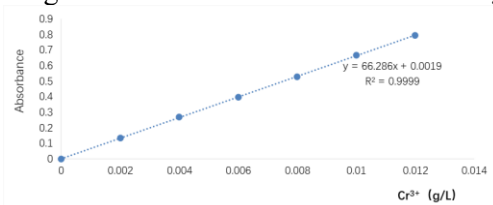


Fig. 5. Cr^{3+} Concentration working curve with potassium dichromate as the standard sample

3.5. Comparative Analysis of Methods

3.5.1 Turbidity

Table 4. Turbidity of Different Chromium Tanning Waste Solutions

Group	Sample 1	Sample 2	Sample 3	Sample 4	Mixed Sample 1
Turbidity/N					
TU	7.07	2.79	78.20	386.67	236

From Table 4, it can be observed that Sample 1 and Sample 2 have lower turbidity, Sample 3 has higher turbidity, while Sample 4 and Mixed Sample 1 have higher turbidity.

3.5.2 Comparison

Table 5. Comparison of Chromium Content Measured by Direct Colorimetric Method and Sodium Chromate Colorimetric Method

Group		Sample 1	Sample 2	Sample 3	Sample 4	Mixed Sample 1
Sodium Chromate Colorimetry						
$\text{C}(\text{Cr}^{3+})/\text{g}\cdot\text{L}^{-1}$		3.37	3.23	0.93	2.42	2.96
Direct Method						
$\text{C}(\text{Cr}^{3+})/\text{g}\cdot\text{L}^{-1}$	C_{427}	3.39	3.29	1.17	6.75	3.42
	C_{591}	3.30	3.10	1.08	4.86	3.34
Relative Error	W_{427}	0.65	1.71	25.32	182.33	15.54
(%)	W_{591}	-2.16	-4.34	15.45	105.63	12.84

From Table 5, it can be observed that the results obtained by the two methods for Sample 1 and Sample 2 are close, with relative errors within $\pm 5\%$. However, the relative errors for Sample 3 and Sample 4 are relatively large. Analysis indicates that the turbidity of the four different chromium tanning waste solutions varies. Combined with Table 4, it can be concluded that turbidity has a significant impact on the accuracy of the direct colorimetric method.

3.6. Analytical Figures of Merit

Apparatus with the three model that can make sure water-waste how much the chrome in the industrial. Provide the apparatus standard curve from the three experience formula. Important of the formula with that point on instrument and method, what trivalent chromium of wasted from the Leather Industry Chrome-tanning. In this part take the $y=0.05807x-0.0017$.

The design considerations for this instrument primarily revolve around the following points. Firstly, the instrument should be capable of detecting trivalent chromium in solutions. Secondly, it should have the ability to overcome interference factors in the solution, such as salt ions and pH. Additionally, it needs to eliminate factors that directly affect the colorimetric method, such as turbidity. In summary, this instrument addresses the impact of the above interferences through the implemented filtration and calibration of the direct colorimetric procedure. However, there are still some limitations that require further improvement in the future.

3.7. Understanding Instrument Software and Hardware Development

Currently, there are several types of products available on the market, including the Shanghai Jingke Yidian 721G, 722N, and 752N UV-Visible Spectrophotometers, the Shanghai Jing 721, 722S,





722N Visible Spectrophotometers, and the 752 and 754 UV Spectrophotometric Analyzers, as well as the Shanghai Meipuda UV-1600/1800PC UV-Visible Spectrophotometer for substance concentration analysis and detection. These products vary in price and functionality, but currently, spectrophotometers on the market do not integrate a lot of code to perform chromium content detection and real-time data analysis. Due to the need for data reading and control, the Shanghai Jingke Yidian 722s model with communication ports was selected.

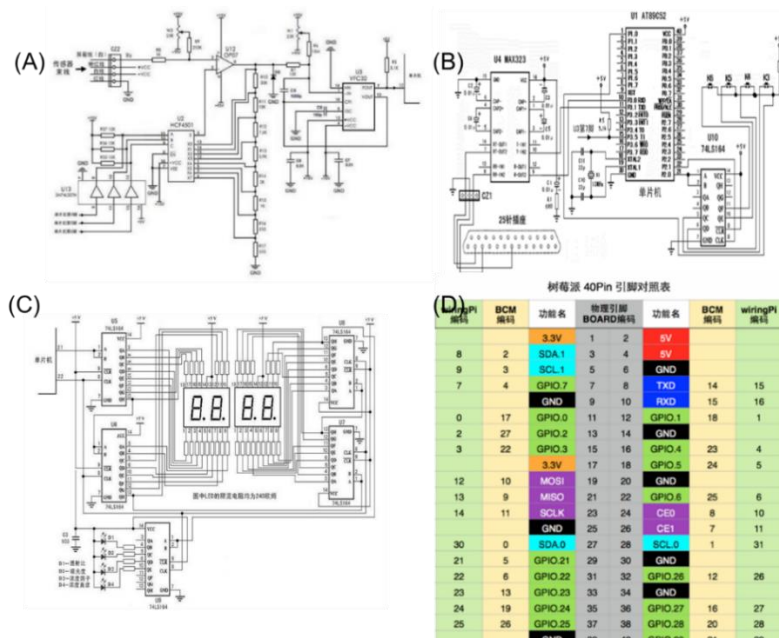


Fig. 6. Reference Diagram for Circuit Modification of the Instrument: (A) Schematic Diagram of the Front-End, Gain, and A/D Circuit of the 722s Spectrophotometer (B) Circuit Diagram of the Control, Keypad, and Communication Sections of the 722s Spectrophotometer (C) Circuit Diagram of the Display Section (D) Raspberry Pi Pinout Table

3.7.1 Data Retrieval and Calculation for Spectrophotometer in Linux Environment Based on QT Language

To analyze the circuit diagram in relation to the actual circuit board, it is necessary to establish communication between the microcontroller inside the visible spectrophotometer and the Linux system on the Raspberry Pi. To achieve this, the research team used Dupont wires to connect the TX, RX, and GND pins of the 722s instrument to the Raspberry Pi and employed the QtSerialPort library for code execution.

3.7.2 Research on Absorbance Data Retrieval Software for the 722s Spectrophotometer Based on Linux System

For the spectrophotometer, the current functionality is to detect the absorbance of a solution and display it on the screen. However, this is insufficient for chromium tanning wastewater detection. Therefore, it is necessary to implement the detection of chromium content in tanning wastewater based on spectrophotometry through later software and hardware upgrades and designs.

3.8. Explanation of the Final Selection of the Maximum Absorption Wavelength

UV-Visible Absorption Spectra of Chromium Tanning Wastewater in Leather Processing Enterprises are shown in Fig. 3. From the graph, it can be observed that there are significant differences in the positions and intensities of the maximum absorption peaks. The main reason for this is the structural differences in the chromium complexes, specifically the ligand structures. Cr^{3+} ions have d^2sp^3 hybrid orbitals and belong to inner sphere-type polymers with a coordination number of 6. The ligands form an octahedral structure. Fig. 8 illustrates the coordination in Cr^{3+} solutions with various ligands. Through the analysis of chromium in tanning wastewater, it was found that the coordination bonds of chromium become more stable at a certain concentration, resulting in higher bond energies and correspondingly higher absorbance coefficients. Therefore, under the same conditions, the absorbance of chromium complexes is higher. Additionally, when using a UV-Visible spectrophotometer to measure





chromium tanning wastewater, it was determined that the maximum absorption peak occurs at 427nm. The wastewater exhibits significant absorption at this wavelength, and based on a consultation of the Lange's Handbook of Chemistry, it was found that there are few substances present below this absorption peak. Therefore, the likelihood of free chromium ions existing in the tanning wastewater at this wavelength is almost negligible.

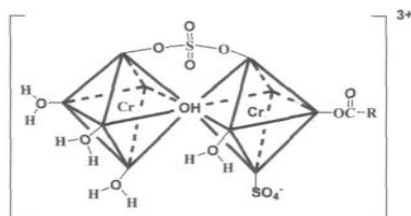


Fig. 8. Schematic Representation of Complex Structure of Low Concentration Cr^{3+} Ions in Aqueous Solution^[13]

4. Conclusion

4.1. Application in Resourceful Treatment of Chromium Tanning Wastewater

When reviewing various methods for rapid determination of chromium content, it is evident that all of them involve using instruments for analysis instead of manual laboratory procedures. However, after summarizing the findings, it is clear that the last method, which is based on direct UV-Visible spectrophotometry using commercially available chromium powder and chromium tanning wastewater, provides a rapid method for determining Cr^{3+} content in chromium tanning wastewater. This method not only simplifies the testing process for a large number of samples but also yields relatively accurate results. Moreover, it can be implemented and optimized using existing instruments and reagents in school and leather processing enterprise laboratories. Based on this method, research and analysis were conducted on leather processing enterprises to empirically determine the impact of components in chromium tanning wastewater on the instrument's measurement of chromium content. The goal was to analyze the components in chromium tanning wastewater, reduce or eliminate any interference with the determination of Cr^{3+} content, and design a rapid method and instrument for determining chromium content in chromium tanning wastewater. This would enable real-time monitoring of chromium content in wastewater generated during leather processing in leather processing enterprises.

For the resourceful utilization of chromium tanning wastewater, it is crucial to first determine the chromium content. By measuring the Cr^{3+} concentration, we can not only evaluate the quality of chromium powder but also determine the residual chromium in the tanning wastewater and the absorption rate of chromium during tanning. However, in contrast to traditional precise testing methods that involve laborious procedures and empirical assessment, we have replaced manual operations with machine-based analysis. This adjustment and automation of the chromium tanning process have significant implications for process improvement. Therefore, the project team members have reviewed and summarized existing methods for chromium content determination and identified a gap in the industry: a lack of specialized instruments for rapid chromium content testing in the leather processing sector. Consequently, we have designed a rapid chromium determination instrument based on spectrophotometry, hoping to achieve fast and accurate measurement of Cr^{3+} content in chromium tanning wastewater during industrial production. This instrument can be employed and optimized using existing equipment and reagents in school laboratories and leather processing enterprise laboratories. Based on this instrument, research and analysis were conducted in leather processing enterprises to empirically determine the impact of components in chromium tanning wastewater on the instrument's measurement of chromium content. The aim was to analyze these components, reduce or eliminate their interference with Cr^{3+} content determination, and design a method and instrument for fast chromium content determination in chromium tanning wastewater. This would enable real-time monitoring of chromium content in wastewater generated during leather processing in leather processing enterprises.

4.2. Enhancing Environmental Monitoring Systems

In environmental online monitoring systems and smart water management systems for leather processing enterprises, various environmental monitoring procedures and systems cover water quality





monitoring, smoke gas monitoring, air quality monitoring, and more. For the rapid chromium content monitoring system, it promotes the enhancement of smart water management systems for leather processing enterprises and fills the gaps in the current rapid chromium content monitoring system for the industry. This has a crucial role in improving the overall production planning capacity of leather processing enterprises.

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