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Multichannel Liquid Phase Microextraction System

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다채널 액상 미세 추출 시스템 설계 및 제작

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ABSTRACT

In this study, a multichannel gas–liquid microextraction system is designed by integrating the automatic elution of extraction line and multichannel gas-purging liquid phase microextraction. The system uses an injection pump and inert gas to push the extraction solvent to a sample bottle of a gas-phase color autosampler and then implements multichannel gas–liquid microextraction and gas chromatography–mass spectrometry. The system also employs a three-way integrated micro-high-temperature heater, syringe pump, and microflow controller to realize the simultaneous processing of multiple groups of samples, thus improving the sample pretreatment speed and reproducibility and reducing human error. Autoinjection experiments were implemented with polycyclic aromatic hydrocarbon standard samples. The experiments show that the average recovery rate of the system exceeds 70%, and the relative standard among the channels is less than 15%.

Keywords : Multichannel Liquid Phase Microextraction(다채널 액상미세추출), Gas Chromatography(가스크로마토그래피), MCU of IAP15W413AS (IAP15W413AS 마이크로 컨트롤러)

1. Introduction

Over the years, with the rapid technical advancements, the intelligence level of various instruments has also steadily increased, promoting the development trend in the technology of simple and integrated operation of instruments for detection and analysis[1]. The emergence of coupling technology makes the sample pretreatment and detection processes closely linked[2], considerably reducing the required manpower and material resources[3]; this is the main priority to achieve a major breakthrough in online analysis.

The combined technology of liquid phase microextraction technology[4] and gas chromatography[5] is in a sample preparation method. The multichannel liquid phase microextraction technique combines extraction, purification, concentration, and pre-dissociation with the gas chromatography (GC) sample pretreatment[6], which is primarily performed to detect and analyze volatile

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components in various samples to be tested. In employing the liquid phase microextraction and GC for sample analysis, the manual operation hinders the accuracy and reproducibility of the entire test result[7]. Consequently, this method cannot satisfy the requirements of modern analytical chemistry for the rapid, simple, and automated sample preparation. To resolve this problem, this study attempts to examine the combined technology of multichannel liquid phase microextraction and gas chromatography in the sample pretreatment and implement online sample detection.

2. System Structure Design

2.1 Combined Structure and Working Principle

The system is mainly composed of a three-way syringe pump, a high temperature heater, three gas flow controllers, an autosampler, and a gas chromatography mass spectrometer. the structure diagram of the system is shown in Fig. 1.

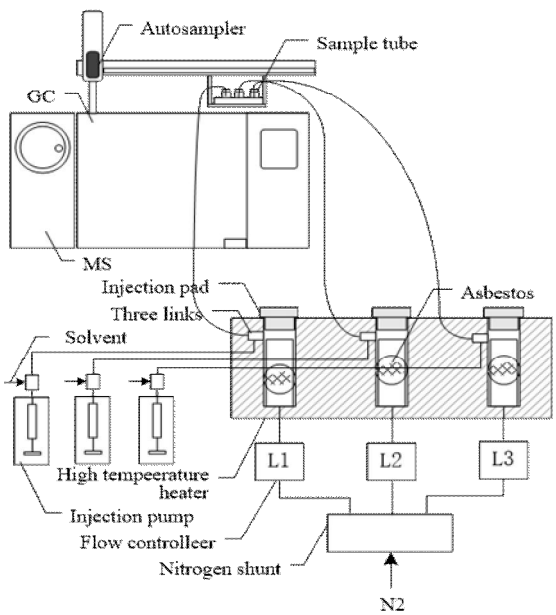

Fig. 1 Structure diagram of combined automatic injection

Fig. 1 shows a syringe pump on the left. the syringe pump uses a stepping motor and a screw rod structure to control the 500μL syringe piston to move up and down. a three-way solenoid valve controls the suction or push channel of the syringe pump. the suction channel is connected with an external solvent bottle. the push channel is connected with a gas outlet through a three-way structure and a polytetrafluoroethylene pipeline is connected to a sample inner cannula in a condenser. Before the extraction experiment, the syringe pump was filled with solvent, and when the extraction experiment was finished and the heater was cooled to below 40℃, the solvent was pushed out by the control syringe pump for pipeline elution.

Fig. 1, a high-temperature heater is located in the middle of the right side. The heating mode is alumina ceramic heating plate. The cylindrical sample cell inside the heater is used to place the Shi Ying sample tube. During the experiment, the sample is placed in the sample tube and sealed with PTFE sample injection pad. The stainless steel gas inlet conduit is connected to the interior of the high temperature heater from the bottom of the heater, inert gas is blown into the heater, and the gas outlet is connected with the elution solvent pipeline and finally leads to the inner cannula in the condenser. The heating temperature range of the sample is 50~350℃.

Fig. 1, the lower part on the right side is the system gas passage. After nitrogen enters the system, the gas is first divided into three paths through the nitrogen splitter. Each of the three paths of gas pipelines is equipped with a flow controller. The gas flow is controlled by the flow controller and then introduced into the heating tank. Finally, it is blown into the sample tube through the three-way passage.

Fig. 1, the upper part is the combined part of the autosampler. The gas-liquid output channel is

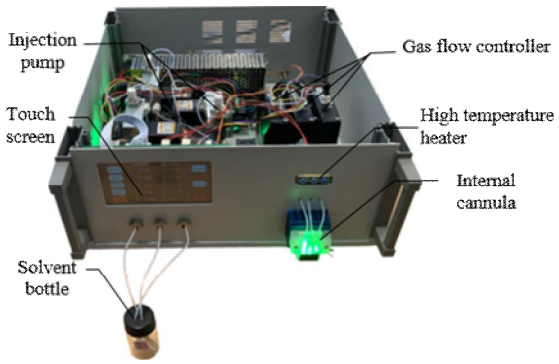

Fig. 2 Microextraction system physical diagram

directly connected to the sample tube placed on the GC sampling table, and the sample tube is placed in the gas phase bottle. After the extraction and automatic elution are completed, the singlechip sends a start signal to the GC, and the sample is put into the Gas chromatography instrument and the mass spectrometer through the automatic sampler for chromatographic analysis.

As shown in Fig. 2, it is a physical map of a multi-channel liquid phase microextraction system. The working principle of the whole system: the sample is placed in the sample tube and placed in the high-temperature heater, and sealed with the sample injection pad. The target analyte in the sample is vaporized in a programmed temperature rise mode, and inert gas output by the flow controller brings the target analyte out of the heater through a gas pipeline. As part of the target object is directly liquefied and remained in the pipeline when it is cooled in the pipeline, the pipeline will be eluted with solvent after the heater is cooled, and the target object is brought into the cannula in the sample through the solvent. After the vaporization process is completed, the inert gas output with a certain flow rate is maintained to prevent the solvent in the inner cannula from backflushing during the cooling process of the heater. After the heating temperature is lower than 40℃, the syringe pump pushes out a certain amount of solvent to complete automatic elution, and a certain inert gas flow rate is maintained to prevent the eluting solvent from flowing into the heater during the elution process.

2.2 Injection Pump Structure

The schematic structural diagram of the syringe pump is shown in Fig. 3. all its components are assembled on an aluminum plate. the micro stepping motor is fixed in the middle of the aluminum plate through screws. the piston end of the injection syringe is connected to the slider of the screw rod of the micro stepping motor. the threaded end of the syringe is connected through one end of a 1/4-28 internal thread interface fixed on the aluminum plate. the screw rod structure controls the piston movement of the syringe by converting the rotation of the stepping motor into the up and down movement of the slider during operation. A positioning aluminum bar is fixed on the other side of the slider. When the slider reaches the bottom, i.e. the system zero position, the positioning aluminum bar will touch the limit sensor. The system controller can detect the change of the output signal of the limit sensor, thus controlling the motor to stop running to achieve the purpose of positioning the injection pump zero position. The common end of the two channels of the electromagnetic

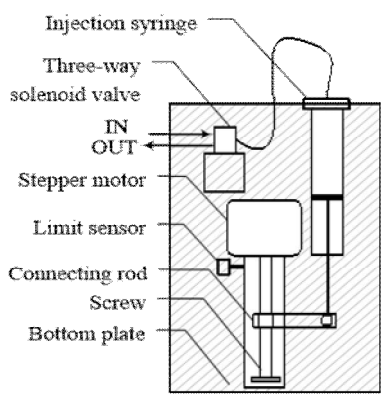

Fig. 3 Structure diagram of syringe pump

valve is connected to the other end of the 1/4-28 internal thread interface, and the two channels of the electromagnetic valve are respectively connected with an external solvent bottle and a heater elution channel.

2.3 Structure of High-Temperature Heater

The structure of the high-temperature heater is shown in Fig. 4. The main material used is copper, which has high thermal conductivity. A cylindrical groove is opened at the center for the sample tube. Stainless steel tubes are drilled and welded on the lower and right sides of the groove to serve as gas pipeline and gas outlet, respectively. An opening on the lower side of the gas outlet is linked to the gas outlet to form a T-shaped structure for passing the elution solvent. A hole is opened on the left side of the heater near the gas outlet for placing a temperature sensor, and a square groove is opened on the left side of the heater for installing an alumina ceramic heating plate. The inside and outside of the high-temperature heater is nickel-plated, improving the overall inertness and surface smoothness of the heater. The Pt1000 platinum resistance sensor is coated with high-temperature heat-conducting silicone grease, and two high-temperature ceramic heating plates are

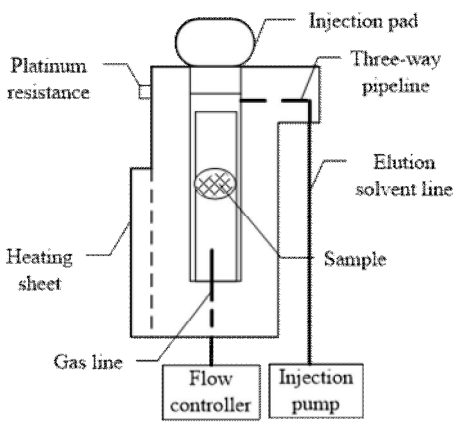

Fig. 4 Structure diagram of high-temperature heater

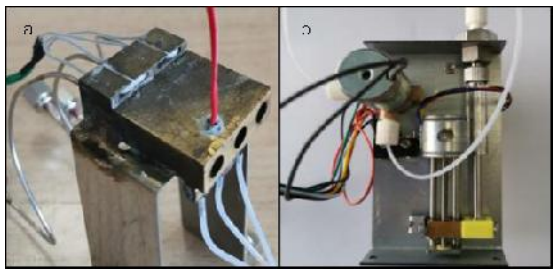

Fig. 5 Physical map of (a) heater and (b) syringe pump

installed at corresponding positions. The gas flow controller and injection pump are connected to the corresponding pipelines; the polytetrafluoroethylene pipeline leads to the outlet. The graphs of the physical maps of the heater and injection pump are shown in Fig. 5, (a) and (b), respectively.

3. System Circuit Design

3.1 System Hardware

The system is mainly composed of a single-chip computer, gas flow controller, syringe pump, platinum resistance sensor, touchscreen, analog-to-digital (AD) converter, ceramic heater, and semiconductor condenser. The principle block diagram of the control system is shown in Fig. 6.

The multipoint control unit of IAP15W413AS is used to regulate the heating and cooling temperatures, gas flow, and fan speed. The syringe pump is used to transmit the liquid in the system pipeline and flush out the accumulated liquefied

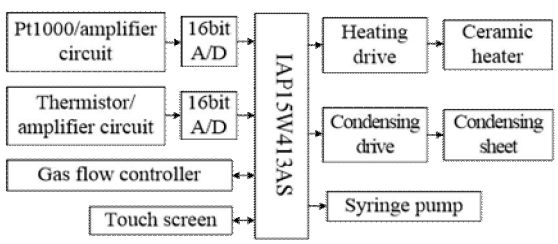

Fig. 6 Hardware block diagram of control system

target substances in the pipes during elution. It also conveys different solvents for the thorough cleaning of the pipeline. The Pt1000 platinum resistance sensor[8] converts the temperature change in the heater into a change in the resistance value and then obtains this value through the bridge circuit. The thermistor sensor converts the temperature change in the condenser into a change in the resistance value and then also derives the change value using the bridge circuit. The 16-bit ADS1286AD conversion chip samples the output voltage of the bridge. The ceramic plate increases the temperature in the heater[9]. The semiconductor condensing sheet[10] ensures that the temperature of the solvent in the inner cannula of the sample is sufficiently low to prevent the solvent in the inner cannula from evaporating due to the high-temperature gas blown out from the pipeline during extraction. At the same time, it liquefies the gaseous target substances in the pipeline. The system simultaneously uses three gas flow controllers to measure and regulate the flow of inert gas introduced into the heater sample tube. The single-chip computer calculates the output pulse-width modulation (PWM) according to the difference between the set flow rate and maximum control flow rate. It also outputs the modulated pulse to the setting end of the flow controller through the AD conversion circuit. Moreover, the output pin of the flow controller is connected to the conversion pin of the single chip for AD conversion to obtain the real-time output (displayed on the touchscreen) of the flow controller.

3.1 System Software

The system programs are written in C51 language, and Keilμ Vision5 is used as the compilation software. The system software includes the main function, temperature detection function, timer function, proportional–integral–derivative (PID) algorithm function, touchscreen control function, AD conversion function, and gas flow control function.

After the startup, the main function is run, the system is initialized, and the system parameters are set; thereafter, the system starts extraction. Upon the completion of extraction, an automatic injection control subroutine is implemented. The system does not require the condenser to start. Hence, it only waits until the heating and elution processes are accomplished before the single-chip computer sends the signal to the GC instrument to initiate the automatic sample introduction; this completes the sample pretreatment process. When the control program is completed, the serial port screen instruction analysis subroutine is called to obtain valid instructions, analyze the instructions, and execute the functions corresponding to the valid instructions displayed on the touchscreen. Finally, it is evaluated whether this cycle has changed the displayed touchscreen data, such as the temperature data. If change has occurred, the single-chip computer sends the modified data to the touchscreen and refreshes the screen display. The functions of the syringe pump control and serial port to send and receive data are all processed during interruption.

The temperature of the heater and condenser is controlled by the incremental PID algorithm. First, the temperature value of ADS1286 is read by the I2C bus, and its difference with the set temperature value is determined. Then, the incremental PID operation is performed to obtain the current increment. After accumulating the increment with the last PID output, the PID is restricted from deriving further current increments. After the output is written into the PWM comparator register, the single-chip microcomputer automatically outputs pulses. At the end of this PID control process, the single-chip microcomputer returns to the main function operation.

4. Experimental Results and Analysis

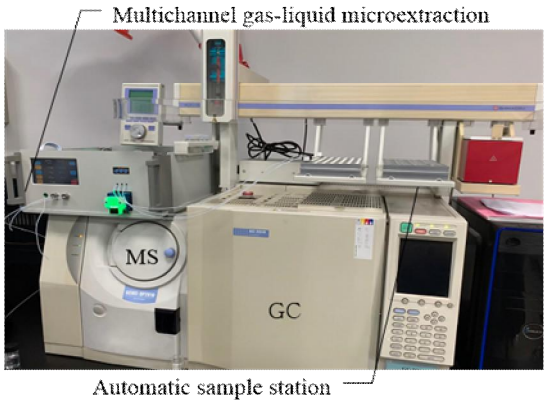

Fig. 7 System physical diagram

4.1 Extraction Experiment Conditions

As shown in Fig. 7, the experimental conditions of the experimental group in the system are as follows: 50 μL of extraction solvent n-hexane; 50 μL of 0.2-ppm polycyclic aromatic hydrocarbon standard sample; heating temperature of 300 ℃; condensation temperature of −5 ℃; 2-mL/min nitrogen flow rate in the extraction process; 40-μL elution solvent volume; 20-μL GC instrument internal standard deuterated phenanthrene. A control group was set up with 60 μL of extraction solvent, 20 μL of standard sample, and 20 μL of instrument internal standard deuterated phenanthrene.

4.2 Analysis of Experimental Data

After the pretreatment experiment in the experimental group, GC was used to analyze the three groups of intubation tubes. The carrier gas flow rate in the capillary column is 1 mL/min, the inlet temperature is 280 ℃, the injection volume is 2 μL, and the split ratio is 50:1. The heating program is 45 ℃ for 1 min, 4 ℃/min until 250 ℃ is reached, and 6 ℃/min until 280 ℃ is attained. The ionization process is electron ionization, the ion source temperature is 280 ℃, and the electron energy is 70 eV.

The list in Table 1 indicates that the average recovery rate of low-boiling point target substances exceeds 90%, and the relative standard deviation among the results of the channels is less than 15%.

Table 1 Results of automatic injection experiment

Target	Recovery 1	Recovery 2	Recovery 3	RSD
Naphthalene	111	133	116	9
Acenaphthy- lene	79	106	96	15
Acenaphthene	84	106	99	12
Fluorene	83	110	103	14
d10-Phenanthrene	100	100	100	0
Phenanthrene	95	103	99	4
Anthracene	87	92	95	4
d10-Fluoranthene	88	77	83	7
Pyrene	86	74	78	8
Benzo[a]-anthracene	75	69	71	4
Chrysene	74	71	71	2
Benzo[b]-fluoranthene	69	71	78	6
Benzo[k]-fluoranthene	70	74	82	8
Benzo[a]-pyrene	72	71	76	4
d-12perylene	70	63	75	9
Dibenz[a,h]-anthracene	78	71	85	9
Benzo[ghi]-perylene	80	85	75	6

Compared with the traditional manual sample injection, the relative standard deviation among the channels for the recovery of low-boiling point target is relatively high. This is because there is no condenser in the experimental device, resulting in the zero loss in the target substance. For the medium-boiling point and high-boiling point targets, the average recovery rate exceeds 70%, and the relative standard deviation is less than 10%. Compared with the traditional manual injection, this recovery rate is lower because the injection pipeline of the device is longer, and some components remaining in the pipeline are not completely eluted. Nevertheless, the deviation between the two experimental groups is small, and the repeatability and accuracy of experimental results satisfy the design requirements.

5. Conclusion

The system has successfully realized the combination of multichannel liquid-phase microextraction and GC. The combined system simultaneously achieves multichannel sample pretreatment and implements the automatic sample introduction to GC. This considerably reduces the time and effort required for the pretreatment process of target compounds in complex samples and allows the sample pretreatment process to integrate extraction with detection and analysis. The automatic sampling method is not only simple and convenient to operate, but also reduces the operation time and unnecessary errors caused by the manual operation in the experimental process; consequently, the required manpower is considerably decreased. The experimental results show that the average recovery rate of the system exceeds 70%, and the relative standard deviation among the channels is less than 15%, indicating the feasibility and reliability of the combined system.

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