I. Outline

The miniaturized ion sensor whose development is the object of this study conventionally comprises a reference electrode (56) separate from a sensing electrode (50), with the electric potential difference between the electrodes measured for determination of ions. As shown below, an ion selective electrode (sensing electrode) (50) contacts the solution to be measured (51) through ion-sensitive film (52), a reference internal solution (53) is provided in the ion selective electrode (sensing electrode) (50), and electrode (54) to measure the electric potential is provided in the internal solution. The following diagram shows a conventional product. [Figure 1]

Figure 2 shows the proposed product of this study, an ion sensor that determines the concentration of ions in a solution with a new completely solid structure, and without any reference electrode.

In this structure, two electrodes are formed in an ion-sensitive film, and the electric-potential gradient in the ion-sensitive film is directly measured.

Thereby, the issues in the miniaturization of the reference electrode which were obstacles in the promotion of the quantification of trace test samples were eliminated.

The purpose of this study is to verify the effectiveness of the ion sensor with this new structure, produce a prototype and perform licensing activities for sales in the market as a new product.

In the prototype, a multi-ion sensor with the features of this ion sensor was made into a laminated structure with the various elements made into chips of various patterns which were stacked together.
II. Superiority of Developed Technology

In order to miniaturize the ion sensor, it was considered necessary to miniaturize the reference electrode as well. However, the reference electrode that is currently widely used because of its reliability uses an Ag/AgCl electrode as an internal electrode, having a porous ceramic or a structure with pinholes between the solution to be measured and the internal solution of the reference electrode so that ion exchange can be performed in trace quantities. Thus, since the reference electrode requires a structure to store an internal solution, examples of miniaturization made the connection between solutions using a polymer material or a MEMS structure. However, there is no reliable reference electrode with an internal solution and with the structure mentioned above at present, and the above structure is difficult to mass-produce. This caused the problem that the overall structure, including the ion sensor and reference electrode, could not be miniaturized.

Consequently, the purpose of this study is to provide an ion sensor which does not need a reference electrode and internal solution and thus can be miniaturized.

III. Marketability and Growth Potential of Technology

The conventional ion sensor requires a reference electrode; however, the new sensor does not require a reference electrode and miniaturization is possible. Therefore, it can be said that the new sensor with this great features will have superiority in the market.

The new sensor is for measuring the ion concentration in solutions, and is used in clinical blood analyzers to measure the electrolyte concentrations in blood, and measure concentrations in solutions used in industry, found in the environment, etc. The new ion sensor can also be used as a micro sensor to monitor local ion concentrations in organisms etc., which was difficult to do with a conventional ion sensor.

Regarding the acquisition of a patent, at the least we would like to obtain all the rights in Japan and the U.S., and while taking advantage of the features of the miniaturized ion sensor, we would like to promote sales to corporations.

IV. Purpose and Necessity of Test Research

The features of the new ion sensor provide a miniaturized and completely solid sensor structure without the reference electrode which was required in a conventional ion sensor. Therefore, the novelty and superiority of the new ion sensor compared to a conventional ion sensor can be demonstrated by the achievement of a new completely solid type ion sensor chip incorporating various ions, making full use of its capacity for miniaturization and completely solid structure. We believe that corporations will come up with great ideas to commercialize this sensor in new products, after corporations actually see and experience the new ion sensor equipped with these functions. In the research and development of this ion sensor up to now, one type of ion sensor has been manually produced. A platinum wire was used for the electrode, and a vinyl chloride cylinder was used for the sensor body. For this reason, the size of the new ion sensor was not very different from the conventional ion sensor, and there were large variations in the
characteristics. In this test research, in order to create a model with an ideal product image, we will produce a prototype integrated ion sensor chip of a multilayer structure where the electrodes, sensor body etc. made with a photo process are all stacked. Accordingly, a new ion sensor which is able to measure multiple items at the same time can be achieved, by only dropping a small amount of a solution sample on the surface of the sensor chip.

V. Method and Steps of Test Research

This test research was for realizing a completely solid type multilayered chip sensor integrated with two types of ion sensors. This prototype integrated ion sensor of a multilayer structure requires, (1) optimization of the sensor chip structure, (2) design and manufacturing of the sensor chip and (3) evaluation of the sensor characteristics. In (1), the relationship between the size and the sensitivity of the upper and lower electrodes is clarified. Regarding sensitivity, it is necessary to capture the dynamic behavior of the ion gradient formation in the film as well as the electrode, and an analysis was performed by an impedance method to clarify the relationship between the sensitivity and the response time. In (2) the design and manufacturing of the sensor chip, the size and thickness of the electrode and the ion-sensitive film are determined, and a layout design is performed for the integration of two or more types of ion sensors. Based on this design, a multilayered sensor board is created, in which a fine pattern is formed by the thick film processing method used in printed circuit board manufacturing etc. A connector to connect the integrated ion sensor and the external measuring circuit is also integrated for overall miniaturization. In order to perform (3) evaluation of the sensor characteristics, it is necessary to connect the sensor chip to the measuring circuit and fix it there. Therefore, a compact measuring device where the sensor chip can be easily attached or removed will be produced.

In order for the prototype sensor chip to gain wide recognition, we will participate in academic conferences and exhibitions where the participation of corporations making commercial analyzers etc. is expected, present this sensor chip and perform licensing activities.

VI. Targets of Test Research

In this test research, the following targets are set for each item of the test research.
(1) Integration of the ion sensors for multiple types of ions (two or more types)
(2) Sensitivity of each ion sensor of 30 mV/decade or more (in the case of univalent ions)
(3) Miniaturized sensor chip with thickness of 2mm or less
(4) Measuring circuit function for simultaneous measurement of two items and evaluation of time response characteristics
(5) Licensing activities while participating in academic conferences and exhibitions (3 times or more)
(6) Obtaining intellectual property rights, publishing theses (One volume or more for each)
Abstract
To provide an ion sensor with which the concentration of ions in a solution can be determined without any reference electrode, an ion sensor is equipped with: a first electrode plate (1-1) : a second electrode plate (3-1) (3-1) which has been disposed opposite the first electrode plate (1-1) and has one or multiple openings (8) ; an ion-sensitive film (2-1) continuously formed so that the film is interposed between the first electrode plate (1-1) and the second electrode plate (3-1) (3-1), blocks up one side of each opening (8) of the second electrode plate (3-1) (3-1), and extends from the periphery of the opening (8) on that side over the inner wall surface of the opening (8) to the outer surface of the second electrode plate (3-1) (3-1) ; and a sensor support (4-1) which supports the second electrode plate (3-1) (3-1) so that when the ion concentration of a test solution is to be examined, the ion-sensitive film (2-1) comes into contact with the test solution only within that opening (8) and at the outer surface of the second electrode plate (3-1) (3-1) ; and a sensor support (4-1) which supports the second electrode plate (3-1) (3-1) so that when the ion concentration of a test solution to be examined is determined, the ion-sensitive film comes into contact with the test solution only in the portions thereof that have been formed in each opening (8) and on the outer surface of the second electrode plate (3-1) (3-1). The ion sensor is configured so that the thickness of the ion-sensitive film (2-1) interposed between the first electrode plate (1-1) and the second electrode plate (3-1) (3-1) is different from the thickness of the ion-sensitive film (2-1) formed on the outer surface of the second electrode plate (3-1) (3-1). A difference in potential between the first electrode plate (1-1) and the second electrode plate (3-1) (3-1) is measured.

Figure 3 Relationship between Ion-sensitive Film and Electrode Plate
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Ion Sensor

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Comparison of Ion Sensors

Conventional

- Potentiometer
- Reference Electrode
- Internal Electrode
- Internal Solution
- Ion-sensitive Film
- Sample Solution

$(a_A)_{\text{sample}}$: Activity of A⁺ Ion in Sample Solution

$(a_A)_{\text{int}}$: Activity of A⁺ Ion in Internal Solution

A⁺: Target Ion
X⁻: Opposite Sign Ion

The Present Invention

- Ion-sensitive Film Inner Layer
- Ion-sensitive Film Outer Layer
- Sensor Support
- Potentiometer
- External Electrode (Ag/AgCl)
- Internal Electrode (Ag/AgCl)

Features
1. Reference electrode unnecessary
2. Internal solution unnecessary

Effectiveness

Miniaturization is achievable
- Trace quantities of specimen measurable
Comparison of Ion Sensors

Conventional
Example: Potassium Ion Electrode
(Horiba, Ltd.)

Reference Electrode
Ion Electrode

The Present Invention

Essentially, this is the entire device

Ion-sensitive Film Inner Layer

Ion-sensitive Film Outer Layer

Dimensions:
- Length: 40 units
- Diameter: 13 units
- Width: 2.0 units
- Thickness: 0.2 units
- Thickness: 0.01 units
Conventional Ion Sensor (Dry-Chem)

Electrolyte Slide

Reference Solution
Specimen
Thread Bridge Reference solution and specimen are passed through.

Multilayer Film Electrode

Distributed Component Reference solution and the specimen are distributed to film electrodes.

Potentiometer

Support
Silver Layer
Silver Chloride Layer
Electrolyte Layer (Na, K electrodes only)
Ion-selective Layer
Distribution Component
Thread Bridge

Problem
The same as a conventional ion selective electrode, a reference electrode and reference solution are required.
Technical Contents of The Present Invention

Result: Sensitivity improved as the hole diameter became larger

Sensitivity: 40 mV/decade when hole diameter is 2.5 mm

Compared with conventional ion-selective electrode
Measuring range: Equivalent
Sensitivity: Low (Conventional product: about 58 mV/decade)
However, since the ion concentration is calculated from the sensor output, there is no problem with the low sensitivity value.
Technical Contents of The Present Invention

Result: Sensitivity improved as the film thickness of the ion-sensitive film became thinner.