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# Use of a Hanging Mercury Drop Electrode in the Alternating Current Polarographic Analysis of Thallium(I)

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The use of a hanging mercury drop electrode (HMDE) in the a.c. polarographic determination of thallium was studied systematically. Analysis was carried out by scanning anodically the potential of HMDE from the limiting-current potential region at a constant scanning rate and by measuring the a.c. peak-height for the anodic stripping process of thallium. Thallium could be concentrated effectively on the HMDE at the initial stage of this procedure and then stripped anodically. By employing this technique, a marked increase in sensitivity could be obtained and $1.0\times10^{-6}$ M thallium(I) in an EDTA solution was determined accurately. The interference effects of lead, cadmium, zinc, and indium on the determination of thallium were also investigated. When the electrolysis was initiated in the limiting-current potential region of lead(II), the peak-height of thallium was found to be enhanced markedly.

Previously,$^{1)}$ we have investigated the characteristics of a hanging mercury drop electrode (HMDE) in alternating current (a. c.) polarography and the possibility of using this electrode in the a.c. polarographic analysis of metal ions. Sensitivity was effectively improved by the pre-electrolysis; the metal ion was reduced to an amalgam in the limiting-current region, and then the metal was anodically stripped.

As was proposed by Underkofler and Shain$^{2)}$ in the a. c. stripping analysis of cadmium(II) using a phase selective detector, the pre-electrolysis and the subsequent electro-dissolution (anodic stripping) processes can be conducted by simply scanning the potential of the working electrode in the anodic direction from the potential, where the limiting current for the metal ion to the amalgam can be observed. In the present paper, the application of this technique to the a. c. polarographic analysis of a micromolar solution of thallium(I) will be discussed.

The interference effects of other metal ions on the determination of thallium(I) in an EDTA solution will also be studied systematically.

## Experimental

**Reagents.** The standard solution of thallium(I) was prepared by a method described previously.$^{3)}$ The solutions of cadmium(II) perchlorate, zinc(II) perchlorate, lead(II) nitrate, and ethylenediaminetetraacetic acid (EDTA) were also prepared as has been described in previous papers.$^{4-6)}$ The standard solution of indium(III) chloride was prepared by dissolving pure indium(III) chloride into dilute nitric acid. Its concentration was determined by titration with a standard EDTA solution.$^{7)}$ The a.c. polarographic analysis showed that indium(III) was not contaminated with lead(II) and thallium(I). All the other chemicals were of an analytical reagent grade and were used without further purification.

**Apparatus and Procedure.** A. c. polarograms were recorded manually or automatically with a Yanagimoto PA-102 pen-recording polarograph. In a. c. polarographic measurements, a 200-$\mu$F condenser was used to minimize the effect of the cell resistance.$^{8)}$ For the accurate measurement of the d. c. potential, a Shimadzu K-2-type potentiometer was used. The Kalousek circuit used in this study was also given in a previous paper.$^{9)}$ A dropping mercury electrode with an $m$ value of $1.24_0$ mg/sec and a drop time, $t_d$, of 4.80 sec at a mercury height of 60 cm in an air-free 0.1 M acetate buffer solution of pH 4.8 at $-0.60$ V *vs.* SCE was used. HMDE was prepared by the method proposed by Ross, Demars and Shain.$^{10)}$ In the preparation of the HMDE, one drop of mercury from the dropping mercury electrode was used.

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## Results and Discussion

**A. C. Polarographic Behavior of Thallium(I) in an EDTA Solution at a Hanging Mercury Drop Electrode.** Previously,[1] we have applied the a. c. polarographic method to the stripping analysis of metals by using a HMDE as an indicator electrode. In that method, the sensitivity was improved considerably by employing the technique which consists of the pre-electrolysis step and the subsequent anodic-dissolution step. The sample was concentrated effectively on the HMDE by conducting the pre-electrolysis in the limiting current region for the reduction of the metal ion to the amalgam. However, an increase in sensitivity by pre-electrolysis could be obtained only in the analysis of metal ions which behave reversibly in a polarographic sense, such as lead(II) and cadmium(II). This may be one of the characteristic disadvantages of an analysis based on a. c. polarographic measurements. As is well known, thallium(I) ion behaves reversibly in almost all supporing electrolyte solutions. Therefore, the a. c. polarographic analysis of thallium(I) can be effected successfully by the method involving the anodic-stripping step. For this reason, the reversibility of the electrode process of thallium(I) in an EDTA solution at HMDE was checked first by the a.c. polarographic method. As is shown in Fig. 1, the reversibility of the electrode reaction was almost perfect in an a. c. polarographic sense; the plot of $\log[(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ against the applied d. c. potential, $E$, gave a straight line with a ±120 mV slope, which is in good agreement with the theoretically-predicted value of ±118 mV.[3,11] Here, $I_p$ and $I$ indicate the a. c. peak-height and the height of the a. c. polarogram at $E$ respectively. Under the present pH conditions, the thallium(I) ion can not form the chelate with EDTA and may exist in a hydrate-ion state.

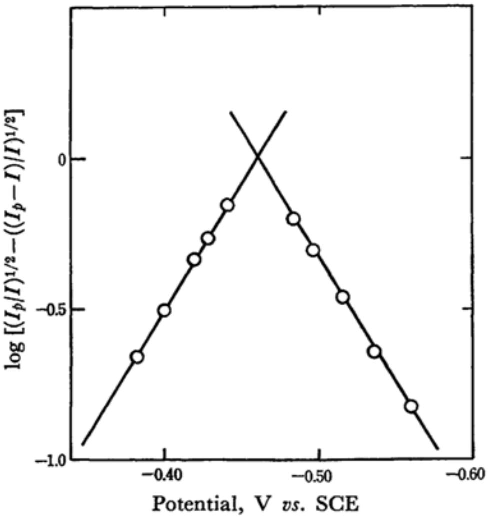

Fig. 1. The plot of $\log[(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ against d.c. potential, $E$.
pH=4.0 (acetate buffer), $\mu=0.50$
Concentration of thallium(I)=$5.0\times10^{-4}$ M
Concentration of EDTA=0.10 M
Normal scanning, non-stirred
Normal scanning means "scanned cathodically"

**The Concentration of Thallium(I) on the HMDE by the Electrodeposition.** Bruckenstein and Nagai[12] have shown that, in the chronopotentiometric analysis of thallium(I), a significant increase in sensitivity can be obtained by emplying the chemical stripping technique, which consists of a pre-electrolysis step and of a subsequent stripping of thallium by chemical oxidation with mercuric ions. In the a. c. polarographic determination of thallium(I), a remarkable increase in sensitivity can also be obtained by emplying the anodic stripping technique. As is illustrated by the a. c. polarograms in Fig. 2, the a. c. peak-height of thallium was greatly increased by the pre-electrolysis and by the subsequent anodic

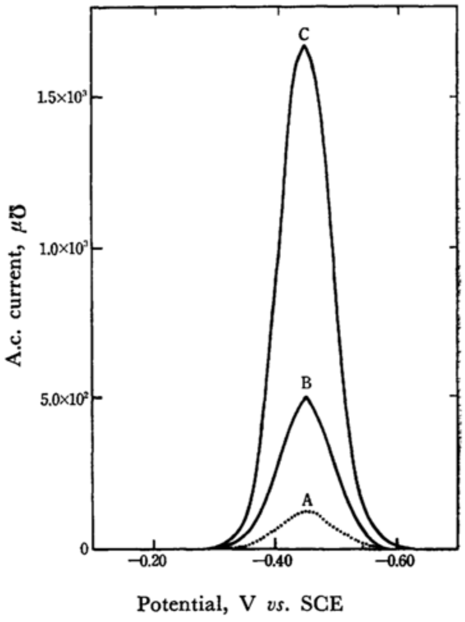

Fig. 2. A.c. polarograms of thallium(I) in 0.05 M EDTA solution.
pH=4.0 (acetate buffer), $\mu=0.50$
Concentration of thallium(I)=$1.0\times10^{-4}$ M
A. normal scanning,
B. reversal scanning, non-stirred, initial potential=−0.80 V vs. SCE,
C. revesral scanning, stirred, initial potential =−0.80 V vs. SCE
Normal and reversal scannings mean "scanned cathodically and anodically," respectively.

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[11] E. R. Brown, T. G. McCord, D. E. Smith and D. D. Deford, *Anal. Chem.*, **38**, 1119 (1966).

[12] S. Bruckenstein and T. Nagai, *ibid.*, **33**, 1201 (1961).

stripping. In a previous paper,[1] the potential of the working electrode was scanned in the cathodic direction from the potential far anodic with respect to the reduction potential of metal ions after a timed pre-electrolysis interval. Alternatively, the pre-electrolysis and the subsequent anodic stripping can be successfully conducted by scanning anodically from the potential where the limiting current for the reduction of metal ions can be obtained. In this study, unless otherwise stated, this technique was employed. An alternating potential was superimposed on the d. c. potential throughout the experiment. However, this had not effect on the pre-electrolysis step.

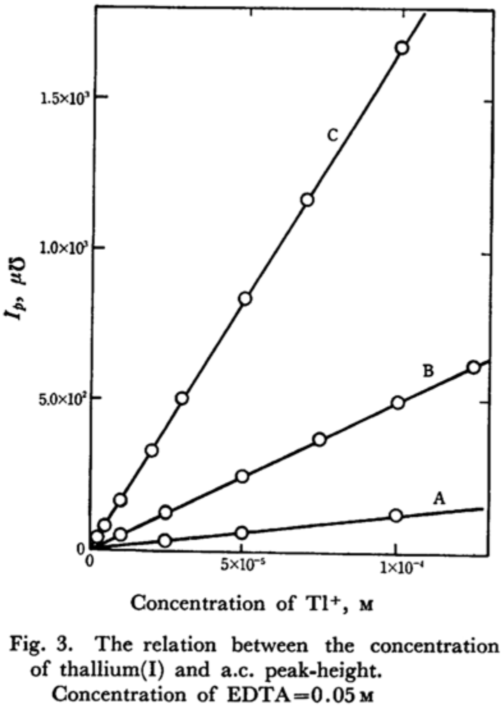

Fig. 3. The relation between the concentration of thallium(I) and a.c. peak-height.
Concentration of EDTA=0.05 M
pH=4.0 (acetate buffer), $\mu$=0.50
A: normal scanning, non-stirred,
B: reversal scanning, non-stirred,
initial potential=−0.80 V *vs.* SCE
C: reversal scanning, stirred,
initial potential=−0.80 V *vs.* SCE
Normal and reversal scannings mean "scanned cathodically and anodically," respectively.

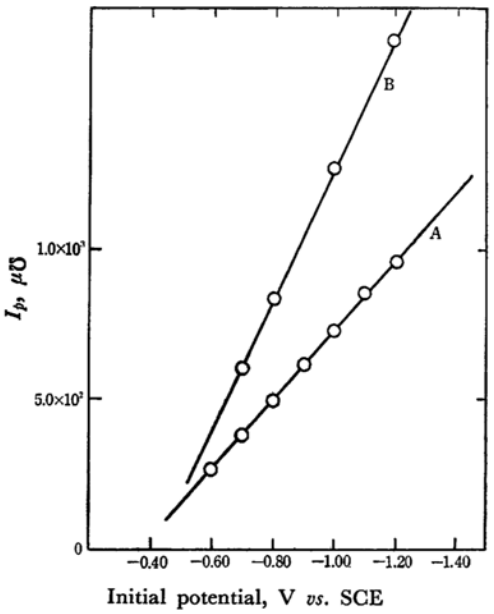

Fig. 4. The relation between a.c. peak-height of thallium(I) and the initial potential.
Concentration of EDTA=0.05 M
pH=4.0 (acetate buffer), $\mu$=0.50
A: reversal scanning, non-stirred,
initial potential=−0.80 V *vs.* SCE
concentration of thallium(I)=$1.0\times10^{-4}$ M
B: reversal scanning, stirred,
initial potential=−0.80 V *vs.* SCE
Concentration of thallium(I)=$5.0\times10^{-5}$ M
Reversal scanning means "scanned anodically."

At a given initial potential, from which the potential of the working electrode was scanned in the anodic direction, the a. c. peak-height of thallium(I) was linear function of the concentration of thallium(I) in the concentration range from $1\times10^{-5}$ to $5\times10^{-4}$ M with non-stirred solutions (Fig. 3). Although a part of the thallium deposited on the mercury electrode is lost by diffusion into the bulk of the mercury electrode, the peak-height of thallium has been found to be a linear function of the effective pre-electrolysis time (Fig. 4). Here, the pre-electrolysis time, *t*, can be calculated approximately by the aid of the following relation:

$$t = (E_p - E_i)/r_s + t_p \qquad (1)$$

where $E_p$ and $E_i$ indicate the peak potential and the initial potential respectively: $r_s$(2.78 mV/sec), the rate of potential scan, and $t_p$, the time interval during which the solution is electrolyzed at $E_i$. This relation can be confirmed by comparing the a.c. peak-height obtained by scanning the potential from −1.10 V *vs.* SCE without the timed interval with that obtained by scanning the potential from −0.70 V *vs.* SCE after a timed pre-electrolysis interval of 144 sec. The former agreed well with the latter within the limit of experimental error.

The a. c. stripping analysis of thallium at the HMDE was also studied in a solution stirred by a magnetic stirring bar driven by a synchronous motor. The stirring was stopped at −0.60 V *vs.* SCE to allow the solution to stand. Without stopping the agitation no improvement in sensitivity could be obtained. As is shown by the polarograms in Fig. 2 and the calibration curves in Fig. 3, the stirring of the solution made it possible to obtain a significant increase in sensitivity: the lower limit of the useful sensitivity range with this technique becomes about $1\times10^{-6}$ M.

**Interference Effects of Other Metal Ions on the Determination of Thallium(I) by the A. C. Stripping Analysis.** To examine the applicability of the above technique to the practical determination of thallium in the presence of a large excess of other metal ions, the effects of the presence of lead(II), cadmium(II), zinc(II), and indium(III) ions on the peak-height of thallium(I) in EDTA solutions were studied. In solutions containing no complex-forming substance, lead(II), cadmium(II), and indium(III) ions are deposited and stripped at potentials very close to the a. c. peak potential of thallium. Therefore, those metal ions may have a considerable effect on the determination of the peak-height of thallium. In solutions containing a large excess of EDTA, however, those metal ions can be deposited on the mercury electrode only at potentials sufficiently negative with respect to the a. c. peak-height of thallium. Therefore, by choosing EDTA as the supporting electrolyte, the interference effects of those metal ions on the determination of thallium may be effectively eliminated. As predicted, when a sample is electrolyzed at the potential of −0.80 V *vs.* SCE, where only thallium(I) is reduced at the mercury electrode, those metal ions have no effect on the a. c. peak-height of thallium. In a 0.05 M EDTA solution of pH 4.0, 0.01 M indium(III) and 0.01 M zinc(II) do not affect the peak-height of $1\times10^{-5}$ M thallium(I), even when the

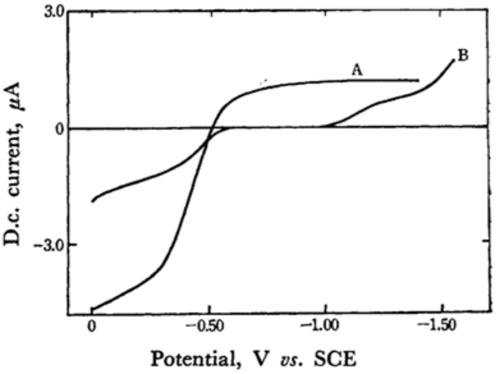

Fig. 5. Kalousek's polarograms.
Concentration of EDTA=0.05 M
pH=4.00 (acetate buffer), $\mu=0.50$
$E_2$9)$= -1.20$ V *vs.* SCE
A: $3.0\times10^{-4}$ M thallium(I)
B: $3.0\times10^{-4}$ M lead(II)

TABLE 1. EFFECT OF THE PRESENCE OF METAL ION ON THE PEAK-HEIGHT OF THALLIUM(I)
0.05 M EDTA, acetate buffer (0.10 M) of pH 4.0, $\mu=0.50$,
concentration of thallium(I)$=1.00\times10^{-5}$ M non-stirred solution

| Metal ion | Concentration of metal ion, M | Initial potential V *vs.* SCE | Time interval sec | Peak-height of thallium, μ℧ |
|---|---|---|---|---|
| — | 0 | −0.60 | 0 | 26.5 |
| — | 0 | −0.80 | 0 | 50.0 |
| — | 0 | −0.90 | 0 | 62.0 |
| — | 0 | −1.10 | 0 | 85.0 |
| — | 0 | −1.50 | 0 | 130.0 |
| Pb(II) | $1.0\times10^{-2}$ | −0.80 | 0 | 48.0 |
| | | −1.10 | 0 | 170.0 |
| | | −0.60 | 72 | 49.0 |
| | | −0.60 | 180 | 84.0 |
| Cd(II) | $1.0\times10^{-2}$ | −0.80 | 0 | 48.0 |
| | | −0.90 | 0 | 60.0 |
| | | −0.60 | 72 | 49.0 |
| | | −0.60 | 108 | 61.0 |
| Zn(II) | $1.0\times10^{-2}$ | −0.80 | 0 | 52.0 |
| | | −1.10 | 0 | 84.0 |
| | | −0.60 | 72 | 51.2 |
| | | −0.60 | 180 | 86.0 |
| In(III) | $1.0\times10^{-2}$ | −1.10 | 0 | 84.0 |
| | | −1.50 | 0 | 132.0 |
| | | −0.60 | 180 | 88.0 |
| | | −0.60 | 324 | 131.0 |
| Pb(II)<br>Cd(II)<br>Zn(II)<br>In(III) | $1.0\times10^{-2}$*<br>$1.0\times10^{-2}$<br>$1.0\times10^{-2}$<br>$1.0\times10^{-2}$ | −0.80 | 0 | 48.0 |
| | | −1.10 | 0 | 180.0 |
| | | −0.60 | 72 | 50.0 |
| | | −0.60 | 180 | 86.0 |

* Concentration of EDTA=0.10 M

solution is electrolyzed at −1.50 V *vs.* SCE. However, in the presence of a large excess of lead(II) over thallium(I), when the solution is electrolyzed at −1.20 V *vs.* SCE, where lead(II) shows the limiting current, the a. c. peak-height of thallium(I) is markedly enhanced. This can be ascribed to the fact that thallium and lead, deposited together on mercury, are also stripped simultaneously. This explanation can be confirmed by Kalousek's polarogram, shown in Fig. 5. The electrode reaction of lead(II) ions in EDTA solution proceeds irreversibly, and the anodic oxidation of lead metal occurs at a potential far from that for the reduction of lead(II) ions, but very close to the peak potential of thallium.

The peak-height observed in the presence of lead(II), however, was considerably lower than the sum of the peak-heights of lead(II) and thallium(I) measured individually. Quite a similar phenomenon was found in the the Bi(III)-Tl(I) system also. When an excess of bismuth(III) is added to a thallium(I) solution (acidic $Na_2SO_4$ solution), the peak-height of the thallium obtained by employing the pre-electrolysis step become considerably lower than that obtained with a solution containing only thallium(I). Bismuth and lead are known to form stable intermetallic compounds with thallium.[13] Therefore, the above phenomenon observed in the thallium-lead system may be attributed to the formation of an intermetallic compound between thallium and lead.

In the case of cadmium, despite the fact that the electrode process also proceeds irreversibly under the present experimental conditions (EDTA solution), cadmium has no effect on the peak-height of thallium, even when the sample is pre-electrolyzed in the limiting current region in order to reduce the Cd(II)-EDTA chelate (−1.25 V *vs.* SCE). This may be ascribed to the fact that, in an EDTA solution, cadmium is stripped anodically from the amalgam at −0.60 V *vs.* SCE. Typical data obtained are given in Table 1.

Although an HMDE has the disadvantage that interference effects due to adsorption, contamination, and other surface phenomena are more frequently encountered than with a DME, where the electrode surface is renewed regularly, this electrode may be used successfully in determining traces of thallium(I) in the presence of lead, cadmium, zinc, and indium by employing the a. c. polarographic method involving pre-electrolysis and stripping.

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13) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, Longmans Green and Co., London (1924).