Feature Article

A Compact Ion Meter Using a Flat Electrode: Applications

Katsuhiko TOMITA   Hiromi OKAWA   Junji KOJIMA

Abstract
This paper introduces and discusses applications of the Cardy series pH meter, ion meters and conductivity meter,; all of which have been developed with a new line of compact testers for chemical analysis. These products feature a newly developed sheet-type electrode, which allows measurements to be made using a very small amount of sample. The discussion centers on possible applications that take advantage of this feature including: (1) measuring acid rain, (2) analyzing the fluid secretions in living bodies, and (3) determining the acidity of paper. Also discussed is the Twin pH meter, which permits measurements to be carried out either by dipping the electrode in a sample (like conventional desk-top pH meters) or by placing a very small amount of sample on the pH sensor.

1. Introduction

As we approach the 21st century, measuring instruments are diverging in two different directions. One path leads to highly sophisticated measurement systems, and the other path leads to lightweight and compact instruments made inexpensive by mass production. The pH meter field, where Horiba has been a leader since its inception, is no exception to this trend. Each model change has seen the addition of new features, and the products have been primarily scientific instruments for use in laboratories. At the same time, there has been a growing demand for the development of a simple and convenient pH meter that can be used outdoors and stored in a desk drawer like a tester or thermometer.

To meet this demand, we began the development of a completely new type of pH meter that is portable and has the look and feel of a "chemist's tester." One possible means of allowing mass production is to create the ion-sensing electrode on a silicon chip like an integrated circuit. We decided that this approach would not produce a product with high reliability and therefore decided to create an ion electrode on film or a sheet, using the same principle used in the conventional stick-shaped electrodes for tabletop pH meters. Our goal was to develop an ultra-small pH meter with a built-in composite sheet electrode that is capable of prolonged use and will perform equal to or better than tabletop pH meters. The result of our efforts was the Cardy (C-1), a reliable, ultra-compact card-type pH meter[2,3]. We also applied this technology to develop a sheet-type sodium ion meter (C-122), a potassium ion meter (C-131), a nitrate ion meter (C-141), a salt meter (C-121), and conductivity meters (C-172 and C-173). In addition, we developed the "Twin" series (B-111 and B-112), which are capable of two types of measurement: immersion of the electrode in the sample (like a conventional tabletop pH meter), and measurement of a small quantity of applied sample (like a card pH meter).

In this article we describe the Cardy and the Twin, and discuss application examples of measuring biological secretions and the acidity of paper. We also discuss applying the product to the measurement of acid rain, a topic related to this edition's focus on environmental problems.

2. The Instruments

2.1 The Structure of the Electrode

Figure 1 shows the structure of the sheet pH combination

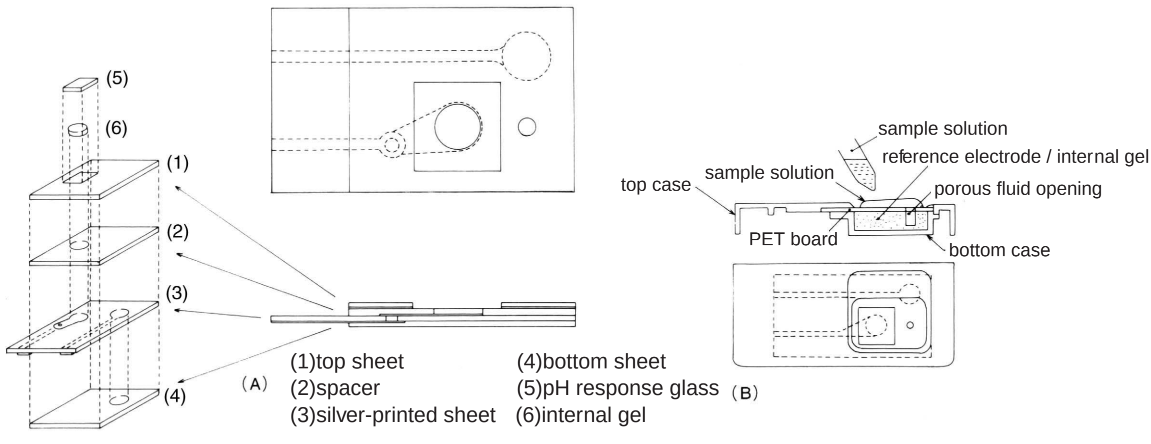


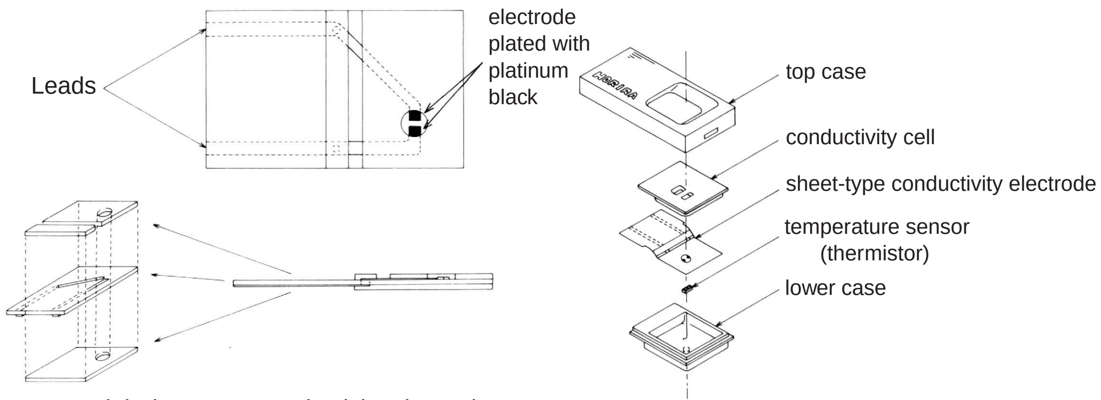
Fig. 1 Structure of sheet-type pH combination electrodes

electrode. **Figure 1(A)** shows that the sheet pH electrode is a multi-layer structure made by laminating four sheets of poly ethylene terephthalate (PET) together (1 to 4). Silver electrodes are printed on both sides of sheet 3, and the response part is chloridated to form an internal Ag/AgCl pole. The inside of the four-layer laminated PET board is filled with a gel, and affixed with a silicon adhesive to thin film of pH response glass, both sides of which have been treated by a high temperature fusing process.

The structure of the reference electrode is shown in **Figure 1(B)**. The four-layer laminated PET board is enclosed in an ABS case and the lower container is filled with a gel consisting primarily of potassium chloride (KCl). The gel is made to contact the internal Ag/AgCl pole on the rear of the PET sheet. A sintered polymer porous material is used for the fluid channel. The fluid channel passes through the PET board so that the pH sensor and fluid channel are joined on the same surface.

The sheet-type ion electrode was developed as an application of the sheet-type pH electrode. We introduced ion concentration meters for measuring nitrite ions, potassium ions, nitrate ions, and salt. A plastic solid film based on poly vinyl chloride (PVC) was used for the response membrane of the ion electrodes. Thus, inner layer 3 (**Figure 1, A**) of the four-layer PET structure was replaced with a PVC sheet.

We also developed a sheet-type conductivity electrode that performs measurements using the AC dual electrode method. **Figure 2** shows the structure of the electrode. Like the sheet-type pH electrode, a silver electrode is printed on a PET sheet. The surface area of the electrode is enlarged and protected against corrosion by platinum plating. Because the current distribution (**Figure 3**) varies with the fluid surface volume when the sample quantity is very small, the sample quantity, though still small, must be sufficient (> 100 μl) to completely fill the conductivity cell shown in **Figure 2**. The conductivity of a solution normally increases by about 2% when the temperature increases by 1℃ at normal temperatures. As the temperature coefficient is comparatively large, we attached a temperature sensor to the rear side of the PET sheet for temperature compensation. Response as a function of temperature is shown in **Figure 4**.



(A) sheet-type conductivity electrode (B) Cardy conductivity sensor

Fig. 2 Structure of sheet-type conductivity electrode

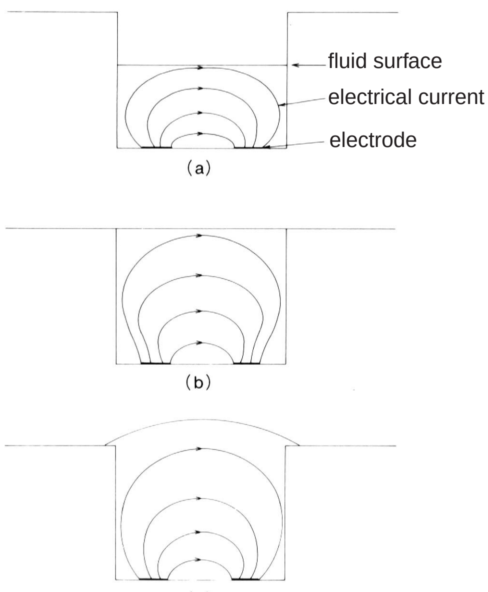


Fig. 3 Current distribution in a conductivity cell

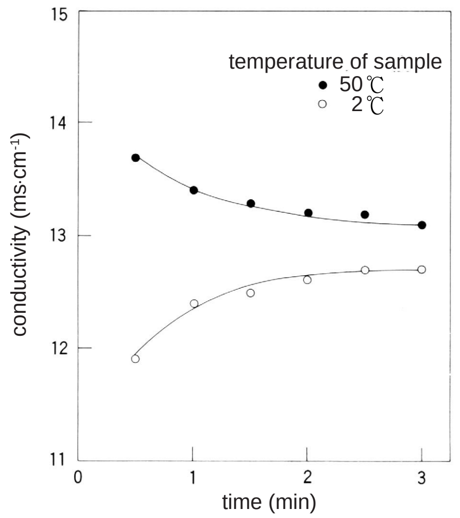


Fig. 4 Time-course change of conductivity depending on the temperature of the sample
(100μl of 0.1 mol KCl (12.9 ms cm^{-1}) was titrated at ambient temperature)

2.2 Fundamental characteristics of the sheet-type pH combination electrode

The electromotive force characteristic of the sheet-type pH combination electrode is shown in **Figure 5**. Within a

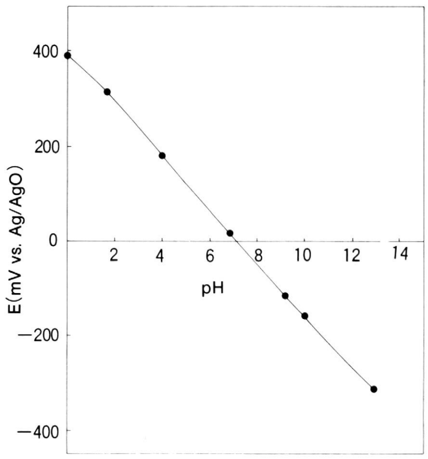


Fig. 5 Electromotive force characteristics of sheet-type combination electrodes

pH range of 2 to 12, the electromotive force of the electrode shows a linear response. The curve deviates slightly from linearity below pH 2 and above pH 12; however, this is probably because the use of a sealed reference electrode (for reasons explained later) can give rise to a slight difference in electric potential between solutions. **Figure 6**

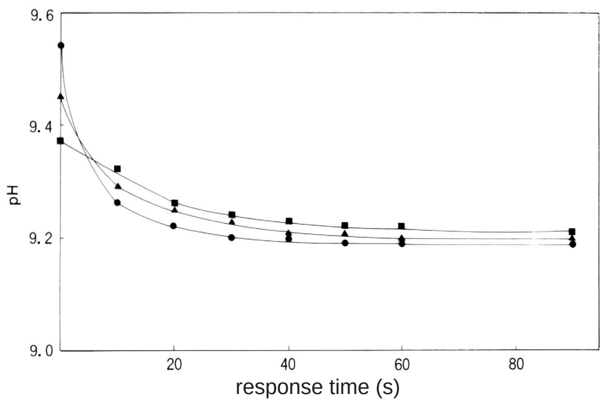


Fig. 6 Time-course change of pH measurement value depending on the temperature of the sample

shows the response when the sample temperatures differ. Phthalate standard solution was dripped on the sheet-type pH combination electrode of the Cardy pH meter (C-1) at 3℃, 25 ℃and 60 ℃, and the changes in the values displayed by the pH meter were plotted. Room temperature at this time was 25.5℃ and the pH of the phthalate standard solution was 9.18 at a fluid temperature of 25℃ .
In all cases the reading stabilized after 40 seconds, and the values were essentially in agreement at 9.2. From this we can see that for a minute sample, even when the temperature of the sample differs from the temperature of the meter (room temperature), the sample temperature adjusts to the meter temperature fairly quickly and an accurate measurement is obtained. For this reason, the Cardy C-1 incorporates a temperature compensation circuit that is based on the meter temperature.

The most important feature of the card-type meter is its ability to perform measurements using only a minute sample. In principle, measurement is possible if the response surface is moistened and the solution thick enough to obtain normal ion conduction. The main problem that occurs when measuring a minute sample is contamination of the sample from contact with the internal solution of the reference electrode. Studies of our design allow us to conclude that the degree of contamination is low compared to ordinary reference electrodes. As an example of minute sample measurement, **Figure 7** shows the result of measurement

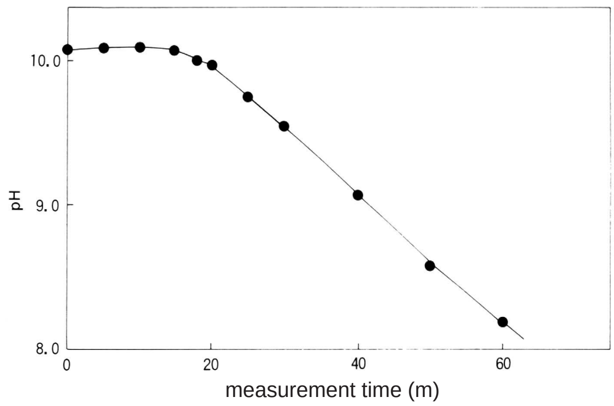


Fig. 7 Measuring the pH of a high-alkali glass surface

of the pH of a high-alkali glass surface using 50 µl of pure water. After measurement begins, alkaline metal ions dissolve from the glass sample surface and hydrate to form hydroxides producing a pH value of 10. The value was initially stable, but after about 15 minutes it gradually began to drop. This was probably due to the effect of CO_2 in the air, but we can still conclude that measurement of minute quantities is possible if performed over a short time period. To perform precise measurements of minute quantities, sufficient consideration must be given to the sample's ion concentration, conductivity, and evaporation (which can reduce the sample quantity), and test conditions must be set accordingly. However for simple measurements, it is very convenient to simply drip the minute sample onto the electrode and then read the measurement. Thus, samples that were previously difficult to measure can now be handled with ease.

The Twin type pH meter is capable of both minute sample measurement and dipping measurement, and the ability to measure by dipping it into a beaker means that the range of application is even greater.

2.3 Specifications

The features of the card-type are as follows:

(1) The world's first card-type meter, exceptionally small and light.

(2) Affordable, ideal for personal use

(3) Measurement is possible with several drops

The meter is shown in **Figure 8(A)**. The sheet-type pH combination electrode is incorporated into the bottom of the meter, and is replaceable. **Figure 8(B)** shows a recently developed stick-type pH meter (the Twin). The electrode configuration is essentially the same as the Cardy. The Twin has the features of the card-type meter but also allows conventional dipping measurement. **Table 1** compares the specifications of the card-type and stick-type pH meters. Specifications for the salt meter and ion concentration meters for sodium, potassium, and nitrate are also shown. A one-chip microprocessor allows these ion concentration meters to display the sample's wt% and ppm concentration. The conductivity meters form a series based on measurement concentrations, and can be broadly classified into meters for measuring water quality of rivers and streams and meters for measuring soil and hydroponics. Specifications are shown in **Table 2**.

(A) The Cardy series (B) The Twin series

Fig. 8 The Cardy series / The Twin series

Table 2 Specifications of Cardy conductivity meter
(measurement outside of range at left also possible)

model name	C-172	C-173
measurement range	0~199 0~1990	0~1.99 0~19.9
display resolution	1 10	0.01 0.1
measurement unit	μS/cm	mS/cm
measuring method:	AC dual-electrode method	←
accuracy	±2% FS (3% FS above 10 mS/cm) ±1 digit (25℃)	←
temperature compensation	automatic 2%/℃ (conversion reference temperature of 25℃	←
ambient temperature conditions		←
	3V × 2 CR-2025 lithium batteries	←
weight	approx. 40 g (excluding accessories)	←
dimensions of meter unit	95 mm ×55 mm ×9 mm	←
meter unit material:	ABS resin	←
battery life	continual use: approx. 200 hours	←
accessories	standard solution (two types), washing solution (deionized water), screwdriver, syringe, instruction manual	←

Table 1 Specifications of Cardy series and Twin series

(A) Cardy pH meter

model name	C-1
measuring method	glass electrode, equivalent to Class III
display	digital LCD display
measurement range	normal measurement range pH 2~12
display resolution	0.01 pH
repeatability	±0.1 pH
measurement temperature	room temperature (5~35℃)
batteries	3V×2 CR-2025 lithium batteries (approx. 1 mW)
weight	approx. 40 g (excluding accessories)
dimensions of meter unit	95 mm × 55 mm × 9 mm
meter unit material	ABS resin
storage temperature	-10~50℃
storage humidity	No condensation
battery life	continual use: approx. 500 hours
accessories	standard solution (two types), washing solution (deionized water), sampling sheet, pincette, syringe, seal for electrode storage, instruction manual.

(B) Twin pH meter

model name	B-111	B-112
measuring method	glass electrode, equivalent to Class III	←
display	digital LCD display	←
measurement range	normal measurement range pH 2~12	←
repeatability	±0.1 pH	←
measurement temperature	(5~40℃)	←
functions	automatic 1-point calibration (backup function for calibration value), manual hold, auto power-off	automatic 2-point calibration (backup function for calibration value), manual and auto hold, auto power-off
dimensions of meter unit	165mm×29mm×19mm	←
batteries	3V×2 CR-2025 lithium batteries	←
meter unit material	ABS resin	←
accessories	standard solution (pH7), test solution, battery, CR-20332 (two), instruction manual.	standard solution (pH7,pH4), washing solution (deionized water), battery, CR-2032 (two), sampling sheet, pincette, syringe, instruction manual.

(C) Cardy salt meter

model name	C-121
measuring method	Na sodium ion electrode method
display	digital LCD display
measurement range	normal measurement range Nacl 0.1~10%(wt/wt)
display resolution	0.01%(0.1~0.99%), 0.1%(1.0~9.9%), 1%(10~25%)
measurement temperature	room temperature (25℃)
batteries	3V×2 CR-2025 lithium batteries (approx. 1 mW)
weight	approx. 40 g (excluding accessories)
dimensions of meter unit	95 mm × 55 mm × 9 mm
meter unit material	ABS resin
battery life	continual use: approx. 500 hours
accessories	standard solution (two types), washing solution (deionized water), sampling sheet, pincette, syringe, seal for electrode storage, instruction manual.

(D) Cardy ion meter

model name	C-122(sodium),C-131(potassium), C-141(nitrate)
measuring method	Na sodium ion electrode method
display	digital LCD display
measurement range	normal measurement range 10^{-3}~10^{-1}mol/1
measurement temperature	room temperature (5~35℃) 0~99 × 100ppm 1ppm(0~99ppm), 10ppm(10~99 × 10ppm), 100ppm(10~99 × 100ppm)
batteries	3V×2 CR-2025 lithium batteries (approx. 1 mW)
weight	approx. 40 g (excluding accessories)
dimensions of meter unit	95 mm × 55 mm × 9 mm
meter unit material	ABS resin
battery life	continual use: approx. 500 hours
accessories	standard solution (two types), washing solution (deionized water), sampling sheet, pincette, syringe, seal for electrode storage, instruction manual.

3. Application to measure acid rain

3.1 The origins of acid rain

We begin with a brief explanation of acid rain based on relevant reference materials. Water free of any pollutants is thought to be in equilibrium with the carbon dioxide in the air (approximately 340 ppm), and its pH, when saturated, is approximately 5.6 (0 ℃, 1 atm). Thus, rainwater with a pH under 5.6 is, in a technical sense, acid rain. However, acid materials from the natural world are normally present in rainwater and thus the term acid rain is generally used only when the pH is less than 5. Acid rain is created when air pollutants such as sulfur oxides, nitrogen oxides, hydrogen chloride, and hydrocarbons dissolve in rainwater. There are natural sources of these air pollutants such as the ocean, soil, and volcanoes; however, manmade sources such as automobiles and factories have been identified as a problem in recent years. Sulfur oxides and nitrogen oxides released into the atmosphere react in gaseous, liquid (in mist or rainwater), and solid surface states (such as aerosols) to eventually become sulfuric acid and nitric acid. Hydroxyl (OH) radicals, ozone, hydrogen peroxide, and metals play important roles in these reactions. Mist drops, raindrops, and snowflakes absorb aerosols and gases containing these catalysts, and the drops eventually fall as acid rain.

3.2 Experiments using artificial acid rain

It has been pointed out, except in cases of severe pollution, that measurement of rainwater pH tends to yield different results with different meters and measured values tend to be unstable. This is due to low ion strength and low pH buffer ability[3)]. At the same time, it is also true that a concrete procedure for measuring rainwater pH including precautions has not been established. Until now, measurement of rainwater pH has generally been performed using a desktop pH meter. To verify the stability of our meters and their measured values, we performed measurements of the pH of artificial acid rain samples using the Cardy, the Twin, and a desktop meter and compared the results. The models used were the desktop F-16 and the Twin B-112. The results are shown in **Table 3**. The measured values from both meters are in good agreement and the time required for the measurements to stabilize was about two minutes. The pH electrode used with the F-16 was the sleeve-shaped 6367-10D with fluid channel, which is also suitable for low-conductivity samples. A beaker was used for measurement with the F-16, and the sample was dripped onto the B-112.

Table 3 pH measurement results of artificial acid rain

Sample	pH meter readings/pH	
	pH meter model	
	Desktop F-16	Twin B-112
Deionized water	5.53	5.6
Acid rain A	5.21	5.2
Acid rain B	4.07	4.0
Acid rain C	3.03	3.0
Acid rain D	4.92	4.9

The deionized water was air-saturated. Acid rains A through C were prepared based on the artificial acid rain of Sato et al.[4)] The composition of acid rain C was H_2SO_4: 5×10^{-4}, HCl: 3×10^{-4}, and HNO_3: 2×10^{-4} mol dm^{-3}. Acid rains A and B were dilutions of acid rain C by factors of 100 and 10, respectively. The details of acid rain D are omitted here due to the large number of components; however, the rain was prepared based on an investigation of the annual average concentrations (1986 and 1987) of a variety of ions conducted by an acid rain analysis group[5)]. We also conducted comparative tests of conductivity using the desktop and card-type meters in the same manner as the pH tests. The results are shown in **Table 4**, and the measured values produced by each type of meter are in good agreement. The conductivity meters used were the desktop (portable) ES-12 and card-type C-172.

Table 4 Conductivity measurement results of artificial acid rain

Sample	conductivity meter readings/ μS cm-1	
	conductivity meter type	
	Desktop (ES-12)	Card type (C-172)
Deionized water	1.42	2
Acid rain A	3.86	3
Acid rain B	39.7	36
Acid rain C	410	410
Acid rain D	27.9	27

3.3 Measurement of natural acid rain

Based on the results of the above tests, we found that the Cardy and Twin Series show performance equal to that of a desktop meter when measuring acid rain. We thereupon conducted measurements of natural rainwater at our Kyoto plant. pH measurements were made using the C-1 and conductivity measurements were made using the C-172. Rain quantities were measured using Isuzu’s rain gage. The measurement procedure consisted of setting up a commercially available rainfall detector outdoors prior to measurement. When rainfall was detected, a clean 300 ml beaker was placed at the rain collection site and left to collect rainwater. Before use the beaker had been washed, rinsed with deionized water and dried. The rainwater collection site was the roof of the two-story Horiba building where there was no dripping or splashing of rainwater. When the rain stopped, we measured the pH and conductivity of the collected water. As **Figure 9** shows, rain with a pH less than 5 was observed. Although we did not analyze all components, the results of the above show that for pH and conductivity, the most important properties of acid rain, measurement is possible without large-scale equipment and by using only several drops of the sample. We believe that this will make a large contribution to the study of acid rain through regional monitoring. It must be noted that the method for collecting rainwater has not been standardized either in Japan or abroad, and we believe that standardization according to the research objective, for example regional monitoring, will be necessary in the future.

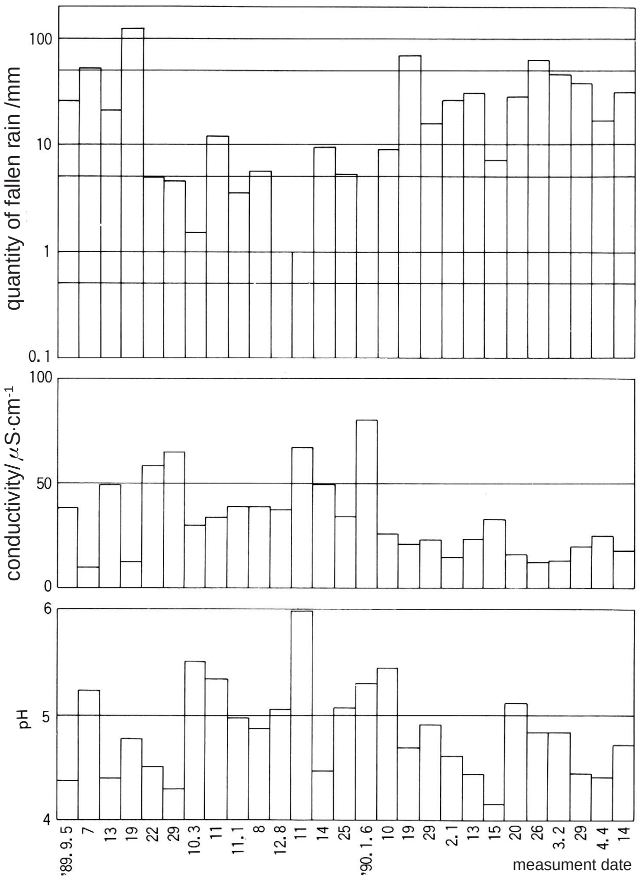


Fig. 9 Measurement results of natural rain by Cardy (C-1)

4. Other application examples

4.1 Biological secretions, particularly tears

Determining the pH and concentrations of sodium and potassium ions in fluids secreted by animals and plants, particularly humans, is very important. However, such fluids are only secreted in minute quantities, and thus it has reviously been impossible to measure these properties without expensive measuring equipment. Furthermore, the values differ widely by individual, and average values (standard values) for sodium and potassium ion concentrations in the blood have not been clearly determined. **Figure 10** shows the results of pH measurements made using the Cardy of tears in 155 eyes of 93 healthy individuals classified by age[6]. The maximum pH observed was 8.23, the lowest was 7.23, and the average was 7.75±0.19. A significant difference was not noted between men and women, with the average for men 7.80±0.18 and the average for women 7.72±0.19. Applications are also possible for measuring saliva, breast milk, and vaginal secretions.

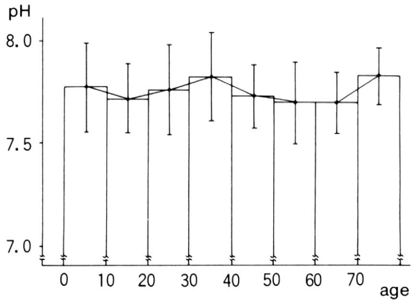


Fig. 10 pH measurement results of human tears by Cardy (C-1)

4.2 Paper and other solids

It is difficult to directly measure the pH of paper, cloth, and other solids. Conventional methods of measurement include soaking the sample in 50 to 100 ml of deionized water and grinding the sample to extract soluble components. With the sheet-type electrode, relative pH measurement is possible by laying the sample on the electrode and moistening it with deionized water to dissolve soluable components into the water. **Figure 11** shows the results of pH measurement of paper using the Cardy correlated with measurements obtained from the conventional JIS cooled-water extraction method.[7] It must be noted that this method does not always yield the same correlation when a number of paper samples are measured.

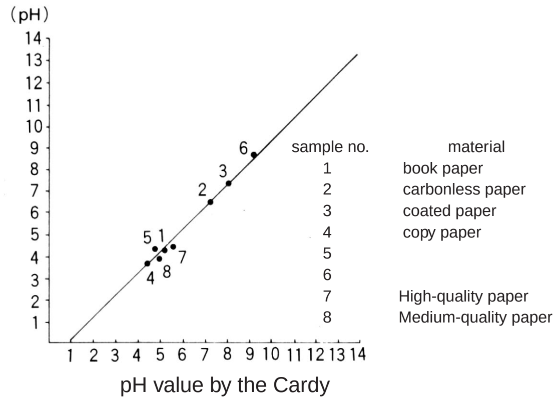


Fig. 11 Correlations between pH measurement results of various types of sheets by Cardy (C-1) and measurement values obtained in the JIS cooled-water extraction method

4.3 Applications of the ion concentration and conductivity meters

The surface of buildings near the ocean tends to be contaminated by ions from salt in the wind and rain from the sea, and painted surfaces are easily oxidized. Damage to forests and crops by acid rain can also be considered a form of ion pollution. Attempts are also being made to measure the pH of human skin as a means of skin protection. In this way there are growing requirements for measuring the state of ion pollution on the surfaces of a variety of materials.

The concentration of surface ions may be measured in the same convenient manner as pH is measured. The surface of the sample is measured by wiping it several times with a non-woven fiber sampling sheet moistened with deionized water. As an example **Table 5** shows the results of measuring

Table 5 Measuring the salt content on human skin using the Cardy Salt Meter (LL shows the measurement range < 0.1 wt%)

measured part	salt meter readings/ _S cm-1 (w / w%)
palm	0.44
arm	0.13
cheek	0.24
forehead	LL
stomack	LL
thigh	LL
leg	0.14
instep of foot	LL
sole of foot	0.11

the salt concentration of a skin surface using the Cardy C-121 salt meter. A sampling sheet was placed on the surface to be measured, three drops of deionized water were dripped onto it, the surface was wiped four or five times using a pair of tweezers, and the sampling sheet was placed on the sensor. In addition, measurement of electrical conductivity is a very convenient means of determining the overall degree of pollution of ions dissolved in water. For reference, **Table 6** shows the results of measurements from a variety of samples using the Cardy C-172 and C-173 conductivity meters.

Table 6 Measurement example of various samples by the Cardy Conductivity Meter

Sample	Conductivity
tap water	100~200 μS/cm
pure water	0.1~2.0 μS/cm
rain	5~100 μ S/cm
pool water	100~500 μS/cm
water in a tropical fish aquarium	0.1~5.0 mS/cm
soil	0.5~2.5 mS/cm
hydroponic water	1.0~3.0 mS/cm
human sweat	10.0~20.1 mS/cm
coffee	0.2~2.0 mS/cm
black tea	0.2~2.0 mS/cm
green tea	0.2~2.0 mS/cm

5. Conclusion

Ion concentration meters and pH meters have until now mainly been used in laboratories and hospitals for clinical testing, factory production control, and other applications. The advent of a handy meter like the Cardy or the Twin will no doubt bring the realm of application closer to our daily lives. There is a growing recognition that knowing ion concentrations, particularly pH, sodium, and potassium, is important in maintaining our health. The harmful effects on human health from excessive intake of salt are only one example of this concern. However, the fact that these instruments have not been accepted in our daily life as a familiar object like a thermometer indicates that room for improvement remains in terms of both the structure of the instrument and its operation. In the future we intend to continue development of a wide range of sensors and strive for improved operation. In conclusion, we would like to thank Messrs. Nakane, Yata, Nakanishi, Ogiwara, and Nakashima for their help in preparing this article.

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Katsuhiko TOMITA

Sinior Manager
R & D Center
Horiba, Ltd.

Hiromi OKAWA

Dep. Manager
Electrodes Manufacturing Dept.
Horiba, Ltd.

Junji KOJIMA

Scientific Instruments R&D Dept.
Horiba, Ltd.