



**"Complex Formation Ability in Water"
(Polarographic Method)**

1. INTRODUCTORY INFORMATION

• Prerequisites

- Suitable analytical method
- Water solubility
- Dissociation constant

• Guidance information

- Structural formula

• Qualifying statement

- This method is applicable only if the water solubility is higher than 10^5 M.
- This method should be applied to pure substances.
- This method is not applicable to the determination of mercury complexes.

• Standard documents

This Test Guideline is based on the consensus method of polarography.

2. METHOD

A. INTRODUCTION, PURPOSE, SCOPE, RELEVANCE, APPLICATION AND LIMITS OF TEST

The ability of a new chemical to form soluble metal complexes may increase the availability to food chains of metals that might otherwise become inaccessible, e.g. by incorporation in sediments. This is of outstanding importance in the case of cadmium, copper, cobalt, chromium, lead and zinc. The ability of a substance to form complexes with the above metals can be assessed by means of polarographic techniques which allow the determination of stability constants for some complexes.

The polarographic method can be applied to substances with a water solubility greater than 10^5 M. Direct measurement of the shift in half-wave potential $E_{1/2}$ can be made, provided that reactions at the dropping-mercury electrode occur reversibly. With suitable modifications,

irreversible cases can occasionally be dealt with. For example, the Gelling's method (6) can be applied to calculate $E_{1/2}$ values for a reversible process from irreversible reduction data. For quasi-reversible systems the method proposed by Grabaric et al. (6) may be conveniently used.

Two or more ions may be determined successively, if their half-wave potentials differ by at least 0.4 V for univalent ions and 0.2 V for bivalent ions, provided that their concentrations are approximately equal.

When a substance forms a series of complexes with a metal ion, the determination of stability constants for intermediate species is also possible, but generally not necessary for environmental assessment. With strong chelating agents care must be taken not to overload the system (i.e. that not all metal is in the complex form).

• Definitions and units

The potential E of the dropping-mercury electrode is given by the equation

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M_a]}{[M_s]}$$

Where E° is the standard electrode potential, R is the gas constant, T the absolute temperature, n the number of electrons involved in the electrode process, F the Faraday constant, and $[M_a]$ and $[M_s]$ the concentrations of simple metals in the amalgam and at the electrode surface, respectively.

The equation given above implies that the diffusion coefficients of the free metal ions and the complexed ones are equal.

The stability constant for the complexation reaction



is given by

$$K = \frac{[MX_p (n - pb)^+]}{[M^{n+}] [X^{b-}]^p}$$

where p is the co-ordination number.

The complex formation constant depends on the temperature and diffusion coefficient.

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By combination of the above equations, the following relation is obtained, which is valid for the reversible reduction of a complex species at 25°C:

$$E_{1/2} = E_m - \frac{0.0591}{n} \log K [X]^p$$

where $E_{1/2}$ is the half-wave potential of the complex, E_m that of the metal ion in the absence of complexing agents, and $[X]$ the concentration of the test compound.

SI unit of the half-wave potential is volt [V].

• Reference substances

The following reference substances need not be employed in all cases when investigating a new substance. They are primarily provided so that calibration of the method may be performed from time to time and to offer the chance to compare the results when another method is applied.

- ethylenediaminetetraacetic acid (EDTA)
- nitrilotriacetic acid (NTA)
- thioglycolic acid
- o-nitrophenol

• Principle of the test method

This method is based on the fact that the reduction potentials of metal ions are shifted, usually to more negative values, as a result of complex formation. A positive shift can also occur, but only if another metal ion is present in the solution that is capable of binding to excess complex-forming agent. The potential at the point on the polarographic wave where the current is equal to one half of the diffusion current is termed the "half-wave potential" ($E_{1/2}$). This parameter is a characteristic constant for each metal ion. In the presence of a complex-forming substance the extent of the $E_{1/2}$ shift depends on its concentration as well as on the stability of the complex. Measurement of $E_{1/2}$ as a function of substance concentrations permit the calculation of both the formulae and the stability constants of some metal complexes. It is assumed that the $E_{1/2}$ shift is entirely due to complex formation, with no contribution from liquid junction potential.

- Quality criteria

Repeatability

Under normal conditions (particularly when working with metal ions in the concentration range 10^{-3} to 10^{-4} M the repeatability can be as good as ± 2 per cent. The temperature coefficient is about 1.5 - 2% per °C. Precise measurements therefore require temperature control to within $\pm 0.2^\circ\text{C}$.

Sensitivity

This depends upon the particular procedure adopted. Generally, metal ion concentrations down to 10^{-5} M can be determined.

Specificity

The method can be applied to substances which are capable of forming stable aqueous solutions at concentrations greater than 10^{-5} M.

Possibility of standardisation: yes

Possibility of automation: not known

B. DESCRIPTION OF THE TEST PROCEDURE

- Preparations

Suitable polarographic apparatus has been fully described in the literature (1 - 8).

- Test conditions

The mercury used in the dropping electrode should be at least redistilled commercial grade and should be filtered before use. Solutions to be tested need to be well-buffered (4). High-quality pure nitrogen should be used to de-oxygenate solutions for 10 to 15 minutes before determining the current-electrode potential curve.

A minimum of four known concentrations of the chemical being tested should be investigated with a known concentration of metal ions. Solutions are most conveniently prepared

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directly within the polarographic cell by means of a precision burette. The chemical being tested should normally be present in at least a 25-fold excess over the metal ion concentrations so that its concentration at the electrode surface will be essentially the same as in the solution bulk. The current should be measured at applied potentials in the range - 0.2 V to -1.0 V.

In order to detect complexes which form slowly, it is necessary to allow the solutions to stand under a nitrogen atmosphere for a minimum period of 24 hours and, by re-examination of a sufficient number of samples, to ensure that complex formation was complete at the time of the original measurements.

The use of buffers and the use of surface-active substances to suppress polarographic maxima should be carefully considered, in order to avoid undesirable effects on the chemical reaction-controlled current as well as on the polarographic wave slope.

- Performance of the test

The performance of the polarographic technique has been fully described in the literature (1 - 8). The test should be run at 25°C ($\pm 0.2^\circ\text{C}$).

3. DATA AND REPORTING

- Treatment of results

The stability constant K can be easily determined by plotting $E_{1/2}$ versus $\log [X]P$ and extrapolating to $[X] = 1.0 \text{ M}$. If a straight line is obtained (whose slope is therefore $0.0591/n$) the formation of a 1:1 complex is assumed. Smooth curves may be caused either by reaction irreversibility or by formation of two or more complex species in equilibrium with each other. In this last case it is necessary to apply the method by De Ford and Hume (8) to calculate stepwise formation constants.

- Test report

The test report should list for each metal ion investigated the half-wave potential $E_{1/2}$, co-ordination number and overall stability constant.

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In addition, the following should also be reported:

- Type of polarisable micro-electrode, the reference electrode and, in the case of the dropping mercury electrode, the flow rate in mg/sec and the drop time
- IR correction (if applied)
- Maxima suppressors (if used)
- Supporting electrolyte
- Buffer
- Temperature of measurement
- Total ionic strength
- Technique applied (pilot ion, standard addition, or other)
- Technical difficulties encountered
- Estimate of accuracy
- Polarographic technique employed (e.g. DC-, AC, polarography, single sweep polarography, radio frequency polarography or square-wave polarography).

• Interpretation and evaluation of results

Stability constants determined for a new substance can be compared with literature values for standard substances (see Reference substances, above) and used therefore to evaluate the strength of its complexing ability.

The system is physically meaningful if (a) the value of the stability constant is positive and (b) the standard error is less than the constant (the t-test should be used as a criterion).

If data are not significant, it is necessary to use methods based on different physicochemical principles, such as spectrophotometry or nuclear magnetic resonance spectrometry.

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