where $\frac{N-1}{N}$ is to be calculated from (A-8). Since the accuracy of the approximations improves sharply with increasing κ, it is sufficient to consider only the case for which $\kappa = 0$ in (A-8). For convenience in manipulation of (A-9) assume that

$$t = \frac{E^\circ - E(0)}{r}$$

Thus, from (A-8) and (A-9) we obtain an expression giving the maximum sweep rate for which C_{ox} will be given by Equation 2 with a relative error less than ϵ:

$$|r| \leqq \left| \frac{RT}{nF} \frac{\pi^2 D}{l^2 \log M} \log\left(\frac{2}{\epsilon + 1} - 1\right) \right| \quad \text{(A-10)}$$

It is easily seen that the relative error in i is twice that in C_{ox}; to assure that the relative error in i will be less than ϵ we must have

$$|r| \leqq \left| \frac{1}{2} \frac{RT}{nF} \frac{\pi^2 D}{l^2 \log M} \log\left(\frac{2}{\epsilon + 1} - 1\right) \right| \quad \text{(A-11)}$$

As examples, if $l^2 = 10^{-6}$ sq. cm., $D = 10^{-5}$ sq. cm./sec., $E^\circ - E(0) = -0.2$ volt, $M = 10^3$, and $T = 298^\circ$ K., Equation (A-11) becomes

$$|r| \leqq \left| \frac{1}{2} \log \left[\frac{2}{1+\epsilon} - 1\right] \right|$$

and if $\epsilon = 0.05$ we must have

$$|r| \leqq 22 \text{ mv./sec.}$$

or if $\epsilon = 0.01$ we must have

$$|r| \leqq 5 \text{ mv./sec.}$$

LITERATURE CITED

(1) Carslaw, H. S., Jaeger, J. C., "Conduction of Heat in Solids," 2nd ed., Section 3.5, Oxford, Clarendon Press, 1959.
(2) Christensen, C. R., Anson, F. C., ANAL. CHEM. **35**, 205 (1963).
(3) *Ibid.*, **36**, 495 (1964).
(4) Grinberg, A. A., *et al.*, *J. Phys. Chem.* (*USSR*) **10**, 661 (1937).
(5) Hubbard, A. T., Anson, F. C., ANAL. CHEM. **36**, 723 (1964).
(6) Hubbard, A. T., Anson, F. C., *J. Electroanal. Chem.* **9**, 163 (1965).
(7) Randles, J. E. B., *Trans. Faraday Soc.* **44**, 327 (1948).
(8) Scott, F. A., Peekema, R. M., Connally, R. E., ANAL. CHEM. **33**, 1024 (1961).
(9) Ševčík, A., *Collection Czech. Chem. Commun.* **13**, 349 (1948).

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Polarography of Metal-Pyrogallol Complexes

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► The polarographic behavior of 22 metal ions in perchlorate media containing pyrogallol is described. Arsenic(V) produces three well-defined waves in a 2M $HClO_4$–0.5M pyrogallol medium ascribed to reduction of an arsenic(V)–pyrogallol complex to arsenic(III), arsenic(0) and AsH_3. Titanium(IV) forms a complex with pyrogallol which yields a single wave in these media, useful in the polarographic determination of titanium. Evidence for complexation of bismuth(III), chromium(III), copper(II), iron(III), molybdenum(VI), uranium(VI), vanadium(V), and tungsten(VI), with pyrogallol is obtained and the polarographic behavior of these metal ions is summarized.

A PERCHLORIC ACID MEDIUM containing pyrogallol (1, 2, 3-trihydroxybenzene) has been shown to be useful for the polarographic determination of tin (IV). In this medium tin(IV) is reduced in reversible, two-electron, steps to tin (II) and tin amalgam (*1*, *7*). The favorable behavior of tin in a pyrogallol-containing medium prompted the investigation of other metals in this medium. These studies were undertaken to provide evidence concerning the formation of metal ion–pyrogallol complexes, to devise new polarographic methods for the determination of metals, and to investigate the interference of metal ions in the polarographic determination of tin(IV).

EXPERIMENTAL

Apparatus. The apparatus and techniques used were generally the same as described previously (*1*). An external saturated calomel electrode (S.C.E.) was used as a reference electrode, and was immersed in supporting electrolyte in one side of an H-cell which was separated from the test solution side by a potassium nitrate–agar plug. The dropping mercury electrode (D.M.E.) capillary had a value of $m^{2/3}t^{1/6}$ of 2.0 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.60 volt *vs.* S.C.E. in a 1*M* perchloric acid, 0.5*M* pyrogallol solution. The height of the mercury column was 80 cm. The total resistance between the D.M.E. and the S.C.E. was about 225 ohms; potentials were not corrected for the small *IR* drop through the cell. All current measurements were made at the maximum value of the instantaneous current. The cell was immersed in a water bath maintained at 25.0° C.

Chemicals. Standard solutions were prepared from reagent grade chemicals used without further purification. The titanium(IV) solution was prepared by adding water to titanium tetrachloride, and was standardized by passage through a Jones reductor and titration of the effluent, received in an excess of ferric ammonium sulfate solution, with potassium permanganate.

Pyrogallol was added as a solid to deaerated solutions to prevent possible air oxidation. All solutions containing a metal ion and pyrogallol, turned black, upon standing overnight, probably because of air oxidation of pyrogallol to purpurogallin, a condensation product of pyrogallol and also a product of the electroxidation of pyrogallol (*3*). Neither pyrogallol itself nor its oxidation products gave reduction waves in the media studies, although Vlček *et al.* reported reduction waves in acidic pyrogallol solutions which had been subjected to extensive air oxidation (*9*).

RESULTS AND DISCUSSION

The polarographic behavior of metal ions was investigated by obtaining a polarogram of the metal ion in the perchlorate supporting electrolyte alone, and then with the addition of different amounts of pyrogallol. The viscosity, η, of a 1*M* $HClO_4$ solution (measured at 25° C. with an Ostwald viscometer) increases about 7% and 12% upon adding sufficient pyrogallol to make the solution 0.5*M* and 1.0*M*, respectively. Therefore, since the diffusion current usually varies as $\eta^{1/2}$ (*5*), addition of pyrogallol should decrease wave heights by no more than about 6% because of viscosity effects alone. Wave height depressions appreciably in excess of this amount, as well as the usual criterion of shifts in half-wave potential, were taken as evidence of complexation with pyrogallol.

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Table I. Summary of Behavior of Metal Ion–Pyrogallol Complexes

Ion	Metal ion stock solution	Supporting electrolyte	$E_{1/2}$ of ion[a] (volt *vs.* S.C.E.)	$E_{1/2}$ of complex[c] (volt *vs.* S.C.E.)	Probable oxid. state[c] changes	Color of complex	$\lvert E_{3/4} - E_{1/4}\rvert$[c] (volt)	Depression of wave height upon addition of pyrogallol (%)	I of complex[d]
As(V)	Na_2HAsO_4	2*M* $HClO_4$	(0.32)[b]	−0.10	V → III		0.096		0.60
			(0.01)	−0.46	III → 0		0.052		
			(−0.84)	−0.72	0 → -III		0.020		
Bi(III)	$Bi(NO_3)_3$	1*M* $HClO_4$	0.02	−0.04	III → 0	Yellow	0.03	10	4.75
Cr(III)	$CrCl_3$	1*M* $NaClO_4$	−0.45	−1.12	III → II	Yellow-brown		65	
Cu(II)	$CuSO_4$	0.1*M* $HClO_4$	0.01	−0.625	II → 0		0.18	60	1.55
Fe(III)	$Fe(NH_4)(SO_4)_2$	1*M* $HClO_4$	(0.53)	−1.2	III → II				
Mo(VI)	Na_2MoO_4	1*M* $HClO_4$	−0.377	−0.339	VI → V	Yellow-brown	0.05	70	12.8[e]
Ti(IV)	$TiCl_4$	1*M* $HClO_4$	−0.84	−0.35	IV → III	Red	0.08	30	1.36
U(VI)	$UO_2(NO_3)_2$	1*M* $HClO_4$	−0.19	−0.24	VI → V		0.13	15	1.55
V(V)	$NaVO_3$	1*M* $NaClO_4$	(0.76)	−0.13	V → IV	Blue	0.07	50	1.44
				−0.815	IV → II		0.04		
W(VI)	Na_2WO_4	1*M* $NaClO_4$	[b]	−1.01	VI → V	Yellow	0.15		1.60

[a] In absence of pyrogallol. Values in parentheses are $E°$'s.
[b] Metal ion not reduced in supporting electrolyte alone.
[c] Supporting electrolyte and 0.5*M* pyrogallol.
[d] $I = i_d/m^{2/3}t^{1/6}C$, for maximum value of instantaneous current.
[e] Probably a catalytic reaction.

The behavior of the ions investigated can be separated into the following groups:

(1) **Metal Ions Not Reduced in 1*M* $HClO_4$, with or without Pyrogallol.** These include zirconium(IV), nickel (II), cobalt(II), lanthanum(III), and strontium(II). The same behavior probably applies to the alkali and other alkaline earth metals.

(2) **Metal Ions Yielding Reduction Waves in 1*M* $HClO_4$ Which Show No or Small Changes upon Addition of Pyrogallol.** These include the following metal ions (numbers in parentheses are half-wave potentials, $E_{1/2}$, in volt *vs.* S.C.E. in 1*M* $HClO_4$): zinc(II) (−1.0), lead(II) (−0.39), thorium(IV) (−1.0), and silver(I) (>0). Cadmium(II) yields a reduction wave at −0.61 volt *vs.* S.C.E. Addition of pyrogallol distorts the wave, but the current rise occurs at about the same potentials, and the solution remains colorless. Selenium(IV) yields two ill-defined waves in 1*M* $HClO_4$; addition of pyrogallol depresses the wave heights about 33%. Antimony(III) precipitates with pyrogallol.

(3) **Metal Ions Showing Shifts in $E_{1/2}$ and Wave-Height Depression.** The behavior of metal ions showing definite evidence of complexation with pyrogallol is summarized in Table I. Data in this table are for the metal ions in the specified perchlorate solutions containing 0.5*M* pyrogallol. Listed for reference are the $E_{1/2}$ values for the ion in the absence of pyrogallol or, where the ion is not reducible in the perchlorate medium alone or is reduced at potentials more positive than the potential at which mercury is oxidized, E° values. In all cases addition of the large excess of pyrogallol caused the wave ascribed to the uncomplexed metal ion to disappear. The behavior of arsenic(V), and titanium(IV), is of special interest and is discussed in greater detail below. The behavior of the tin(IV)–pyrogallol complex has been reported (*1*).

Table II. Half-Wave Potentials and Diffusion Currents for First(1), Second(2), and Third(3) Waves for Polarographic Reduction of Arsenic(V)

Concentration arsenic (V), m*M*	$E_{1/2}$ for wave indicated (volt *vs.* S.C.E.) First	Second	Third	i_d for wave indicated, μa. First	Second	Third
0.5	−0.104	−0.461	−0.728	0.66	1.00	0.8
1.0	−0.107	−0.464	−0.725	1.22	1.94	1.52
1.5	−0.108	−0.464	−0.716	1.84	2.88	2.32
2.0	−0.108	−0.464	−0.729	2.48	3.60	3.20

The solution contained 2*M* $HClO_4$ and 0.5*M* pyrogallol. m = 2.21 mg./sec. at −0.405 volt, where $i_d(1)$ was measured.

Table III. Half-Wave Potentials and Diffusion Currents for First(1) and Second(2) Waves for Polarographic Reduction of Arsenic (III)

(Solution contained 2*M* $HClO_4$)

Concn. arsenic(III), m*M*	$E_{1/2}$ for wave indicated (volt *vs.* S.C.E.) First	Second	i_d for wave indicated, μa. First	Second
0.5[a]	−0.465	−0.74[c](?)	8.00	...[c]
0.5[b]	−0.460	−0.740	6.36	5.0
1.0[b]	−0.453	−0.743	15.40	13.2

[a] In absence of pyrogallol.
[b] Containing 0.5*M* pyrogallol.
[c] Second wave ill-defined, with pronounced maxima (Figure 2).

Arsenic. Arsenic(V) is reduced in a $HClO_4$–pyrogallol medium yielding three well-defined waves (Figure 1). Since arsenic(V) does not yield well-developed polarographic waves in any other supporting electrolytes (*5*), the polarographic reduction of arsenic (V) in a pyrogallol medium may be of interest in its electrochemical determination. Meites (*6*) reported that the polarographic reduction of arsenic(V) in 11.5*M* HCl occurred as a double wave corresponding to the scheme As(V) → As(0) and As(0) → AsH_3. The first wave started from zero applied voltage and the $E_{1/2}$ of the second wave was −0.52 volt *vs.* S.C.E. The wave shape in 11.5*M* HCl became complex at arsenic(V) concentrations above 0.4m*M*, so that the useful concentration range was small.

Polarographic data for the reduction of arsenic(V) at different concentrations are shown in Table II. The relative wave heights suggest the ratio

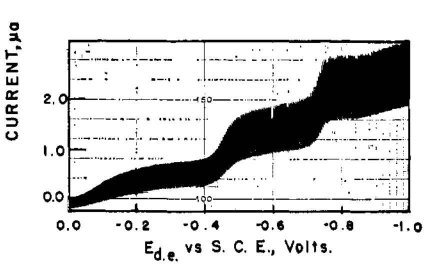

Figure 1. Polarographic reduction of arsenic(V) in pyrogallol medium

Solution contained 2M $HClO_4$, 0.5M pyrogallol, and 0.5mM arsenic(V)

of electron changes of the three waves to be 2:3:3, corresponding to reduction of arsenic(V) to the III, 0, and −III states. The values of $|E_{3/4} - E_{1/4}|$ are given in Table I and may be compared to the values for reversible 2 and 3 electron reactions, 0.028 and 0.019 volt, respectively. The diffusion coefficient of the arsenic(V)–pyrogallol complex, calculated by applying the unmodified Ilkovic equation to the first wave, is 1.7×10^{-7} sq. cm. per sec. This small value suggests a rather bulky and slow moving arsenic(V)–pyrogallol complex.

The $E_{1/2}$ values for the three reduction waves are independent of $HClO_4$ concentration in the range of 1 to 3M. At $HClO_4$ concentrations below 1M, the second and third waves become less well-defined. Above 3M $HClO_4$ the third wave develops a maximum.

The polarographic reduction of arsenic(III) in the presence and absence of pyrogallol is shown in Figure 2, and data for the reduction are given in Table III. The agreement of $E_{1/2}$ values in the absence and presence of pyrogallol and the fact that the diffusion coefficient of arsenic(III) in the pyrogallol medium is about 1.0×10^{-5} sq. cm. per sec. suggests that arsenic(III) is not complexed by pyrogallol. The correspondence of these $E_{1/2}$ values with those for the second and third waves in the reduction of arsenic(V) indicates that the reduction of the arsenic(V)–pyrogallol complex proceeds to uncomplexed arsenic(III). This is analogous to the polarographic reduction of the tin(IV)–pyrogallol complex, which proceeds to uncomplexed tin(II) (*1*). Rosenheim and Thon (*8*) prepared salts of arsenate ion and pyrogallol and showed that the composition of these corresponded to three pyrogallol molecules per arsenic.

Titanium. Titanium(IV) is irreversibly reduced in 1M $HClO_4$ with an $E_{1/2}$ of −0.84 volt *vs.* S.C.E.; the $E°$ for the Ti(IV), Ti(III) couple is −0.14 volt *vs.* S.C.E. Addition of pyrogallol shifts the wave to more positive potentials (Table IV), indicating that the reduction of the titanium–pyrogallol complex proceeds more reversibly than that of the uncomplexed ion. Polarographic data for the reduction of titanium(IV) at different concentrations of $HClO_4$, pyrogallol, and titanium are given in Tables IV and V; the analytically useful range can be judged from these tables. The data indicate that the reduction of the titanium (IV)–pyrogallol complex proceeds most reversibly in the 0.1M $HClO_4$–0.9M $NaClO_4$ electrolyte at higher concentrations of pyrogallol. The essentially constant $E_{1/2}$ values in this medium for pyrogallol concentrations of 0.5 to 1.1M (Table IV) under conditions approaching polarographic reversibility suggests that both titanium(IV) and titanium(III) contain the same number of pyrogallol molecules per titanium. The diffusion coefficients for titanium(IV) in the 1M and 7M $HClO_4$-pyrogallol media (Table V) are 3.7×10^{-6} and 3.0×10^{-6} sq. cm. per sec. Spectrophotometric studies on the titanium(V)–pyrogallol system have been reported (*2*, *4*).

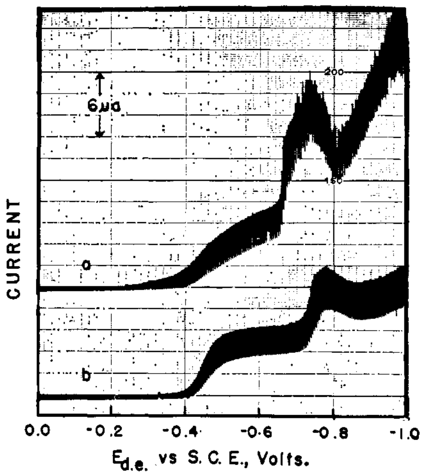

Figure 2. Polarographic reduction of arsenic(III) in absence and presence of pyrogallol

Solution containing (a) 2M $HClO_4$ and 0.5 mM arsenic(III) alone, and (b) with 0.5M pyrogallol

Table V. Half-Wave Potentials and Diffusion Currents for Polarographic Reduction of Titanium(IV) in Various Solutions

Titanium(IV) concn., *C*. (mM)	i_d, μa.	i_d/C, μa./mM
0.1M $HClO_4$, 0.9M $NaClO_4$, 1.0M pyrogallol. m = 2.18 mg./sec., t = 4.1 sec., $E_{1/2}$ = −0.38 volt *vs.* S.C.E., $|E_{3/4} - E_{1/4}|$ = 0.06		
0.331	2.48	7.50
0.656	3.84	5.86
0.970	4.80	4.95
1.290	5.64	4.35
1.600	6.60	4.12
1.900	7.20	3.79
1.0M $HClO_4$, 1.0M pyrogallol. m = 2.03 mg./sec., t = 3.9 sec., $E_{1/2}$ = −0.35 volt *vs.* S.C.E., $|E_{3/4} - E_{1/4}|$ = 0.08		
0.331	0.96	2.90
0.656	1.88	2.86
0.970	2.64	2.73
1.290	3.24	2.51
1.600	4.24	2.65
1.900	5.08	2.65
7.0M $HClO_4$, 0.28M pyrogallol (saturated solution), m = 2.07 mg./sec., t = 3.9 sec., $E_{1/2}$ = −0.14 to −0.11 volt *vs.* S.C.E., $|E_{3/4} - E_{1/4}|$ = 0.07 to 0.13 volt		
0.500	1.16	2.32
0.748	2.00	2.68
1.090	2.64	2.42
1.770	4.24	2.40
2.100	5.40	2.57

Table IV. Half-Wave Potentials and Diffusion Currents for Polarographic Reduction of Titanium(IV) at Different Pyrogallol Concentrations

Pyrogallol Concn., M	$E_{1/2}$ (volt *vs.* S.C.E.)	i_d, μa.	$|E_{3/4} - E_{1/4}|$ (volt)
0.1	−0.364	2.92	0.094
0.3	−0.355	3.52	0.094
0.5	−0.381	4.48	0.065
0.7	−0.378	4.48	0.072
0.9	−0.379	4.24	0.054
1.1	−0.382	4.28	0.060

The solution contained 0.1M $HClO_4$, 0.9M $NaClO_4$, and 1.06mM titanium (IV). m = 2.03 mg./sec. and t = 3.5 sec. at −0.6 volt where i_d was measured.

LITERATURE CITED

(1) Bard, A. J., Anal. Chem. **34**, 266 (1962).
(2) Caulfield, P. H., Robinson, R. J., *Ibid.*, **25**, 982 (1953).
(3) Doskocil, J., *Collection Czech. Chem. Commun.* **15**, 599 (1950).
(4) Ikenberry, L., Martin, J. L., Boyer, W. J., Anal. Chem. **25**, 1340 (1953).
(5) Kolthoff, I. M., Lingane, J. J., "Polarography," Interscience, New York, 1952.
(6) Meites, L., *J. Am. Chem. Soc.* **76**, 5927 (1954).
(7) Phillips, S. L., Morgan, E., Anal. Chem. **33**, 1192 (1961).
(8) Rosenheim, A., Thon, S., *Z. Anorg. Allgem. Chem.* **167**, 1 (1927).
(9) Vlček, A. K., Špalek, E., Krátký, L., Havlíček, E., *Chem. Obzor* **25**, 81 (1950); *C.A.* **44**, 11147 (1950).

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