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# Spectrochemical Analysis by Means of a Newly Devised Soak Up Electrode

(Received Sept. 17, 1959)

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## Abstract

An electrode which soaks up the sample has been designed and used for the determination of submicrogram quantities of magnesium in the solution. This electrode which can excite a sample solution of 0.1ml is made from a graphite rod which has a fine hole along the axis with some powder of the same graphite stuffed in it.

The electrode is set vertically on the sample solution, with lower end dipped in. Then liquid is soaked up to the upper end of the electrode through the hole in the center in which powdered graphite has been filled. A counter electrode of cone-shaped graphite rod is used as the negative end of the arc of an intermittent d. c. (1.5A, 1:8).

The dimensions of the electrode were as follows: length, 25mm; outside diameter, of hole, 1.5mm $\phi$ ; grain size of powder stuffing, 120-200 meshes. The solution was prepared as hydrochloric (1:5). Zinc was chosen for the internal standard and  $10^{-7}$ /ml of magnesium was determined with good reliability.

## I. Introduction

Generally speaking, the sensitivity of analysis is raised by concentrating the sample solution, but extreme decrease of the volume of the liquid sample makes the procedure difficult. Also, integrating capacity of the photographic emulsion can be used for increasing sensitivity in spectrographic analysis,<sup>1) 2)</sup> if the excitation of the aliquot is done in suitable conditions.

Some attempt has been made along this line, such as a capillary electrode<sup>3)</sup> which raised the liquid sample by capillary effect through a fine hole drilled in a copper electrode along its axis. But this single capillary electrode is often unstable in

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1) W. R. Brode: "Chemical Spectroscopy", 2nd Ed., pp. 53 (1946)

2) Y. Uzumasa: "Emission and Absorption Spectrochemical Analysis", pp. 64 (1939)

3) Leo D. Frederickson, Jr.: Appl. Spectroscopy, 7, No. 1.19 (1953)

excitation of the samples.

The authors designed a new type of electrode which makes it possible to excite small quantities of the liquid sample very effectively.

Our soak up electrode is made from a 6 mm $\phi$  graphite rod for spectrographic use, along the axis which a fine hole is drilled and some powder of the same graphite is filled firmly in the hole. This electrode is set vertically on the liquid sample with its lower end dipped in, and it is arced or sparked against a counter electrode. The liquid sample is supplied to the top of the electrode through the capillary among the fine grains of graphite powder. As soaking capacity depends on the shape of the electrode, the size of graphite grains, properties of liquids etc., these conditions should be previously investigated.

## II. 1 Liquids

Water cannot be soaked up in this soak up electrode, but some kinds of liquid can be. This is because of the difference in surface tension. Therefore, difference in capillary effect for each soaking liquid must be tested at first.

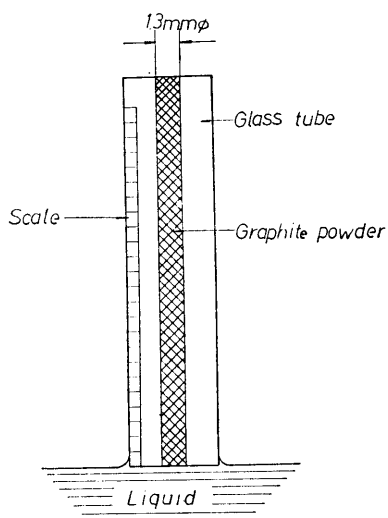


Fig. 1. Measurement of the soaking rate by the glass tube.

For this purpose the authors measured the rate of soaking up of some kinds of liquids in the capillary along the grains of powder filled firmly. As the soaking rate of the electrode cannot be easily measured, the rate in a glass tube filled with the graphite powder was measured, and the relative values were compared (Fig. 1). A glass tube, with the inside diameter of 1.5 mm $\phi$  was filled with the graphite powder of 80-120 meshes and a section paper of 1 mm scale was put outside the tube. To fill the graphite powder, the bottom of the tube was covered with a bit of paper and the powder was poured in by the use of a pencil cap made of polyethylene, and tapped strongly on the table. This glass tube was set vertically in the testing liquids as is seen in Fig. 1.

With aqueous solutions of Tween 20\*, the surface active reagent, the soaking height within one minute (called "the soaking rate" hereafter) increases proportionally with the concentration of Tween 20 when less than one percent (Fig. 2).

Although the soaking rate is not always poor, the necessity of adding more than one percent of matter is unfavourable in spectrographic analysis. Then acid solutions were sought for the purpose. In Fig. 3 the results of some kinds of acids are

\* A commercial name of kind of fatty acid ester of polyoxyethylene-sorbitane.

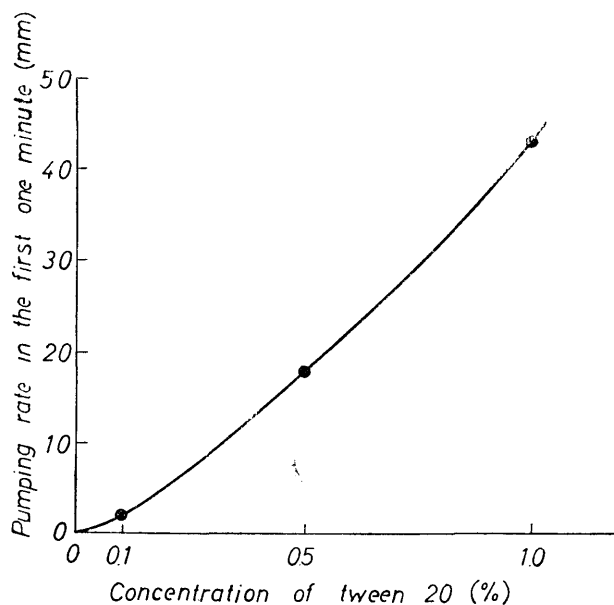


Fig. 2. Relation between concentration of Tween 20 and soaking rate.

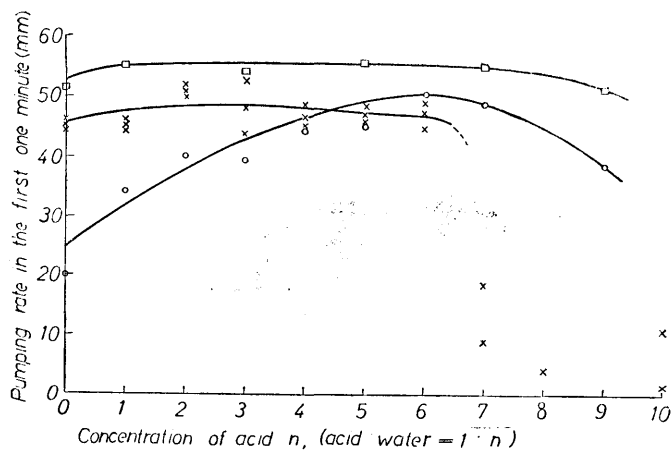


Fig. 3. Relation between concentration of acid and soaking rate.

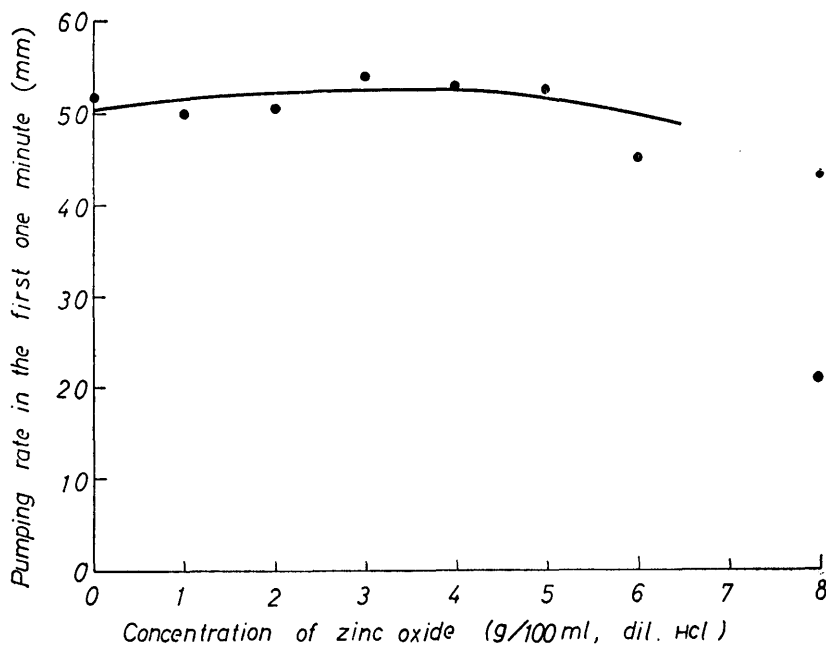


Fig. 4. Relation between concentration of zinc oxide and soaking rate.

seen. Nitric acid has a good rising capacity and it does not vary with concentration, but sulfuric acid varies probably due to its high viscosity\*\*. Hydrochloric acid shows lower reproducibility in concentrations less than 1:6. From these results and for easy treatments the authors selected hydrochloric acid as a soaking solution and the operating concentration was decided at 1:5.

As zinc is to be used as an internal standard in the spectrographic determination of magnesium, the soaking rate of the hydrochloric acid solution of zinc oxide was measured and found to be suitable for less than several grams of oxide in 100 ml (Fig. 4).

## II. 2 Size of the grains of graphite powder

The filling graphite powder is made from graphite electrode for spectrographic use by shaving with a pencil sharpener. Shaved powder was sieved and the soaking capacities of powders of various size were compared in the same method as described in the former section. Table 1 shows that the powder of 120-200 meshes have the largest soaking powder.

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\*\* Soaking length of a liquid in a capillary<sup>4)</sup> is shown as follows;

$$l^2 = \frac{r \gamma \cos \theta}{2\eta}$$

$r$  : diameter of a capillary  
 $\gamma$  : surface tension of a liquid  
 $\theta$  : contact angle  
 $\eta$  : viscosity of a liquid

4) E. W. Washburn: Phys. Rev., 17, 273 (1921)

Table 1. Influence of the size of the grains of graphite powder. (Comparison of soaking rate represented in mm within the first one minute.)

Liquid	The size of the grains of graphite powder (mesh)				
	<200	120-200	80-120	>80	No filling
HCl (1:5)	33	56	41	15	23
ZnO in HCl (1:5)	28	49	31	13	21
H <sub>2</sub> SO <sub>4</sub> (1:9)	25	40	24	10	21
Zn in H <sub>2</sub> SO <sub>4</sub> (1:9)	26	47	34	17	22
Water	0	0	0	0	0

The sieved graphite powders are mixtures of various sizes of graphite grains and each grain is an irregular lump, but the crystals of graphite are microscopically observed on the surface of grains.

Although it may be easily considered that the finer the grains become the better the soaking rate, due to increases in the capillary effect, the experiments show the middle size of grains has the maximum rate. This is supposed as effects due to relations between the contact angle between liquid and graphite grains.

### II. 3 Diameter of capillary

The former tests were made with the glass tube filled with the graphite powder, but determination of the best capillary diameter must be made with the actual graphite electrode, because the material of the inside wall directly influences the rate.

The graphite electrodes of various length from 1 to 3 cm with the holes from 0.7 mm or 1.5 mm $\phi$  drilled along the axis were filled with the powder of 120-200 meshes for the purpose. As the head of the liquid rising in the capillary cannot be observed from outside, a blue flag of lithmus paper was set in the powder at the top of the electrode and hydrochloric acid (1;5) was used as the rising liquid, and then the time between the dipping one end of the electrode in the acid and the change of color of the flag from blue to red was measured with a stop-watch (Fig. 5).

The right half of Table 2 shows the results. It is interesting that a 1.5 mm $\phi$  capillary has the better rate than a 0.7 mm $\phi$  one. This is perhaps due to the ununiformity of the filling of the graphite powder in the fine capillary. Soaking

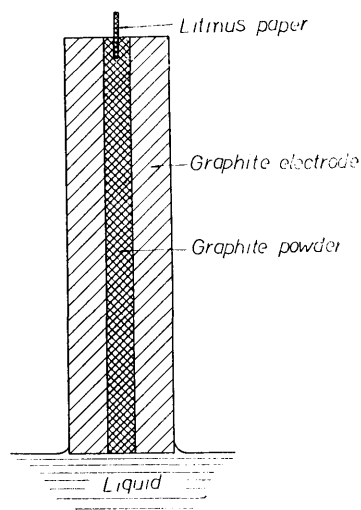


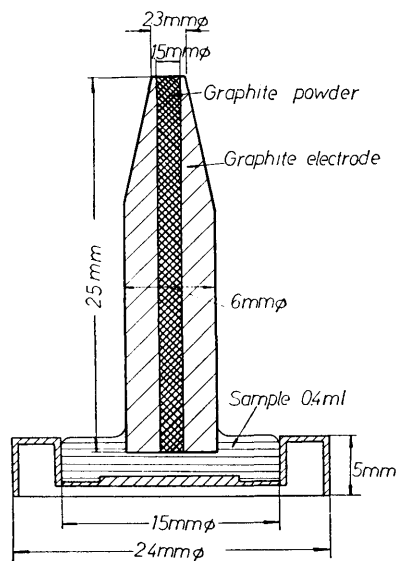
Fig. 5. Measurement of soaking rate

**Table 2.** Influence of the capillary diameter. (Comparison of soaking time through the length of the electrode.)

Length of the electrode (cm)	Diameter			
	No filling		Filling	
	0.7 mm $\phi$	1.5 mm $\phi$	0.7 mm $\phi$	1.5 mm $\phi$
1	0 sec	0 sec	5-20 sec	6-20 sec
1.5	0 "	0 "	12-18 "	8-22 "
2	0 "	No reaching to the upper end	60-80 "	15-22 "
2.5	0 "		200-260 "	50-90 "
3	0 "		250-300 "	120-150 "

capacities of the capillary electrode in which powder is not filled are shown at the left half of Table 2 for reference. From the results, a 0.7 mm $\phi$  electrode seems to have some soaking capacity, but this type of electrode has two faults of uncertainty of rising of liquids and instability of discharging characteristics.

#### II. 4 Dimensions of the electrode



**Fig. 6.** Dimension of the soak up electrode and the sample supplier.

From considerations of the above results, the soaking electrode was designed as follows (Fig. 6);

1.5 mm $\phi$  capillary is drilled along the axis of the 5 mm $\phi$  or 6 mm $\phi$  graphite electrode and 120-200 meshes of graphite powder is filled in it. The length must be less than 2.5 cm and the upper end shape is required to be a pencil-like conical form with a 2.3 mm $\phi$  top. A counter electrode is a similar one with a 1 mm $\phi$  top. The blank solution is 1:5 hydrochloric acid and contains 50 mg/ml of zinc. The dish from which the sample solution is supplied is an inner stopper of a reagent bottle made of polyethylene, and its reserving volume is 0.4 ml. This electrode is set and its lower end is dipped more than 1.5 min. before excitation, and at the beginning of discharge a bit of litmus paper is touched to ascertain that the soaked solution has reached

the top.

Table 3 shows the relations between quantities of the filled powder and quantities of the liquid in the capillary. As the volume of capillary is about 0.05 cm<sup>3</sup>, the liquid is almost all contained within the capillary before discharging, but two minutes after discharging the electrode itself contains much more liquid than the

volume of the capillary. This shows that the liquid is contained not only in the capillary but in the porous graphite cylinder around the capillary. Occasionally, this soaking electrode does not soak up the liquid sample even when it is stood a long time, but the reason for this is not yet studied.

**Table 3.** Capacity of the electrode for liquid

No.	1	2	3	4	5
Weight (mg)	898.0	901.7	834.1	935.8	786.7
Length (mm)	25.0	24.5	24.5	26.5	23.5
Powder filled (mg)	28.3	25.1	24.5	33.6	23.1
Liquid contained (mg) (before discharge)	29.2	22.1	24.5	28.0	22.4
Liquide contained (mg) (2 min. after discharge)	76.6	82.2	99.3	105.1	82.5

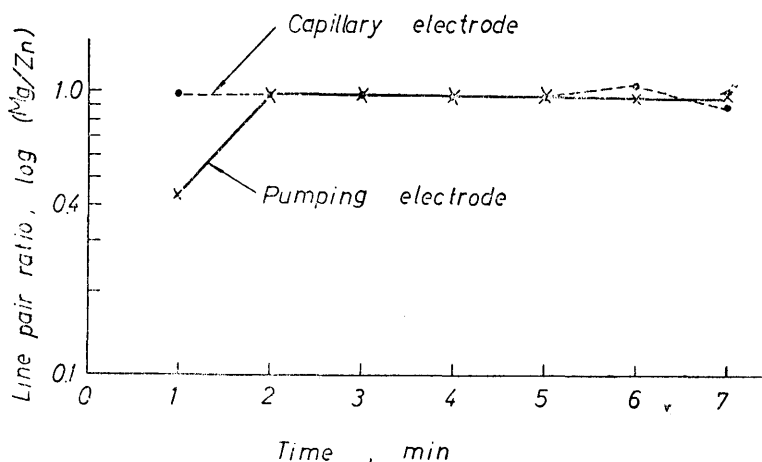
### III. Determination of Magnesium

Determination of magnesium was made by the use of the above mentioned soaking up electrode. Zinc was used as an internal standard for its easily purifying quality and suitable spectrum in magnesium determination. In this case the most sensitive line pair is Mg 2795.5 A/ Zn 2765.4 A.

#### III. 1 Analytical conditions

As the soaking up electrode soaks up the liquid sample little by little, a large current arc is not effective and not recommended.

At first, change of intensity ratios of Mg/Zn with exciting time was investigated under conditions of arc current, intermittent number and intermittent ratio respectively 1.5 A, 40 times/min. and 1:8, and analytical gap is set as 2 mm through all the experiments. From Fig. 7 one minute preliminary arcing is found to be necessary.



**Fig. 7.** Variation of line pair ratios with time



Leaving the conditions as they are, except intermittent ratio, line pair ratio was plotted against time for each intermittent ratio and the results are shown in Fig. 8.

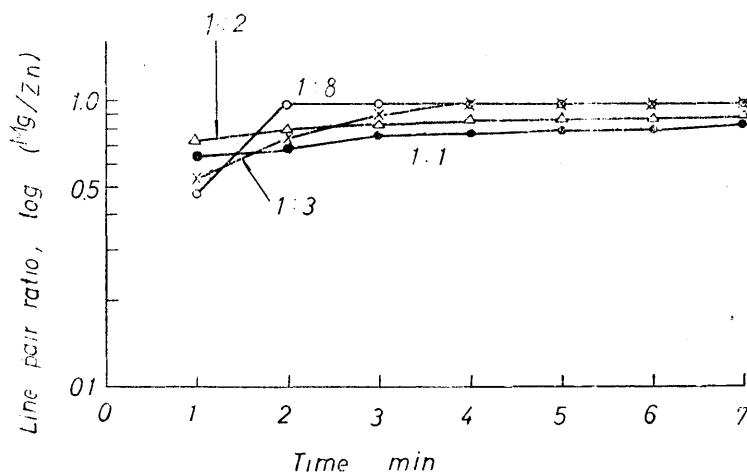


Fig. 8. Relation between line pair ratio and intermittent ratio

Increased intermittent ratios take more stable values of Mg/Zn but continuous arcing cause random results. This teaches us that longer time the arcing is required to supplement the consumption of the sample solution at the top during arcing.

Relation between intermittent number and line pair ratio curve is shown in Table 4. The line pair ratio has a slight inclination to decrease with the intermittent number. In this table, stability of arcing is not evident but larger intermittent

Table 4. Effect of rate of intermittence on the line pair ratio

Intermittence (times/mine.)	Line pair ratio (Mg/Zn)
22	0.96
24	0.98
28	0.99
31	1.00
40	1.01
50	1.05

numbers are empirically recommended for making stable excitation.

Analytical conditions were decided upon the basis of the data mentioned above. The term 'polarity' in Table 5 means the polarity of the soaking up electrode if it is positive or negative. The soaking up electrode should be set on the negative side, as it gets much heat and consumes much samples when set on the positive side.

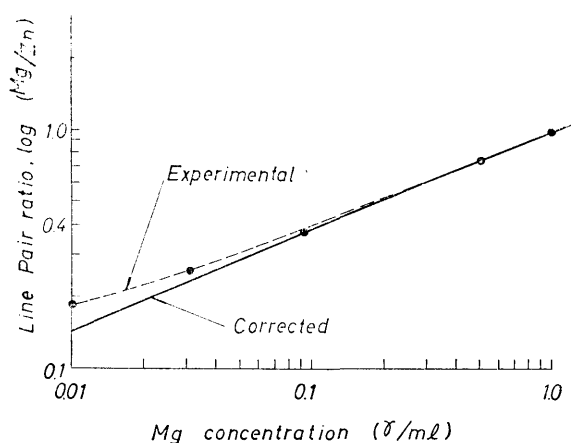
**Table 5.** Conditions for analysis

Spectroscopic	Spectroscope	Cornu, Medium type, Riken (Co.)
	Light source	Intermittent arc apparatus D. C., 110 v, 1.5 A Intermittence; 1:8, 40/min.
	Optical system	Slit focusing
Photographic	Analytical gap	2 mm
	Polarity	Minus for the soak up electrode
	Development	FD-31, 20°C, 5 min.
	Plate	Fuji, Process hard, for spectrographic

### III. 2 Calibration curve

In preparing standard series of solution, analytical grade zinc oxide was dissolved in hydrochloric acid (1:5) so as to make it 50 mg/ml concentration; to this was added 0.05–50  $\gamma$  of magnesium per one ml. With these standard solutions, the calibration curve was drawn and found to be straight line in the range of 0.1–5  $\gamma$ /ml. at one minute exposure. In this case one minutes exposure means net exposure of 6.6 seconds, for arcing time in 1:8 intermittent arc is one ninth of the full exposure.

A curve drawn by two minute exposure is shown in Fig. 9 as a dotted line. Influence by blank magnesium in zinc oxide appears and 'the curve' bends in the part of lower concentrations. Blank value obtained by trial and error method, is 0.009  $\gamma$ /ml, and the upper limit lowered to 1  $\gamma$ /ml.

**Fig. 9.** Calibration curve

The synthesized samples were assayed by this corrected calibration curve and the results are seen in Table 6. Some results in the table have very large errors. They were intentionally contaminated by dust in the analytical laboratory by leaving the sample dishes open in the room during a day. This fact shows how important it is to keep the samples and instruments from contamination: The preparations of all samples were done in a "dustless" laboratory and all vessels such

as reagent bottles and beakers used in the experiments were those made of high quality polyethylene, and hydrochloric acid was carefully redistilled.

**Table 6.** Analytical results by the use of the corrected calibration curve (Soak up electrode)

No.	Mg taken	Mg found	Error	
	( $\gamma/ml$ )	( $\gamma/ml$ )	$\gamma/ml$	%
1	1.0	1.0	0	0
2	0.50	0.42	-0.08	-16
3	0.50	0.50	0	0
4	0.50	0.54	+0.04	+8
5	0.20	0.24	+0.04	+20
6	0.11	0.10	-0.01	-5
7	0.10	0.70	+0.60	*
8	0.040	0.046	+0.006	+15
9	0.040	0.031	-0.009	-22
10	0.030	0.90	+0.87	*
11	0.030	0.52	+0.49	*
12	0.019	0.019	0	0
13	0.019	0.023	+0.004	+21
14	0.010	0.010	0	0

\* These values show contaminations from the dishes which were left open in the room through a day.

### III. 3 Examples

Determination of magnesium in a well water was done by the use of the above described calibration curve. To give the well water the same quality as above described, double concentration of hydrochloric acid (1:2) containing 1 mm/ml of zinc was prepared and mixed one part to one part of the well water. The sample solutions was excited by the use of the soak up electrode and spectrographed. Table 7. shows the results of determinations.

**Table 7.** Determination of Mg in a well water

No.	Mg/Zn	Mg concentrations ( $r/ml$ )
1	0.85	1.70
2	0.87	1.80
3	0.91	1.92
4	0.81	1.52
5	0.89	1.88
6	0.90	1.92
7	0.82	1.53
8	0.86	1.78
9	0.89	1.88
10	0.77	1.34

$$S = \sqrt{\frac{1}{N} \sum (x - \bar{x})^2} = 0.19r$$

#### **IV. Conclusion**

The soak up electrode is suitable for exciting small quantities of aliquots and able to assay with good sensitivity. If the standard materials and electrode graphite are further purified, further sensitivity will be reached.

This electrode is superior to a single capillary electrode, in sure soaking and suitable discharge. With a capillary electrode, the soaking power is promoted not only by capillary effect but also by discharging or arcing, and so the excess solution overflows from the top of the electrode and flows down along the outside wall of the electrode, and instability of discharging or arcing results.

#### **Acknowledgement**

The authors wish to express their deep thanks to Mr. Hiroshi Kuno, an assistant professor in the Faculty, for giving some valuable advices.