

# 浙江大学



## 本科实验报告

### Chemical Sensors

课程名称： 生物医学传感与检测

姓名：

学院： 生物医学工程与仪器科学学院

专业： 生物医学工程

学号：

指导老师： 张芬妮

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实验名称: Chemical Sensors 实验类型: \_\_\_\_\_ 同组学生姓名: \_\_\_\_\_

## 1. Principle of Two Chemical Sensors

### (1) Definition of Chemical Sensors

The definition of chemical sensors by Wolfbeis (Wolfbeis, 1990) in 1990 is as follows: Chemical sensors are small-sized devices comprising a recognition element, a transduction element, and a signal processor capable of continuously and reversibly reporting a chemical concentration. The description above is pragmatic while the definition by the IUPAC (International Union of Pure and Applied Chemistry) in 1991 is general: A chemical sensor is a device that transforms chemical information, ranging from concentration of a specific sample component to total composition analysis, into an analytically useful signal. As a kind of analytical device, chemical sensors are so effective that they can detect the object molecules in the presence of interfering substances. This sensing principle is shown in Figure 1.

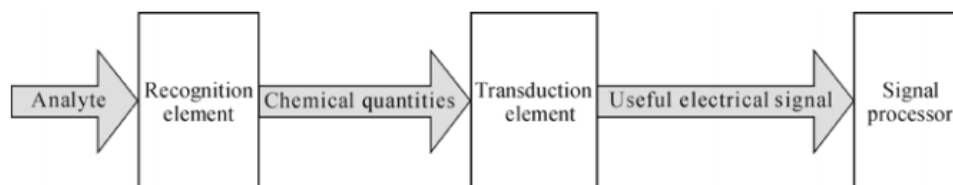


图 1: Sensing principles of chemical sensors

According to these definitions, here are the principles of two common types of chemical sensors:

### (2) Ion-Selective Electrode (ISE) Sensors

- **Definition:** An ISE is an electroanalytical sensor with a membrane whose potential indicates the activity of a specific ion in a solution.
- **Principle:** The core of an ISE is a selective membrane that interacts with the target ion. When the determinand ion (the ion to be measured) with charge number  $z$  influences the membrane potential, its value is given by:

$$\Delta\phi_M = \frac{RT}{zF} \ln \left( \frac{\alpha_x}{\alpha_{x0}} \right)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant, and  $\alpha_x$  and  $\alpha_{x0}$  are the activities of  $x$  in the analyte solution and the internal reference solution,

respectively. This interaction creates a potential difference across the membrane, which is then measured against a stable reference electrode. The overall EMF (electromotive force) of the cell is the difference between the electrode potentials of the reference electrodes and the membrane potential.

- **Mechanism:** The membrane potential is influenced by the concentration of the target ion. For example, in a pH glass electrode, a thin glass membrane responds to the  $H^+$  concentration.

### (3) Semiconductor Gas Sensors

- **Definition:** These sensors utilize changes in the electrical conductivity of semiconductor materials upon exposure to specific gases.
- **Principle:** The working principle is based on band theory, which describes how the interaction of a target gas with the surface of a metal oxide film changes the material's charge carrier concentration.
- **Mechanism:**
  - **Adsorption/Desorption:** Gas molecules (often through surface adsorbed oxygen ions) interact with the semiconductor material's surface, leading to adsorption or desorption.
  - **Conductivity Change:** This interaction causes a change in the concentration of charge carriers (electrons or holes) within the semiconductor.
  - For an n-type semiconductor (majority carriers are electrons), interaction with a reducing gas increases conductivity, while an oxidizing gas decreases it.
  - For a p-type semiconductor (majority carriers are positive holes), an oxidizing gas increases conductivity, and a reducing gas decreases it.
  - This change in conductivity (or resistivity) is then measured as the sensor's output.
- **Example:**  $SnO_2$  (tin dioxide) semiconductor gas sensors are widely used, where oxygen adsorption on the surface makes the electrical resistance high. When a reducing gas reacts with the oxygen, the resistance drops.

## 2. Liquid Junction Potential and How to Eliminate It

### (1) What is Liquid Junction Potential?

Liquid junction potential is generated by ion diffusing from one side of the porous membrane to the other. Different ions have distinct diffusion speed and an electrical double layer of positive and negative charges will be produced at the junction of the two solutions. The potential difference at the junction caused by the ionic transfer is called liquid junction potential.

The major causes of the liquid junction potential are as follows:

**Same solution with different concentrations** Diffusion from high concentration to low concentration is due to the difference of hydrogen ion and chloride mobility. The hydrogen ion with higher speed will be accumulated more on the right side. Thus the right side possesses a positive potential while the left is negative. When this phenomenon appears, the transfer speed of hydrogen ion will slow down while that of chloride will speed up. As a result a balance is obtained. The liquid junction potential can be described as follows:

$$E = -\frac{RT}{ZF} \cdot \frac{U^+ - U^-}{U^+ + U^-} \ln \frac{C_1}{C_2}$$

where  $C_1$ ,  $C_2$  represents the two concentrations,  $U^+$  and  $U^-$  is the ionic mobility of cations and anions.

**Same concentration with different electrolytes** This shows the condition of same concentration with different electrolytes except a common ion. Due to the similar electrolyte concentration of both sides, chloride is regarded motionless while hydrogen ions diffuse to the left and potassium ions diffuse to the right. The speed of hydrogen is larger than that of potassium. So the left obtains positive charge while the right obtains negative ones.

## (2) How to Eliminate It?

To eliminate the liquid junction potential, salt bridge is inserted between the two solutions as shown in Figure 2.

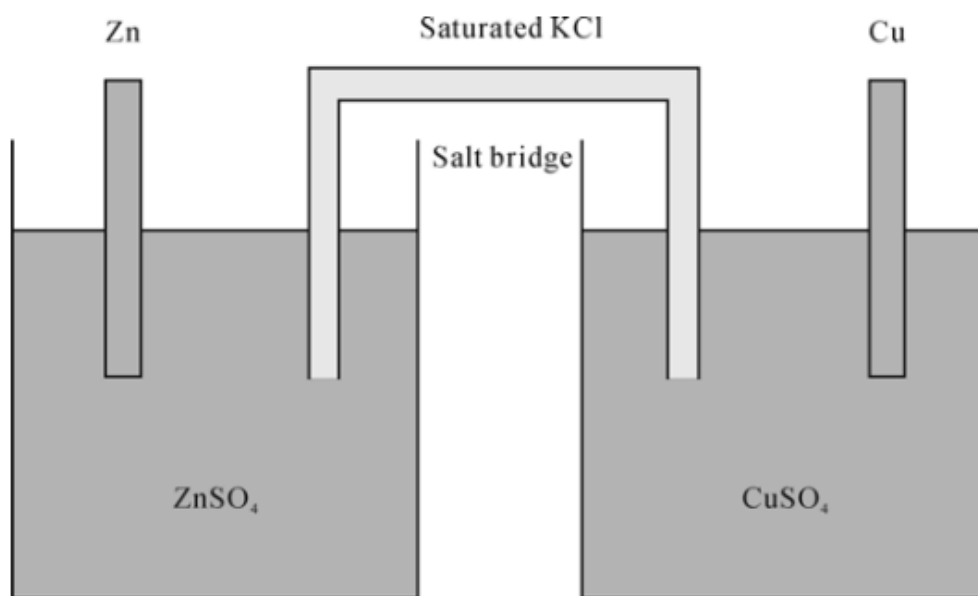


图 2: Salt bridge for eliminating liquid junction potential

The solution in salt bridge normally is saturated potassium chloride. Due to the high concentration, ions in the salt bridge will diffuse to both sides. And there is no much difference between the speeds of potassium and chloride ions, thus the liquid junction potential is pretty small, which is only several millivolts. The requirements of the solution in salt bridge are high concentration, the speeds of anode and cathode are similar, and it has no chemical reaction with the electrolyte.

### 3. Generation Process of Electrode Potential and Diffusion Layer

#### (1) Generation of Electrode Potential

The generation of electrode potential occurs when an electrode is submerged in an electrolyte solution, leading to chemical reactions at the interface between the electrode and the electrolyte.

##### **Process (Example: Zinc electrode in Zinc Sulfate):**

- (1) If the chemical potential of zinc atoms in the electrode is greater than that of zinc ions in the electrolyte, zinc atoms from the electrode lattice will tend to depart into the solution as zinc ions ( $\text{Zn}^{2+}$ ).
- (2) This process leaves behind excess electrons on the electrode surface, making the electrode negatively charged.
- (3) Conversely, the positively charged zinc ions entering the solution will accumulate near the electrode surface, forming a layer of counter-ions.
- (4) This separation of charge creates a **double electrode layer** at the interface, which in turn generates a potential difference. This generated potential obstructs further motion of zinc ions into the solution.
- (5) At equilibrium, a narrow potential difference is established at the interface, known as the **equilibrium electrode potential**. The magnitude and polarity of this potential depend on the type of electrode material and the concentration of metal ions in the solution.

#### (2) Generation Process of Diffusion Layer

The diffusion layer is a component of the interface potential distribution that arises from the interaction of ion thermal motion and static electricity when an electrode is submerged in an electrolyte.

##### **Process:**

- (1) When charge separation occurs at the electrode-electrolyte interface (leading to the formation of the double electrode layer), the leftover charge on the electrode surface attracts counter-ions from the solution.
- (2) These counter-ions arrange themselves into distinct layers:
  - **Compact Layer (Helmholtz Layer):** A layer of ions that are strongly adsorbed and directly attached to the electrode surface, typically with a thickness comparable to the ionic radius of the hydration layer.
  - **Diffusion Layer (Gouy-Chapman Layer):** Beyond the compact layer, ions are still influenced by the electrode's charge, but their distribution is less rigid due to thermal motion. This layer shows an exponential decay of potential with increasing distance from the electrode surface.
- (3) The combination of the compact layer and the diffusion layer forms the overall electrical double layer. The diffusion layer's magnitude and polarity significantly influence electrode reactions and depend on factors like solution characteristics, ion concentration, and active substance adhesion at the interface.

#### 4. Kinds of Electrodes and Reference Electrode

##### (1) Classification of Electrodes

According to the role of electrodes playing in the electrochemical measurement, they can be classified as indicator electrode, working electrode, reference electrode, and auxiliary electrode.

**Indicator electrode** Indicator electrode serves as a transducer responding to the excitation signal and to the composition of the solution being investigated, but that does not affect an appreciable change of bulk composition within the ordinary duration of a measurement. The most commonly used indicator electrode includes ion-selective electrode, gas-sensing electrode, and bioelectrode.

The simplest type of direct indicator electrode is a metal, M, in contact with a solution containing its own cation,  $M^+$ . At the metal-solution interface, a potential develops that is proportional to the activity of the metal ion in solution. The potential can be measured directly with respect to a reference electrode using the simple arrangement shown in Figure 3.

The voltage measured is simply the difference between the potential at each electrode:

$$E_{cell} = E_{indicator} - E_{reference}$$

Inert metal electrodes like Pt or Au can be used as indicator electrodes for ions involved in redox reactions that occur in solution but do not include the metallic form of the analyte.

**Working electrode** Working electrode serves as a transducer responding to the excitation signal and the concentration of the substance of interest in the solution being investigated, and which permits the flow of current sufficiently large to effect appreciable changes of bulk composition within the ordinary duration of a measurement. The working electrode represents the most important component of an electrochemical cell. It is at the interface between the working electrode and the solution that electron transfers of greatest interest occur. The most commonly used working electrode includes hanging mercury electrode, mercury thin-film electrode, glassy carbon electrode, graphite electrode and metal electrode such as gold electrode, platinum electrode and copper electrode.

**Reference electrode** A reference electrode is used in measuring the working electrode potential of an electrochemical cell. It should be constructed using half-cell components that are stable over time and with changing temperature, present at well-defined values of activity and should possess fixed, reproducible electrode potentials. The most common reference electrode is standard hydrogen electrode, which compose of an inert solid like platinum on which hydrogen gas is adsorbed, immersed in a solution containing hydrogen ions at unit activity.

Practical application of the standard hydrogen electrode is limited by the difficulties in preparing solutions containing  $H^+$  at unit activity and maintaining unit activity for  $H_2$  (g) in the half-cell. Most experiments carried out in aqueous solutions utilize one of two other common reference half-cells: saturated calomel electrode or silver-silver chloride electrode ( $Ag/AgCl$ ) as shown in Figure 4.

**Auxiliary electrode (Counter electrode)** The purpose of the auxiliary electrode is to provide a pathway for current to flow in the electrochemical cell without passing significant current through the reference electrode. There are no specific material requirements for the electrode beyond it not

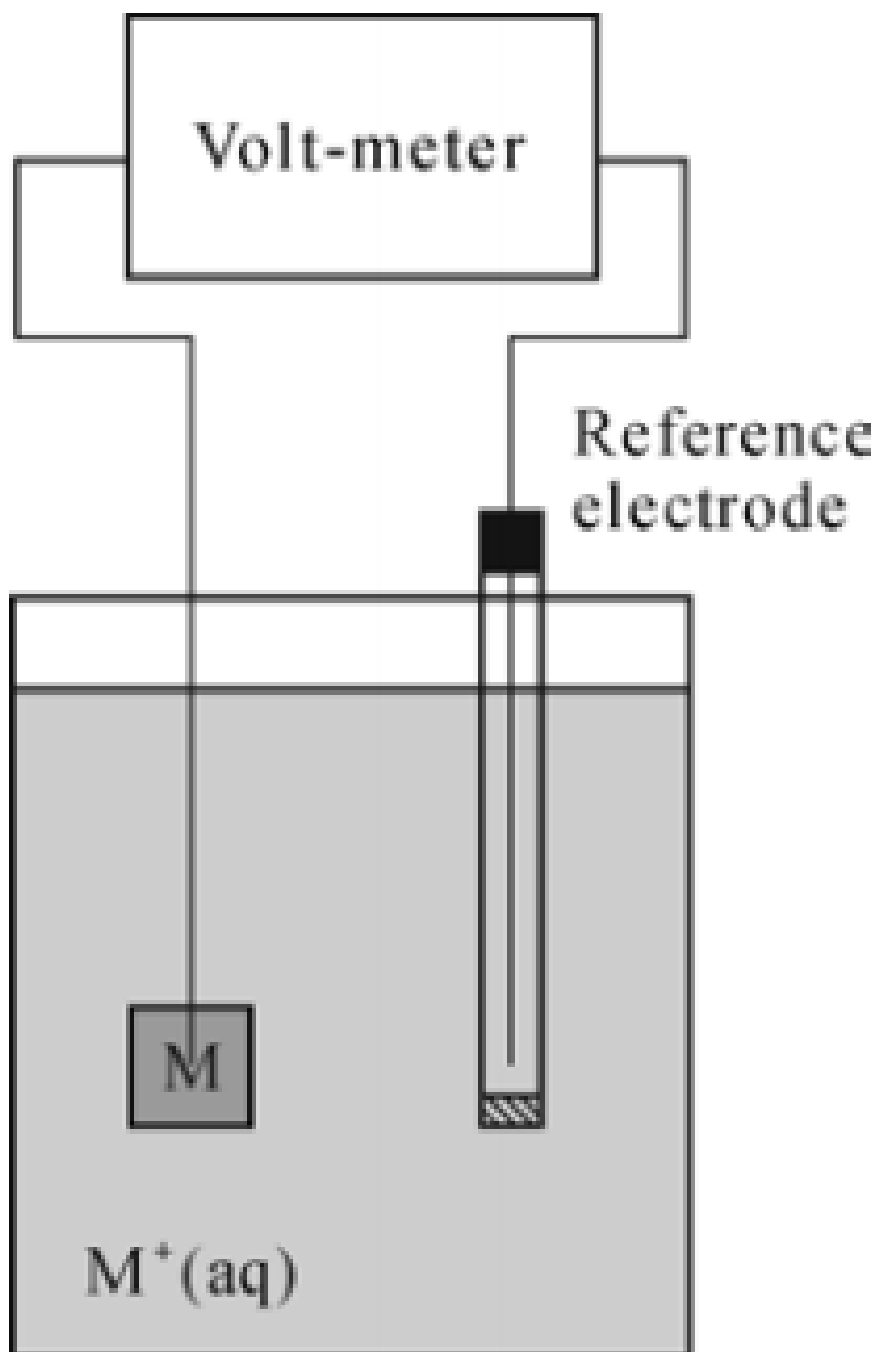


图 3: Electrochemical cell for a potentiometric measurement with a metallic indicator electrode

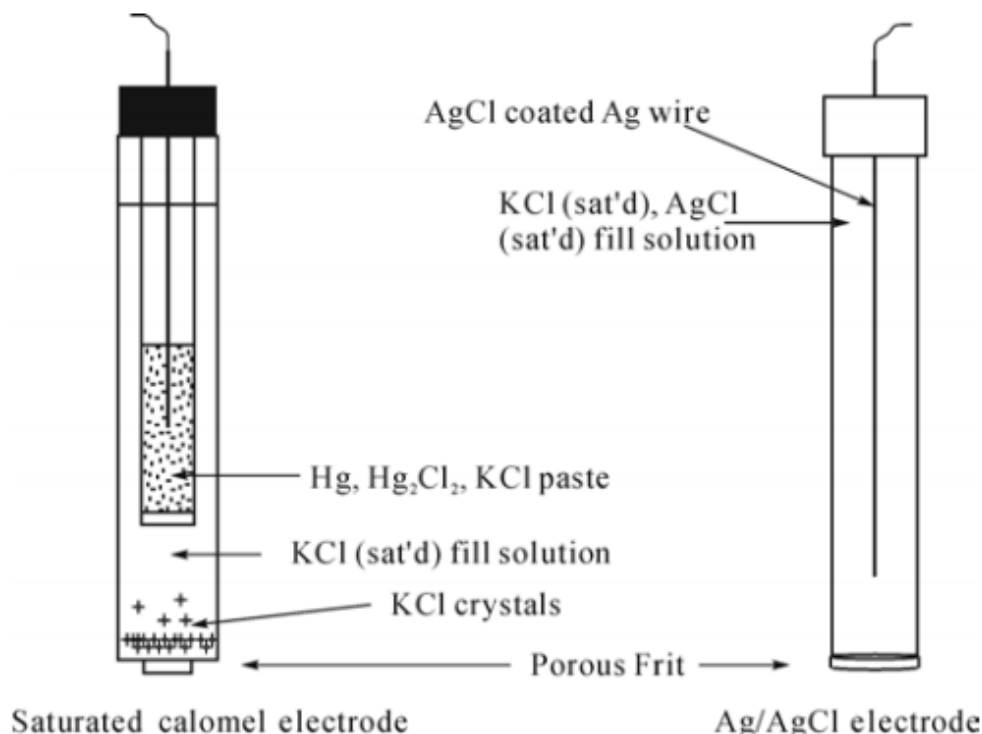


图 4: Schematic of saturated calomel electrode and Ag/AgCl electrode

adversely influencing reactions occurring at the working electrode. Remember that if a reduction occurs at the working electrode, there must be an oxidation that takes place at the auxiliary electrode. Care should be taken that electrode products formed at the auxiliary electrode do not interfere with the working electrode reaction. The auxiliary electrode can be physically separated from the working electrode compartment using a fritted tube, but one should be aware that under certain circumstances this can have a deleterious effect.

The most commonly used material for the auxiliary electrode is platinum, due to its inertness and the speed with which most electrode reactions occur at its surface. Other less expensive materials may also be used as auxiliary electrodes. Choices include carbon, copper, or stainless steel if corrosion is not an issue for a particular electrolyte solution or reaction.

## (2) Structure and Function of Reference Electrode

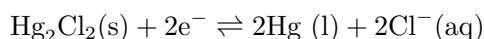
**Function of Reference Electrode** The primary function of a reference electrode is to provide a stable and well-defined potential against which the potential of an indicator or working electrode can be measured. Because a single electrode potential cannot be measured directly, a reference electrode with a defined zero potential (or a known fixed potential) is crucial for determining the potential of other electrodes.

**Structure of Common Reference Electrodes** Two of the most common and practical reference electrodes are the Saturated Calomel Electrode (SCE) and the Silver-Silver Chloride (Ag/AgCl) Electrode.



**(1) Saturated Calomel Electrode (SCE):**

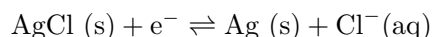
- **Structure:** The SCE typically consists of a mercury (Hg) electrode in contact with a paste of mercury(I) chloride (calomel,  $\text{Hg}_2\text{Cl}_2$ ) and saturated potassium chloride (KCl) solution. This inner assembly is usually housed within a glass tube that has a porous plug or frit at its lower end to allow contact with the external analyte solution via a liquid junction.
- **Electrode Reaction:** The half-cell reaction is:



- **Potential Stability:** The potential of the SCE is stable because it is determined by the concentration of chloride ions, which is kept constant by using a saturated KCl solution.

**(2) Silver-Silver Chloride (Ag/AgCl) Electrode:**

- **Structure:** This electrode consists of a silver (Ag) wire coated with silver chloride (AgCl). The Ag/AgCl wire is immersed in a solution containing a known concentration of chloride ions (e.g., saturated KCl or 3.5 M KCl). Similar to the SCE, it often has a porous frit for contact with the external solution.
- **Electrode Reaction:** The half-cell reaction is:



- **Potential Stability:** The potential is stable because the concentration of chloride ions is constant, and AgCl is sparingly soluble.

Both SCE and Ag/AgCl electrodes provide stable and reproducible potentials, making them ideal for use as reference electrodes in various electrochemical measurements.

**5. Steps of Your Thinking on How to Monitor Air Quality in a Room**

Monitoring air quality in a room involves identifying and quantifying common indoor pollutants. Here's a thought process for designing such a system:

**(1) Identify Key Pollutants:**

- **Particulate Matter (PM2.5/PM10):** Dust, pollen, smoke, aerosols.
- **Volatile Organic Compounds (VOCs):** From paints, furniture, cleaning products, cooking. Common examples: formaldehyde, benzene, toluene.
- **Carbon Dioxide (CO2):** Indicator of ventilation, human occupancy.
- **Carbon Monoxide (CO):** From incomplete combustion (e.g., faulty gas appliances).
- **Humidity:** Affects comfort and mold growth.
- **Temperature:** Basic comfort parameter.

**(2) Select Appropriate Sensors for Each Pollutant:**

- **PM2.5/PM10:** Optical dust sensors (e.g., based on light scattering).

- **VOCs:** Semiconductor gas sensors (e.g., SnO<sub>2</sub>-based MOS sensors). These are sensitive to a range of VOCs and reducing gases. For more specific VOCs like formaldehyde, specialized electrochemical or optical sensors might be needed.
- **CO<sub>2</sub>:** Solid electrolyte gas sensors (e.g., NASICON-based) or NDIR (Non-Dispersive Infrared) sensors.
- **CO:** Electrochemical gas sensors (e.g., 3-electrode fuel cell type) or specialized MOS sensors.
- **Humidity:** Capacitive humidity sensors (based on dielectric changes due to water vapor uptake) or resistive humidity sensors (based on impedance changes of a hygroscopic medium).
- **Temperature:** Thermistors (NTC/PTC) or integrated temperature sensors (e.g., diode-based).

### (3) Consider Sensor Array and Data Processing:

- **Sensor Array:** A single sensor array, akin to an "electronic nose", can be designed. This involves using multiple gas sensors with differing selectivities. While each sensor might be sensitive to several volatile molecules, they will react in their specific way.
- **Pattern Recognition:** Since individual sensors often have cross-sensitivity, a sophisticated pattern recognition system is crucial. This system would analyze the unique "fingerprint" of electrical signals from the array. Techniques like Principal Component Analysis (PCA) for dimension reduction and Artificial Neural Networks (ANN) for classification can be used. ANNs learn to identify different odors or gas mixtures by example.
- **Microcontroller/Microprocessor:** A central processing unit (MCU/DSP) will collect data from all sensors, perform necessary calculations (e.g., unit conversions, linearizations), and execute the pattern recognition algorithms.

### (4) Hardware Architecture:

- **Sensor Interface Circuits:** Each sensor will require a specific interface circuit (e.g., Wheatstone bridge for resistance changes, current-voltage converters, amplifiers) to convert non-electrical signals into electrical signals suitable for the MCU.
- **Signal Pre-processing:** This includes amplification, filtering (e.g., low-pass filters to remove noise), and Analog-to-Digital Conversion (ADC) to prepare analog sensor outputs for digital processing by the MCU.
- **Power Supply:** A stable power supply for all components. For a room monitor, a mains power adapter would be suitable, possibly with a small battery backup.
- **Display/Output:** A simple LCD or LED display to show real-time air quality readings (e.g., numerical values, color-coded indicators for air quality levels), or a wireless module (e.g., Wi-Fi, Bluetooth) to send data to a smartphone app or cloud platform for remote monitoring.

### (5) Software and Algorithms:

- **Sensor Data Acquisition Firmware:** Code running on the MCU to interface with sensors, read data, and perform initial processing (e.g., debouncing, basic scaling).

- **Calibration:** Periodically calibrate sensors (e.g., against known gas concentrations) to maintain accuracy. Software can store calibration curves or compensation parameters.
- **Environmental Compensation:** Implement algorithms to compensate for temperature and humidity effects on gas sensor readings, as many gas sensors are temperature-dependent.
- **Alerting System:** Define thresholds for each pollutant. If a pollutant exceeds its threshold, trigger an alarm (e.g., sound buzzer, change display color, send notification).
- **Data Logging:** Store historical data (e.g., on an SD card or internal memory) for analysis and trend tracking.

(6) **Physical Design and Placement:**

- **Enclosure:** Design a compact and aesthetically pleasing enclosure that allows for proper air circulation to the sensors.
- **Placement:** Position the device in a central location in the room, away from direct drafts, heat sources, or windows, to get a representative reading of the room's air quality.

By following these steps, a comprehensive and effective system for monitoring room air quality can be designed.

## 6. Relative Humidity and Absolute Humidity. How to Detect Them?

(1) Humidity Sensors

Humidity and temperature are the most frequently measured physical quantities in measurement science. Whereas the measurement of temperature can nowadays be done with a satisfactory accuracy, measurement of the water vapour content of gaseous atmosphere, i.e. hygrometry, appears much more complex. Water vapour is a natural component of air, and it plays an important role in a wide and various ranges of practical measurement situations. Today, different humidity sensors are developed for miscellaneous application. The requirements that humidity sensors must meet in order to satisfy a wide range of application are: (1) a good sensitivity over a wide range of both humidity and temperature, (2) a short response time, (3) a good reproducibility and a small hysteresis, (4) a good durability and long life, (5) resistance against contaminants, (6) negligible temperature dependence and (7) low cost.

In hygrometry, it is common to measure the relative humidity  $rh$  along with the temperature  $T$ . The  $rh$  is defined as:

$$rh = \frac{p_w}{p_s} \times 100\%$$

where  $p_w$  is the vapour pressure and  $p_s$  is the saturation pressure.

A parameter that is frequently measured is the dew point  $T_d$  ( $^{\circ}\text{C}$ ), i.e. the temperature and pressure at which gas begins to condense into liquid. Other ways to define the humidity are the absolute humidity ( $\text{g}/\text{m}^3$ ), the ratio with respect to the dry air, i.e. mixing ratio  $m_r$  (ppmv), and the deficit with respect to the saturation, i.e. saturation deficit  $p_{sd}$  (mbar). The vapour saturation pressure of water is plotted versus temperature as shown in Figure 5.

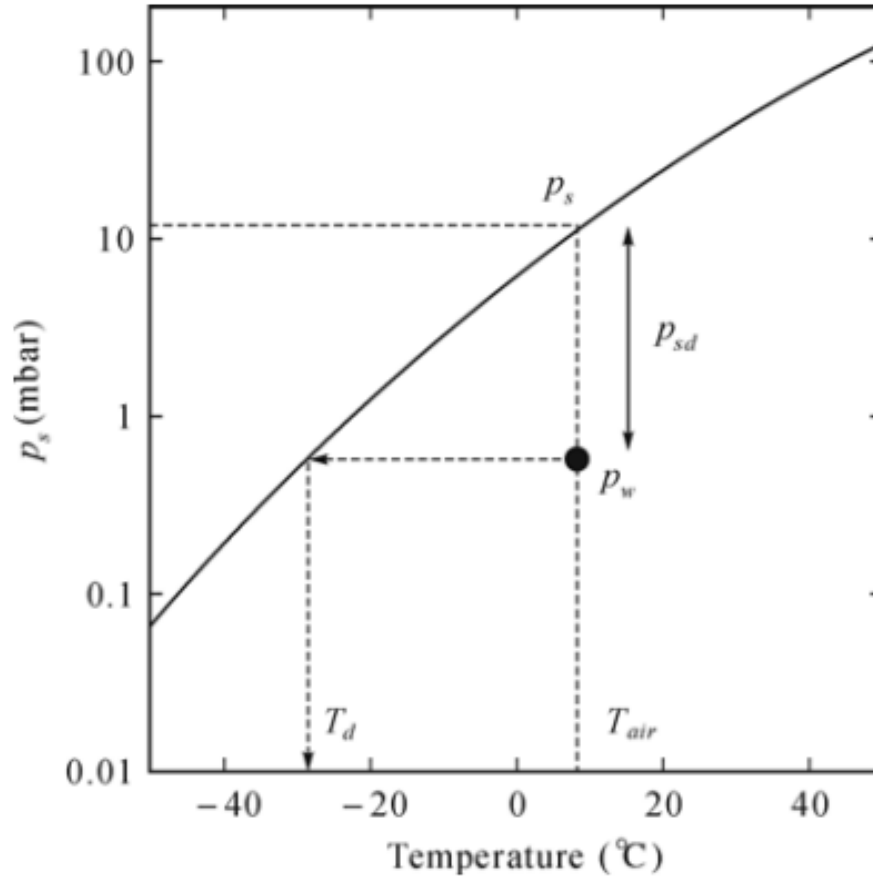


图 5: Water saturation pressure vs. temperature

## (2) Relative Humidity (RH)

- **Definition:** Relative humidity (RH) is defined as the ratio of the actual water vapor pressure ( $p_w$ ) to the saturation vapor pressure ( $p_s$ ) at a given temperature, expressed as a percentage:

$$\text{rh} = \frac{p_w}{p_s} \times 100\%$$

- **Meaning:** It indicates how close the air is to saturation with water vapor. At 100% RH, the air is fully saturated, and condensation may occur.

**Detection Method: Capacitive Humidity Sensors** Capacitive humidity sensors are based on dielectric changes caused by the water vapour uptake on thin films. The properties of these sensors are determined by the hygroscopic material and the electrode geometry. Electrode geometry allows the vapour to diffuse freely into the dielectric, e.g., interdigitated electrodes (IDE) are favourable for rapid responses, but a thin top electrode (typically 10–80 nm Au), will result in a more uniform field distribution.

A capacitive humidity sensor is actually a plate capacitor. A polymer layer is placed between a metal electrode and a coated glass substrate as shown in Figure 6.

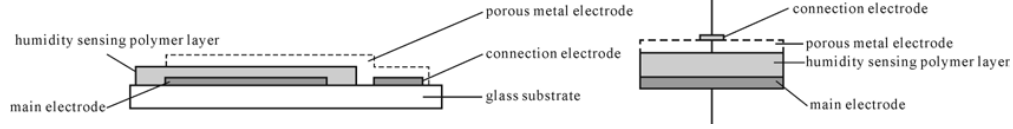


图 6: Schematic construction of a capacitive humidity sensor and its equivalent diagram

The dielectric permittivity of the polymer depends on its water content which can be written in complex number form:

$$\varepsilon_{rh} = \varepsilon'_{rh} - j\varepsilon''_{rh} = \varepsilon'_{rh} - j\frac{\sigma}{\omega}$$

where  $\varepsilon'_{rh}$  is the real part and  $\varepsilon''_{rh}$  is the dielectric loss factor. In a capacitive humidity sensor, change in dielectric permittivity is almost directly proportional to relative humidity in the environment. The sensor capacity at relative humidity rh can be described as:

$$C_{rh} = \frac{\varepsilon_0 \varepsilon_{rh} A}{d}$$

where  $\varepsilon_0$  is the permittivity of vacuum, A is the area of the electrodes, d is the distance between the electrodes.

**Detection Method: Resistive Humidity Sensors** Resistive humidity sensors measure the change in electrical impedance of a hygroscopic medium such as a conductive polymer, salt, or a treated substrate. The impedance change is typically an inverse exponential relationship to humidity. Resistive sensors usually consist of noble metal electrodes either deposited on a substrate by photoresist techniques or wire-wound electrodes on a plastic or glass cylinder. The substrate is coated with a salt or conductive polymer as shown in Figure 7.

The sensor absorbs water vapor and ionic functional groups are dissociated, resulting in an increase in electrical conductivity. There are three groups of materials: (1) ceramics, (2) polymers and (3) electrolytes.

An example of the electrolyte based humidity sensors is the LiCl dew point hygrometer fabricated with a composite of porous polymer and the salt as shown in Figure 8.

**Detection Method: Sling Psychrometer** This instrument contains two thermometers: a dry bulb (open to air) and a wet bulb (immersed in a wet cloth). Evaporation from the wet bulb causes it to cool, and the degree of cooling (the "wet bulb depression") is a function of the relative humidity. By rotating the psychrometer, the temperatures of both bulbs are read, and the RH can be determined from psychrometric charts or calculations based on the temperature difference.

### (3) Absolute Humidity (AH)

- **Definition:** Absolute humidity (AH) is the mass of water vapor present in a unit volume of moist air, typically expressed in grams per cubic meter ( $\text{g}/\text{m}^3$ ).
- **Meaning:** It represents the actual amount of water vapor, regardless of temperature.

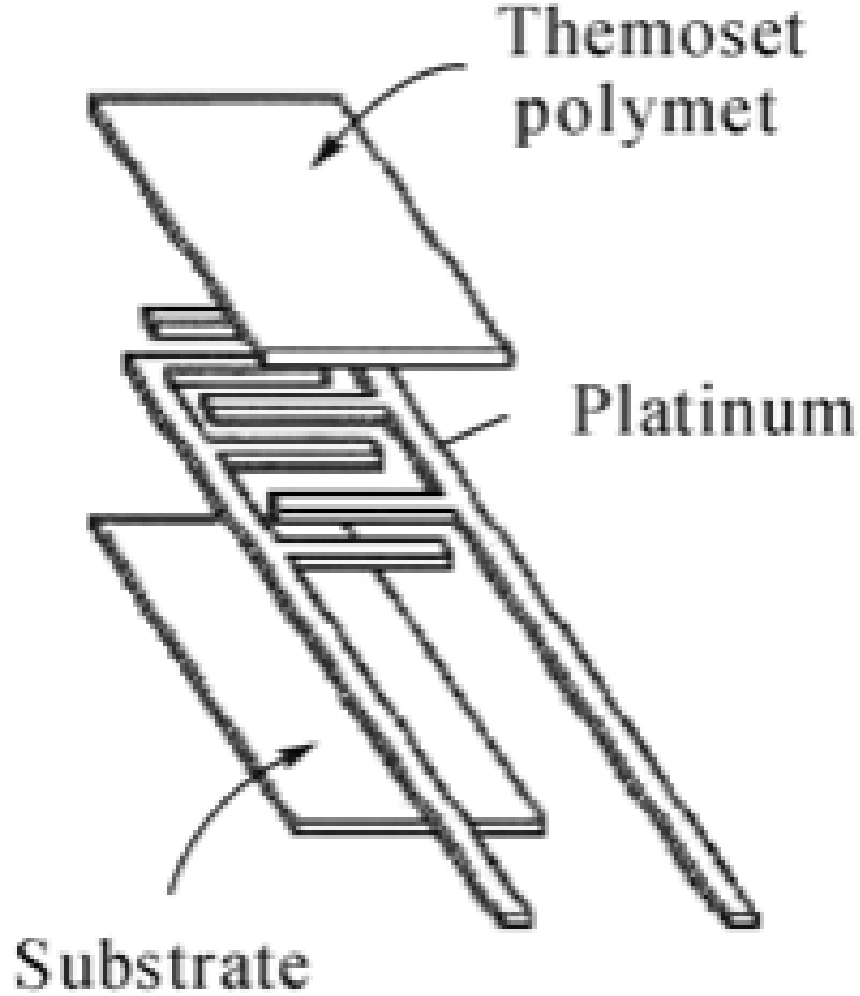


图 7: Typical resistive humidity sensor configuration consisting of polymer coated electrodes on a suitable substrate

**Detection Method: Thermal Conductivity Humidity Sensors** Thermal conductivity humidity sensors, also known as absolute humidity sensors, measure absolute humidity by calculating the difference between the thermal conductivity of dry air and air containing water vapor.

Thermal conductivity humidity sensors can be accomplished by a thermistor-based sensor. Two tiny thermistors ( $R_{t1}$  and  $R_{t2}$ ) are supported by thin wire to minimize thermal conductivity loss to the housing. The left thermistor is hermetically sealed in dry air. Both thermistors are connected into a bridge circuit ( $R_1$  and  $R_2$ ), which is powered by voltage  $E$  as shown in Figure 9.

The bridge output is given by:

$$V_{out} = E \left( \frac{R_1}{R_1 + R_{t1}} - \frac{R_2}{R_2 + R_{t2}} \right)$$

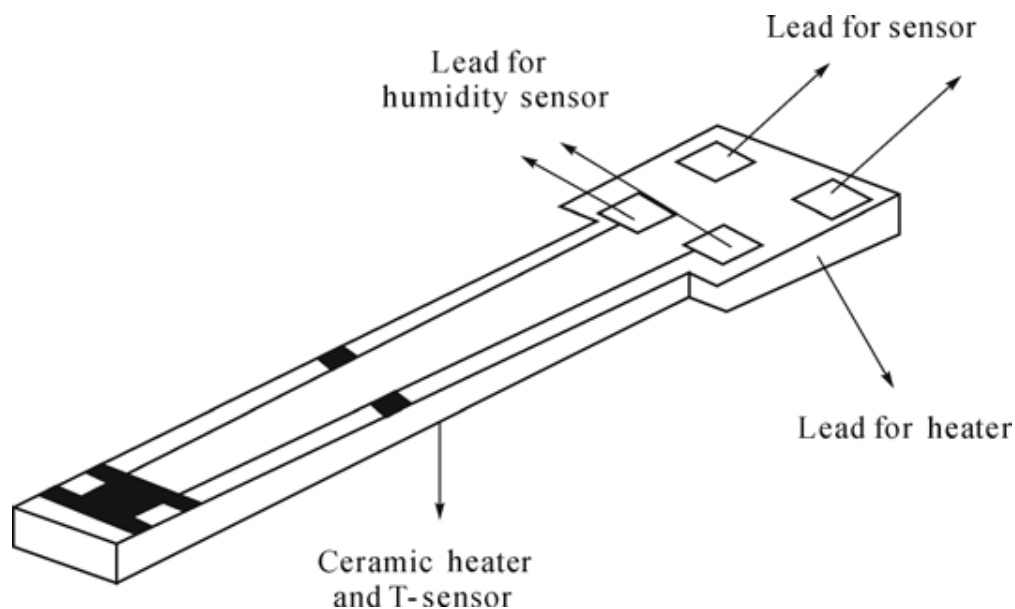


图 8: A prototype of the dew point hygrometer

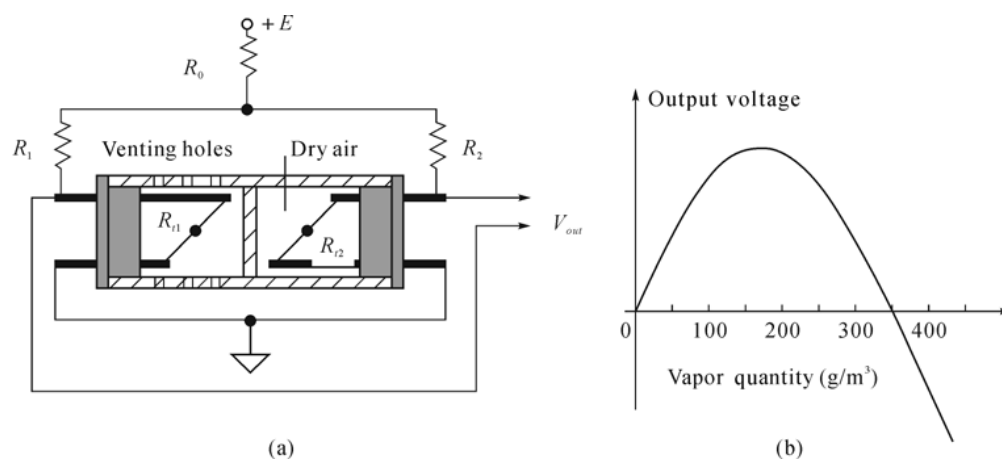


图 9: Absolute humidity sensor with self-heating thermistors: (A) design and electrical connection; (B) output voltage

The thermistors develop self heating due to the passage of electric current. Their temperature rises up to 170 °C over the ambient temperature. Initially, the bridge is balanced in dry air to establish a zero reference point. The output of this sensor gradually increases as absolute humidity rises from zero.

#### (4) Application Examples

Figure 10 shows relative humidity sensors that are based on the psychrometer principle.

The sensor consists of two thermistors (thermal resistors), one inside a sealed (dry) chamber and the other open to the air. Both thermistors are operated close to the self-heating point so that relatively small temperature changes create large resistance changes. When operated in a Wheatstone bridge

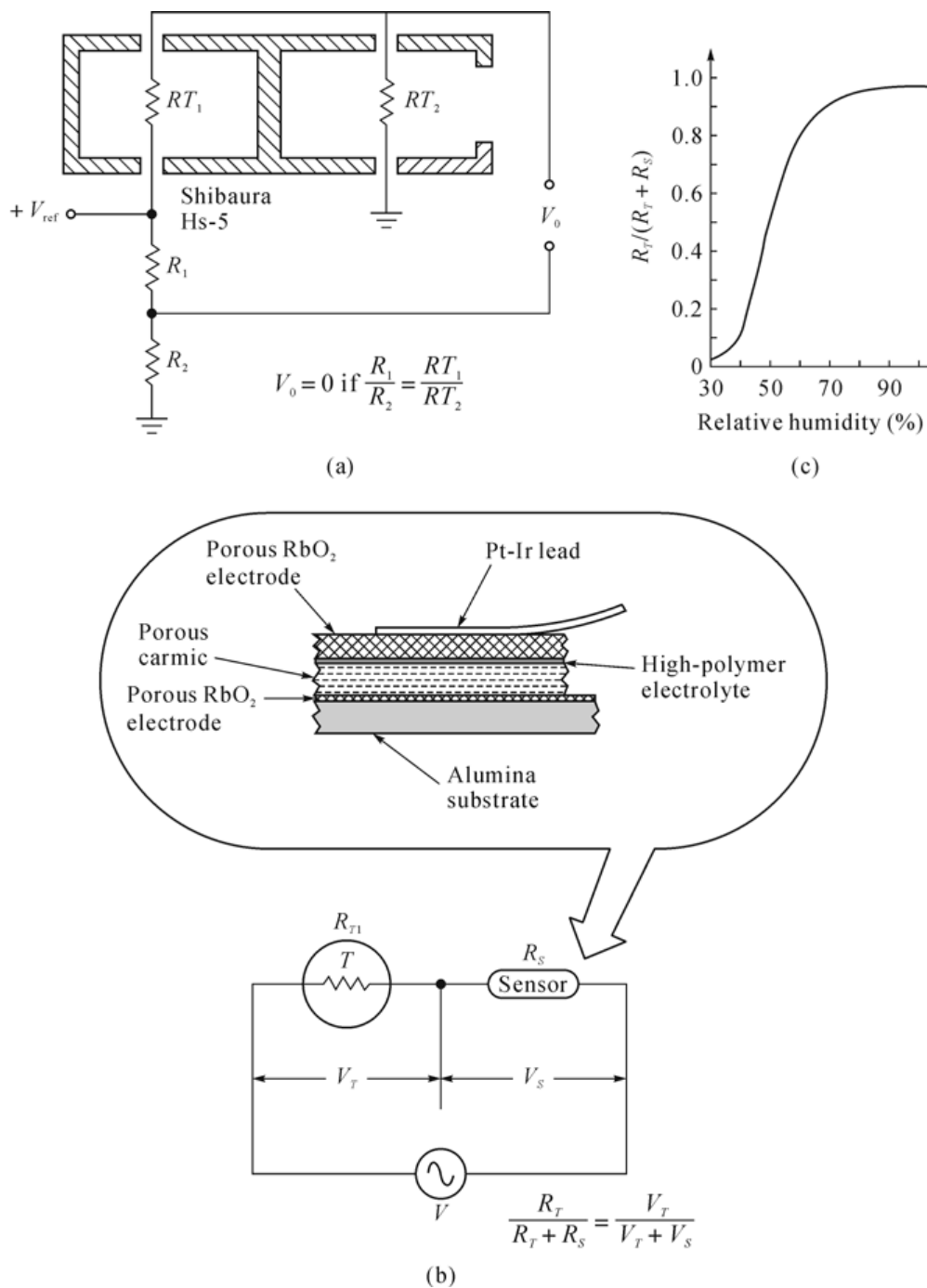


图 10: (a) Shibaura resistive relative humidity sensor; (b) Structure of the sensor element; (c) Calibration curve



configuration, the sensor will produce a voltage that can be used to determine the relative humidity.

In summary, relative humidity is a percentage indicating saturation, often detected by capacitive or resistive sensors. Absolute humidity measures the actual water vapor mass, typically detected by thermal conductivity sensors.

## 7. Similarity and Difference between Electronic Tongue and Electronic Nose

Electronic tongue (e-Tongue) and electronic nose (e-Nose) are both intelligent chemical sensor arrays designed to mimic biological sensory systems for qualitative and/or quantitative analysis. They share fundamental similarities in their architectural approach but differ significantly in their target analytes and specific applications.

### (1) Similarities

- (1) **Biomimicry:** Both e-Nose and e-Tongue are inspired by biological sensory organs –the human nose for e-Nose and the tongue/taste buds for e-Tongue. They aim to replicate the complex recognition and perception mechanisms of these biological systems.
- (2) **Multi-Sensor Array:** Both systems rely on an array of multiple chemical sensors, rather than a single sensor. This array provides a unique "fingerprint" or pattern of responses for a given sample, similar to how different receptors in biological systems respond to various stimuli.
- (3) **Cross-Sensitivity:** A key feature of both is the use of cross-sensitive sensors. Individual sensors in the array are not perfectly selective to a single substance but respond to a group of chemicals, and even to other chemicals of a different nature. This cross-sensitivity is crucial for generating complex patterns.
- (4) **Pattern Recognition System:** Both systems integrate a sophisticated computer-based pattern recognition system as their "brain". This system processes the raw electrical signals from the sensor array using intelligent algorithms (e.g., Principal Component Analysis, Artificial Neural Networks) to identify, distinguish, and quantify the samples. ANNs, for example, learn by example to identify various chemicals or odors.
- (5) **Application Areas:** Both find applications in quality control (food, beverage), environmental monitoring, and medical diagnosis, by analyzing complex mixtures.

### (2) Differences

The most obvious difference between e-Nose and e-Tongue is their target detection object.

In essence, while both e-Nose and e-Tongue represent intelligent sensor technologies employing multi-sensor arrays and advanced data processing, their fundamental distinction lies in whether they analyze **gaseous** or **liquid** samples to derive qualitative and quantitative information.

Feature	Electronic Nose (e-Nose)	Electronic Tongue (e-Tongue)
Target Analyte	Gases, vapors, or odors (volatile compounds)	Liquids (taste substances in solution)
Sensing Principle	Detection of volatile organic compounds (VOCs) in the air.	Detection of non-volatile taste substances dissolved in liquids.
Sensor Types	Primarily metal oxide semiconductors (MOS), conducting polymers (CP), quartz crystal microbalance (QCM), surface acoustic wave (SAW), field-effect transistors (MOSFET), electrochemical gas sensors.	Often utilize potentiometric sensors, such as PVC membrane sensors, chalcogenide glass membrane sensors, or Langmuir-Blodgett membrane sensors.
Sample Introduction	Utilizes pumps and sampling systems to bring gaseous samples to the sensor array.	Involves direct immersion of the sensor array into liquid samples.
Biological Analogy	Olfactory system (sense of smell).	Gustatory system (sense of taste).
Application Examples	Lung cancer diagnosis from breath, air quality monitoring, industrial process control, food spoilage detection.	Water pollution assessment, food quality assessment (e.g., distinguishing mineral water, beverages, wine, coffee), pharmaceutical analysis.

## 8. How to Drive the Micro Flow in a Microfluidic Chip?

### (1) Driving and Control of Micro Flow

The basis of a microfluidic chip operation is the technique for micro flow driving and control. Since the invention of the microfluidic chip, it has always been an important topic in the basic research field of microfluidic chip and new techniques and methods are progressively appearing. Here, we will briefly introduce two techniques for micro flow driving, which are electroosmotic driving and micropump driving. Also, two techniques for micro flow control will be introduced, which are electroosmotic control and microvalve control.

### (2) Electroosmotic Driving

At present, electroosmotic driving is one of the most widely used methods in micro flow driving. Its basic principle is using the fixed charges on the inner surface of microchannels to drive the micro flow. Its advantages include lack of mechanical components, simple configuration, convenient operation, flat flow, and no pulsation. However, this method is sensitive to the influences of external electrical fields, channel surface, properties of micro flow, and the effect of heat transfer. So, it is not so stable and can only be applied to electrolyte solutions.

Electroosmosis cannot only be used to directly drive the charged flow, but also can be used as the energy source of the micropump, which is called the electroosmotic pump. The method to achieve

this kind of electroosmotic pump is as follows: electrodes with certain intervals are fabricated on the surface of a chip basis by using lithography. Then it is sealed with PDMS microchannels to form a hermetic electroosmotic driving system. When it works, the voltage is applied to the electrodes to generate an electroosmotic flow. As the electroosmotic flow only exists between the two electrodes, the flow outside the two electrodes can be driven by the electroosmotic flow. Consequently, the function of the electroosmotic pump can be realized.

- **Principle:** Electroosmotic flow (EOF) utilizes the fixed charges on the inner surface of microchannels to drive the fluid. When an electric field is applied across a microchannel containing an electrolyte solution, ions in the electrical double layer near the channel walls are dragged by the field, in turn dragging the bulk fluid.
- **Mechanism:** The density and polarity of charges on the inner surface of microchannels determine the velocity and direction of the electroosmotic flow. By modifying the surface properties (e.g., coating with polyelectrolyte layers), the flow direction can be changed, enabling complex flow operations.
- **Advantages:**
  - Lack of mechanical components, leading to simple configuration and convenient operation.
  - Produces flat flow profiles (plug flow) with no pulsation, which is beneficial for minimizing band broadening in separations.
  - Can be used to drive charged fluid directly or as the energy source for electroosmotic pumps.
- **Disadvantages:**
  - Sensitive to external electrical fields, channel surface properties, and micro flow properties.
  - Less stable and primarily applicable to electrolyte solutions.
  - Affected by heat transfer effects.

### (3) Micropump Driving

Pneumatic micropump in the mechanical driving system is composed of multiple pneumatic microvalves. When the pressure is applied, PDMS thin film deformed under the effect of gas pressure, leading to the block of channel and the closing of the valve. When there is no pressure applied, the restitution of the PDMS thin film can be achieved by its own elastic force, thus the channel becomes unobstructed and the valve sits open. By the sequential control of the opening and closing of three valves, the driving of micro flow can be obtained.

Micropumps are mechanical components designed to actively move fluids within microfluidic systems. They often involve a movable membrane or other mechanical elements.

- **Principle:** Micropumps generate fluid movement through mechanical actuation, similar to macroscopic pumps.
- **Mechanism (Example: Pneumatic Micropump):**
  - These pumps are typically composed of multiple pneumatic microvalves.

- When pressure is applied (e.g., air pressure), a flexible membrane (e.g., PDMS thin film) deforms, blocking the channel and closing the valve.
  - When pressure is released, the membrane restitutes due to its elasticity, opening the channel.
  - By sequentially controlling the opening and closing of three such valves, a pumping action can be achieved, driving the micro fluid in a desired direction.
- **Advantages:** Can handle a wider range of fluids (including non-electrolytes) and potentially provide higher flow rates or pressures compared to electroosmotic methods.
  - **Disadvantages:** Involves mechanical components, which can be more complex to fabricate and integrate, and may be prone to wear or leakage over time.

#### (4) Micro Flow Control Methods

Micro flow control is the central principle of microfluidic chip operations. It is related to almost all the processes such as sampling, mixing, reaction, and separation, which are necessary to be finished in the controllable flow. Valve is the central component for flow control both in macro and micro scale. Due to its importance, microvalve has been deeply studied before the invention of the microfluidic chip. In the primary stage of its development, microfluidic chips are normally a kind of capillary electrophoresis on a chip, which is dependent on the electroosmotic driving. So, until now, electroosmotic driving is still the most widely used technique for micro flow control.

**Electroosmotic Control** Electroosmosis is a type of phenomenon that the solution in the microchannel can move in the desired direction along the inner surface of the channel under the effect of the electrical field. It has been widely used in micro flow control. Compared to other types of micropumps, the most important feature of electroosmotic valves is their simple and flexible operation. The velocity and direction of flow can be controlled by adjusting the voltage applied to different nodes of the microchannel. Consequently, operations such as complex mixing, reaction, and separation can be realized. Besides the voltage, electroosmotic microvalves can be affected by such factors as the chemical composition of channel surface, ingredients of buffer solution, and temperature.

Besides driving the flow, electroosmosis can be used for precise flow control. The velocity and direction of flow can be adjusted by varying the voltage applied to different nodes of the microchannel. This allows for complex operations like mixing and separation.

**Microvalve Control** There are various kinds of microvalves. Theoretically, all components that can control the opening and closing of the channel can be used as microvalves in microfluidic chips. An ideal microvalve can be characterized as follows: low leakage, low energy consuming, fast responses, linear operation, and wide range of adaptation. According to the necessity of the excitation source during microvalve operations, microvalves can be classified into passive valves and active valves.

Microvalves are fundamental components for flow control. They can be passive (e.g., one-way valves that allow flow in only one direction based on pressure differentials) or active (requiring an external excitation source for opening and closing).

**Channel Structure and Surface Modification** In addition, the structure of channel, surface modification of the chip, laminar flow, and the effect of diffusion also play an important role in micro flow control. The physical design of the microchannels (e.g., serpentine, zigzag patterns) and chemical modification of their inner surfaces (e.g., creating hydrophobic/hydrophilic regions) can influence flow patterns, enhance mixing through chaotic advection, or achieve flow limitations.

**Laminar Flow and Diffusion** At the micro scale, flows are typically laminar (low Reynolds number), meaning fluids move in parallel layers without turbulent mixing. Mixing primarily relies on molecular diffusion. To improve mixing efficiency, principles like extending flow shear (to increase contact area) and splitting/recombining fluid streams (to reduce diffusion distance) are employed.

#### (5) Sample Introduction and Pretreatment

Sample introduction is the first step of microfluidic chip analysis. It includes the process of sampling from the analysis object and the introduction of sample into the microchannel for sample handling. Before detection, a series of pretreatment and reaction steps are necessary to be done to the sample, such as pre-separation, pre-concentration, and dilution.

Currently, in most microfluidic analysis systems, sample, reagent, and buffer solution are stored in a well type storage chamber located on the chip. Sample introduction methods usually add the sample to the well type storage chamber manually or automatically. Then the sample is imported into the channel for pretreatment or directly separated and analyzed.

A commonly used method is to set an auxiliary channel on the chip, which is perpendicular to the sample processing channel. The sample zone can be generated in the cross of the two channels. This method is called the single channel aid sample introduction. It includes two steps, loading and sampling. Loading refers to the process of sample load to the auxiliary channel through a storage chamber and is filled within the cross of channels. Sampling is the process of introducing the sample that is located in the cross to the sample processing channel by electrical forces or pressure.

Sample for microfluidic analysis systems are usually related to the biological sample containing complex composition. So, the techniques for sample pretreatment are very important, which often include sample pre-separation and pre-concentration. Pre-separation includes liquid-liquid extraction, solid phase extraction, filtration, chromatography, and membrane separation. Pre-concentration includes isoelectric focusing, isotachopheresis, and field amplified stacking.

#### (6) Micro Mixer, Reactor and Separator

Reaction is the central process of chemical and biological experiments. Also mixing and separation are necessary for the process of reaction, especially in the micro scale. So, micro mixer, reactor, and separator are important components of microfluidic chips.

**Micro Mixer** Micro mixer is very useful in the biological process that requires rapid responses such as the hybridization of DNA, cell activation, enzyme reaction, and protein folders. In microfluidic systems, the size of the channels is in the micrometer scale. The velocity of the solution is usually low and the solution mixing is mainly based on the mechanisms of laminar flow, which can be greatly influenced by the molecular diffusion. In order to improve the efficiency of laminar flow mixing, some

principles should be followed: (1) extending the flow shear to increase the contact area of solution; (2) splitting and recombining the solution by the utilization of distributed mixing design, consequently reducing the solution thickness to realize more efficient mixing.

**Micro Reactor** Micro reaction technique is the application of micro structure advantages to the process of chemical reaction. Micro reactor is a mini chemical reaction system with unit reaction interface in a micrometer scale. Its basic features include a small linear scale, high physical quality gradient, high surface to volume ratio, and low Reynolds number. Also, by its parallel units, a micro reactor can realize flexible and scale up production, and rapid and high throughput screening.

**Micro Separator** Recently, great progress has been achieved in the micro separation techniques. Now, various chromatography and electrophoresis separation modes can be realized on chips. Micro separator has become one of the fastest developing and maximum maturity technical units, which has greatly advanced the integration trends of microfluidic chips. Taking the integrated capillary electrophoresis chip as an example, microchannels and other functional units can be etched on the chip in a few centimeter square areas using micro processing technology. Consequently, a micro analysis device integrated with functions of sample introduction, separation, reaction, and detection can be realized, which is characterized with rapid, high efficiency, low sample consuming, low cost, and portability.

In essence, microfluidic chips leverage a combination of electrokinetic phenomena and miniature mechanical devices to precisely manipulate fluids, enabling complex laboratory functions on a miniaturized scale.

# 浙江大学实验报告

专业： 生物医学工程  
姓名： \_\_\_\_\_  
学号： \_\_\_\_\_  
日期： 2025 年 5 月 25 日  
地点： \_\_\_\_\_

课程名称： 生物医学传感与检测 指导老师： 张芬妮 成绩： \_\_\_\_\_  
实验名称： 化学传感器 实验类型： \_\_\_\_\_ 同组学生姓名： \_\_\_\_\_

## 1. 两种化学传感器的原理

### (1) 化学传感器的定义

Wolfbeis 在 1990 年对化学传感器的定义如下：化学传感器是由识别元件、转换元件和信号处理器组成的小型器件，能够连续且可逆地报告化学浓度。上述描述是实用性的，而 IUPAC（国际纯粹与应用化学联合会）在 1991 年的定义是通用的：化学传感器是一种将化学信息（从特定样品组分的浓度到总组成分析）转换为分析有用信号的器件。作为一种分析器件，化学传感器非常有效，能够在干扰物质存在的情况下检测目标分子。这种传感原理如图 1 所示。

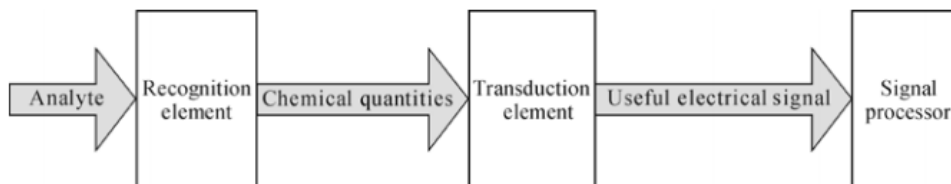


图 1: 化学传感器的传感原理

根据这些定义，以下是两种常见化学传感器的原理：

### (2) 离子选择性电极（ISE）传感器

- **定义：** ISE 是一种电分析传感器，其膜电位指示溶液中特定离子的活度。
- **原理：** ISE 的核心是与目标离子相互作用的选择性膜。当被测离子（待测离子）的电荷数为  $z$  时，影响膜电位的值由下式给出：

$$\Delta\phi_M = \frac{RT}{zF} \ln \left( \frac{\alpha_x}{\alpha_{x0}} \right)$$

其中  $R$  是气体常数， $T$  是绝对温度， $F$  是法拉第常数， $\alpha_x$  和  $\alpha_{x0}$  分别是分析溶液和内参比溶液中  $x$  的活度。这种相互作用在膜两侧产生电位差，然后与稳定的参比电极进行测量。电池的总电动势（EMF）是参比电极电位与膜电位的差值。

- **机理：** 膜电位受目标离子浓度的影响。例如，在 pH 玻璃电极中，薄玻璃膜对  $H^+$  浓度产生响应。

### (3) 半导体气体传感器

- **定义：**这些传感器利用半导体材料在暴露于特定气体时电导率的变化。
- **原理：**工作原理基于能带理论，描述目标气体与金属氧化物薄膜表面的相互作用如何改变材料的载流子浓度。
- **机理：**
  - **吸附/脱附：**气体分子（通常通过表面吸附的氧离子）与半导体材料表面相互作用，导致吸附或脱附。
  - **电导率变化：**这种相互作用引起半导体内载流子（电子或空穴）浓度的变化。
  - 对于 n 型半导体（多数载流子为电子），与还原性气体的相互作用增加电导率，而氧化性气体则降低电导率。
  - 对于 p 型半导体（多数载流子为正空穴），氧化性气体增加电导率，还原性气体降低电导率。
  - 这种电导率（或电阻率）的变化然后被测量作为传感器的输出。
- **例子：**SnO<sub>2</sub>（二氧化锡）半导体气体传感器被广泛使用，其中表面氧吸附使电阻很高。当还原性气体与氧反应时，电阻下降。

## 2. 液接电位及其消除方法

### (1) 什么是液接电位？

液接电位是由离子从多孔膜的一侧扩散到另一侧而产生的。不同离子具有不同的扩散速度，在两种溶液的界面处会产生正负电荷的电双分子层。由离子转移在界面处引起的电位差称为液接电位。

液接电位的主要原因如下：

**相同溶液，不同浓度** 从高浓度向低浓度的扩散是由于氢离子和氯离子迁移率的差异。具有较高速度的氢离子将在右侧积累更多。因此右侧具有正电位，而左侧为负电位。当这种现象出现时，氢离子的转移速度会减慢，而氯离子的速度会加快。结果达到平衡。液接电位可以描述如下：

$$E = -\frac{RT}{ZF} \cdot \frac{U^+ - U^-}{U^+ + U^-} \ln \frac{C_1}{C_2}$$

其中  $C_1$ 、 $C_2$  表示两种浓度， $U^+$  和  $U^-$  是阳离子和阴离子的离子迁移率。

**相同浓度，不同电解质** 这显示了除了一个共同离子外，相同浓度但不同电解质的情况。由于两侧电解质浓度相似，氯离子被认为是不动的，而氢离子向左扩散，钾离子向右扩散。氢的速度大于钾的速度。所以左侧获得正电荷，右侧获得负电荷。

### (2) 如何消除？

为了消除液接电位，在两种溶液之间插入盐桥，如图 2 所示。

盐桥中的溶液通常是饱和氯化钾。由于高浓度，盐桥中的离子会向两侧扩散。钾离子和氯离子的速度没有太大差异，因此液接电位很小，只有几毫伏。盐桥中溶液的要求是高浓度，阳极和阴极的速度相似，并且与电解质没有化学反应。



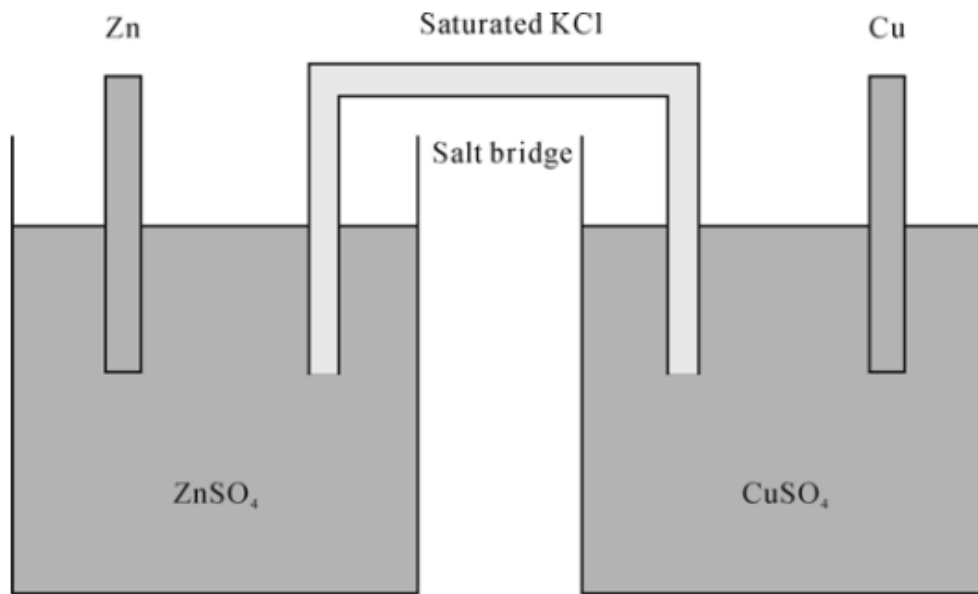


图 2: 用于消除液接电位的盐桥

### 3. 电极电位和扩散层的产生过程

#### (1) 电极电位的产生

当电极浸入电解质溶液中时，在电极与电解质的界面处发生化学反应，产生电极电位。

**过程（例子：锌电极在硫酸锌中）：**

- (1) 如果电极中锌原子的化学势大于电解质中锌离子的化学势，电极晶格中的锌原子将倾向于作为锌离子（ $\text{Zn}^{2+}$ ）离开进入溶液。
- (2) 这个过程在电极表面留下过量电子，使电极带负电。
- (3) 相反，进入溶液的带正电锌离子将在电极表面附近积累，形成反离子层。
- (4) 这种电荷分离在界面处产生**双电极层**，进而产生电位差。这个产生的电位阻碍锌离子进一步运动到溶液中。
- (5) 在平衡时，在界面处建立一个窄的电位差，称为**平衡电极电位**。这个电位的大小和极性取决于电极材料的类型和溶液中金属离子的浓度。

#### (2) 扩散层的产生过程

扩散层是当电极浸入电解质中时，由离子热运动和静电相互作用产生的界面电位分布的组成部分。

**过程：**

- (1) 当电极-电解质界面发生电荷分离（导致双电极层的形成）时，电极表面的剩余电荷吸引溶液中的反离子。
- (2) 这些反离子排列成不同的层：

- **紧密层 (Helmholtz 层):** 强烈吸附并直接附着在电极表面的离子层, 厚度通常与水合层的离子半径相当。
- **扩散层 (Gouy-Chapman 层):** 在紧密层之外, 离子仍受电极电荷影响, 但由于热运动, 它们的分布不那么刚性。这一层显示电位随距离电极表面距离增加而指数衰减。

(3) 紧密层和扩散层的组合形成整体电双分子层。扩散层的大小和极性显著影响电极反应, 取决于溶液特性、离子浓度和界面处活性物质吸附等因素。

#### 4. 电极的种类和参比电极

##### (1) 电极的分类

根据电极在电化学测量中所起的作用, 可以将其分类为指示电极、工作电极、参比电极和辅助电极。

**指示电极** 指示电极作为传感器响应激励信号和被研究溶液的组成, 但在普通测量持续时间内不会对整体组成产生明显变化。最常用的指示电极包括离子选择性电极、气敏电极和生物电极。

最简单的直接指示电极类型是金属 M 与含有其自身阳离子  $M^+$  的溶液接触。在金属-溶液界面, 产生与溶液中金属离子活度成正比的电位。可以使用图 3 所示的简单装置直接相对于参比电极测量电位。测量的电压简单地是每个电极电位的差值:

$$E_{\text{cell}} = E_{\text{indicator}} - E_{\text{reference}}$$

像 Pt 或 Au 这样的惰性金属电极可以用作涉及在溶液中发生但不包括分析物金属形式的氧化还原反应的离子的指示电极。

**工作电极** 工作电极作为传感器响应激励信号和被研究溶液中感兴趣物质的浓度, 并允许足够大的电流流动, 在普通测量持续时间内对整体组成产生明显变化。工作电极代表电化学电池最重要的组成部分。最感兴趣的电子转移发生在工作电极和溶液之间的界面处。最常用的工作电极包括悬汞电极、汞薄膜电极、玻碳电极、石墨电极和金属电极, 如金电极、铂电极和铜电极。

**参比电极** 参比电极用于测量电化学电池中工作电极的电位。它应该使用随时间和温度变化稳定的半电池组分构建, 以明确定义的活度值存在, 并应具有固定、可重现的电极电位。最常见的参比电极是标准氢电极, 由吸附氢气的惰性固体 (如铂) 组成, 浸入含有单位活度氢离子的溶液中。

标准氢电极的实际应用受到制备含有单位活度  $H^+$  的溶液和在半电池中维持  $H_2(g)$  单位活度的困难限制。在水溶液中进行的大多数实验使用两种其他常见参比半电池之一: 饱和甘汞电极或银-氯化银 ( $Ag/AgCl$ ) 电极, 如图 4 所示。

**辅助电极 (对电极)** 辅助电极的目的是为电化学电池中的电流流动提供路径, 而不通过参比电极传递显著电流。除了不对工作电极发生的反应产生不利影响外, 对电极没有特定的材料要求。请记住, 如果在工作电极发生还原, 则必须在辅助电极发生氧化。应注意在辅助电极形成的电极产物不会干扰工作电极反应。辅助电极可以使用烧结管与工作电极室物理分离, 但应注意在某些情况下这可能产生有害影响。

辅助电极最常用的材料是铂, 由于其惰性和大多数电极反应在其表面发生的速度。如果对于特定电解质溶液或反应腐蚀不是问题, 也可以使用其他较便宜的材料作为辅助电极。选择包括碳、铜或不锈钢。

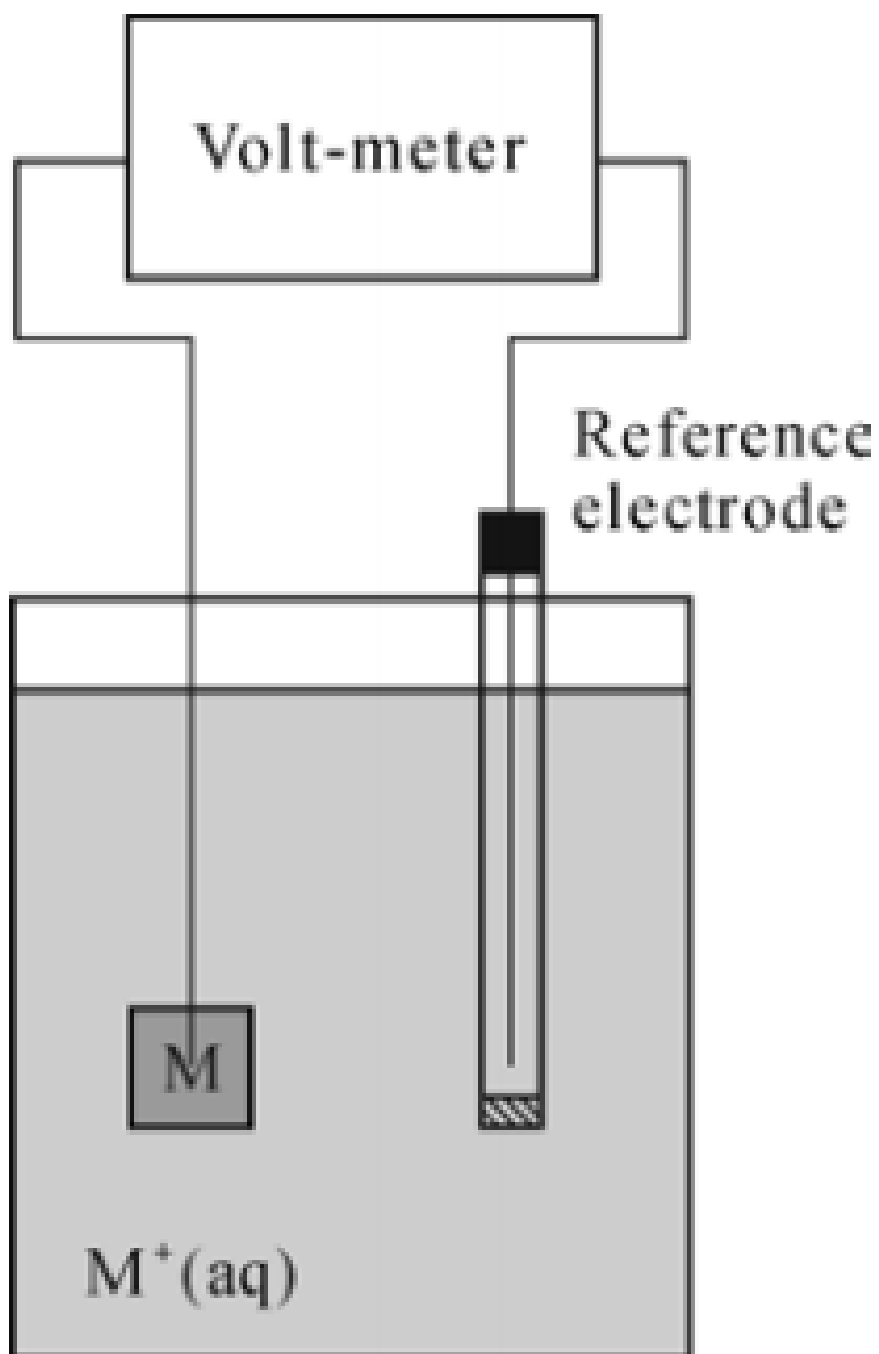


图 3: 使用金属指示电极进行电位测量的电化学电池

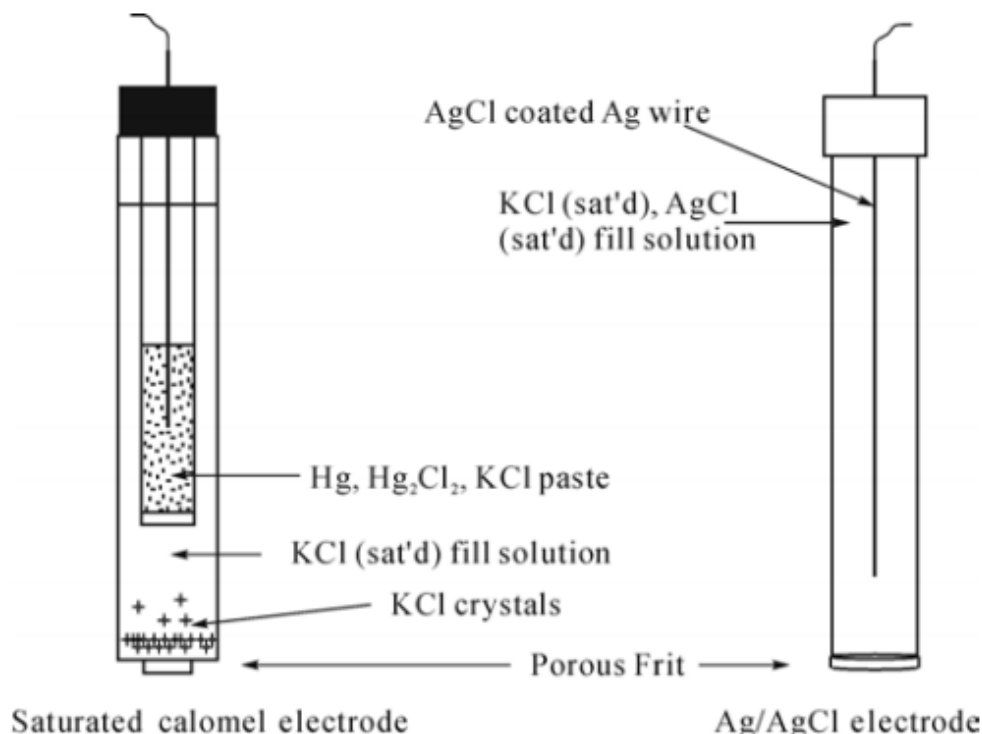


图 4: 饱和甘汞电极和 Ag/AgCl 电极示意图

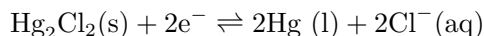
## (2) 参比电极的结构和功能

**参比电极的功能** 参比电极的主要功能是提供稳定和明确定义的电位，用于测量指示电极或工作电极的电位。由于单个电极电位不能直接测量，具有定义零电位（或已知固定电位）的参比电极对于确定其他电极的电位至关重要。

**常见参比电极的结构** 两种最常见和实用的参比电极是饱和甘汞电极（SCE）和银-氯化银（Ag/AgCl）电极。

### (1) 饱和甘汞电极（SCE）:

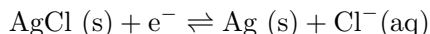
- **结构:** SCE 通常由汞（Hg）电极与氯化汞（I）（甘汞，Hg<sub>2</sub>Cl<sub>2</sub>）糊状物和饱和氯化钾（KCl）溶液接触组成。这个内部组件通常装在玻璃管中，底端有多孔塞或烧结玻璃，通过液接与外部分析溶液接触。
- **电极反应:** 半电池反应是：



- **电位稳定性:** SCE 的电位稳定，因为它由氯离子浓度决定，通过使用饱和 KCl 溶液保持恒定。

### (2) 银-氯化银（Ag/AgCl）电极:

- **结构：**这种电极由涂有氯化银（AgCl）的银（Ag）丝组成。Ag/AgCl 丝浸入含有已知浓度氯离子的溶液中（例如，饱和 KCl 或 3.5 M KCl）。与 SCE 类似，它通常有多孔烧结玻璃与外部溶液接触。
- **电极反应：**半电池反应是：



- **电位稳定性：**电位稳定，因为氯离子浓度恒定，AgCl 微溶。

SCE 和 Ag/AgCl 电极都提供稳定和可重现的电位，使它们成为各种电化学测量中参比电极的理想选择。

## 5. 室内空气质量监测系统思路

监测室内空气质量涉及识别和定量常见的室内污染物。以下是设计这样系统的思路：

### (1) 识别关键污染物：

- **颗粒物（PM2.5/PM10）：**灰尘、花粉、烟雾、气溶胶。
- **挥发性有机化合物（VOCs）：**来自油漆、家具、清洁产品、烹饪。常见例子：甲醛、苯、甲苯。
- **二氧化碳（CO2）：**通风、人员占用的指标。
- **一氧化碳（CO）：**来自不完全燃烧（例如，燃气设备故障）。
- **湿度：**影响舒适度和霉菌生长。
- **温度：**基本舒适参数。

### (2) 为每种污染物选择合适的传感器：

- **PM2.5/PM10：**光学粉尘传感器（例如，基于光散射）。
- **VOCs：**半导体气体传感器（例如，基于 SnO2 的 MOS 传感器）。这些对一系列 VOCs 和还原性气体敏感。对于特定 VOCs 如甲醛，可能需要专门的电化学或光学传感器。
- **CO2：**固体电解质气体传感器（例如，基于 NASICON）或 NDIR（非分散红外）传感器。
- **CO：**电化学气体传感器（例如，3 电极燃料电池型）或专门的 MOS 传感器。
- **湿度：**电容式湿度传感器（基于水蒸气吸收引起的介电变化）或电阻式湿度传感器（基于吸湿介质的阻抗变化）。
- **温度：**热敏电阻（NTC/PTC）或集成温度传感器（例如，基于二极管）。

### (3) 考虑传感器阵列和数据处理：

- **传感器阵列：**可以设计类似“电子鼻”的单一传感器阵列。这涉及使用具有不同选择性的多个气体传感器。虽然每个传感器可能对几种挥发性分子敏感，但它们会以特定方式反应。
- **模式识别：**由于单个传感器通常具有交叉敏感性，复杂的模式识别系统至关重要。该系统将分析阵列电信号的独特“指纹”。可以使用主成分分析（PCA）进行降维和人工神经网络（ANN）进行分类等技术。ANN 通过例子学习识别不同的气味或气体混合物。

- **微控制器/微处理器：**中央处理单元（MCU/DSP）将从所有传感器收集数据，执行必要的计算（例如，单位转换、线性化），并执行模式识别算法。

(4) 硬件架构：

- **传感器接口电路：**每个传感器需要特定的接口电路（例如，电阻变化的惠斯通电桥、电流-电压转换器、放大器）将非电信号转换为适合 MCU 的电信号。
- **信号预处理：**包括放大、滤波（例如，低通滤波器去除噪声）和模数转换（ADC），为 MCU 的数字处理准备模拟传感器输出。
- **电源：**所有组件的稳定电源。对于室内监测器，主电源适配器合适，可能配有小型备用电池。
- **显示/输出：**简单的 LCD 或 LED 显示器显示实时空气质量读数（例如，数值、空气质量等级的颜色编码指示器），或无线模块（例如，Wi-Fi、蓝牙）将数据发送到智能手机应用或云平台进行远程监控。

(5) 软件和算法：

- **传感器数据采集固件：**在 MCU 上运行的代码，用于与传感器接口、读取数据并执行初始处理（例如，去抖动、基本缩放）。
- **校准：**定期校准传感器（例如，对已知气体浓度）以保持准确性。软件可以存储校准曲线或补偿参数。
- **环境补偿：**实施算法补偿温度和湿度对气体传感器读数的影响，因为许多气体传感器对温度敏感。
- **报警系统：**为每种污染物定义阈值。如果污染物超过其阈值，触发报警（例如，声音蜂鸣器、改变显示颜色、发送通知）。
- **数据记录：**存储历史数据（例如，在 SD 卡或内部存储器上）用于分析和趋势跟踪。

(6) 物理设计和放置：

- **外壳：**设计紧凑美观的外壳，允许传感器适当的空气循环。
- **放置：**将设备放置在房间的中央位置，远离直接气流、热源或窗户，以获得房间空气质量的代表性读数。

通过遵循这些步骤，可以设计出全面有效的室内空气质量监测系统。

## 6. 相对湿度和绝对湿度及其检测方法

### (1) 湿度传感器

湿度和温度是测量科学中最常测量的物理量。虽然温度测量现在可以达到令人满意的精度，但气态大气中水蒸气含量的测量，即湿度测量，显得更加复杂。水蒸气是空气的天然组成部分，在广泛和各种实际测量情况中起着重要作用。今天，针对各种应用开发了不同的湿度传感器。湿度传感器必须满足的要求以满足广泛的应用包括：(1) 在湿度和温度的宽范围内具有良好的灵敏度，(2) 短响应时间，(3) 良好的重现性和小滞后，(4) 良好的耐久性和长寿命，(5) 抗污染物，(6) 可忽略的温度依赖性和 (7) 低成本。

在湿度测量中，通常测量相对湿度  $rh$  和温度  $T$ 。 $rh$  定义为：

$$rh = \frac{p_w}{p_s} \times 100\%$$

其中  $p_w$  是蒸气压， $p_s$  是饱和压力。

经常测量的参数是露点  $T_d(^{\circ}\text{C})$ ，即气体开始凝结成液体的温度和压力。定义湿度的其他方法有绝对湿度 ( $\text{g}/\text{m}^3$ )，相对于干空气的比率，即混合比  $m_r(\text{ppmv})$ ，以及相对于饱和的不足，即饱和不足  $p_{sd}(\text{mbar})$ 。水的蒸气饱和压力与温度的关系如图 5 所示。

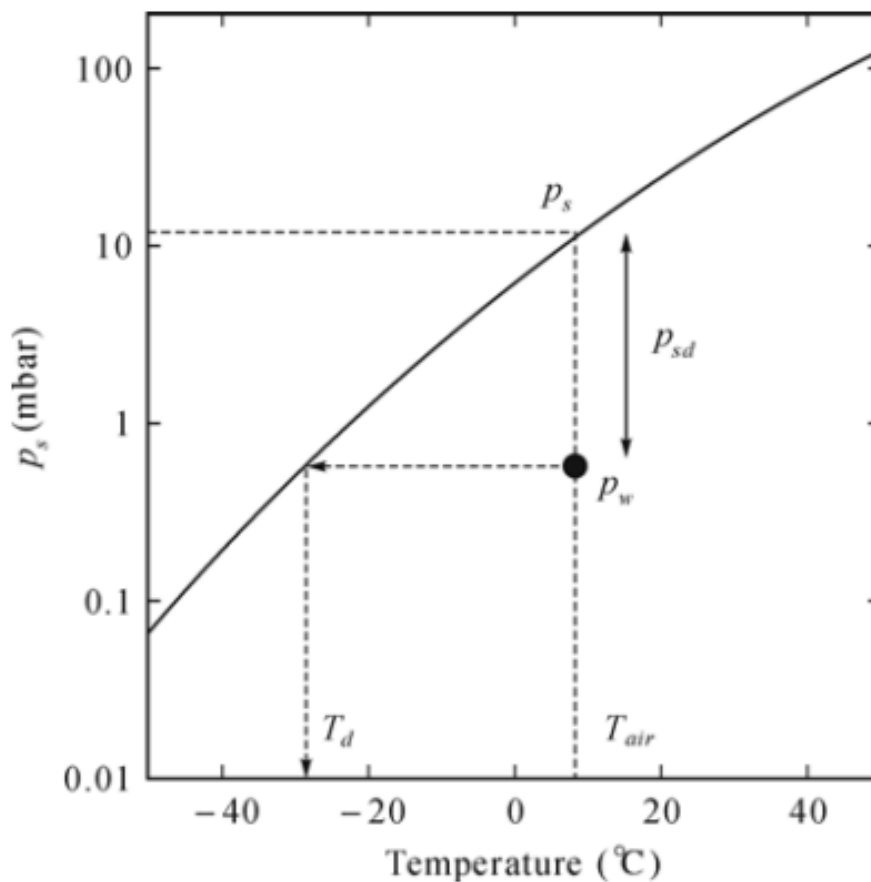


图 5: 水饱和压力与温度的关系

## (2) 相对湿度 (RH)

- **定义：**相对湿度 (RH) 定义为实际水蒸气压 ( $p_w$ ) 与给定温度下饱和蒸气压 ( $p_s$ ) 的比值，以百分比表示：

$$rh = \frac{p_w}{p_s} \times 100\%$$

- **含义：**它表示空气接近水蒸气饱和的程度。在 100% RH 时，空气完全饱和，可能发生冷凝。

**检测方法：电容式湿度传感器** 电容式湿度传感器基于薄膜上水蒸气吸收引起的介电变化。这些传感器的性质由吸湿材料和电极几何形状决定。电极几何形状允许蒸气自由扩散到介电质中，例如，叉指式电极 (IDE) 有利于快速响应，但薄顶电极 (通常 10-80 nm Au) 将产生更均匀的场分布。

电容式湿度传感器实际上是平板电容器。聚合物层放置在金属电极和涂层玻璃基板之间，如图 6 所示。

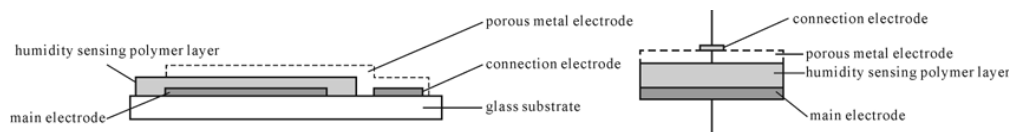


图 6: 电容式湿度传感器的示意结构及其等效图

聚合物的介电常数取决于其含水量，可以用复数形式表示：

$$\varepsilon_{rh} = \varepsilon'_{rh} - j\varepsilon''_{rh} = \varepsilon'_{rh} - j\frac{\sigma}{\omega}$$

其中  $\varepsilon'_{rh}$  是实部， $\varepsilon''_{rh}$  是介电损耗因子。在电容式湿度传感器中，介电常数的变化几乎与环境中的相对湿度成正比。相对湿度 rh 时的传感器电容可以描述为：

$$C_{rh} = \frac{\varepsilon_0 \varepsilon_{rh} A}{d}$$

其中  $\varepsilon_0$  是真空介电常数，A 是电极面积，d 是电极间距离。

**检测方法：电阻式湿度传感器** 电阻式湿度传感器测量吸湿介质（如导电聚合物、盐或处理过的基板）的电阻抗变化。阻抗变化通常与湿度呈反指数关系。电阻式传感器通常由贵金属电极组成，这些电极通过光刻技术沉积在基板上或在塑料或玻璃圆柱体上绕线电极。基板涂有盐或导电聚合物，如图 7 所示。

传感器吸收水蒸气，离子官能团解离，导致电导率增加。有三组材料：(1) 陶瓷，(2) 聚合物和 (3) 电解质。

基于电解质的湿度传感器的一个例子是 LiCl 露点湿度计，由多孔聚合物和盐的复合材料制成，如图 8 所示。

**检测方法：旋转湿度计** 这种仪器包含两个温度计：干球（暴露在空气中）和湿球（浸在湿布中）。湿球的蒸发使其冷却，冷却程度（“湿球抑制”）是相对湿度的函数。通过旋转湿度计，读取两个球的温度，RH 可以从湿度图或基于温差的计算确定。

### (3) 绝对湿度 (AH)

- **定义：**绝对湿度 (AH) 是单位体积湿空气中存在的水蒸气质量，通常以克每立方米 ( $\text{g}/\text{m}^3$ ) 表示。
- **含义：**它表示实际的水蒸气量，与温度无关。

**检测方法：热导率湿度传感器** 热导率湿度传感器，也称为绝对湿度传感器，通过计算干空气和含水蒸气空气的热导率差异来测量绝对湿度。

热导率湿度传感器可以通过基于热敏电阻的传感器实现。两个微小的热敏电阻 ( $R_{t1}$  和  $R_{t2}$ ) 由细线支撑，以最小化到外壳的热导率损失。左侧热敏电阻密封在干空气中。两个热敏电阻连接到桥式电路 ( $R_1$  和  $R_2$ ) 中，由电压 E 供电，如图 9 所示。



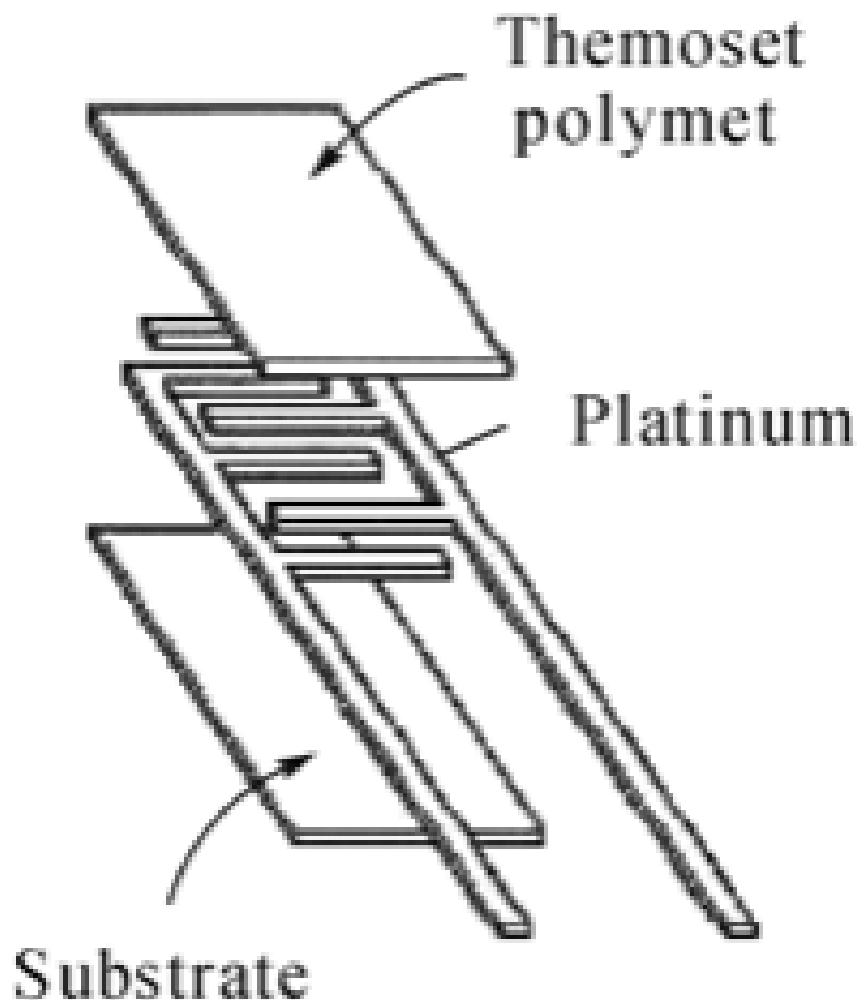


图 7: 典型的电阻式湿度传感器配置，由合适基板上的聚合物涂层电极组成

桥式输出由下式给出：

$$V_{out} = E \left( \frac{R_1}{R_1 + R_{t1}} - \frac{R_2}{R_2 + R_{t2}} \right)$$

热敏电阻由于电流通过而产生自加热。它们的温度比环境温度升高 170°C。最初，桥在干空气中平衡以建立零参考点。当绝对湿度从零开始上升时，该传感器的输出逐渐增加。

#### (4) 应用实例

图 10显示了基于湿度计原理的相对湿度传感器。

传感器由两个热敏电阻（热电阻）组成，一个在密封（干燥）室内，另一个暴露在空气中。两个热敏电阻都在接近自加热点的地方工作，因此相对较小的温度变化会产生较大的电阻变化。当在惠斯通电桥配置中工作时，传感器将产生可用于确定相对湿度的电压。

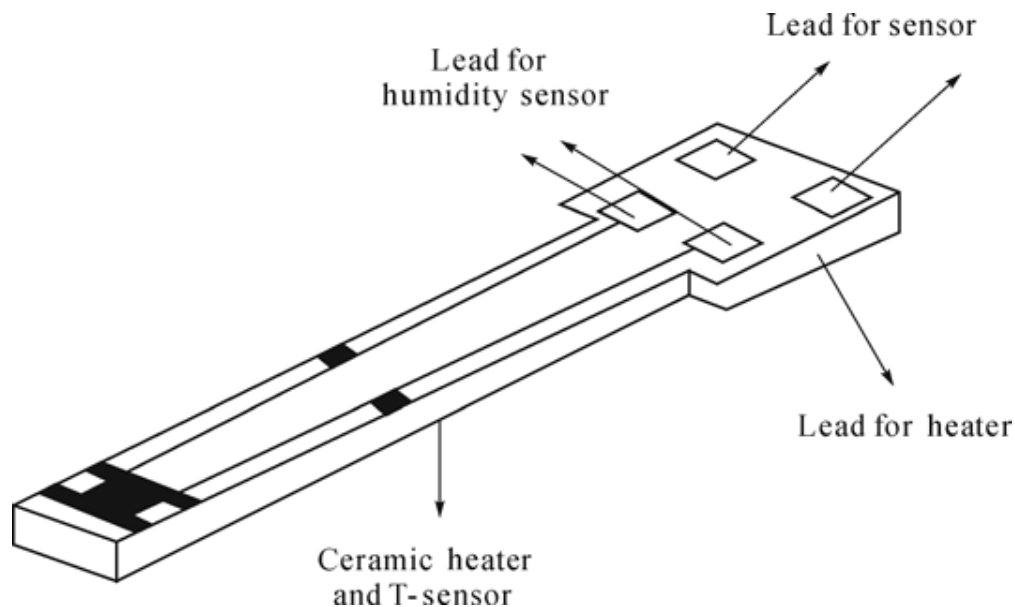


图 8: 露点湿度计原型

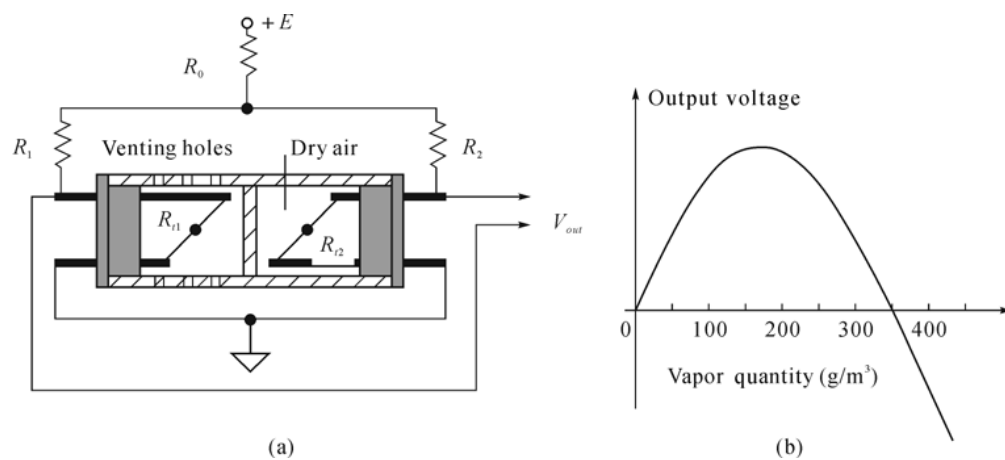


图 9: 自加热热敏电阻绝对湿度传感器: (A) 设计和电气连接; (B) 输出电压

总之，相对湿度是表示饱和度的百分比，通常由电容式或电阻式传感器检测。绝对湿度测量实际水蒸气质量，通常由热导率传感器检测。

## 7. 电子舌和电子鼻的相似性和差异

电子舌（e-Tongue）和电子鼻（e-Nose）都是智能化学传感器阵列，旨在模拟生物感觉系统进行定性和/或定量分析。它们在架构方法上有根本相似性，但在目标分析物和具体应用方面有显著差异。

### (1) 相似性

- (1) **仿生学**：e-Nose 和 e-Tongue 都受生物感觉器官启发——e-Nose 模拟人类鼻子，e-Tongue 模拟舌头/味蕾。它们旨在复制这些生物系统的复杂识别和感知机制。

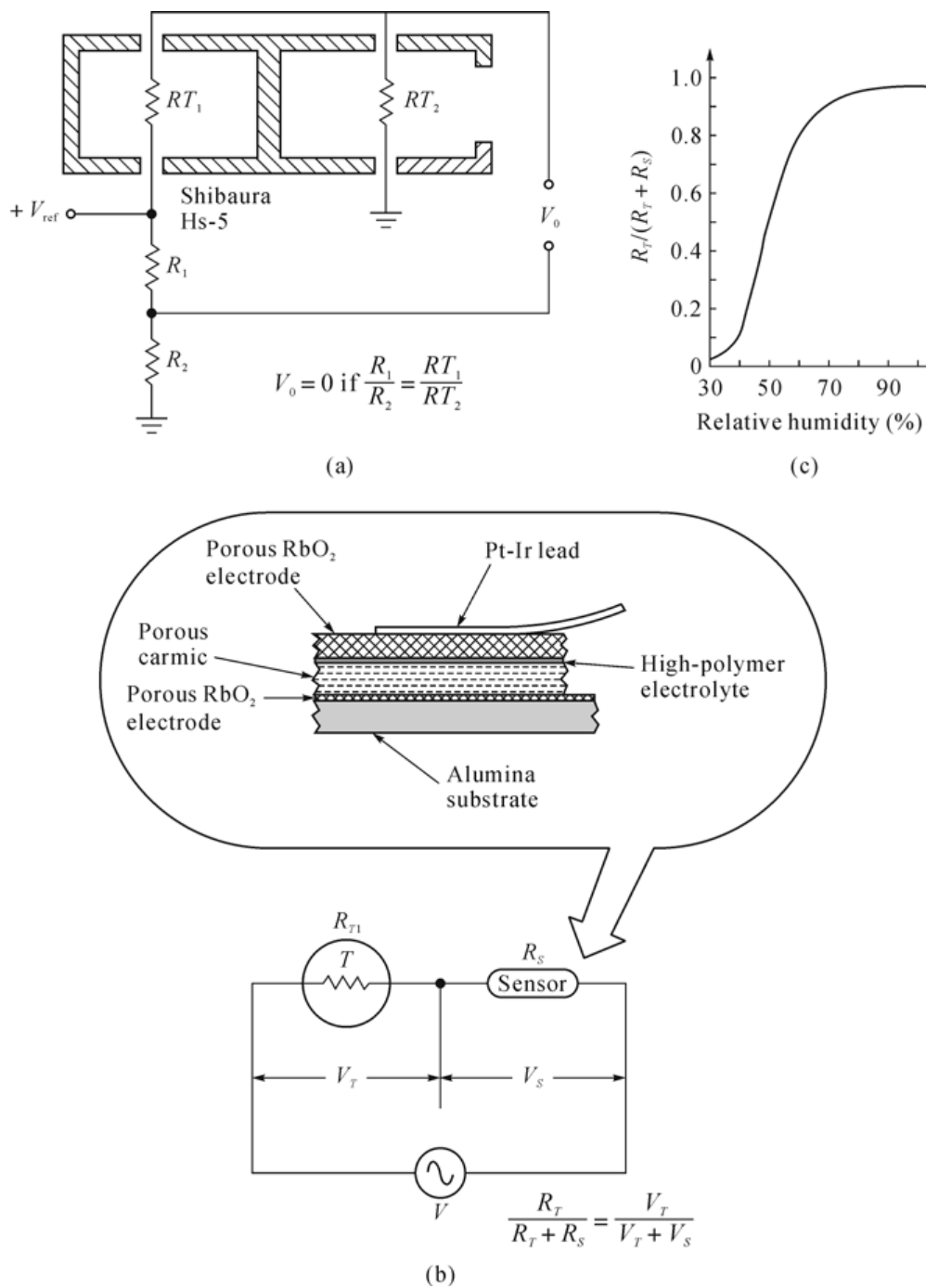


图 10: (a)Shibaura 电阻式相对湿度传感器; (b) 传感器元件结构; (c) 校准曲线

- (2) **多传感器阵列**：两个系统都依赖多个化学传感器的阵列，而不是单个传感器。这个阵列为给定样品提供独特的“指纹”或响应模式，类似于生物系统中不同受体对各种刺激的响应方式。
- (3) **交叉敏感性**：两者的关键特征是使用交叉敏感传感器。阵列中的单个传感器不是对单一物质完全选择性的，而是对一组化学物质响应，甚至对不同性质的其他化学物质也有响应。这种交叉敏感性对于产生复杂模式至关重要。
- (4) **模式识别系统**：两个系统都集成了复杂的基于计算机的模式识别系统作为它们的“大脑”。该系统使用智能算法（例如，主成分分析、人工神经网络）处理传感器阵列的原始电信号，以识别、区分和量化样品。例如，ANN 通过例子学习识别各种化学物质或气味。
- (5) **应用领域**：两者都在质量控制（食品、饮料）、环境监测和医学诊断中找到应用，通过分析复杂混合物。

## (2) 差异

e-Nose 和 e-Tongue 之间最明显的差异是它们的目标检测对象。

特征	电子鼻 (e-Nose)	电子舌 (e-Tongue)
目标分析物	气体、蒸气或气味（挥发性化合物）	液体（溶液中的味觉物质）
感应原理	检测空气中的挥发性有机化合物（VOCs）。	检测溶解在液体中的非挥发性味觉物质。
传感器类型	主要是金属氧化物半导体（MOS）、导电聚合物（CP）、石英晶体微天平（QCM）、表面声波（SAW）、场效应晶体管（MOSFET）、电化学气体传感器。	通常利用电位传感器，如 PVC 膜传感器、硫族化物玻璃膜传感器或 Langmuir-Blodgett 膜传感器。
样品引入	利用泵和采样系统将气态样品带到传感器阵列。	涉及将传感器阵列直接浸入液体样品中。
生物类比	嗅觉系统（嗅觉）。	味觉系统（味觉）。
应用例子	从呼吸诊断肺癌、空气质量监测、工业过程控制、食品变质检测。	水污染评估、食品质量评估（例如，区分矿泉水、饮料、葡萄酒、咖啡）、药物分析。

本质上，虽然 e-Nose 和 e-Tongue 都代表采用多传感器阵列和先进数据处理的智能传感器技术，但它们的根本区别在于是分析气态还是液态样品来获得定性和定量信息。

## 8. 微流控芯片中微流体的驱动方法

### (1) 微流体的驱动和控制

微流控芯片操作的基础是微流体驱动和控制技术。自微流控芯片发明以来，它一直是微流控芯片基础研究领域的重要课题，新技术和新方法不断涌现。这里教材简要介绍了两种微流体驱动技术，即电渗驱动和微泵驱动。同时，还将介绍两种微流体控制技术，即电渗控制和微阀控制。

## (2) 电渗驱动

目前，电渗驱动是微流体驱动中最广泛使用的方法之一。其基本原理是利用微通道内表面的固定电荷来驱动微流体。其优点包括缺乏机械组件、配置简单、操作方便、流动平坦且无脉动。然而，这种方法对外部电场、通道表面、微流体性质和传热效应的影响敏感。因此，它不太稳定，只能应用于电解质溶液。

电渗不仅可以用于直接驱动带电流体，还可以用作微泵的能源，称为电渗泵。实现这种电渗泵的方法如下：使用光刻技术在芯片基底表面制造具有一定间隔的电极。然后用 PDMS 微通道密封，形成密闭的电渗驱动系统。工作时，向电极施加电压以产生电渗流。由于电渗流只存在于两个电极之间，电极外的流体可以被电渗流驱动。因此，可以实现电渗泵的功能。

- **原理：**电渗流（EOF）利用微通道内表面的固定电荷来驱动流体。当电场施加在含有电解质溶液的微通道上时，通道壁附近电双分子层中的离子被电场拖拽，进而拖拽整体流体。
- **机理：**微通道内表面电荷的密度和极性决定电渗流的速度和方向。通过修改表面性质（例如，用聚电解质层涂覆），可以改变流动方向，实现复杂的流动操作。
- **优点：**
  - 缺乏机械组件，导致配置简单，操作方便。
  - 产生平坦的流动剖面（塞流），无脉动，有利于最小化分离中的谱带展宽。
  - 可用于直接驱动带电流体或作为电渗泵的能源。
- **缺点：**
  - 对外部电场、通道表面性质和微流体性质敏感。
  - 稳定性较差，主要适用于电解质溶液。
  - 受传热效应影响。

## (3) 微泵驱动

机械驱动系统中的气动微泵由多个气动微阀组成。当施加压力时，PDMS 薄膜在气压作用下变形，导致通道阻塞和阀门关闭。当没有施加压力时，PDMS 薄膜可以通过自身的弹性力实现复位，因此通道变得畅通，阀门打开。通过顺序控制三个阀门的开启和关闭，可以获得微流体的驱动。

微泵是设计用于在微流控系统内主动移动流体的机械组件。它们通常涉及可移动膜或其他机械元件。

- **原理：**微泵通过机械驱动产生流体运动，类似于宏观泵。
- **机理（例子：气动微泵）：**
  - 这些泵通常由多个气动微阀组成。
  - 当施加压力（例如，气压）时，柔性膜（例如，PDMS 薄膜）变形，阻塞通道并关闭阀门。
  - 当压力释放时，膜由于其弹性而恢复，打开通道。
  - 通过顺序控制三个这样阀门的开启和关闭，可以实现泵送作用，在所需方向驱动微流体。
- **优点：**可以处理更广泛的流体（包括非电解质），与电渗方法相比可能提供更高的流速或压力。
- **缺点：**涉及机械组件，制造和集成可能更复杂，随时间可能容易磨损或泄漏。

#### (4) 微流体控制方法

微流体控制是微流控芯片操作的核心原理。它涉及几乎所有过程，如采样、混合、反应和分离，这些都需要在可控流动中完成。阀门是宏观和微观尺度流动控制的核心组件。由于其重要性，微阀在微流控芯片发明之前就已经得到深入研究。在其发展的初期阶段，微流控芯片通常是芯片上的一种毛细管电泳，依赖于电渗驱动。因此，直到现在，电渗驱动仍然是微流体控制最广泛使用的技术。

**电渗控制** 电渗是一种现象，即微通道中的溶液可以在电场作用下沿着通道内表面向所需方向移动。它已广泛用于微流体控制。与其他类型的微泵相比，电渗阀最重要的特征是其简单灵活的操作。可以通过调节施加到微通道不同节点的电压来控制流动的速度和方向。因此，可以实现复杂的混合、反应和分离等操作。除了电压外，电渗微阀还可能受到通道表面化学组成、缓冲溶液成分和温度等因素的影响。

除了驱动流动外，电渗可用于精确流动控制。通过改变施加到微通道不同节点的电压，可以调节流动的速度和方向。这允许复杂的操作如混合和分离。

**微阀控制** 微阀有各种类型。理论上，所有能够控制通道开启和关闭的组件都可以用作微流控芯片中的微阀。理想的微阀可以具有以下特征：低泄漏、低能耗、快速响应、线性操作和广泛的适应范围。根据微阀操作期间是否需要激励源，微阀可以分为被动阀和主动阀。

微阀是流动控制的基本组件。它们可以是被动的（例如，基于压差仅允许单向流动的单向阀）或主动的（需要外部激励源进行开启和关闭）。

**通道结构和表面修饰** 此外，通道结构、芯片表面修饰、层流和扩散效应也在微流体控制中起重要作用。微通道的物理设计（例如，蛇形、之字形图案）和其内表面的化学修饰（例如，创建疏水/亲水区域）可以影响流动模式，通过混沌对流增强混合，或实现流动限制。

**层流和扩散** 在微尺度，流动通常是层流（低雷诺数），意味着流体在平行层中移动而没有湍流混合。混合主要依赖分子扩散。为了提高混合效率，采用延长流动剪切（增加接触面积）和分割/重组流体流（减少扩散距离）等原理。

#### (5) 样品引入和预处理

样品引入是微流控芯片分析的第一步。它包括从分析对象采样和将样品引入微通道进行样品处理的过程。在检测之前，需要对样品进行一系列预处理和反应步骤，如预分离、预浓缩和稀释。

目前，在大多数微流控分析系统中，样品、试剂和缓冲溶液存储在位于芯片上的井型存储室中。样品引入方法通常手动或自动将样品添加到井型存储室。然后将样品导入通道进行预处理或直接分离和分析。

常用的方法是在芯片上设置垂直于样品处理通道的辅助通道。样品区可以在两个通道的交叉处产生。这种方法称为单通道辅助样品引入。它包括两个步骤，加载和采样。加载是指通过存储室将样品加载到辅助通道并在通道交叉处填充的过程。采样是通过电力或压力将位于交叉处的样品引入样品处理通道的过程。

微流控分析系统的样品通常与含有复杂组成的生物样品有关。因此，样品预处理技术非常重要，通常包括样品预分离和预浓缩。预分离包括液-液萃取、固相萃取、过滤、色谱和膜分离。预浓缩包括等电聚焦、等速电泳和场放大堆积。

## (6) 微混合器、反应器和分离器

反应是化学和生物实验的核心过程。混合和分离对于反应过程也是必要的，特别是在微尺度。因此，微混合器、反应器和分离器是微流控芯片的重要组成部分。

**微混合器** 微混合器在需要快速响应的生物过程中非常有用，如 DNA 杂交、细胞激活、酶反应和蛋白质折叠。在微流控系统中，通道的尺寸在微米尺度。溶液的速度通常很低，溶液混合主要基于层流机制，这可能受到分子扩散的很大影响。为了提高层流混合的效率，应遵循一些原则：(1) 延长流动剪切以增加溶液的接触面积；(2) 通过利用分布式混合设计分割和重组溶液，从而减少溶液厚度以实现更有效的混合。

**微反应器** 微反应技术是将微结构优势应用于化学反应过程。微反应器是具有微米尺度单元反应界面的微型化学反应系统。其基本特征包括小的线性尺度、高物理质量梯度、高表面体积比和低雷诺数。此外，通过其并行单元，微反应器可以实现灵活的放大生产和快速高通量筛选。

**微分离器** 最近，微分离技术取得了很大进展。现在，各种色谱和电泳分离模式都可以在芯片上实现。微分离器已成为发展最快、成熟度最高的技术单元之一，极大地推进了微流控芯片的集成趋势。以集成毛细管电泳芯片为例，使用微加工技术可以在几平方厘米的芯片区域内蚀刻微通道和其他功能单元。因此，可以实现集成样品引入、分离、反应和检测功能的微分析设备，其特点是快速、高效、低样品消耗、低成本和便携性。

本质上，微流控芯片利用电动现象和微型机械设备的组合来精确操纵流体，在微型化尺度上实现复杂的实验室功能。