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Electronic Tongue Detection System with Automatic Sampling and Constant Temperature Control

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Abstract: The electronic tongue has better stability and repeatability than sensory evaluation and it also has the advantages of easy-operated and faster detection speed relative to traditional equipments. At present, the research of electronic tongue is mainly focused on sensor development, and the research on system integration and automation is rare. Thus, a voltammetric electronic tongue was designed, which can automatically adjust the temperature of sample, feed into sample, clean the electrode and detect sample. It included the upper computer, control module, electrode, signal acquisition module, automatic sampling module, thermostatic bath module and display module, etc. The control interface was based on LabVIEW. The upper computer sent commands to control module to drive the automatic sampling module, thermostatic bath module and other modules through the serial port. Signal acquisition module connected the upper computer through USB cable. It contained a three electrodes system, and the signal curve of the sample was obtained by pulse voltammetry. The test results showed that all the modules were stable and reliable and the temperature control accuracy of the sample was (25 ± 1)℃. The area between the signal curve and the *X* axis was used as the signal characteristic value. The drift of signal characteristic values of 20 d was below 5.6%. The characteristic value was affected significantly by the sample temperature. When the sample temperature departure was ±5℃, the error of the characteristic value was 36%. Under the control of temperature bath (25 ± 1)℃, the error of the characteristic value was 5.8%, which indicated that the temperature control can effectively improve the accuracy of electronic tongue detection result. In the detection application, the electronic tongue can distinguish among four different kinds of beer, milk, water and different grades of tea with the principal component analysis (PCA).

Key words: electronic tongue; automatic feeding; thermostatic bath; detection system

0　Introduction

The electronic tongue (ET) is composed of series of low selective and interactive sensor arrays, which processes the signal by mathematical method, and is able to complete either the qualitative or quantitative analysis[1]. It is different from the traditional detection equipment, whose sensors focus on pursuing high selectivity and specificity. By contrast, ET sensors have low selectivity and interactive sensing, which are important features[2-4].

Compared with traditional sensory evaluation, ET has better stability and repeatability, is less susceptible to subjective feelings, and has a good ability to distinguish and lower detection limit. Compared with chemical analysis, gas chromatography and other detection methods, the electronic tongue has advantages of simple operation, fast detection speed and no complicated pretreatment.

Electronic tongue is highly versatile. It can not only identify the sample with different treatments, but also can accurately predict the content of related components in the sample[5-7] with the multivariate data analysis. Due to the promising application prospects of electronic tongue, it has been applied in many fields, such as food and beverage[8-9], environmental monitoring[10-12], biological medicine[13-15], security detection[16], etc.

At present, the researches of electronic tongue is mainly focused on the development of sensor[17-21]. On the contrary, the studies, such as automatic processing, sampling and system integration are less

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published. Furthermore, most of the existing electronic tongues need manual feed, cleaned electrodes and sample temperature control. The manual feed process is complex, and the workload of personnel is large. Now only a few of business electronic tongues, such as the French MOS INSENT company's ASTREE and Japan's TS - 5000Z company's Alpha, have automatic sampling and automatic detection function. But, neither of them has the ability to control the sample temperature. In addition, those business ETs are expensive, the sensor life is short, and the single detection time is long.

Therefore, this paper developed a voltammetric electronic tongue. It's easy to operate, low price, with the automatically adjusting temperature unit, feeding unit, cleaning electrode unit and detection sample function.

1 Hardware design

As shown in Fig. 1, the electronic tongue system designed in this paper is composed of the electrode and signal acquisition module, control module, automatic sampling module, thermostat module, keyboard & display module and the upper computer.

1.1 Upper computer and control module

The upper computer is a PC which installs LabVIEW software and LabVIEW DAQ software. It is the operation and display terminal of system. The core of control module is STC12 - microcontroller, which is used to control electrical equipments.

The upper computer communicates with control module through the serial cable, and communicates with signal acquisition module through the USB cable.

The upper computer sends command string through the serial port to control module to drive sampling, cleaning and thermostat temperature control operation. The control module operates I/O ports to control the corresponding electrical or scans I/O ports to obtain information after receiving the instruction. The upper computer drives the data acquisition card to generate a trigger signal and get working electrode loop signal in real-time when sample detecting.

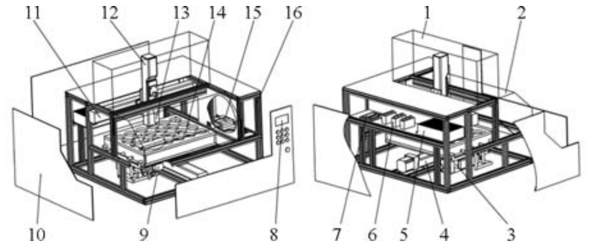

Fig. 1 Schematic diagram of electronic tongue

1, 2. Acrylic cover 3. Semiconductor refrigerating and heating components 4. *Y* direction stepper motor sliding 5. Switching power supply 6. Stepper motor drive control module 7. Control module 8. OLED display, Keyboard 9. Water circulating pump 10. Aluminum alloy shell 11. *X* direction stepper motor sliding 12. *Z* direction stepper motor sliding 13. Electrode 14. Constant temperature tank 15. The signal acquisition module 16. The frame of the device

1.2 Electrode and signal acquisition module

The module are composed of electrodes, conditioning circuit and NI data acquisition card. The detection part, which is a three electrodes system, is crucial. It includes working electrodes (WE), counter electrode (CE), reference electrode (RE) and conditioning circuit. The electrode part includes Au, Rh, Ag, Pt working electrodes, 1 Pt counter electrode and 1 Ag/AgCl reference electrode.

Its working principle is as follows: when the voltage between the working electrode and the reference electrode is applied, the electric double layer and redox reaction is formed between the electrode surface and the solution. The working circuit flows through the non redox current and the redox current. The relevant characteristics of the solution can be obtained by analyzing the superposition current. The counter electrode is used for conducting the current. The

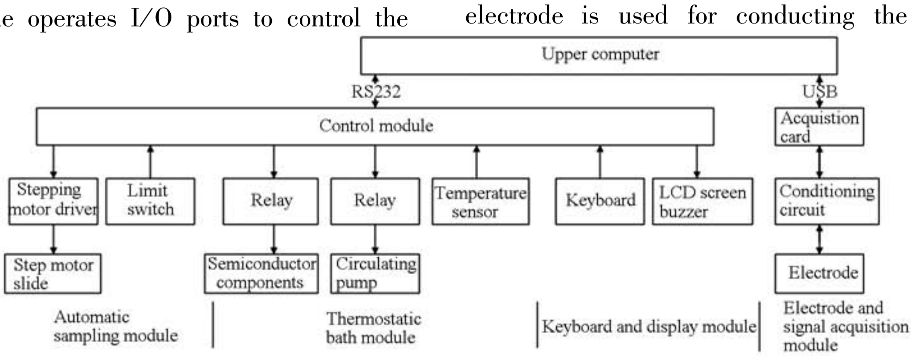

Fig. 2 Electrical structure diagram of electronic tongue

counter electrode and the working electrode form a current loop. Reference electrode provides a stable reference potential to determine the working electrode potential.

As shown in Fig. 3, the conditioning circuit mainly includes signal excitation circuit and signal acquisition circuit. P2 – 6 in the signal excitation circuit connects to reference electrode, P4 – 8 connects to the signal output of the signal acquisition card, P2 – 5 connects to one of working electrdoes. Signal excitation circuit from left to right is divided into three parts: 1 : 1 following circuit, voltage comparison circuit and the same direction amplifier circuit. The 1 : 1 following circuit is mainly used for impedance transformation, which provides the suitable input for the next part, voltage comparison circuit. The role of the voltage comparison circuit is to amplify the difference. The role of the same amplifier circuit is to adjust the output amplification.

P2 – 1 in signal acquisition circuit connects to the counter electrode, and P4 – 2 connects to the NI acquisition card signal acquisition port. The circuit is circuit for converting current into voltage. Because of the difficulty in measuring the current through the working electrode circuit, the current on the measuring circuit is replaced by the voltage. The voltage signal is collected by the NI – 6009 acquisition card and transmitted to the upper computer display and stored.

The other three signal excitation circuits and signal acquisition circuits have similar structure, as in Fig. 3.

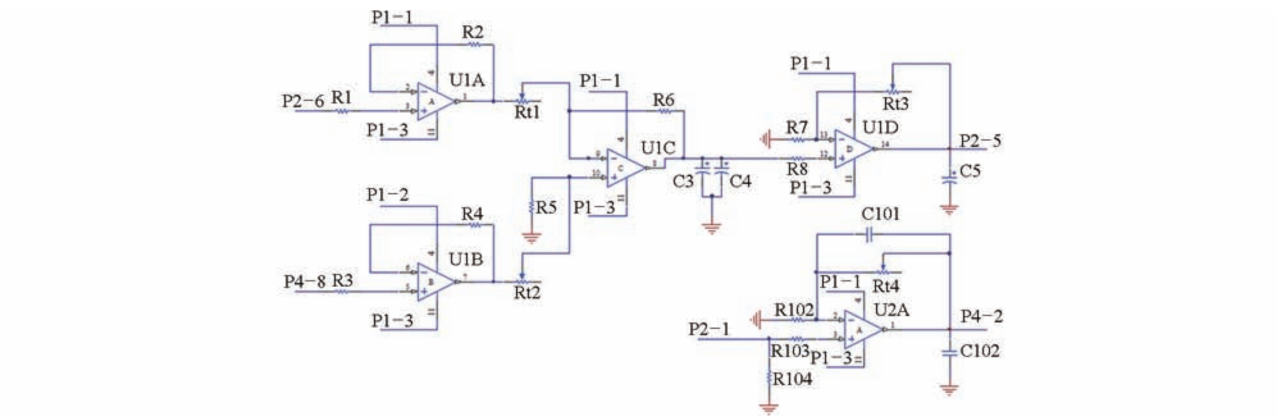

Fig. 3 Schematic diagram of circuit

The working process of the module is as follows: the upper computer controlsthe excitation signal of the NI acquisition card, and the voltage between the working electrode and the reference electrode is changed under the action of the conditioning circuit.

The potential between the working electrode and the solution is changed with the excitation signal. Because the potential of the reference electrode is always constant. The signals on the working electrode and the auxiliary electrode loop signal can be measured, displayed and saved in real time when the excitation signal is applied.

1.3 Automatic sampling module

According to Fig. 1, sampling mechanism is rectangular coordinate system structure with three degrees of freedom. The structure includes 100, 300 and 400 mm of step motor slides, which can realize the movement of *Z*, *X*, *Y* directions. *Z* direction slide is used to move the electrode up and down. *Z* direction slide is installed on the *X* direction slide. Furthermore, *Z* direction slide is driven by the *X* direction slide from the left or right. Thermostat bath module is installed on top of *Y* direction slide and driven by it.

Open loop control is applied in step motor slide. When single chip output a pulse signal, the slide moves a certain distance. The slide is equipped with a limit switch which is used to determine the zero point and eliminate the error caused by overstepping. The calculation formula of moving speed and moving distance of the slide is as follows.

$$S = nP/N \quad (1)$$

$$V = fP/N \quad (2)$$

where S—the moving distance of the slide, mm

V—the moving speed of the slide, mm/s

n—the number of pulses send fromsingle chip

P—pitch, mm

N—micro-step number of step motor driver

f—the frequency of the input pulse fromsingle chip, Hz

There is a process of acceleration and deceleration when stepper motor starts and stops. The slide is driven by trapezoidal curve output signal. It reduces the impact and noise, prolongs the service life of slide at the starting and stopping movement stage[22-23].

1.4 Constant temperature bath module

Temperature changes will cause difference of the physical and chemical characteristics of the solution, resulting in the operation of the electrical signal drift. The thermostatic bath module can control sample temperature automatically, which reduces the signal deviation caused by the temperature fluctuation effectively. The module includes a relay, a semiconductor refrigerating and heating components, a circulating water pump, temperature sensor s and a tank (as shown in Fig. 4).

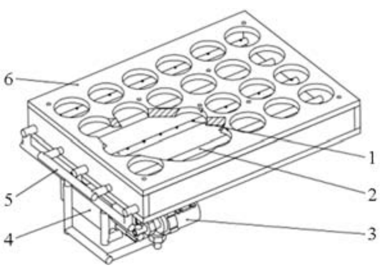

Fig. 4 Schematic diagram of thermostatic bath module

1. Water-in pipe 2. Water-out pipe 3. Circulating water pump 4. Semiconductor refrigerating and heating components, Relay 5. Connecting pipe 6. Tank

The 4 × 5 left holes place sample cups. The 4 × 1 right holes place electrode cleaning cups. Tank is filled with water as working medium. The water pipes with holes set at the bottom of tank. Water is pumped from the tank out of the water-out pipe into semiconductor refrigerating and heating components to adjust the temperature. Then, water is pumped from the water-out pipe into the tank to regulate temperature of water in tank.

Semiconductor refrigerating and heating components is based on the Peltier effect of semiconductor materials[24]. The heating, cooling and stopping operation of three kinds of working states of semiconductor components are controlled by the relay. The temperature sensor is DS18B20 (temperature range from −55℃ to 125℃, the error range ±0.5℃). There are four temperature sensors arranged in the device. The first one is installed in water tank to measure water temperature. One is installed on electrode to measure sample temperature. One is installed in device shell to measure air temperature. The last is installed in semiconductor component to monitor device status.

The temperature of water in the tank is detected every 10 s after the thermostatic bath is started. When the temperature of the water temperature is 0.5℃ lower than the preset temperature, the semiconductor component will heat. If the temperature is 0.5℃ higher than the preset temperature, it will refrigerate. The component will stop working in the range of ±0.5℃. At that time, temperature sensor started to detect sample temperature. The component and sensor will work until the sample temperature close to the preset temperature.

2 Software design

2.1 Upper computer program

The upper computer program is written in LabVIEW graphical language. On the left side of program interface are the waveform display which shows signals of four working electrodes and a excitation signal. On the right side of interface are options for changing waveforms, waveform cycle times and so on. The below part of the right side of the interface is for manual and automatic control mode.

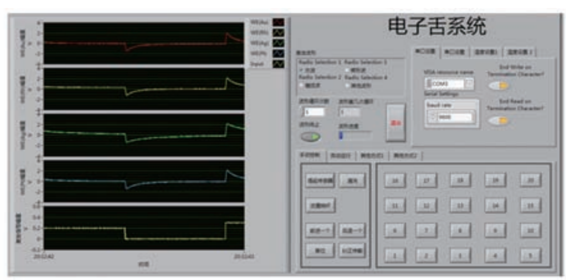

Fig. 5 Upper computer interface

The main function of the upper computer program includes the following parts: sending instructions to control module and receiving feedback signal to control the device according to the procedure or the keyboard operation; controlling signal acquisition card NI − 6009's analog voltage port to generate multi frequency pulse; collecting and saving data and display in the interface. Its' work processes is shown in Fig. 6.

2.2 Lower computer program

The lower computer program is written in KEIL and burn into the control module. The control module receives the keyboard input or PC commands to control

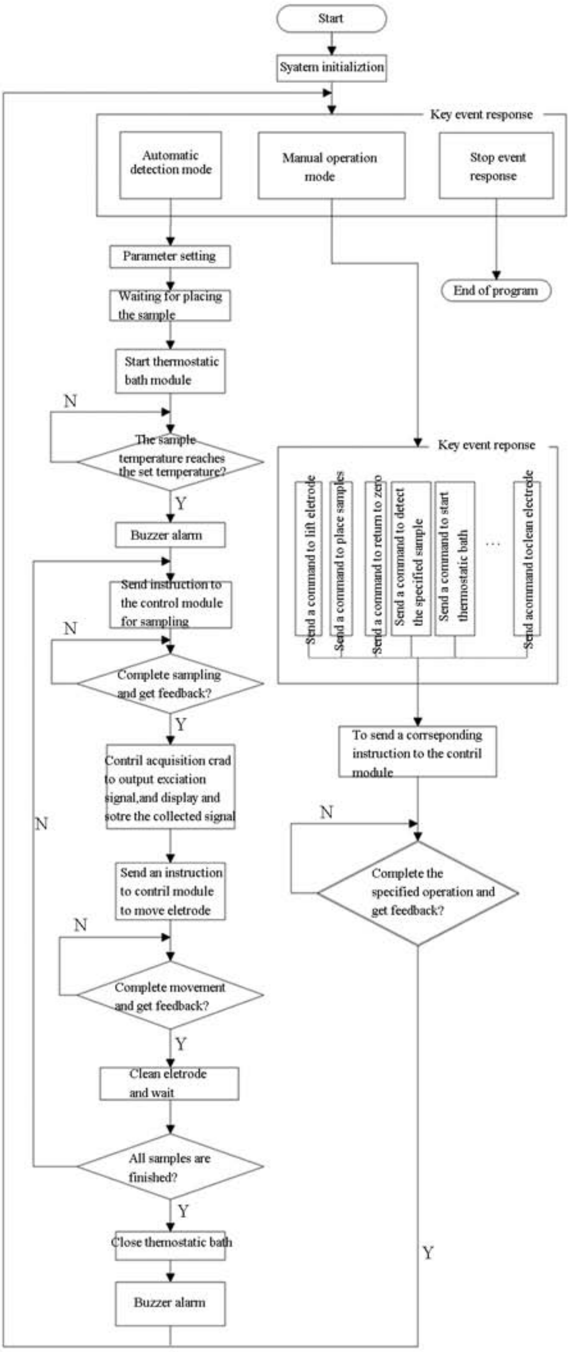

Fig. 6 Flow chart of upper computer program

sampling module, display module, thermostat bath, etc. It feedbacks information to the upper computer at the same time. The flow diagram is shown in Fig. 7.

3 Test of main modules of electronic tongue

3.1 Automatic sampling module test

The three groups of stepper motor slides reset automatically before the electronic tongue starting. Then the thermostat bath moves out and waits for placing sample cups and cleaning cups. Then it begins to detect samples automatically one by one.

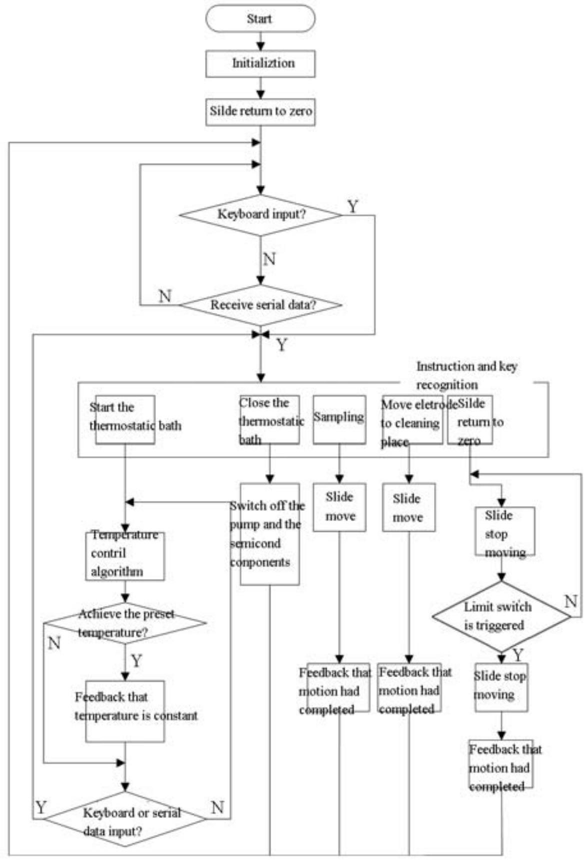

Fig. 7 Flow chart of lower machine program

The electrode moves to the top of the sample cup and then inserts into the sample cup. It moves to the top of the cleaning cup inserts into the cleaning cup which contains pure water after finishing the detection. Stepper motor slide drives thermostat bath moving back and forth to accelerate to clean the electrode. Electrode moves to the next after cleaning and repeats the detection work until completing all tests.

The device ran automatically sampling process 10 times every day, running a total of 200 times. Automatic sampling module work flow is accurate. It can complete the specified sampling and cleaning accurately. At the same time, there are no any collision between electrode and the sample cups or the cleaning cups in the whole process.

3.2 The thermostat module test

Fig. 8 is the thermostat temperature curve in two cases. Fig. 8a is a heating temperature curve when environment temperature, working medium and the sample temperature were 15℃. The sample temperature reached (25 ± 0.5)℃ after 11 min. Fig. 8b is a cooling curve when external temperature is 30℃. The sample temperature reached (25 ± 0.5)℃ after 17 min. The temperature sensor error range is ±0.5℃, so the actual sample temperature is (25 + 1) ℃.

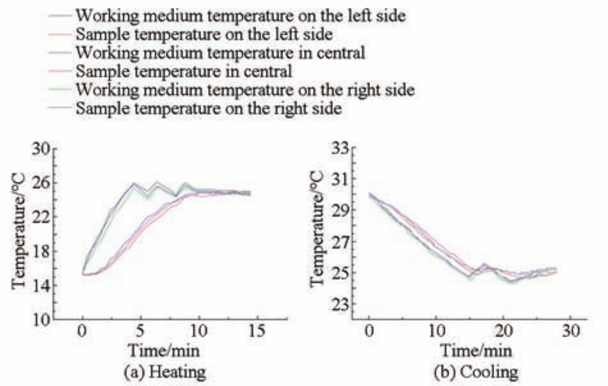

Fig. 8 Temperature adjustment curves under thermostat control

3.3 Electrode and signal acquisition module test

3.3.1 The time drift of signal characteristic value

The Nongfu spring mineral water is selected as the test object. Fig. 9 is a single signal excitation and acquisition curve at 25℃. The detection time is 7 s for a sample. The excitation waveform is comprised of a group of 1, 10, 100 Hz waves. There are four response curves obtained.

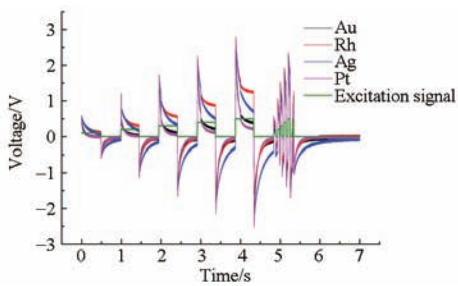

Fig. 9 Single signal acquisition curves

Ten samples were detected every day under the same sample temperature (25℃). The absolute value of the surrounding area of the response curve and the X axis is used as the signal characteristic value. The average value of these ten value is calculated and the test was carried out for 20 days As shown in Fig. 10, the drift of the four working electrode in 20 d is small. Further analysis of the data of 20 d, including the maximum deviation of the signal characteristic value of the signal collected by each electrode, is no more than 5.6% which is acceptable.

3.3.2 Influence of sample temperature on signal characteristic value

AA grade Longjing tea in six kinds temperature (20℃, 25℃, 30℃, 35℃, 40℃, 45℃) were detected. As shown in Fig. 11, the signal characteristic values are gradually increasing with the increasing of the sample temperature.

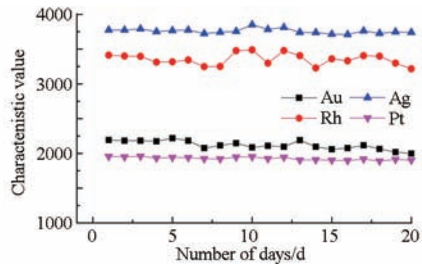

Fig. 10 Drift of the characteristic value with time

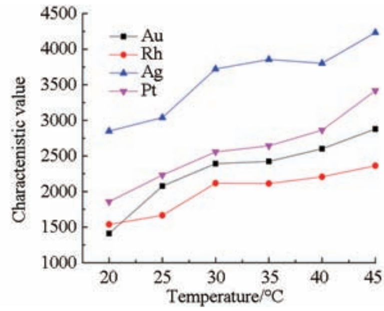

Fig. 11 Effect of temperature on signal

The maximum deviation of the characteristic value was calculated when the sample temperature deviate from 25℃. The maximum deviations were 5.8%, 12.2%, 19.2%, 27.1%, 36% when the temperature deviation were ±1℃, ±2℃, ±3℃, ±4℃, ±5℃. If the thermostat bath module temperature works and sample temperature deviation is ±1℃, the maximum deviation is under 5.8%. By controlling the sample temperature through the thermostat bath module, the detection accuracy of electronic tongue can be improved effectively.

3.3.3 Application of electronic tongue

The electronic tongue distinct four kinds of samples: milk, beer, water and tea. The milk samples were Yizhiyezi milk (m1), Jindianyouji milk (m2), Telunsu milk (m3) and Mengniuchun milk (m4). The beer samples were Qiandaohu beer (b1), Tsingtao beer (b2), Xuehuadanshuang beer (b3) and Xuehuayongchuangtianya beer (b4). Water samples were Binglu mineral water (w1), Nongfuspring water (w2) and Wahaha pure water (w3) and tap water (w4). Tea samples were the same batch purchased from Hangzhou tea company. There are some grades of Longjing tea (AAA, AA, A, B). The proportion of tea and water is 50 mL/g. Tea brew 5 min with 100℃ deionized water. Then filter out tea leaves to get tea soup.

All the tea samples were detected in (25 ± 1)℃. The absolute value of the surrounding area of the response curve and the X axis is used as the signal characteristic value. The four response curves were used to obtain 4 features, and the data were analyzed by principal component analysis (PCA).

As shown in Fig. 12, the output of the four kinds of samples were analyzed by PCA. The cumulative contribution rate of the first two principles of the four kinds of samples is more than 89%, which meant that it contained most of the information of the original data. Fig. 12 of the same sample data points together between different sample data points without overlap. Electronic tongue can be used to distinguish different kinds of milk, beer, water and different grades of tea. The data points of the same sample are gathered together, and there is no overlap between the data points of different kinds of samples. Electronic tongue can be used to distinguish different kinds of milk, beer, water and different grades of tea.

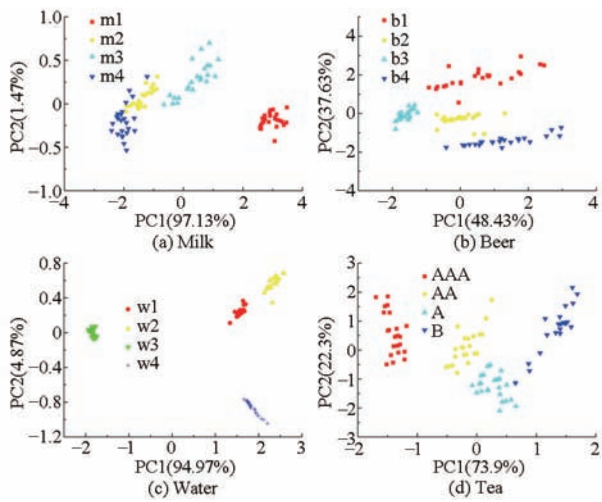

Fig. 12 PCA discrimination diagrams for four kinds of samples

4 Conclusion

(1) A voltammetric electronic tongue detection system is designed using modular design, including electrode and the signal acquisition module, automatic feed module, thermostat bath module, keyboard and display module, control module and the upper computer. It has automatic temperature control, sample injection, cleaning electrode and automatic detection functions.

(2) The test shows that the automatic sampling module is accurate and reliable, and the temperature control range of the thermostatic bath module is (25 ± 1)℃. The drift of signal characteristic value of the electronic tongue in 20 d is less than 5.6%, and it has good stability. The signal characteristic value is affected by the sample temperature changing significantly. The error is as high as 36% when the sample temperature deviation is ± 5℃. Under the control of the constant temperature bath, the sample temperature is kept in (25 ± 1)℃ and signal characteristic value of the sample temperature deviation is less than 5.8%. The use of thermostatic bath temperature control can improve the accuracy of electronic tongue effectively.

(3) Different kinds of milks, beers, waters and different grades of tea were detected by this electronic tongue. The detecting data used PCA to analyse. Results shows that different kinds of sample data points were separated clearly and same sample data point gather together. The electronic tongue has good detection efficiency.

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自动进样与恒温控制型电子舌检测系统

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摘要：针对现有电子舌集成化、自动化程度较低的问题，设计了一台能自动调节样品温度、进样、清洗电极和检测样品的伏安型电子舌，包括上位机、控制模块、电极与信号采集模块、自动进样模块、恒温槽模块和按键显示模块。系统的控制界面基于LabVIEW设计开发，通过串口向控制模块发送指令，进而控制自动进样、恒温槽等模块协同工作。电极与信号采集模块采用了三电极检测体系，由贵金属裸电极阵列、调理电路、采集卡构成，运用脉冲伏安法获得样品的信号曲线，并与上位机之间通过USB互传数据。对设备的进样和调温性能试验结果表明，自动进样模块能可靠运行，恒温槽对样品的温度控制范围为(25±1)℃。对设备的检测性能试验表明，检测信号特征值随时间漂移较小，有良好的稳定性。样品温度波动会引起特征值显著变化，恒温槽控温能有效提高电子舌检测精度。使用电子舌对不同类型的啤酒、牛奶、水和不同等级的茶叶4大类样品进行检测，对数据运用主成分分析(PCA)，结果显示电子舌对它们均能有效区分。

关键词：电子舌；自动进样；恒温槽；检测系统

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Abstract: The electronic tongue has better stability and repeatability than sensory evaluation and it also has the advantages of easy-operated and faster detection speed relative to traditional equipments. At present, the research of electronic tongue is mainly focused on sensor development, and the research on system integration and automation is rare. Thus, a voltammetric electronic tongue was designed, which can automatically adjust the temperature of sample, feed into sample, clean the electrode and detect sample. It included the upper computer, control module, electrode, signal acquisition module, automatic sampling module, thermostatic bath module and display module, etc. The control interface was based on LabVIEW. The upper computer sent commands to control module to drive the automatic sampling module, thermostatic bath module and other modules through the serial port. Signal acquisition module connected the upper computer through USB cable. It contained a three electrodes system, and the signal curve of the sample was obtained by pulse voltammetry. The test results showed that all the modules were stable and reliable and the temperature control accuracy of the sample was (25±1)℃. The area between the signal curve and the X axis was used as the signal characteristic value. The drift of signal characteristic values of 20 d was below 5.6%. The characteristic value was affected significantly by the sample temperature. When the sample temperature departure was ±5℃, the error of the characteristic value was 36%. Under the control of temperature bath (25±1)℃, the error of the characteristic value

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was 5.8%, which indicated that the temperature control can effectively improve the accuracy of electronic tongue detection result. In the detection application, the electronic tongue can distinguish among four different kinds of beer, milk, water and different grades of tea with the principal component analysis (PCA).

Key words: electronic tongue; automatic feeding; thermostatic bath; detection system

引言

电子舌(Electronic tongue,ET)由一系列低选择性、交互感知的传感器阵列组成,能将采集到的信号通过多元统计分析方法对检测对象进行定性、定量分析[1]。有别于传统检测设备对传感器追求高选择性、专一性,电子舌传感器的低选择性和交互感知是其重要的特点[2-4]。

电子舌相对于传统的感官评定有着更好的稳定性、重复性,不易受主观感受影响,同时有着良好的区分能力和更低的检测下限;电子舌相对于化学分析、气相色谱等检测方法,又有操作简单、检测速度快、无复杂前处理的优势。

电子舌配合化学计量学、丰富的多元数据分析手段,不但能识别检测对象,还能精确预测样品中的多种相关成分含量,使用范围广、通用性强[5-7]。由于电子舌良好的应用前景以及相关技术的进步,已被应用于食品饮料、环境监测、生物医药、安保检测等领域[8-16]。

目前,国内外学者对电子舌研究主要集中在传感器开发上,对自动化前处理、进样、系统集成等方面研究较少[17-21]。现有大部分电子舌检测时需要手工完成进样、清洗电极和控制样品温度等工作,操作过程复杂、人员工作量大。现阶段,国际上也只有少数商业电子舌,如法国 Alpha MOS 公司的 ASTREE 和日本 INSENT 公司的 TS-5000Z,具备自动进样、自动检测功能,但存在无法自动控制样品温度、价格昂贵、传感器寿命短、单次检测耗时长等缺点。

本文设计一台结构简单、价格低廉,具备自动调节样品温度、进样、清洗电极和检测样品功能的伏安型电子舌。

1　系统硬件设计

设计的电子舌系统由电极与信号采集模块、控制模块、自动进样模块、恒温槽模块、按键显示模块和上位机组成,如图 1 所示。

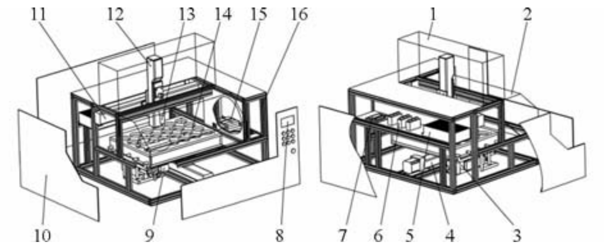

图 1　电子舌构成示意图

Fig. 1　Schematic diagram of electronic tongue

1、2. 亚克力护罩　3. 半导体制冷制热部件　4. Y 方向步进电动机丝杆滑台　5. 开关电源　6. 步进电动机驱动器　7. 控制模块　8. OLED 显示屏、按键　9. 循环水泵　10. 铝合金外壳　11. X 方向步进电动机丝杆滑台　12. Z 方向步进电动机丝杆滑台　13. 电极　14. 恒温槽槽体　15. 信号采集模块　16. 设备主体框架

1.1　上位机和控制模块

上位机为预装了 LabVIEW 软件和 LabVIEW DAQ 驱动软件的计算机,是系统的操作、显示终端。控制模块的核心是 STC12 系列单片机,用于控制底层电器设备。如图 2 所示,上位机与控制模块通过串口通讯,与信号采集模块通过 USB 通讯。

当需要进行进样、清洗、恒温槽温度控制等操作时,上位机通过串口向控制模块发送字符串指令。控制模块收到指令后,操作对应的通用 I/O 口输出以控制相应电器工作或扫描对应的 I/O 口以获取相关信息。样品检测时,上位机直接控制数据采集卡

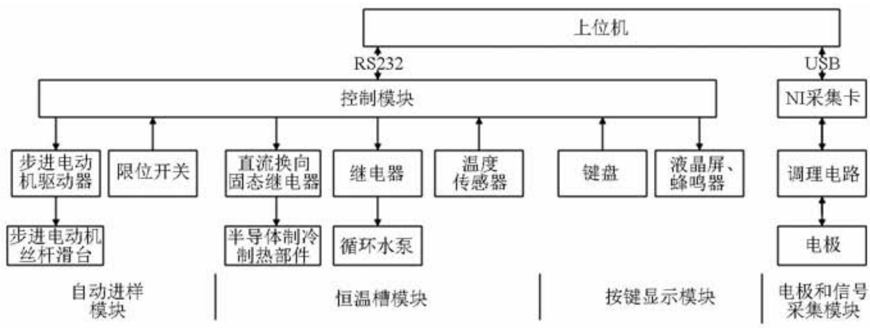

图 2　电子舌电器控制结构示意图

Fig. 2　Electrical structure diagram of electronic tongue

产生激发信号并实时采集工作电极回路的信号。

1.2 电极与信号采集模块

该模块由电极、调理电路、NI采集卡组成。核心的检测部分为三电极体系，由工作电极（WE）、辅助电极（CE）、参比电极（RE）和调理电路组成。电极部分集成了4根材料分别为Au、Rh、Ag、Pt的工作电极、1根Pt辅助电极和1根饱和Ag/AgCl参比电极。

其工作原理为：在工作电极与参比电极间施加一定变化规律的电压，电极表面与待测溶液间形成双电层充放电与氧化还原反应，工作回路流过非氧化还原电流和氧化还原电流，通过分析叠加电流，可得出溶液的相关特性。辅助电极用于传导电流，与工作电极构成电流回路。参比电极提供一个稳定的参考电位，以确定工作电极电位。

如图3所示，调理电路主要包括信号激发电路和信号采集电路。信号激发电路中P2-6连接参比电极，P4-8连接采集卡的激发信号输出端，P2-5连接一路工作电极。信号激发电路从左到右分3级，分别为1∶1跟随电路、电压比较电路和同向放大电路。1∶1跟随电路主要起阻抗变换作用，为下一级电压比较电路提供合适的输入。电压比较电路主要作用是差分放大。同向放大电路主要作用是调整输出的放大倍数。

信号采集电路中P2-1接辅助电极，P4-2接NI采集卡的一路信号采集口。该电路是一个电流转电压电路。由于直接测量通过工作电极回路的电流比较困难，所以采用测量回路上分压电阻的电压代替。电压信号由NI-6009采集卡采集，并传输到上位机显示和保存。

其余3路信号激发电路和信号采集电路与图3相同。

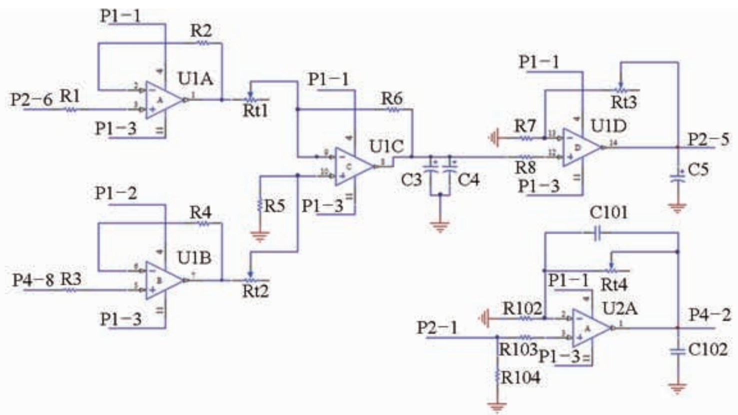

图3 调理电路原理图

Fig. 3 Schematic diagram of circuit

该模块的工作过程是：上位机控制NI采集卡输出特定波形的激发信号，在调理电路的作用下，工作电极和参比电极间电压跟随激发信号变化。由于参比电极电势始终保持恒定，即工作电极和溶液间电势跟随激发信号变化。在信号激发的同时，实时测量工作电极和辅助电极回路上的信号，并将信号显示和保存。

1.3 自动进样模块

如图1所示，进样机构为一个三平动自由度直角坐标系结构。该结构分别由3根有效行程为100、300、400 mm的步进电动机丝杆滑台组成，分别完成Z、Y、X方向的运动。Z方向滑台用于带动电极上下运动。Z方向滑台安装在X方向滑台上，由X方向滑台带动完成左右运动。Y方向滑台能带动安装在它上面的恒温槽模块前后运动。

步进电动机丝杆滑台采用开环方式控制。单片机每向驱动器输入一个脉冲信号，滑台移动相应距离。滑台一端装有限位开关用于确定零点和消除失步或越步造成的误差。滑台的移动距离和移动速度的计算公式为

$$S = nP/N \tag{1}$$

$$V = fP/N \tag{2}$$

式中 S——滑台的移动距离，mm

V——滑台的移动速度，mm/s

n——单片机累计向驱动器输入的脉冲数

P——丝杆的螺距，mm

N——驱动器细分步数

f——单片机向驱动器输入的脉冲频率，Hz

滑台驱动采用梯形曲线控制，步进电动机启动和停止阶段有加减速过渡，可以有效避免启停阶段单片机输出的脉冲变化过大，电动机产生失步和越步现象[22-23]。同时也有效减轻了启停阶段运动冲击造成丝杆寿命缩短、设备振动、噪声等不良影响。

1.4 恒温槽模块

温度变化会引起溶液理化特性改变，导致工作回路电信号发生漂移。恒温槽模块能自动控制待测

样品的温度，可有效降低由温度波动引起的信号偏差，如图 4 所示。该模块包括直流换向固态继电器、半导体制冷制热部件、循环水泵、温度传感器和槽体。

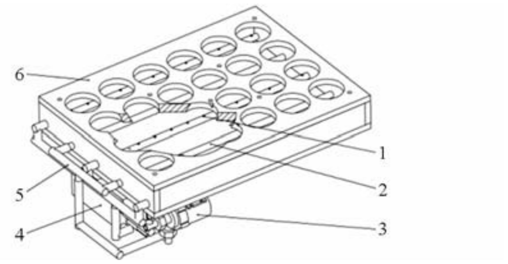

图 4　恒温槽模块结构示意图

Fig. 4　Schematic diagram of thermostatic bath module

1. 出水管　2. 排水管　3. 循环水泵　4. 半导体制冷制热部件、直流换向固态继电器　5. 管道　6. 槽体

槽体左侧 4 ×5 的圆孔位放置待测样品杯，右侧 4 ×1 的圆孔位放置清洗电极的水杯。槽内盛 1/2 的水作为工作介质，底部间隔分布多根带小孔的进出水管。水被从槽中出水管抽出后，泵入制冷制热部件中制冷或加热，最后从出水管喷出以调节槽内水温。

半导体制冷制热部件利用的是半导体材料的 Peltier 效应[24]。直流换向固态继电器控制半导体制冷制热部件的加热、制冷、停止运行 3 种工作状态。温度传感器采用 DS18B20 型，测温范围 －55 ~ 125℃，误差范围 ±0.5℃。设备中设置有 4 个温度传感器，分别安装在水槽内部测水温、电极头部测样品温度、机箱内部测室温和水冷交换器上监控温度，防止结冰或者烧毁。

恒温槽启动后，每隔 10 s 检测槽内水温，当槽内水温低于设定温度 0.5℃时，半导体部件加热，高于 0.5℃时制冷，在 ±0.5℃范围内则停止工作。此时温度传感器不断检测样品温度，等待水浴中的样品温度接近设定温度。

2　系统软件设计

2.1　上位机程序

上位机程序采用 LabVIEW 图形化语言编写。程序界面左侧波形显示器（图 5）分别显示 4 个工作电极回路上采集到的电信号和发出的激发波形；界面右侧上部分别是波形、波形循环次数等功能选项；界面右侧下部为仪器手动控制模式下的手动进样、滑台归零等功能键，切换到自动检测模式下，则是显示设置样品个数、全自动运行等功能键。

上位机程序主要功能包括：根据程序流程或按键操作向控制模块发送指令和接收反馈信号，控制进样、恒温槽等模块工作；控制 NI－6009 采集卡模拟电压口产生多频脉冲信号；从采集卡接收采集到的数据，并显示在界面上和保存成文件。其工作流程如图 6 所示。

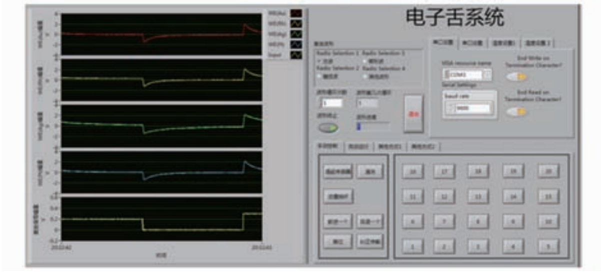

图 5　上位机界面

Fig. 5　Upper computer interface

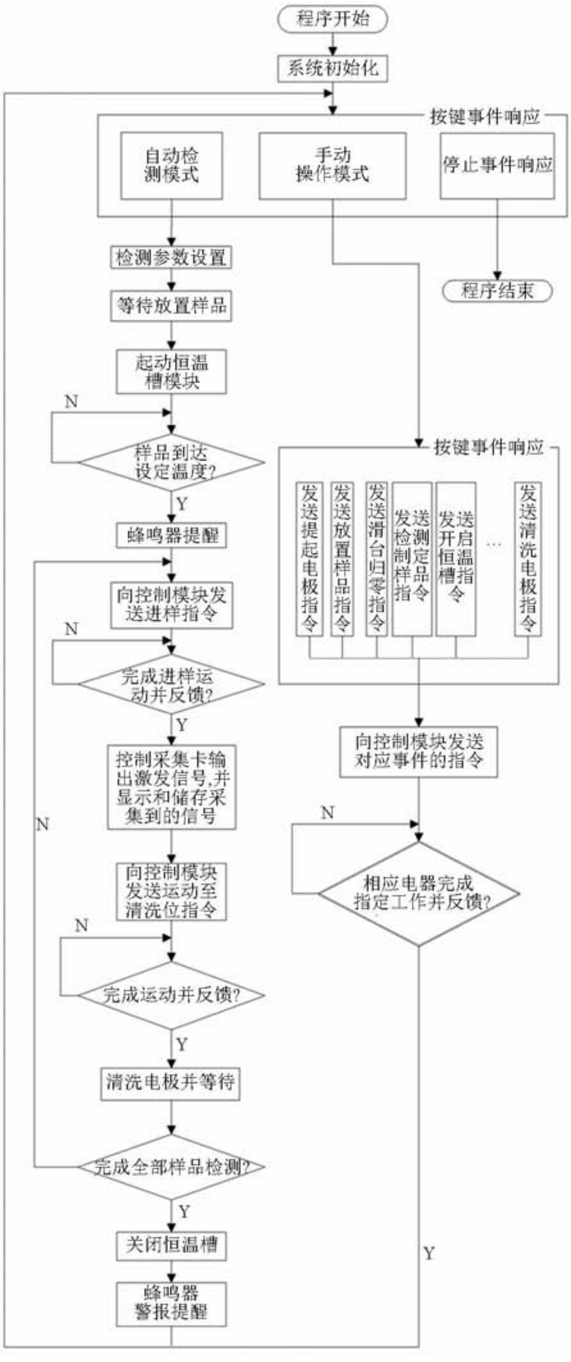

图 6　上位机程序流程图

Fig. 6　Flow chart of upper computer program

2.2　下位机程序

下位机程序在 KEIL 中编写，烧录到控制模块的单片机中。控制模块接受按键输入或上位机的指令控制进样模块、恒温槽模块、显示屏等工作，同时将设备的信息反馈给上位机。其工作流程如图 7 所示。

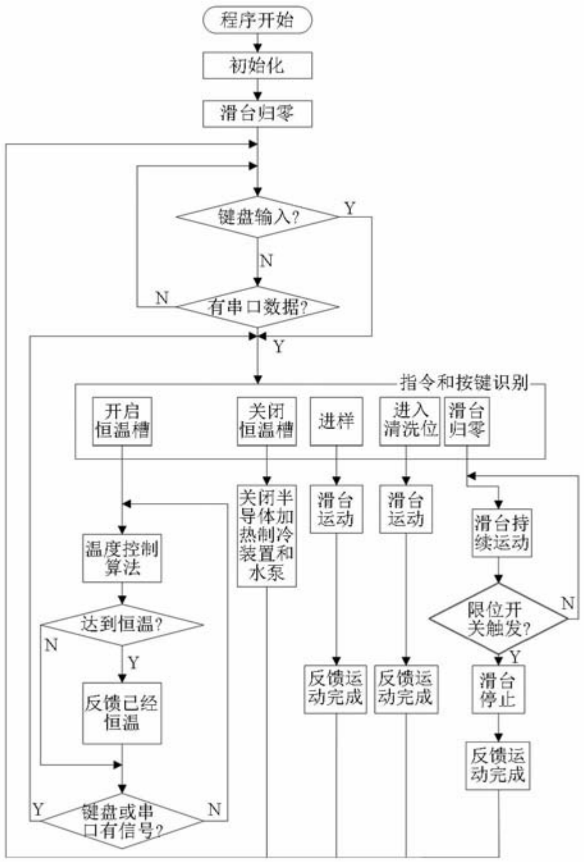

图 7　下位机程序流程图

Fig. 7　Flow chart of lower machine program

3　电子舌主要功能模块性能试验

3.1　自动进样模块测试

启动设备后 3 组步进电动机丝杆滑台自动复位，恒温槽移出等待放置样品杯和清洗杯。放置完成后，点击全自动运行，设备开始自动依次检测样品。电极移动至样品杯上空，头部准确插入样品杯中部，并浸入样品中。完成检测后，自动移动到清洗杯上空，并准确插入超纯水中浸泡。此时恒温槽在滑台的驱动下反复前后移动，晃动清洗杯加速清洗。完成清洗后，电极依次移至下一个样品检测，直至完成全部检测。

设备连续 20 d 每天重复完整的全自动进样流程 10 次，累计运行 200 次。自动进样模块的工作流程准确无误，能准确完成指定位置样品的进样和清洗，同时在整个流程中未发生电极碰撞样品杯和清洗杯的现象。

3.2　恒温槽模块测试

图 8 为 2 种情况下的恒温槽调温曲线。图 8a 是环境温度、工作介质和样品温度均为 15℃时的升温调温曲线，经过 11 min，槽内各处位置样品温度均达到(25 ± 0.5)℃；图 8b 是环境温度、工作介质和样品温度均为 30℃时降温调温曲线，经过 17 min，槽内各处位置样品温度均达到(25 ± 0.5)℃。由于温度传感器误差范围为 ±0.5℃，所以实际样品温度为(25 ± 1)℃。

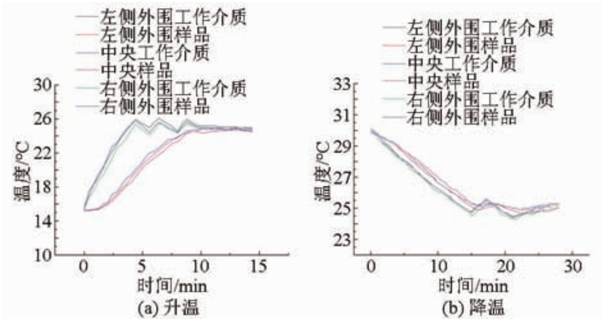

图 8　恒温槽控制下的样品温度调节曲线

Fig. 8　Temperature adjustment curves under thermostat control

3.3　电极和信号采集模块测试

3.3.1　信号特征值随时间的漂移

考虑到样品品质的稳定性，试验用了同一批次的农夫山泉矿泉水作为检测对象。如图 9 所示的是以农夫山泉矿泉水为样品，在 25℃时做的单次信号激发和采集曲线。单次检测时间为 7 s，激发波形为 1、10、100 Hz 的一组方波，4 个工作电极分别得到 4 条响应曲线。

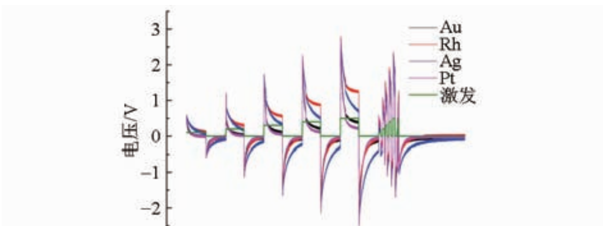

图 9　单次信号采集曲线

Fig. 9　Single signal acquisition curves

每天控制在相同的样品温度下(25℃)重复检测 10 个样品。以响应曲线与 X 轴上下包围面积绝对值的和作为信号特征值，对每天的 10 个样品的特征值求平均值，连续检测 20 d。从图 10 中可以看出 4 个工作电极 20 d 内漂移较小。进一步对 20 d 的数据进行偏差分析，每根电极采集到的信号特征值的 20 d 内的最大偏差不超过 5.6%，在可接受范围内。

3.3.2　样品温度对电信号特征值的影响

在 20、25、30、35、40、45℃ 6 个温度下检测 AA

级龙井茶茶汤。如图 11 所示，随着样品组温度逐渐上升，4 根电极信号特征值均随样品温度升高而逐渐变大。

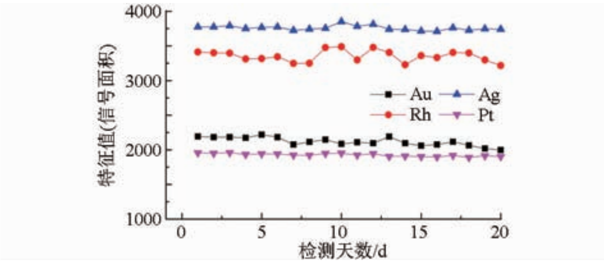

图 10　电极信号特征值随时间的漂移

Fig. 10　Drift of characteristic value with time

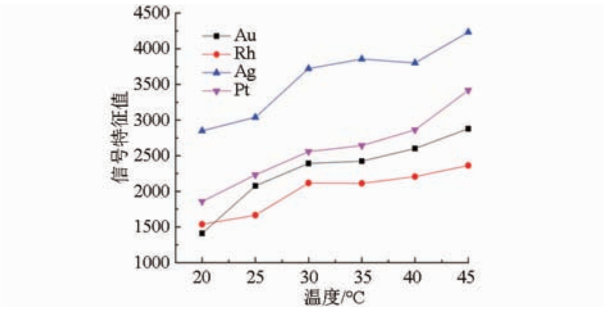

图 11　样品温度对电信号的影响

Fig. 11　Effect of temperature on signal

将图 11 中特征值随温度变化的曲线作 4 次多项式拟合，计算样品温度偏离 25℃时特征值的最大偏差。温度偏差为 ±1℃、±2℃、±3℃、±4℃、±5℃时，特征值最大偏差分别为 5.8%、12.2%、19.2%、27.1%、36.0%。当采用恒温槽模块调温，样品温度偏差为 ±1℃时，特征值的最大偏差为 5.8%，恒温槽模块对样品的温度调节能有效提高电子舌检测精度。

3.3.3　电子舌检测应用

使用电子舌检测区分 4 大类样品：牛奶、啤酒、水和茶叶。牛奶类样品分别为光明一只椰子牛奶、金典有机奶、蒙牛纯牛奶和特仑苏。啤酒类样品分别为千岛湖原生态、青岛啤酒经典款、雪花淡爽和雪花勇闯天涯。水类样品分别是冰露矿泉水、农夫山泉、娃哈哈纯净水和自来水。茶叶样品为购自杭州茶叶公司的同一批次 AAA、AA、A、B 4 种等级的西湖龙井茶。茶叶使用 100℃ 去离子水按液料比 50 mL/g 冲泡 5 min，滤掉茶叶得到茶汤待测。

所有样品均调温至(25 ±1)℃下检测。以响应曲线与 *X* 轴上下包围面积绝对值的和作为信号特征值，4 根响应曲线得到 4 个特征值数据，并对数据采用主成分分析(PCA)。

如图 12 所示，分别对 4 类样品的检测数据进行 PCA 分析。4 类样品的前 2 个因子累计贡献率均超过 89%，都能很好地反映原始数据的大部分信息。图 12 中同种样品的数据点聚集在一起，不同种样品的数据点之间基本没有重叠。电子舌能有效区分不同种类的牛奶、啤酒、水和不同等级的茶叶。

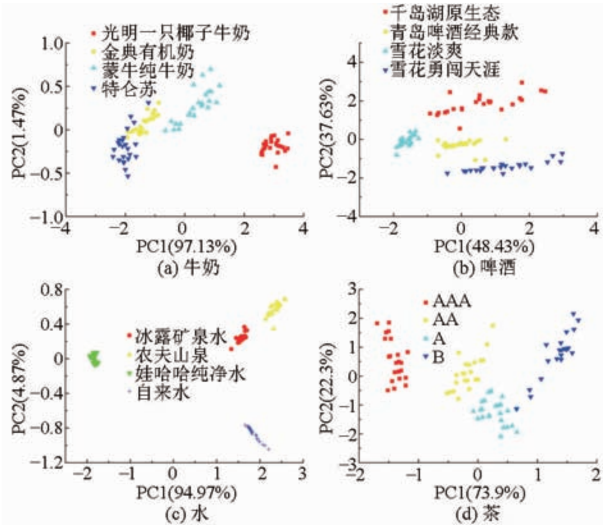

图 12　电子舌对 4 类样品的 PCA 分析

Fig. 12　PCA discrimination diagrams for four kinds of samples

4　结论

(1)设计了一台伏安型电子舌检测系统，采用模块化设计，包括电极与信号采集模块、自动进样模块、恒温槽模块、按键显示模块、控制模块和上位机，具备自动样品温度控制、进样、清洗电极和检测的功能。

(2)对样机试验表明，自动进样模块工作准确可靠，恒温槽模块温度控制范围为(25 ±1)℃。电子舌 20d 内检测信号特征值随时间的漂移小于 5.6%，有较好的稳定性。检测信号特征值受样品温度变化影响显著，在样品温度偏差 ±5℃时误差高达 36%。在恒温槽控制下，样品温度保持在(25 ±1)℃时，样品温度偏差产生的信号特征值漂移小于 5.8%，运用恒温槽控温能有效提高电子舌检测精度。

(3)应用电子舌对不同种类的牛奶、啤酒、水和不同等级的茶叶进行检测试验，对检测数据运用 PCA 分析，结果显示不同种类样品数据点之间明显分离，同种类样品数据点间聚拢效果良好，该电子舌对上述样品均有良好的效检测区分效果。

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