Differential Pulse Polarographic Determination of Tellurium by Use of Maximum Wave

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A differential pulse polarographic method for the rapid and simple determination of tellurium by use of maximum wave has been studied. Differential pulse polarographic (DP) peak of tellurium(IV) in 1 mol dm^{-3} phosphoric acid is observed in the potential range −0.7—−1.0 V *vs.* SCE. The peak current is very large in comparison with that in d.c. mode, or in normal pulse mode, being proportional to the concentration of tellurium(IV) between 10^{-8} and 10^{-7} mol dm^{-3} contents. The relative standard deviation for 3.94×10^{-8} mol dm^{-3} tellurium(IV) under representative sets of good conditions was 0.0342. The method has been applied to the determination of tellurium in carbon steel.

Tellurium is an important substance in the steel industry and alloy production. However, tellurites and hydrogen telluride are more toxic and dangerous than the corresponding selenium compounds. Thus it is most important to know the tellurium content in the fields of toxicology, industrial hygiene, and environmental pollution. Determination of tellurium can be carried out by the solvent extraction-spectrophotometric[1)] and spectrophotometric[2)] methods by use of Bismuthiol II (3-phenyl-5-mercapto-1,3,4-thiadiazole-2-thione). However, these methods involve complicated steps for clean-up and color development, requiring much time. On the other hand, differential pulse (DP) polarography as well as atomic absorption spectrometry[3)] provide reliable determination of the micro-amount of tellurium.

Since polarographic investigation was carried out in 1935 by Schwaer and Suchy,[4)] many reports have appeared on the reduction of tellurium concerning the polarographic maximum wave, mainly in view of establishing reaction mechanisms.[5—14)]

For the purpose of working out a reliable analytical method, the author has studied the effect of supporting electrolytes, coexisting ions and surfactants on the DP peak, the effects of instrumental parameters such as modulation amplitude (ΔE) and scan rate (ν) in the DP mode, and also sensitivity and relative standard deviation for tellurium.

Experimental

Reagents. Chemicals used were of reagent grade and dissolved in deionized water. A standard tellurium solution (1.00×10^{-2} mol dm^{-3}) was prepared by dissolving 0.1276 g of tellurium lump (purity 99.999%, Wako Chemical Ind. Ltd.) in 50 cm^3 of 7 mol dm^{-3} nitric acid and diluting to 100 cm^3. All dilute solutions were prepared from a stock solution.

Apparatus. The pulse polarographic determination was carried out with a Model 174A polarographic analyzer and a Model 174/70 drop timer (Princeton Applied Research, U.S.A.) and an Omnigraphic 2000 Recorder (Houston Instrument, U.S.A.). The polarographic solutions were deaerated before and during the course of electrolysis with pure nitrogen by passing through a trap containing a solution of the same supporting electrolyte. Except for temperature dependence studies, all the measurements were carried out at room temperature (21±1) °C. Conditions for the dropping mercury electrode (d.m.e.): drop time $t=3.66$ s (open circuit in 1 mol dm^{-3} phosphoric acid), rate of mercury flow $m=2.156$ mg s^{-1}, height of mercury reservoir $h=79$ cm. The electrolysis circuit was a three electrode system consisting of a d.m.e., a carbon rod as counter electrode and a SCE. Small volumes of tellurium(IV) solutions were supplied from Eppendorf micropipetters.

Results and Discussion

Characteristics of Tellurium(IV) Reduction. Reduction wave or peak of tellurium with catalytic hydrogen evolution was observed in the potential range −0.7—−1.0 V. The mechanism of electrode processes has been discussed by many investigators.[5,6,8,11,12)] According to Shinagawa *et al.*,[11)] and Volaire *et al.*,[12)] the electrode process after the reduction of Te(IV)—Te(0) is as follows:

$$Te^0_{ads} + 2H_{ads} = HTe^-_{ads} + H^+$$
$$HTe^-_{ads} + e = 1/2H_2 + Te^{2-}_{ads}$$
$$Te^{2-}_{ads} + H^+ = HTe^-_{ads}$$

If tellurium undergoes two-electron reduction due to formation of telluride as a whole, we can reexamine the process by means of the dependence of peak half width, $W_{1/2}$, on pulse amplitude, ΔE, for various values of n[15)] in order to confirm total number of electrons in electrode reaction, n. The results for the $W_{1/2}$-ΔE dependence are given in Table 1. The values agree with the theoretical ones for $n=2$. The instantaneous current-time curve of 1×10^{-6} mol dm^{-3} tellurium(IV) in 1 mol dm^{-3} phosphoric acid was observed in the potential in the range −0.70—−0.94 V by the potential-step method. The slope of lg i-lg t was 0.480, lying in the range between the maximum of first kind and the kinetic current. No brown mist formed on the d.m.e., convection in the vicinity of the d.m.e., not being observed

TABLE 1. DEPENDENCE OF MODULATION AMPLITUDE ON DP PEAK HALF WIDTH FOR $n=2$

$W_{1/2}$ (mV)	Modulation amplitude, ΔE (mV)		
	−10	−25	−50
Theoretical	46	50	63
Observed	48	50	70

Concentration: 1.00×10^{-7} mol dm^{-3} Te(IV); scan rate, ν: 5 mV s^{-1}; mechanically controlled drop time, t_d: 1 s.

because of the low concentration of tellurium(IV).[11] The relative temperature coefficient of the DP peak current for tellurium-reduction in the temperature range 1—44 °C was 3.02% K^{-1} at 20 °C, the value being reasonable because of maximum wave. No maximum wave was observed in the potential range −1.0—−1.9 V in 1 mol dm^{-3} sodium hydroxide. The reduction is irreversible, the slope of lg $i/(i_d-i)$ *vs.* potential, E in normal pulse (NP) mode and the peak half width, $W_{1/2}$ in DP mode being 80 and 144 mV, respectively, at $\Delta E = -50$ mV. The peak current in 1 mol dm^{-3} sodium hydroxide is much less than that in 1 mol dm^{-3} phosphoric acid.

Choice of Supporting Electrolyte. Several investigators have recommended alkaline or ammoniacal supporting electrolytes for the determination of tellurium.[6—8,11] Itsuki *et al.*[9] used phosphoric acid for s.w. polarographic determination of tellurium in crude copper, silver and selenium. Maienthal and Taylor[10] determined tellurium in cartridge brass and in white cast iron by cathode-ray polarography in 1.5 mol dm^{-3} phosphoric acid, getting good results. Milner and Slee[16] recommended phosphoric acid as a suitable supporting electrolyte for square wave (s.w.) polarographic determination of heavy metals. Phosphoric acid was thus chosen as the supporting electrolyte. In solutions with phosphoric acid, there was no variation in DP current in the concentration range 0.1—2 mol dm^{-3}.

In a.c. mode, the background current practically does not change because of the irreversible reduction of dissolved oxygen in acid solutions,[17] nevertheless that in DP mode altered remarkably and affected the DP current of tellurium(IV) markedly. Thus it was necessary to monitor the residual current in order to make analytical error minimum. The effects of hydrochloric acid, sulfuric acid and nitric acid were studied. The DP peak for 1×10^{-7} mol dm^{-3} tellurium(IV) remained constant even in the presence of 1 mol dm^{-3} nitric acid in the polarographic solution. The presence of 0.1 mol dm^{-3} hydrochloric acid or 0.1 mol dm^{-3} sulfuric acid in the solution gave practically no influence on the DP peak current.

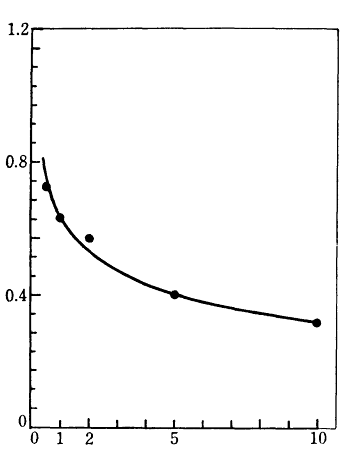

Fig. 1. Effect of scan rate on DP peak of tellurium(IV). Concentration: 1.00×10^{-7} mol dm^{-3} Te(IV); modulation amplitude, ΔE: −50 mV; mechanically controlled drop time, t_d: 1 s.

Effect of Modulation Amplitude and Scan Rate. For the reduction process with catalytic reaction, the peak height-pulse amplitude relationship was found to be linear up to 100 mV pulse amplitude. In general, small pulse amplitude gives better resolution and less instrumental error.[15] However, it is more advantageous to work at larger pulse amplitudes in order to obtain better sensitivity.

Figure 1 shows the effect of scan rate on DP peak height for the reduction of tellurium(IV). It should be noted that the specially slow scan rate for the reduction of tellurium(IV) gives better sensitivity sufficiently reliable for routine analytical operation but its use is time consuming and tedious. However, in the case of lower concentrations as low as 10^{-9} mol dm^{-3} content, it is desirable to use lower scan rates of 0.1—0.5 mV s^{-1}.

TABLE 2. EFFECT OF MAXIMUM SUPPRESSOR CONCENTRATION ON DP PEAK

Concentration of Triton X-100(%)	Tellurium concentration (mol dm^{-3})	
	1.00×10^{-7}	1.00×10^{-6}
None	1.00[a)]	1.00[a)]
5×10^{-4}	0.99	—
1×10^{-3}	0.96	—
5×10^{-3}	0.93	0.99
1×10^{-2}	—	0.60
2×10^{-2}	—	0.31

a) Relative value against the peak current without Triton X-100. Conditions as in Table 1.

Effect of Surfactants. If surfactants are present in the polarographic solution, the current should decrease due to change in interfacial phenomena such as adsorption. Table 2 gives the effect of surfactants on the maximum peak current for the reduction of tellurium(IV). In general, gelatine and Triton X-100 are used for maximum suppressor at concentration lower than 10^{-2}%. These concentrations usually suppress the maximum wave sufficiently. However, none of them affected the current at concentrations less than 10^{-3}% in spite of the fact that the depolarizer concentration was as low as 10^{-7} mol dm^{-3}. In the present method it is not necessary to pay attention to the presence of surfactants. The results of the DP peak current-concentration of Triton X-100 relationship are similar to those obtained in the "suspension polarogram" of tellurium powder in 1 mol dm^{-3} ammonium chloride and in 4×10^{-4} mol dm^{-3} K_2TeO_3.[11]

Calibration Curve. Figure 2 shows typical DP polarograms of tellurium(IV) in 1 mol dm^{-3} phosphoric acid. The DP peak height is proportional to the concentration of tellurium(IV) between 5×10^{-8} and 4×10^{-7} mol dm^{-3} (Fig. 3). The relative standard deviation for 3.94×10^{-8} mol dm^{-3} tellurium(IV) was 0.0342. If the current offset in the instrument, modulation amplitude of −100 mV, and scan rate of 0.5 mV s^{-1} as low as possible are used, detection limits are about 10^{-9} mol dm^{-3} content. The large amount of iron(III) and

TABLE 3. CONTENTS OF CONSTITUENTS OF CARBON STEEL SPECIMEN

Specimen	Concentration (%)										
No. 1	C	Si	Mn	P	S	Ni	Cr	Cu	Mo	Te	Se
	0.20	0.24	0.59	0.012	0.013	0.15	0.15	0.18	0.05	0.020	0.020

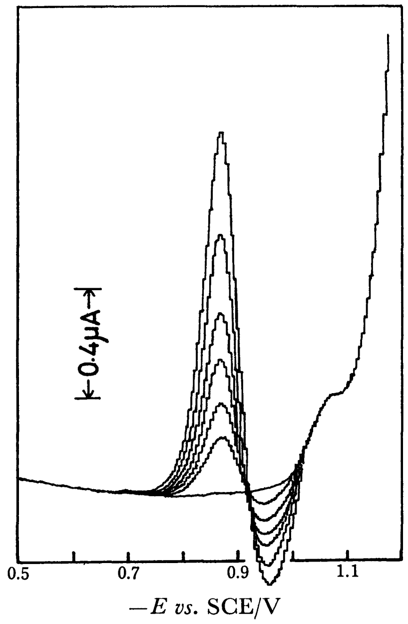

Fig. 2. Differential pulse polarograms of tellurium(IV) in 1 mol dm^{-3} phosphoric acid.
Concentration: 0, 5.00, 10.00, 15.00, 20.00, 30.00, and 40.00 × 10^{-8} mol dm^{-3} Te(IV); scan rate, v: 5 mV s^{-1}; ΔE: -50 mV; t_d: 1 s.

the elements given in Table 3 did not interfere with the determination of tellurium(IV).

The maximum wave was also observed in NP mode, but it was difficult to measure the wave height accurately.

Analytical Application. An analytical procedure was established from the results. Contents of constituents of carbon steel used as a sample are given in Table 3.

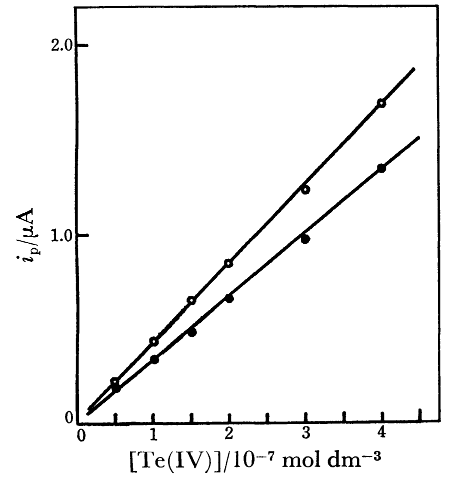

Fig. 3. Calibration curve of tellurium(IV) by DP mode. Conditions are the same as in Fig. 2.
○: Current measured as a height of peak-to-peak.
●: Current measured as a height of background-to-the peak at more positive potential.

Dissolve *ca.* 0.1 g of the sample weighed accurately in a mixture of 3 cm^3 of nitric acid and 0.1 cm^3 of hydrochloric acid, and keep it in a water-ice bath to prevent fuming. Filter through a No. 5C filter paper when necessary. Wash the paper with a few cm^3 of 4 mol dm^{-3} nitric acid, and dilute to 10 cm^3 accurately with 4 mol dm^{-3} nitric acid. Pipette an adequate amount of the sample solution into the supporting electrolyte solution. After deaeration, measure the tellurium peak in DP mode in the potential range -0.7—-1.0 V, and then calibrate the amount by means of a calibration curve or standard addition method. The results of analyses, given in Table 4, are in good agreement with the prescription of sample within experimental error.

TABLE 4. ANALYSIS OF CARBON STEEL

Method	Found values of tellurium (%), × 10^2		
Calibration curve	1.95	1.96	1.95
Standard addition	1.97	1.98	1.96

Conditions are the same as in Fig. 2.

As compared to many analytical procedures the present one was found to be the simplest, giving the highest reliability as the anodic stripping voltammetry for heavy metal determination.

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