

# 1

## Sensor and measurement

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### 1.1 What is a sensor?

Humans have five senses: sight, hearing, touch, smell and taste, as illustrated in Fig. 1.1. These senses are very important because humans act after receiving information from the outside world.

Automatic doors open by checking for the presence of people using the device that corresponds to the sense of sight. These devices are common throughout the world. In fact, when we come across a nonautomatic door, we often assume that it must be self-operating and wait for a while for it to open, and then we become aware that it is nonautomatic. The infra-red light is usually used in detecting a person at automatic doors. The history of the automatic door is very old; in fact, it was used in Alexandria, the capital of ancient Egypt, more than 2000 years ago. It was made in such a way that it could open when fire was started at the altar in front of the door of the temple.

The sensor plays the role of reproducing the five senses or surpassing them. Figure 1.2 shows the correspondence between the biological system and the artificial system in the process of reception and the following action. The sensor is the device that mechanizes the ability of five organs, i.e., eye, ear, skin, nose and tongue, in the senses of sight, hearing, touch, smell and taste, respectively. With the development of computers, we often use the term sensor in the global sense by combining the data-processing part with the receptor part (i.e., the sensor in the narrow sense). In this case, the sensor plays roles of recognition as well as reception. This is the direction in which development of intelligent sensors is moving.

The actuator implies the mechanical part that moves the object by transforming the output from the sensor to rotation and displacement.

In the above example of the automatic door in ancient Egypt, the air under the altar is expanded by fire (sensor part); this causes water to flow into another vessel through a tube. The resulting water pressure moves the rotating apparatus of the door (actuator part).

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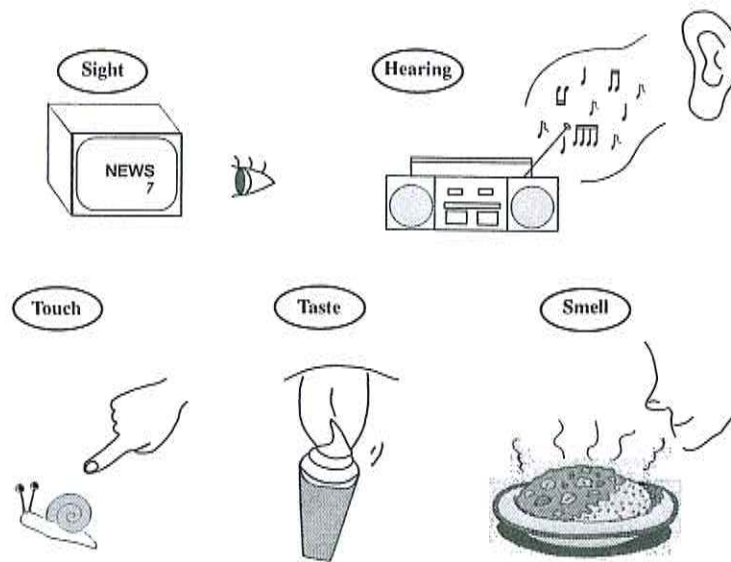


Figure 1.1. Five senses of humans.

Table 1.1 summarizes the correspondence between the sensor and the five senses. “Odor sensor” and “taste sensor” are entered in the lists of the senses of smell and taste, respectively. This is based on the expectation that these two kinds of sense can be realized at the reception level if good sensing materials are developed successfully. As explained in Chapter 2, the primitive

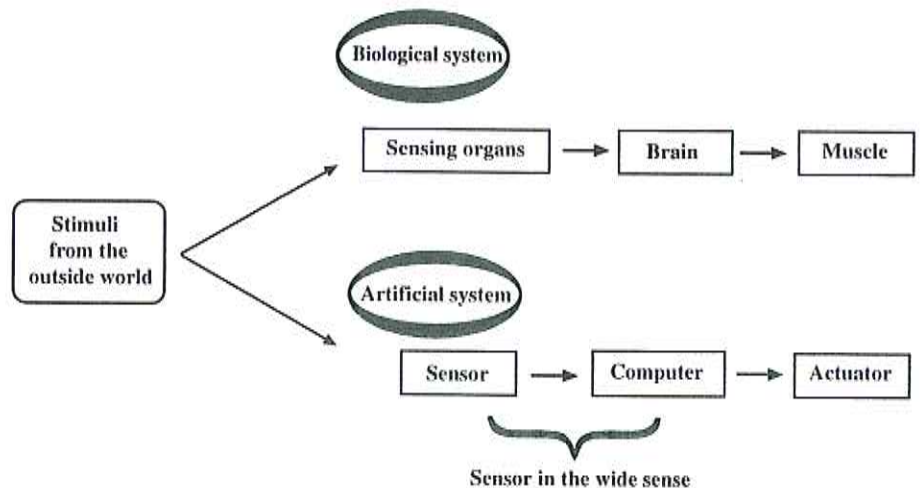


Figure 1.2. Correspondence between the biological system and the artificial system in the process of reception and the following action.

Table 1.1. Five senses and sensors

Five senses	Sensing organ	Object	Sensor	Principle
Sight	Eye	Light	Optical sensor	Photovoltaic effect (photon → electric change <sup>a</sup> )
Hearing	Ear	Sound wave	Pressure sensor	Piezoelectric effect (sound wave → electric change)
Touch	Skin	Pressure	Pressure sensor	Piezoelectric effect (pressure → electric change)
		Temperature	Temperature sensor	Seebeck effect (temperature → electric change)
Smell	Nose	Chemical substances	Gas sensor	Chemical reaction (gas adsorption → electric resistance change)
			Odor sensor	Adsorption effect (mass change → frequency change)
Taste	Tongue	Chemical substances	Ion sensor	Selective ion permeation (ion → electric change)
			Taste sensor	Electrochemical effect (interactions → electric change)

<sup>a</sup> The term "electric change" implies changes in electric resistance, electric voltage or electric current.

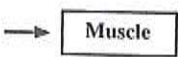
discriminations of quality of taste and chemical substances to produce smell are made in gustatory and olfactory cells, respectively.

The sensor can surpass the ability of the five senses of humans in the following two ways. The first is that living organisms including human beings cannot live in severe conditions; for example, humans cannot experience the temperature in a blast furnace themselves. It is the sensor that can achieve this. The second concerns the limited sensory range, depending on the species, of living organisms. For example, humans cannot recognize propane gas or carbon dioxide and cannot hear the supersonic sound generated by a bat or a dolphin. Humans can perceive these quantities by using a sensor that surpasses their abilities.

In the history of sensor development, the sensors (in the narrow sense) corresponding to the receptor parts of sight, hearing and touch have been developed for many years. By comparison, the sensors for simulating the senses of smell and taste have been proposed only recently. This difference



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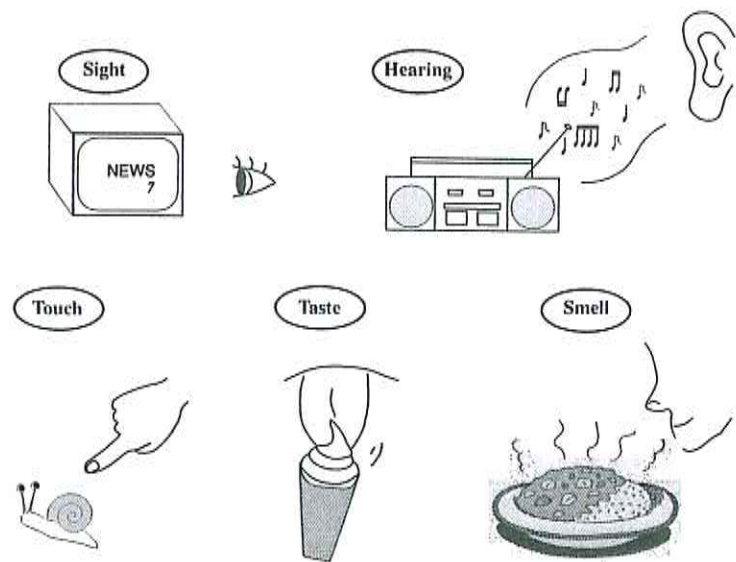


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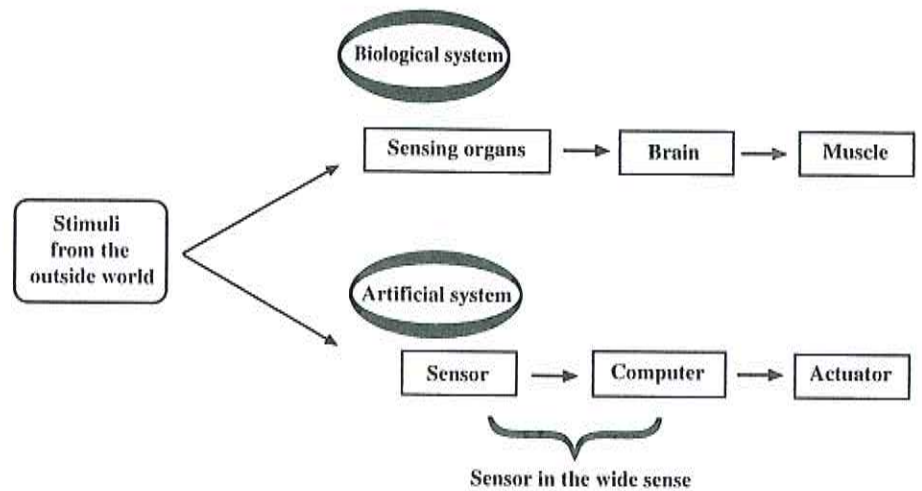


Figure 1.2. Correspondence between the biological system and the artificial system in the process of reception and the following action.

is a consequence of the mechanisms involved in these two kinds of sensor. In the senses of sight, hearing and touch, only one physical quantity – light, sound wave and pressure (or temperature), respectively – is received. Hence the sensors have only to transform this physical quantity to another tractable quantity such as an electric signal. On the contrary, many kinds of chemical substance must be assessed at once for smell and taste to be transformed into meaningful quantities to represent these senses.

As a result, sensors for sight, hearing and touch use popular materials such as semiconductors to receive the physical quantity. For smell and taste, however, it has been less clear what materials can be adequately used to receive the many kinds of chemical substance. For example, when we eat something, we express its taste by using the terms “sweet”, “bitter” and “sour”. It is said that there are about 1000 kinds of chemical substance in tea or coffee. We have no idea of the mechanism by which information contained in these substances is transformed into meaningful, simple expressions such as “sweet” and “bitter”. However, it should be noted that the classification into these taste expressions is made at the first stage of reception of chemical substances by taste cells.

The sensors that play the roles of receptor in the senses of sight, hearing and touch are called physical sensors, because physical quantities are received. The sensors playing the role of receptor in the senses of smell and taste can be classified as the so-called chemical sensors. Nevertheless, the approach used to construct chemical sensors seems to have been almost the same as that in physical sensors, because it is based on high selectivity and sensitivity. One of the fruitful results is an enzyme sensor or an ion-selective electrode. They are very powerful and useful for detecting a specific chemical substance with high selectivity and sensitivity.

However, taste or smell cannot be measured if we fabricate many chemical sensors with high selectivity for different chemical substances when there are more than 1000 in one kind of foodstuff. The original role of smell and taste was to detect and assess information within a large mass of external information (enormous numbers of chemicals). The sense of smell is powerful in detecting the smell of an enemy or prey in the dark of a forest. The sense of taste is used to judge whether anything to be taken into the mouth is beneficial or poisonous for the body. There are too many kinds of chemical substance involved in producing taste and smell, and hence it seems important to obtain useful information quickly rather than to discriminate a single chemical species from others. This tendency is evident in unicellular living organisms, which have no sense of sight.

The above argument may need one comment concerning the sense of smell. Recent studies have revealed that there are numerous types of specific protein for odor molecules, as detailed in Chapter 2. In addition, there is no basic smell, whereas five basic taste qualities are known in the sense of taste. These facts may imply a large difference between the senses of smell and taste: the sense of smell has a specific property in real biological systems while the sense of taste keeps a nonspecific property to some extent. For this reason, the above argument concerning the fabrication of sensors may be good in the technical meaning for odor sensors, while for taste sensors it holds also in the biomimetic meaning.

As a summary, it can be said that the sensors that are used for smell and taste must have a fabrication principle that differs from the physical sensors or the conventional chemical sensors. Recently developed taste and odor sensors have outputs well correlated with the human sensory evaluations, and the taste sensor particularly has an intelligent ability to break down the information included in chemical substances to the basic information of taste quality. We are now standing at the beginning of a new age when sensors can be used to reproduce all five senses.

We have huge numbers of sensors that can be considered in terms of three factors: the materials selected for measuring the object, the purpose and use of the sensor and the physical effect or chemical reaction used in achieving the measurement (Fig. 1.3). For example, let us consider a situation where we measure pressure or acceleration. For this purpose, it seems good to use a

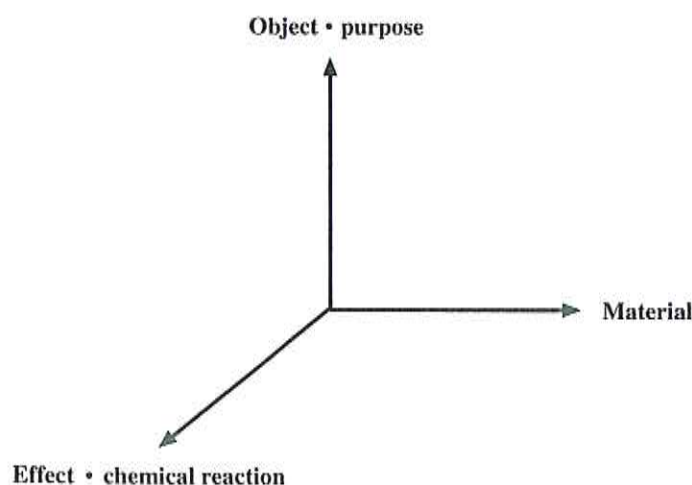


Figure 1.3. Various kinds of sensor with different effects and materials according to the object.

Table 1.2. *Various effects utilized in sensors*

Classification	Effect
Light	Zeeman
	Stark
	Doppler
	Raman
	Brillouin
	Nonlinear
Sound wave	Optical parametric
	Doppler
	Acoustoelectric
	Acoustomagnetic
Semiconductor	Masking
	Diffraction
	Tunnel
	Zener
Magnetism	Electric field
	Gun
	Josephson
Thermal	Superconducting quantum
	Barkhausen
Photovoltaic	Seebeck
	Peltier
	Thomson
	Photoconductive
	Photoelectron emission
Piezoelectricity	Photoelectromagnetic
	Pockels
	Kerr
	Piezoelectric

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combination of the piezoelectric effect in Table 1.2 and the semiconductor material in Table 1.3. However, other combinations may be possible. To measure temperature, we can use the Seebeck effect, which transforms temperature change into electromotive force, and a metal that shows this effect as the sensing material.

What are the materials and effects that are adequate to measure the senses of taste or smell? It is not too much to say that a novel material and effect have been found in the development of sensor technology. If we can visualize taste and smell quantitatively, a new world will be opened.

Table 1.3. *Materials used for sensors*

Materials	Examples
Ceramics	SnO <sub>2</sub> , ZnO, TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , BaTiO <sub>3</sub> , SiO <sub>2</sub>
Semiconductor	Si, Ge, GaAs, InSb, CdSe
Metal	Cu, Fe, Ni, Pt
Polymer, enzyme <sup>a</sup>	Polyvinyl chloride, poly(pyrrole), glucose oxidase, valinomycin, crown ether
Living-organ material	Microbe, lipid, collagen, protein, catfish barb, frog skin, bacteriorhodopsin

<sup>a</sup> There is not a strict division between polymer/enzymes and material from living organisms.

## 1.2 Fundamental units

We can find the sentence "Time travels in diverse paces with diverse persons" in *As You Like It* written by Shakespeare. It implies a subjective factor in the concept of time, i.e., mental time. However, we can also have physical and objective time. We are always troubled by the dilemma between mental and objective time.

Measurement implies the ability to compare some obtained quantity with a fundamental value ("measure") deduced from some scale and to express it using the quantitative value. Let us consider a situation where we measure some quantity and get the value  $L$ , then the measured value becomes  $L/U$  if the fundamental value is  $U$ . If the quantity is concerned with length with a unit of m, we can say that the length of the object is  $L/U$  m.

While many units of length have been proposed so far, the most convenient way may be to use the human body (Fig. 1.4). Protagoras in ancient Greece said that "man is the measure of all things; of what is, that it is; of what is not, that it is not". While he meant the standard of the truth of all things by "measure of all things", we can apply this saying to our body. The fact that humans have tried to develop a common unit based on their bodies can also be found in a famous sentence in *Rongo* written by Koshi in ancient China; Koshi says that we know one *sun* by stretching our fingers, one *shaku* by our hand, and one *hiro* by our elbow. One *sun* is 3.03 cm, one *shaku* 30.3 cm, and one *hiro* 1.515 m. The unit cubit has an old history from over 4000 years ago in Mesopotamia and Egypt, and one cubit corresponds to 45 to 70 cm depending on the race and period. One yard, which might originate from double cubits, is equal to 3 feet (0.914 m). The same situation holds for the units inch, ell, fathom and so on.

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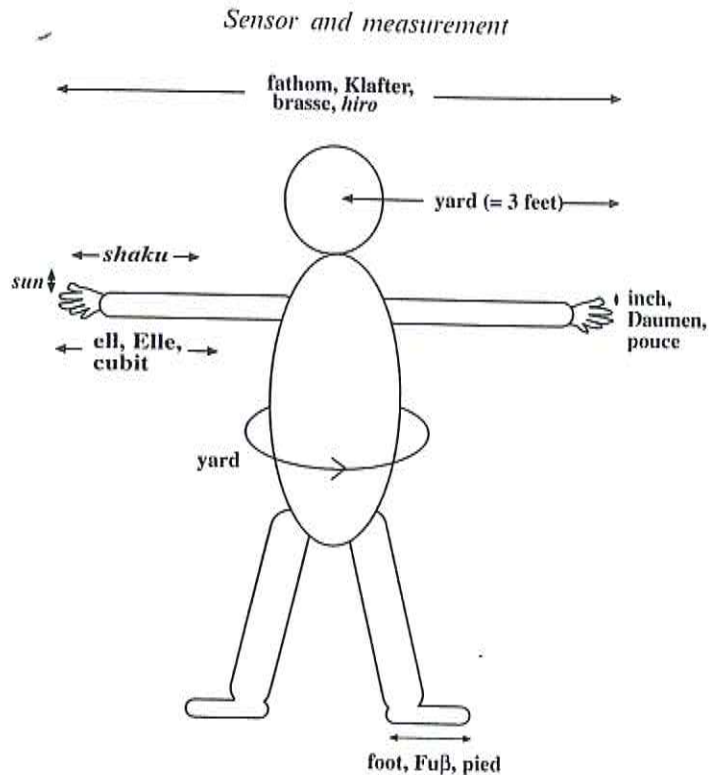


Figure 1.4. Scales based on the human body. The scales based on anatomy such as the length of elbow do not always have the same value, presumably because of differences in race, period and tradition.

With time, the unit was determined using a phenomenon that occurred repeatedly with an accurate period. The annual overflow of the Nile in ancient Egypt occurred when Sirius rises in the sky in the same direction as sunrise, and it promised a good harvest by carrying fertile soil from the upper stream. The unit “one year” (i.e., solar year) was determined from a period of the revolution of the earth.

In 1889, 30 meter prototypes (Fig. 1.5) were produced. One of them was assigned as an international meter prototype, the length of which at 0 °C was defined as 1 meter. The system unified on the base of this meter unit is the international system of metric units (SI: *Système International d’Unités*). The SI unit was accepted during a number of meetings of the *Conférence Générale des Poids et Mesures*.<sup>2</sup>

The SI system consists of seven base quantities (shown in Table 1.4), two additional quantities and numerous derived quantities. The units of the length and time have been improved and now they are defined within the framework of quantum mechanics. However, mass is based on the international kilogram

Table 1.4. The seven base quantities of the SI system

Base quantity	Name	Symbol	Definition
Length	meter	m	Distance travelled by light in vacuum during a time interval of $1/299\,792\,458$ second
Mass	kilogram	kg	Weight of an international platinum-iridium alloy prototype kept at the International Bureau for Weights and Measures in Sèvres, France
Time	second	s	Duration of $9\,192\,631\,770$ periods of electromagnetic radiation, corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom
Electric current	ampere	A	Current that produces a force of $2 \times 10^{-7}$ newton per meter of length between two straight parallel conductors of infinite length placed 1 meter apart in a vacuum
Thermodynamic temperature	kelvin	K	$1/273.16$ of the thermodynamic temperature of the triple point of water
Amount of substance	mole	mol	Amount of a substance of a system containing as many elementary entities as there are atoms in $0.012$ kilogram carbon-12
Luminous intensity	candela	cd	Intensity in a given direction of a source emitting monochromatic radiation of a frequency $540 \times 10^{12}$ hertz with a radiant intensity in that direction of $1/683$ watt per steradian

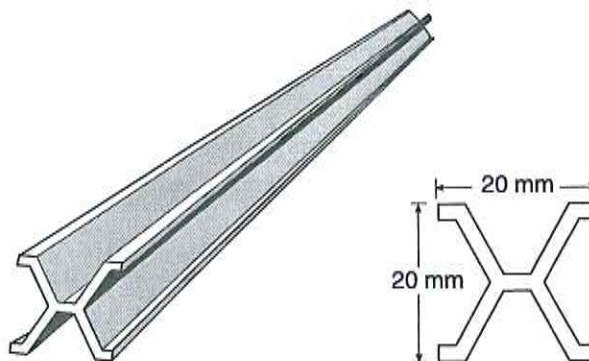


Figure 1.5. The meter prototype.

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prototype, which is made of 90% Pt and 10% Ir, from 1889. It is cylindrical and is kept at the International Bureau for Weights and Measures (BIPM) in Sèvres, France.

Galileo found that the period of a simple pendulum is determined by the length of the pendulum and does not depend on the weight. The period of a 1 m simple pendulum is about 2.01 s, and hence half a period is about 1 s. It is easy to visualize the relationship between 1 m and 1 s.

The unit for the amount of substance, as atoms, molecules or ions, is the mole. Because there is an unimaginably large number of molecules, we use a "unit" called the Avogadro constant (originally termed Avogadro number), which is  $6.02 \times 10^{23}$ . The reference "prototype" is the number of atoms in 0.012 kg carbon-12. How large this number is can be grasped by the following hypothetical experiment. Let us fill a cup with water when we go to the sea. Then we put the water back into the sea and let the giant in the Aladdin's lamp stir the sea with a large spoon. After a sufficient stir, we again fill the cup with water from the sea. How many molecules that first filled the cup come back into the cup? The result is very surprising; some molecules will come back to the cup. As this example illustrates, the world we deal with is composed of an unimaginably large number of molecules.

Using a mol, we can define the unit for concentration in solution. A 1 M aqueous solution is 1 mol of molecules dissolved in 1 l ( $1000 \text{ cm}^3$ ) water. The NaCl content of sea water is 0.5 M (500 mM). The threshold for detection of chemical substances to produce taste and smell for ordinary individuals lies between  $1 \times 10^{-6} \text{ M}$  (1  $\mu\text{M}$ ) and 0.1 M (100 mM). The decimal prefixes that are used to describe these multiples and submultiples of a thousand are given in Table 1.5.<sup>2</sup>

Figure 1.6 shows large numbers using hieroglyphics:  $10^4$  implies the form of bending a figure,  $10^5$  the form of some animal, a burbot, and  $10^6$  shows a person surprised. The sign for  $10^7$  may be an indication of unknown because the number is just too huge.

Figure 1.7 shows what we can see when the scale is increased. We human beings can imagine such a microscopic object as a quark, which cannot be observed by the naked eye, and further can think of such a huge object as the universe.

Recently, environmental pollution has become a social problem, and pollution of the atmosphere and rivers and the destruction of the ozone layer must be considered carefully from now on. We often hear the term ppm (parts per million) in our daily life. The unit ppm implies a ratio. For example, if 1  $\mu\text{g}$  materials are included in 1 g water, it amounts to 1 ppm. More recently, we hear ppb (parts per billion). The appearance of this small unit may not be

Table 1.5. Decimal prefixes

Factor	Prefix	Abbreviation	Factor	Prefix	Abbreviation
$10^{18}$	exa	E	$10^{-1}$	deci	d
$10^{15}$	penta	P	$10^{-2}$	centi	c
$10^{12}$	tera	T	$10^{-3}$	milli	m
$10^9$	giga	G	$10^{-6}$	micro	$\mu$
$10^6$	mega	M	$10^{-9}$	nano	n
$10^3$	kilo	k	$10^{-12}$	pico	p
$10^2$	hecto	h	$10^{-15}$	femto	f
$10^1$	deca	da	$10^{-18}$	atto	a

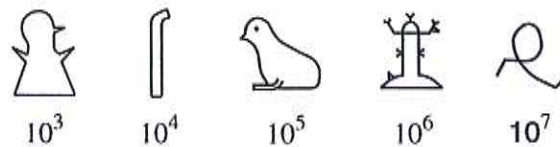


Figure 1.6. Hieroglyphics to express large numbers.

independent of the fact that humans produce chemical substances that are harmful in quantities as low as  $10^{-9}$  (1 ppb).

### 1.3 Classification of measurement methods

Measurement methods can be divided into the following categories depending on the object and the properties of the measured quantity.

#### 1.3.1 Direct and indirect measurements

Direct measurement implies a method to measure by directly comparing the measured quantity with the scale, for example reading the divisions of a scale in the case of measuring length. On the contrary, indirect measurement needs some calculation to get the result, for example to get velocity by the division procedure using the distance and the necessary time, which must be measured separately.

The accuracy of the indirect measurement is determined from the accuracy of each measurement. Let  $x_1, x_2, \dots, x_n$  denote the quantity obtained by the measurement and  $y$  denote the quantity to be obtained as a result, then  $y$  can be expressed by:<sup>3,4</sup>

$$y = f(x_1, x_2, \dots, x_n), \quad (1.1)$$

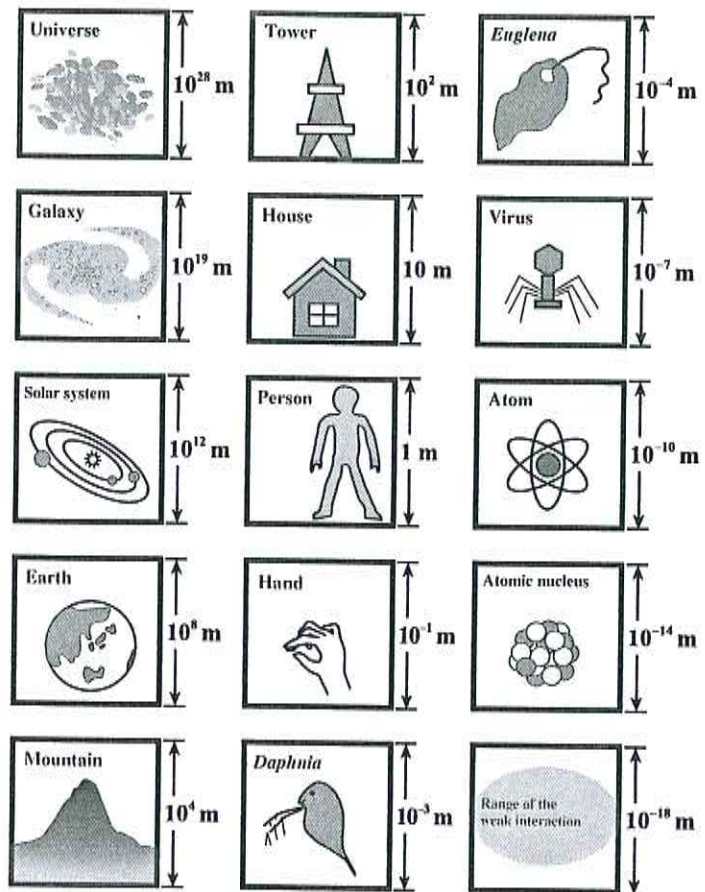


Figure 1.7. From microscopic scale to macroscopic scale.

where  $f$  implies some calculation procedure. The errors  $\delta x_1, \delta x_2, \dots, \delta x_n$  are generated in the measurements of  $x_1, x_2, \dots, x_n$ , respectively. In this case, the resulting error of  $y$  becomes

$$\delta y = \frac{\partial f}{\partial x_1} \delta x_1 + \frac{\partial f}{\partial x_2} \delta x_2 + \dots + \frac{\partial f}{\partial x_n} \delta x_n. \quad (1.2)$$

Each error  $\delta x_i$  affects the total error  $\delta y$  by the weight of  $\partial f / \partial x_i$ .

Let us consider one example of obtaining the moment of inertia of the cylinder with mass  $M$ , diameter  $d$  and length  $l$ . The moment of inertia  $y$  is given by

$$y = M \left( \frac{l^2}{12} + \frac{d^2}{16} \right). \quad (1.3)$$

From eq. (1.1) we get

$$\frac{\delta y}{y} = \frac{\delta M}{M} + \frac{8}{4 + 3d^2/l^2} \frac{\delta l}{l} + \frac{6}{3 + 4l^2/d^2} \frac{\delta d}{d} \quad (1.4)$$

For the cylinder with  $l = 10$  cm and  $d = 1$  cm,  $\delta y/y$  becomes

$$\frac{\delta y}{y} \approx \frac{\delta M}{M} + 2 \frac{\delta l}{l} + 0.015 \frac{\delta d}{d} \quad (1.5)$$

This result means that the measurement of the diameter  $d$  scarcely affects the moment of inertia.

As illustrated in this example, there are instances where we must make careful measurements and others where we can make somewhat rough measurements according to the particular factor in the indirect measurement.

### 1.3.2 Absolute and relative measurements

In absolute measurement, the measured quantity is an absolute value, as found when measuring light velocity ( $c = \lambda f$ ) using the values of the wavelength  $\lambda$  and the frequency  $f$ . Here we can get the magnitude of velocity in itself if the wavelength and frequency are measured accurately. The same situation holds for the measurement of length.

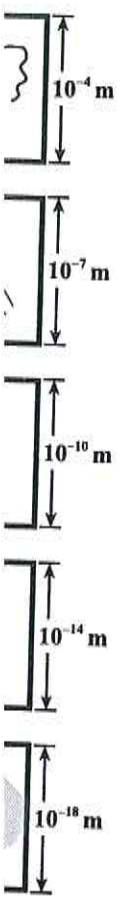
By comparison, relative measurement implies that the method measures the difference from the value at a reference point, which can be set arbitrarily. A typical example is the measurement of electric potential at some point, because it depends on the reference point of zero electric potential.

Whereas the value at a reference point should be constant during the measurement, it changes in some cases. The difference method for cancelling the changeable value at the reference point is effective in this instance (see an example in Fig. 4.11).

### 1.3.3 Deflection and null methods

In the spring balance, we read the deflection of the sign attached to the spring, which is expanded by the weight of an object, as shown in Fig. 1.8(a). In the ammeter to measure electric current, we read the angle achieved by the rotational force caused by the electric current that induces the electromagnetic force in the magnet. These are deflection methods. Here we must obtain beforehand a relationship between the deflection and the measured quantities, i.e., a calibration line.

The null method is one whereby the unknown quantity is measured by balancing it with a known reference quantity. The indication is zero when



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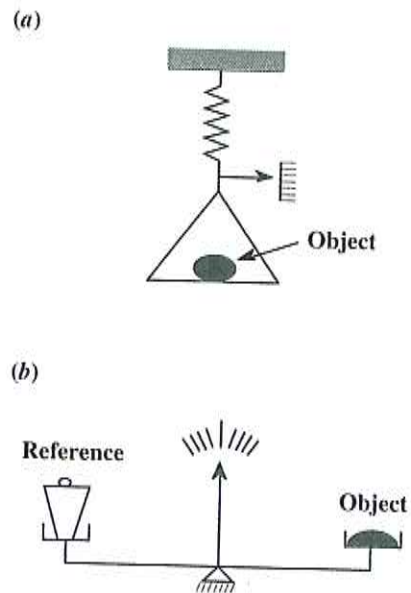


Figure 1.8. (a) The deflection method and (b) the null method.

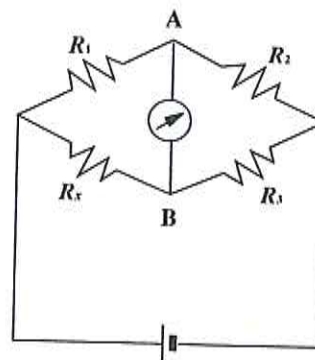


Figure 1.9. Wheatstone bridge.

the reference quantity is adjusted to the same value as the unknown quantity, as shown in Fig. 1.8(b).

One of the null methods is the measurement of electric resistance using the Wheatstone bridge, shown in Fig. 1.9. The unknown resistance  $R_x$  can be expressed using the known resistances  $R_1$ ,  $R_2$ ,  $R_3$  by

$$R_x = \frac{R_1 R_3}{R_2} \quad (1.6)$$

When the above equation holds, the electric current does not flow between points A and B because of zero electric potential difference.

In the null methods, a type of feedback procedure to adjust the known quantity is necessary.

### 1.4 Multiple regression analysis

In multiple regression analysis, we consider deriving a linear equation to give a relationship between several measured quantities. As one of the simplest examples, Fig. 1.10 shows the change in electric resistance  $R(\Omega)$  of some material with increasing temperature  $T(^{\circ}\text{C})$ . Let us try to express the relationship between  $R$  and  $T$  by the following linear equation:

$$R = b_1 T + b_0, \tag{1.7}$$

where  $b_1$  and  $b_0$  are the constants to be determined to give a best fit to all the measured data. Since the number of pieces of data is generally greater than two, there cannot exist two constants ( $b_1, b_0$ ) that will satisfy eq. (1.7) for all the data. So, what we can do is to search for the method for determining  $b_1$  and  $b_0$  in an approximate equation to reproduce all the data in the best way.

This subject can be extended to the case with more variables,  $y, x_1, x_2, \dots, x_p$ . The expected value  $Y$  for the experimental value  $y$  can be expressed by the following equation:

$$Y = b_1 x_1 + b_2 x_2 + \dots + b_p x_p + b_0. \tag{1.8}$$

This equation is called a multiregression equation with the explanatory variables  $x_i$  (predictor variables) and one dependent variable  $Y$ .

The two constants  $b_1$  and  $b_0$  in eq. (1.7) can be determined as follows. The error of each measurement  $i$  is given by

$$z_i = R_i - (b_1 T_i + b_0) \quad \text{for} \quad i = 1, 2, \dots, n, \tag{1.9}$$

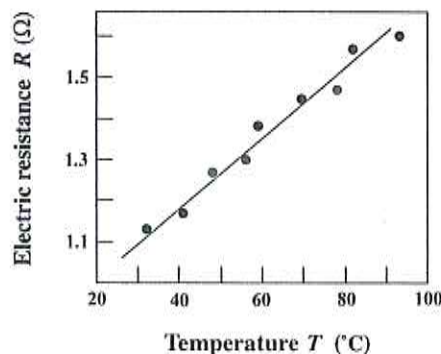


Figure 1.10. Change of electric resistance with temperature.

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(1.6)



where  $R_i$  is the measurement value of the electric resistance and  $n$  is the total number of measurements. From the method of least squares, the error is smallest when  $\sum z_i^2$  becomes a minimum with respect to  $b_0$  and  $b_1$  (see Fig. 1.11).

By minimizing  $\sum z_i^2$  with respect to  $b_0$  and  $b_1$ , we get

$$\begin{aligned}\frac{\partial}{\partial b_0} \sum_i z_i^2 &= \sum_i [R_i - (b_1 T_i + b_0)] = 0, \\ \frac{\partial}{\partial b_1} \sum_i z_i^2 &= \sum_i [R_i - (b_1 T_i + b_0)] T_i = 0.\end{aligned}\quad (1.10)$$

From this equation, we get

$$\begin{aligned}b_0 &= \frac{\sum_i R_i \sum_i T_i^2 - \sum_i R_i T_i \sum_i T_i}{n \sum_i T_i^2 - (\sum_i T_i)^2}, \\ b_1 &= \frac{n \sum_i R_i T_i - \sum_i R_i \sum_i T_i}{n \sum_i T_i^2 - (\sum_i T_i)^2}.\end{aligned}\quad (1.11)$$

The above case comprises only one explanatory variable. In more general cases with many predictor variables, the following set of equations holds for each measurement:

$$\begin{aligned}Y_1 &= b_1 x_{11} + b_2 x_{21} + \cdots + b_p x_{p1} + b_0, \\ Y_2 &= b_1 x_{12} + b_2 x_{22} + \cdots + b_p x_{p2} + b_0, \\ &\vdots \\ Y_n &= b_1 x_{1n} + b_2 x_{2n} + \cdots + b_p x_{pn} + b_0.\end{aligned}\quad (1.12)$$

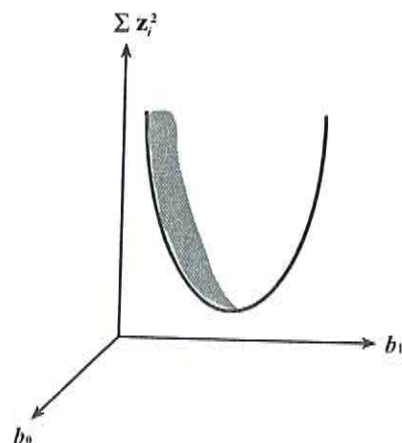


Figure 1.11. Minimization of errors.

Minimization of  $\sum z_i^2$  leads to

$$\sum_i (y_i - Y_i) = 0, \quad (1.13a)$$

$$\sum_i (y_i - Y_i)x_{ji} = 0. \quad (1.13b)$$

Equation (1.13a) implies that the average value  $\bar{y} (= \sum y_i/n)$  of the measured quantity is equal to the average of the expected value  $\bar{Y} (= \sum Y_i/n)$ . By multiplying  $b_j$  in eq. (1.13b) and making a summation about  $j$ , we get

$$\sum_i (y_i - Y_i)Y_i = 0, \quad (1.14)$$

by taking into account eq. (1.13a). Using eq. (1.14) we get

$$\sum_i (y_i - \bar{y})^2 = \sum_i (Y_i - \bar{Y})^2 + \sum_i (y_i - Y_i)^2. \quad (1.15)$$

This equation implies that the square sum ( $S_T$ ) of the observed value from which the average is subtracted is equal to the sum ( $S_R$ ) of the square sum of expected value, from which the average is subtracted, and that of error ( $S_E$ ).

$$\frac{S_E}{S_T} = 1 - \frac{S_R}{S_T}. \quad (1.16)$$

For the smaller  $S_E$ , the multiregression equation can explain the experimental data.

The ratio  $S_R/S_T$  can be expressed by

$$\frac{S_R}{S_T} = r^2, \quad (1.17)$$

where  $r$  is the multicorrelation coefficient defined by

$$r = \frac{\sum_i (y_i - \bar{y})(Y_i - \bar{Y})}{\sqrt{\sum_i (y_i - \bar{y})^2 \sum_i (Y_i - \bar{Y})^2}}. \quad (1.18)$$

From the above equations, it can be concluded that if  $r$  is near 1, the multiregression equation can also explain the experimental data.

The multiregression analysis is used with the smallest number of predictor variables. In general cases,  $n$  is larger than  $p$  in eq. (1.12). A peculiar situation arises in the case of  $n = p + 1$ . The number of unknown coefficients  $b_0, b_1, \dots, b_p$  agrees with the number of equations. So,  $b_i$  can be solved exactly except for a special case where one equation coincides with another equation because of the same data values that were obtained casually. This leads to zero errors; that is, eq. (1.8) can express the observed data strictly. Therefore, it is expected that we can obtain a multiregression equation to explain the observed data only if we increase the number of explanatory variables that

and  $n$  is the total  
squares, the error is  
 $b_0$  and  $b_1$  (see Fig.

(1.10)

(1.11)

In more general  
equations holds

(1.12)

have no relationship with the phenomenon concerned. Then,  $r^2$  increases artificially by adding meaningless explanatory variables. This is very strange. It is an unfavorable artifact brought about by the increasing degree of space constructed from the explanatory variables, i.e. the degree of freedom.

To prevent the meaningless increase in correlation coefficient, the adjusted  $r^2$  is proposed as follows:

$$\hat{r}^2 = 1 - \frac{n-1}{n-p-1}(1-r^2). \quad (1.19)$$

As can be understood from the above equation,  $\hat{r}^2$  can decrease if meaningless explanatory variables are added to the multiregression model. Using  $\hat{r}^2$ , we can compare the correlation between cases with different numbers of explanatory variables.

In some cases, cross-terms consisting of  $x_i$  and  $x_j$  are necessary to express  $Y$ . The same procedure is possible by regarding the cross-term as a new explanatory variable.

### 1.5 Principal component analysis

When we make measurements, we usually wish to express some components quantitatively. In the case of direct measurement, the measured quantity is the object itself. In the case of indirect measurement, however, the object (dependent variable) is expressed by a set of measured quantities (explanatory variables). The method to achieve this was described in Section 1.4. In this section, we treat the case where there is no dependent variable, which occurs frequently. For example, let us assume that we have a detailed investigation in a hospital. The investigation produces a number of measurements, total bilirubin, GOT, GPT, . . . , in the list of functional tests (the explanation of GOT, GPT is unnecessary; we only need to know that they are important quantities measured in assessing our health). When we want to know the hepatic function, we must search the equation by which the hepatic function is expressed using the above measured quantities.

Let us consider an example, shown in Table 1.6, where scores of language and mathematics of 16 students are listed. Using this result, it may be possible to say whether student E is good at language or mathematics. It implies the formulation to express the term "good at language" (or "good at mathematics") using the score of language  $x_1$  and the score of mathematics  $x_2$ . In this case, the decrease in information occurs always because the two variables (scores of language and mathematics) are reduced to one variable ("good at language"). Our intention is to adopt the method to obtain useful information

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 This is very strange.  
 ing degree of space  
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Table 1.6. Scores of language and mathematics of 16 students

Student	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Language	78	75	61	88	86	65	63	87	75	67	80	83	87	90	72	82
Mathematics	71	73	79	67	65	79	82	74	76	78	72	70	64	65	76	80
PCI	1.5	-2.0	-17.2	12.2	11.4	-13.7	-16.9	8.0	-3.5	-11.5	2.8	6.4	12.8	15.0	-6.1	0.7

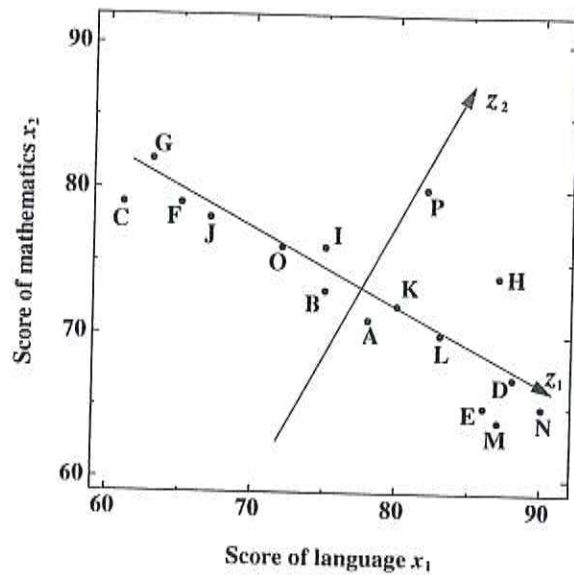


Figure 1.12. Scattering diagram of the scores of language and mathematics of 16 students.

without losing information.<sup>5,6</sup> This method is called a principal component analysis, which is often abbreviated as PCA.

The scores in Table 1.6 are rewritten in Fig. 1.12. By examining this figure, it would appear that the students who are good at mathematics are bad at language, while the students who are good at language are bad at mathematics. Therefore, it may be natural to define the lower right direction as the term “good at language” by drawing a straight line, as shown in Fig. 1.12. It means the introduction of a new variable  $z_1$ :

$$z_1 = a_{11}x_1 + a_{12}x_2, \quad (1.20)$$

where  $x_1$  and  $x_2$  are the values after the average was subtracted from the original values. Eq. (1.20) is nothing but rotation of axis.

We must do our best in determining  $a_{11}$  and  $a_{12}$  without losing information. It implies that the new axis is determined by the direction of the large spread of data points. To keep the magnitude in the transformation in eq. (1.20), the following condition is set:

$$a_{11}^2 + a_{12}^2 = 1. \quad (1.21)$$

Figure 1.13 shows schematically a relationship among the original information, the new information and loss of information. We get

$$\overline{OP}_i^2 - \overline{OQ}_i^2 = \overline{PQ}_i^2. \quad (1.22)$$

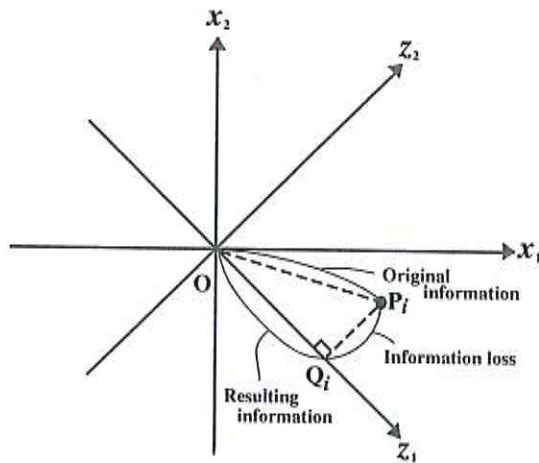


Figure 1.13. Concept of principal component analysis to obtain meaningful information.

This equation implies that  $\overline{OQ}_i^2$  can be maximized in order to minimize  $\overline{PQ}_i^2$  (loss of information). This is a problem in that we maximize  $\overline{OQ}_i^2$  by summing up over 16 pieces of data under the condition of eq. (1.21).

For this purpose, the Lagrange's method of undetermined multipliers is powerful. We maximize the following equation including the undetermined multiplier  $\lambda$ :

$$g(a_{11}, a_{12}) = \sum_{i=1}^N (a_{11}x_{1i} + a_{12}x_{2i})^2 - \lambda(a_{11}^2 + a_{12}^2 - 1), \quad (1.23)$$

where  $N$  is equal to 16 in the present example. By maximizing eq. (1.23) with respect to  $a_{11}$  and  $a_{12}$ , we get

$$\begin{aligned} \frac{\partial g}{\partial a_{11}} &= s_{11}a_{11} + s_{12}a_{12} - \lambda a_{11} = 0, \\ \frac{\partial g}{\partial a_{12}} &= s_{12}a_{11} + s_{22}a_{12} - \lambda a_{12} = 0, \end{aligned} \quad (1.24)$$

with

$$\begin{aligned} s_{11} &= \sum_i x_{1i}^2, \\ s_{12} &= \sum_i x_{1i}x_{2i}, \\ s_{22} &= \sum_i x_{2i}^2. \end{aligned} \quad (1.25)$$

The quantities obtained by dividing  $s_{11}$  and  $s_{22}$  by  $N$  are called a variance and the quantity  $s_{12}/N$  is called a covariance.

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 (1.22)

For the non-zero values of  $a_{11}$  and  $a_{12}$  in eq. (1.24),

$$\begin{vmatrix} s_{11} - \lambda & s_{12} \\ s_{12} & s_{22} - \lambda \end{vmatrix} = 0 \quad (1.26)$$

is a necessary and sufficient condition. The eigenvalue is given by

$$\begin{aligned} \lambda_1 &= \left[ s_{11} + s_{22} + \sqrt{(s_{11} - s_{22})^2 + 4s_{12}^2} \right] / 2, \\ \lambda_2 &= \left[ s_{11} + s_{22} - \sqrt{(s_{11} - s_{22})^2 + 4s_{12}^2} \right] / 2. \end{aligned} \quad (1.27)$$

Since the relation

$$g(a_{11}, a_{12}) = \lambda \quad (1.28)$$

holds, the magnitude of eigenvalue  $\lambda$  is equal to that of new information. The axes  $z_1$  and  $z_2$  are determined by  $\lambda_1$  and  $\lambda_2$ , respectively, because  $\lambda_1 > \lambda_2$ . The following expressions can be obtained for  $a_{11}$  and  $a_{12}$ , if we take  $a_{11} > 0$ :

$$\begin{aligned} a_{11} &= \frac{|s_{12}|}{\sqrt{(\lambda_1 - s_{11})^2 + s_{12}^2}}, \\ a_{12} &= \frac{\lambda_1 - s_{11}}{s_{12}} a_{11}. \end{aligned} \quad (1.29)$$

For the example in Table 1.6, we get  $a_{11} = 0.88$  and  $a_{12} = -0.48$ . The line  $z_1$  in Fig. 1.12 is drawn using eq. (1.20) with these values. The positive value of  $a_{11}$  and negative value of  $a_{12}$  means  $z_1$  increases for better at language and worse at mathematics. It really expresses the students who are better at language than at mathematics. The fact of  $|a_{11}| > |a_{12}|$  implies that the axis  $z_1$  is determined more by the score of language than that of mathematics. This axis has the largest information contained in  $x_1$  and  $x_2$ , and hence it is called a first principal component (PC1). The axis  $z_2$  determined from another eigenvalue  $\lambda_2$  is called a second principal component (PC2).

As shown in eq. (1.28), the magnitude of eigenvalue reflects information. The ratio of the eigenvalue to the sum of all the eigenvalues is called a contribution rate. In the present example, the contribution rates are 92.9% and 7.1% for PC1 and PC2, respectively. Therefore, PC1 has almost all the information.

Figure 1.12 implies that the student E is very good at language because his PC1 value is high. On the contrary, the student G is very bad at language because of the low score of PC1. In this way, we could extract information regarding the term "good at language" from two scores of language and mathematics.

The axis  $z_2$  is given by

$$z_2 = a_{21}x_1 + a_{22}x_2. \quad (1.30)$$

where the vector  $(a_{21}, a_{22})$  belonging to the eigenvalue  $\lambda_2$  becomes  $(0.48, 0.88)$ . The fact that  $a_{21} > 0$  and  $a_{22} > 0$  means that  $z_2$  reflects the students who are relatively good at both language and mathematics. The student P takes the largest value of  $z_2$ . The value of PC2 can be regarded as a kind of total score of examinations.

This can be understood clearly from the next example, shown in Table 1.7. By using the same procedure as above, we get

$$A = \begin{pmatrix} 0.73 & 0.68 \\ -0.68 & 0.73 \end{pmatrix}, \quad (1.31)$$

where

$$\mathbf{z} = A\mathbf{x} \quad (1.32)$$

with  $\mathbf{z} = (z_1, z_2)'$  and  $\mathbf{x} = (x_1, x_2)'$ , the superscript  $t$  implying the transpose vector. The contribution rates to PC1 and PC2 are 77.6% and 22.4%, respectively. As can be understood from the expression of eq. (1.31),  $z_1$  becomes the sum of  $x_1$  and  $x_2$  with different weights.

This expression is similar to the simple sum of scores and sometimes is more effective for evaluating the result of examinations. If all the students get the same score, for example 80 for mathematics, the addition of the score in mathematics to those for examinations of other subjects is meaningless. In this case, the score in mathematics has no value in evaluating differences in the ability of students (no ability difference or problems too bad). If the PCA is made, one eigenvalue becomes zero because there is no dispersion of the score in mathematics. As a result, PC1 is determined by other examinations.

The PCA was made here using the variance and covariance. However, it is not adequate to perform the analysis when there are variables with different characteristics, for example weight (kg) for  $x_1$  and height (m) for  $x_2$  in assessing obesity. If the unit g is chosen for the weight, the dominant term becomes the weight, and obesity can be determined by only the weight  $x_1$  independent of the height  $x_2$ . In such a case, the method using the nondimensional quantities is usually convenient: dividing  $x_i$  by the root of variance of  $x_i$ . It leads to  $s_{ii} = 1$ , and  $s_{ij}$  becomes the correlation coefficient  $r_{ij}$ .

Two variables were reduced to one variable in the above example. Of course, the same procedure can be applied to more general cases including many variables. The ultimate goal of sensor technology is to mimic the human senses and exceed them. For this aim, we sometimes get necessary information by using several sensors of different types and properties. In this case, we must relate all the information from these sensors to the intended quantities without losing information. The PCA is very useful for this purpose. In some cases, however, a relationship between input and output of the sensor



Table 1.7. Another example of scores of language and mathematics

Student	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Language	80	72	75	87	63	75	66	85	78	67	68	82	80	77	71	85
Mathematics	64	66	80	85	62	73	76	76	79	70	62	70	62	68	75	83
PCI	-2.8	-7.2	4.6	18.8	-16.5	-0.2	-4.7	9.1	6.1	-8.1	-12.8	2.8	2.7	-2.2	-1.7	13.9

becomes strongly nonlinear. A neural network algorithm can be used in those cases, as will be found in Chapter 5 for odor sensors.

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## 8

### Toward a sensor to reproduce human senses

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#### 8.1 Discrimination of wine flavor using taste and odor sensors

Earlier chapters have reviewed a range of sensor types. Recently, there have been striking developments in odor and taste sensors. As shown in Fig. 8.1, it may not be impossible to discuss deliciousness of foods by combining the sensors corresponding to the five senses. We can use an optical sensor for the color, a thermometer for the temperature, a pressure sensor for the texture, a taste sensor for the taste and an odor sensor for the odor. Analysis of outputs from the above sensors, together with environmental and personal information, may lead to quantification of deliciousness. The following example describes a first step of this trial.

Wine has both taste and odor qualities resulting from different aromatic molecules in the liquid and vapor phases. The average wine contains about 80–85% water and over 500 different substances, some of which are very important to the wine flavor in spite of their low concentrations. The main groups are acids, alcohols, esters, sugars and tannins. The difference in the color of wine comes mainly from tannins (which are also responsible for the flavor). The tannins are present in the solid part of the grapes, which are fermented together with the liquid part when a red wine is made; for white wines only the liquid from grapes is used. It is known that tannins are responsible for the astringency of a solution whereas some acids are responsible for “freshness” and others for peculiar odor nuances.<sup>1</sup>

Among this huge number of molecules, those which can easily pass in a vapor phase represent potential stimulus for the human olfaction when they reach the bulb in the nasal cavity and interact with the odor receptors. Molecules in the liquid phase are responsible for the perceived taste when they interact with taste buds on the tongue. The overall perception of a substance as far as its chemical properties are concerned results from a combination of odor and taste senses and also from the so-called trigeminal sense (responsive to irritant chemical species). This perception is hereafter

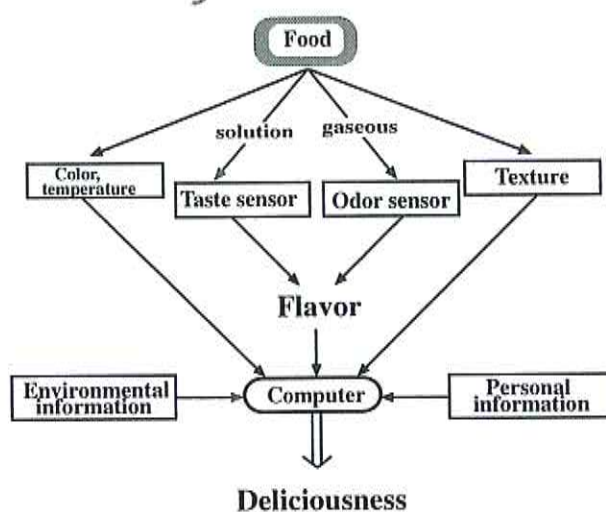


Figure 8.1. Measurement of deliciousness.

referred to as flavor. Wine, therefore, is a suitable candidate for testing the performance of the sensory fusion of taste and odor sensors.<sup>2</sup> The odor-sensor array used in this study is composed of four different novel conducting polymers that have been recently developed.<sup>3</sup> The monomer (25 mg) is dissolved in trichloroethylene (2 ml) and the oxidizing salt previously dissolved in acetonitrile is added in a dropwise manner. The polymerization process then occurs and the resulting solution is sprayed onto an alumina substrate where four interdigitated electrodes were previously evaporated. After evaporating the solvent, the conducting polymer is connected with the four electrodes, as shown in Fig. 8.2. Four different sensing elements were obtained by combining two different monomers and two oxidizing salts (see Table 8.1).

The electric resistance between the inner electrodes of these sensing elements ranged from 1 to 100 k $\Omega$ . The resistance measured at the inner electrodes varied when volatile molecules were adsorbed at the surface of the polymer film. The average sensitivity, expressed as the ratio of the resistance change to the base resistance value, was almost always less than 2% for the elements used in wine sensing. These sensors show broad and overlapped sensitivities to many compounds such as alcohols, amines, hydrocarbons and phenols. They also show a cross-sensitivity to water vapor (relative humidity; RH) so that monitoring of RH was necessary during the experiments.

The taste-sensor array is composed of eight different polymer/lipid membranes, as shown in Table 6.1 (p. 116). After preparation, the electrodes were immersed in a solution of a Japanese red wine for four weeks (the wine used as a standard solution) before they were used for the experiments

Table 8.1. Materials used for the conducting polymer forming process

Channel	Monomer	Oxidizer
1	3DPO2BT	Fe(ClO <sub>4</sub> ) <sub>3</sub>
2	3,3'-DPTTT	Fe(ClO <sub>4</sub> ) <sub>3</sub>
3	3,3'-DPTTT	Cu(ClO <sub>4</sub> )
4	3DPO2BT	Cu(ClO <sub>4</sub> )

3DPO2BT, 3,3'-dipentoxy-2,2'-bitiophene;  
3,3'-DPTTT, 3,3'-dipentoxy-2,2': 5',2''-  
tertiophene.

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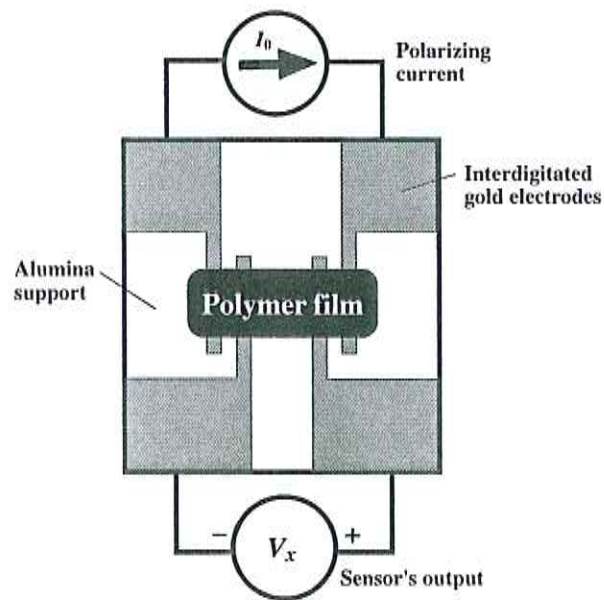


Figure 8.2. Layout of a single odor-sensing element on alumina substrate.  
(With permission from Baldacci *et al.*<sup>2</sup>)

(preconditioning method). The four different wines used for the experiments are listed in Table 8.2.

The raw data were normalized by the following method. Let  $\bar{S}_{ix}$  be the set of measurements taken with the multichannel odor sensor:

$$\bar{S}_{ix} = \begin{bmatrix} S_{11} & S_{21} & S_{31} & S_{41} \\ \vdots & & & \vdots \\ \vdots & & & \vdots \\ S_{1N} & \cdots & \cdots & S_{4N} \end{bmatrix}, \quad (8.1)$$

Table 8.2. Four different wines used in the experiments

Wine	Brand name
Wine 1 (white)	Est! Est! Est! di Montefiascone 1995, Italy
Wine 2 (red) (standard solution)	Bon Marche' Mercian, Japan
Wine 3 (white)	Chablis 1994, France
Wine 4 (red)	Rosso di Montalcino, Fattoria dei Barbi, 1994, Italy

where  $i$  is the channel number,  $s$  is the  $s$ -th measurement and  $N$  is the number of measurements. Each element of the matrix represents the response of a single element of the odor-sensor array expressed as the ratio of the maximum resistance change, upon exposure to the vapors, to the base resistance measured in presence of clean air flowing through the exposition chamber. Let  $\bar{T}_{is}$  be the set of measurements taken with the multichannel taste sensor:

$$\bar{T}_{is} = \begin{bmatrix} T_{11} & \dots & \dots & T_{81} \\ \vdots & & & \vdots \\ \vdots & & & \vdots \\ T_{1N} & \dots & \dots & T_{8N} \end{bmatrix}, \tag{8.2}$$

where  $i, s$  and  $N$  have the same meanings as above. Each element of the matrix represents the response of a single electrode of the taste sensor expressed as the difference between the electric potential in the testing solution and the electric potential in the standard solution.

The mean values of the responses for each channel are

$$\bar{S}_i = \frac{1}{N} \sum_{s=1}^N \bar{S}_{is} \tag{8.3a}$$

for the odor sensor, and

$$\bar{T}_i = \frac{1}{N} \sum_{s=1}^N \bar{T}_{is} \tag{8.3b}$$

for the taste sensor.

Computing the average of the square errors of the responses first among the samples and then among the channels we obtain

$$\sigma_o^2 = \frac{1}{4N} \sum_{i=1}^4 \sum_{s=1}^N (\bar{S}_{is} - \bar{S}_i)^2 \tag{8.4a}$$

(8.1)

for the odor sensor and

$$\sigma_o^2 = \frac{1}{8N} \sum_{i=1}^8 \sum_{s=1}^N (\bar{T}_{is} - \bar{T}_i)^2 \quad (8.4b)$$

for the taste sensor.

Now the original sets of data can be normalized as follows:

$$\bar{s}_{is} = \frac{\bar{S}_{is} - \bar{S}_i}{\sigma_o} \quad (8.5a)$$

for the odor sensor, and

$$\bar{t}_{is} = \frac{\bar{T}_{is} - \bar{T}_i}{\sigma_t} \quad (8.5b)$$

for the taste sensor. Combining the normalized sets of data we obtain the data set:

$$\bar{F}_{is} = [\bar{s}_{is} \quad \bar{t}_{is}], \quad (8.6)$$

that is, a  $12 \times N$  dimensional data array.

From each measurement using the taste sensor, an eight-dimensional vector representing eight membrane potentials was extracted. One cycle of measurements consisted of four different acquisitions made by rotating the testing samples in the following order: wine 1, wine 2, wine 3 and wine 4 (note here that wine 2 was also used as the standard solution). PCA was made after normalizing. The distribution of data in the principal component space is shown in Fig. 8.3.

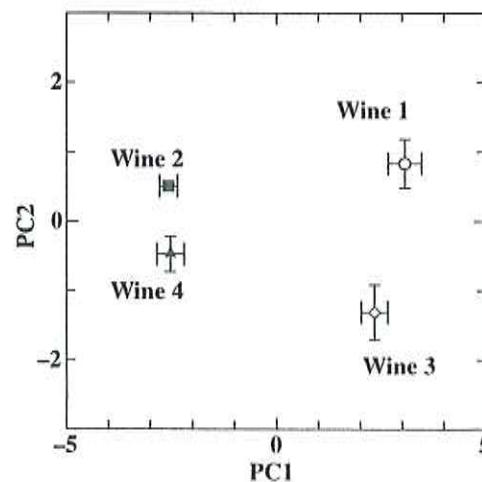


Figure 8.3. Results of the PCA applied to the data set from the taste sensor. Wines 1 and 3 are white; wines 2 and 4 are red. (With permission from Baldacci *et al.*<sup>2</sup>)

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(8.5a)

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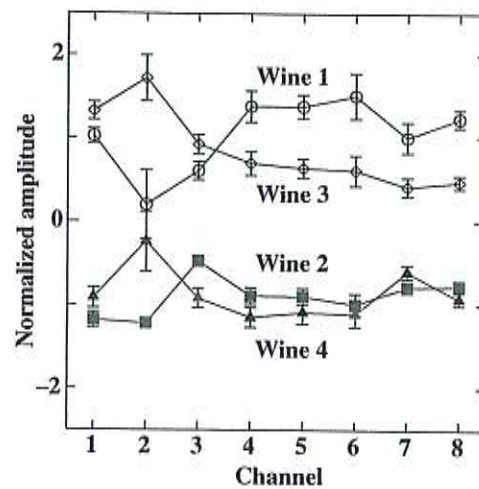


Figure 8.4. Eight-dimensional taste patterns of the testing wines. (With permission from Baldacci *et al.*<sup>2</sup>)

We can observe that the data are clustered in four well-separated groups representing the four different wines used. The PC1 accounts for the differences between red and white wines, whereas the PC2 accounts for the differences between wines of the same color. As mentioned above, the color of wine is mainly from the content of tannins. The sensitivity of the taste sensor to tannins was investigated in a previous work<sup>4</sup> to show that the array's element, DOP : TOMA 3 : 7, was the most sensitive for tannic acid. This agreed with the present result because the element DOP : TOMA 3 : 7 is the larger contributor to the PC1, which, in turn, accounts for the discrimination between red and white wines.

Figure 8.4 shows the averaged taste patterns of the four wines. The taste pattern can be seen as the fingerprint of a wine in the eight-dimensional space represented by the taste sensor. Each wine is characterized by its own taste pattern.

From each measurement using the odor sensor, a four-dimensional data vector representing the peak values of the electric resistance changes was extracted. The PCA was computed after normalizing the data in the same way as for the taste sensor. The plot in Fig. 8.5 shows the distribution of clusters in the principal component space. Again, discrimination among different wines was achieved. At this stage no data were available concerning the sensitivity of odor sensors to the main components of wines and therefore no quantitative consideration can be put forward to account for these results. Nevertheless, in this case the mutual distribution of clusters differs from that in Fig. 8.3 and this can be considered as evidence that the information concerning the samples



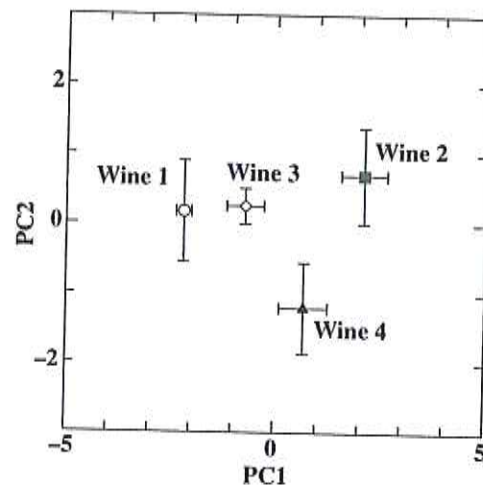


Figure 8.5. Results of the PCA applied to the data set from the odor sensor. (With permission from Baldacci *et al.*<sup>2</sup>)

provided by the odor sensors accounts for different characteristics of the wines themselves. In this case, the PC1 is still responsible for the discrimination between red and white wines and also for the differences between the two white wines and the two red wines. The PC2 gives information about further differences between the two red wines. Note here, in the PCA plot, how the overall information about the set of samples is topologically distributed in a different way compared with that from the taste sensor.

Figure 8.6 shows the averaged odor patterns for the four wines tested. Again, the odor patterns are the representation of the wines in

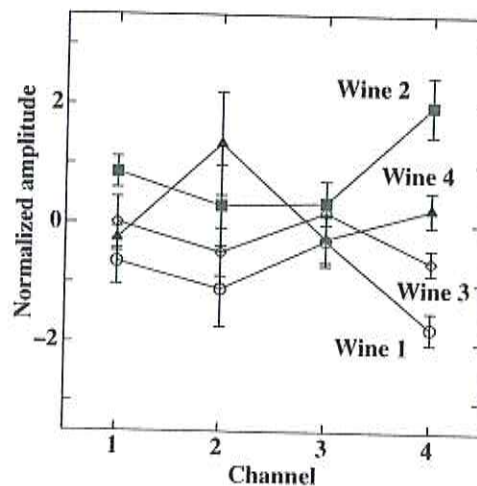


Figure 8.6. Four-dimensional odor patterns of the testing wines. (With permission from Baldacci *et al.*<sup>2</sup>)

the four-dimensional space of the odor-sensing elements. Each sample has its own odor pattern, which differs slightly among samples belonging to the same kind of wine because the responses of the odor sensor and the fluid-dynamic conditions<sup>5</sup> were not highly reproducible, as in the case of the taste sensor.

After either set of data was normalized, according to the method described, a 12-dimensional data array was obtained for each measurement. The 12-dimensional data array is composed of the four-dimensional data array of the odor sensor and the eight-dimensional data array of the taste sensor. Another PCA was performed on this new set of data and the results are shown in Fig. 8.7.

The relative positioning of the clusters in the principal component plane was similar to that for the odor sensor, and the relatively large distance between clusters of the red (2 and 4) and white (1 and 3) wines were successfully achieved by the contribution of the taste sensor, as in Fig. 8.3. The combination of the two sets of data has led to a new representation of the samples in the 12-dimensional space, which we refer to as flavor pattern. A flavor pattern simultaneously contains information from odor and taste sensors concerning the sample measured.

The feasibility of a sensory fusion between taste and odor sensors has been investigated with the aim of discriminating among substances with subtle differences, such as the wines used here. The same method was applied to detect the change in flavor after opening wine, using five samples of the same

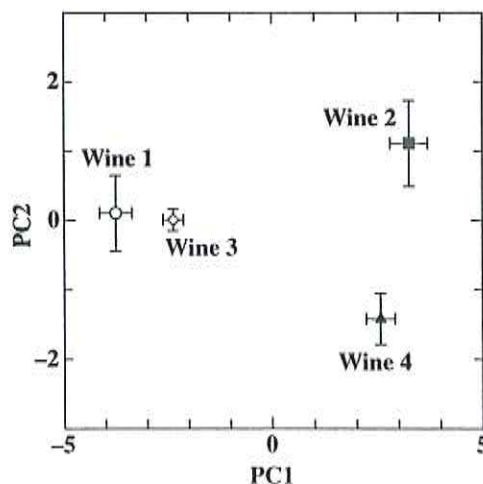


Figure 8.7. Results of the PCA applied to the combination of the data set from the odor sensor with the data set from the taste sensor. (With permission from Baldacci *et al.*<sup>2</sup>)

wine opened for different times.<sup>2</sup> Discrimination of wines, having the same denomination but coming from different vineyards, was successfully made using an array of metal oxide semiconductor gas sensors.<sup>6</sup> The sensor fusion is very effective because the information provided by each array is to some extent independent from the others; the arrays account for different characteristics of the wines themselves since the relative positioning of clusters in the principal component space differs from one wine to the next. Conventional multiple sensor arrays have several sensing elements produced by similar technology, e.g., conducting polymer sensor, metal oxide sensor and lipid-membrane sensor. These sensors show broad sensitivities to certain groups of substances but are not sensitive to other compounds. If different types of sensor technology are simultaneously applied, provided that the data from the different sources are independent, it is worthwhile to combine them to obtain a broader viewpoint of the samples measured.

## 8.2 Perspective

A multichannel taste sensor, i.e., electronic tongue, utilizes lipid membranes as the sensing part. This sensor can discriminate and quantify the taste of chemical substances that is really felt by humans. A recent study<sup>7</sup> shows that measurement of the electric potential of the membrane electrode in standard KCl solution without rinsing the electrode, onto which chemical substances such as quinine and tannin were adsorbed by measuring the sample solution, is very effective for quantifying the taste. This measurement is called a CPA measurement, because the change of electric potential caused by adsorption of chemical substances is measured. The CPA measurement provides information that is different from the usual measurement of electric potential of the sample (i.e., the response electric potential) as described in Chapter 6. Briefly speaking, the CPA measurement reflects the adsorbed amount of chemical substances on the lipid/polymer membranes mainly from hydrophobic interactions. If we combine the CPA measurement with the usual measurement, which detects the electric potential of the sample, we can obtain more information of the overall taste comprising salty, sour, sweet, bitter, umami taste and astringency components. The overall taste of green tea, where amino acids and tannin are main taste substances, was quantified using this method, and high correlations with the results of sensory tests were found.<sup>8</sup>

One of the main features of the taste sensor utilizing lipid membranes is its ability to quantify the taste of amino acids, as seen in Section 6.4. The taste sensor can classify the taste of amino acids into tastes such as bitter, sweet,

sour and umami taste. The mixed taste composed of bitterness and sweetness shown by L-methionine and L-valine can be reproduced using the taste sensor by a mixture of L-alanine, which tastes sweet, and L-tryptophan, which tastes bitter. The bitter taste of amino acids is intimately related to the hydrophobicity. The taste of dipeptides can also be discriminated by the response pattern of the taste sensor, which is characteristic of each taste quality. Figure 8.8 shows a taste map of five taste qualities elicited by typical chemical substances, amino acids and dipeptides (K. Toko and T. Nagamori, unpublished data).

The taste of seafoods such as abalone, sea-urchin, crab, scallop and short-necked clam is determined by the content of amino acids.<sup>9</sup> For example, the taste of sea-urchin can be expressed by L-glutamate, glycine, L-alanine, L-valine and L-methionine at 103, 842, 261, 154 and 47 mg/100 g and an adequate quantity of NaCl. The aqueous solution of this mixture was measured using the taste sensor, and the result was compared with the measurements for sea-urchin, which was crushed and homogenized with a mixer. The correlation coefficient was 0.995 for one of the sea-urchins tested (S. Takagi and K. Toko, unpublished data). There was a tendency for the correlation to become higher for expensive sea-urchins; it is related to the quantity of NaCl compared with that of amino acids. As the sea-urchin is more expensive, the weight of amino acids playing a role in producing the main taste becomes larger.

As mentioned in Chapter 2, the reception mechanism of gustatory systems is as yet unclear. However, the taste sensor using lipid membranes can reproduce the taste experienced by humans in most cases except for sweetness elicited by sugars, as detailed in the last two chapters. The response patterns for five taste qualities differ, and hence these tastes are separated well on the three-dimensional taste map (see Fig. 6.7, p. 122). The response patterns for bitter amino acids such as L-tryptophan resemble that for quinine, which is a typical bitter substance belonging to the alkaloids. The detected threshold is almost the same in both the taste sensor and the gustatory system for each taste quality. Suppression of bitterness by sweet substances and phospholipids can be reproduced well using the taste sensor. The tastes of many foodstuffs such as beer, coffee, milk, mineral water, sake and tomatoes can be quantified and the sensor outputs can agree with sensory tests by humans. How should we interpret these facts?

It may be reasonable to consider that in real systems the lipid membrane plays a role in the reception of bitter substances such as quinine and amino acids, sour substances such as acetic acid and citric acid, and salty substances such as NaCl, KCl and FeCl<sub>3</sub>. The response patterns are large for these taste

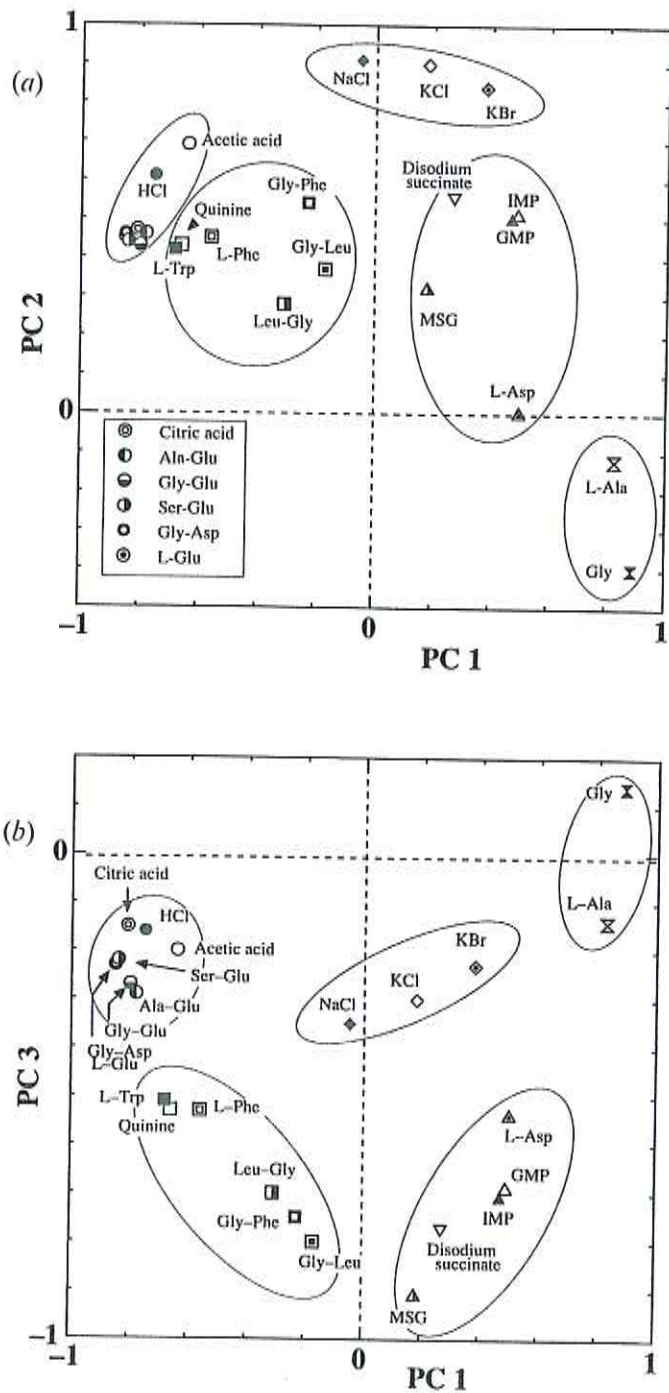


Figure 8.8. Taste map comprising typical chemical substances such as HCl, NaCl, quinine, amino acids and dipeptides. (a) PC 1-PC 2, (b) PC 1-PC 3 plane.

qualities and differ from one taste quality to another; similar patterns are obtained for chemical substances producing the same taste. Within the group of sweet substances, sugars can be hardly detected using the multi-channel potentiometric taste sensor that uses lipid membranes; however, amino acids (glycine, L-alanine) and artificial sweeteners can be measured. Interestingly, a different reception and transduction mechanism in gustatory systems is proposed for these two species, as mentioned in Section 2.3.

The fifth taste quality, umami taste, can be detected using the taste sensor. Three umami taste substances (MSG, IMP and GMP) with very different chemical structures (MSG is an amino acid; IMP and GMP are nucleotides) show almost the same response electric patterns, as seen in Fig. 6.6 (p. 121). There is a possibility that umami taste substances are received at the lipid membrane part of biomembranes, because a similar response pattern can be obtained for other umami substances such as monosodium L-aspartate.<sup>10</sup> It can be considered that umami taste is related to chemical substances that have a common structure as neutral salts of weak acids with moderate hydrophobic properties.<sup>11</sup> The hydrophilic group and hydrophobic chains of the lipid membrane interact with the chemical substances that have this structure. A well-known phenomenon that saltiness of NaCl is decreased by coexistent umami taste substances can be reproduced using the taste sensor.<sup>12</sup> However, the reproduction of the synergistic effect experienced by humans is not completely achieved by the taste sensor because the increase in umami taste strength is weaker for the taste sensor than for humans.

Kurihara suggested the importance of the hydrophobic part of lipid membranes for the reception of bitter substances.<sup>13</sup> The results of the taste sensor studies using lipid membranes support this suggestion and furthermore suggest that other taste qualities such as sourness and saltiness can also be detected by the lipid membrane, which can use both its hydrophobic and its hydrophilic parts in reception of chemical stimuli. Living organisms must check the safety of all chemical substances quickly before eating them and it may well be that they use the lipid membrane as well as the proteins embedded in it to achieve this.

Although lipid molecules have a more simple structure than most proteins, they can self-organize into macroscopic multimolecular structures such as the lipid bilayer and liposomes. Once such a structure is formed, it can function as a barrier to ions, a supporting/modulating material for proteins, an electron-transfer medium and as a recognition system at the cell surface.

The studies using the taste sensor described in this book and the results achieved may contribute to our understanding of the reception mechanisms

involved in the gustatory system and add new light to the role of lipid membranes.

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