

ELECTROCHEMICAL REDUCTION OF COMPLEX SPECIES IN SOLUTION WITH METAL ACCUMULATION AT THE ELECTRODE

Peter Grundler

Karl Marx University Leipzig
Chemical Department, Analytical Center
Talstr. 35, Leipzig, DDR-7010

(Received June 2, 1987 ; revised April 28, 1988)

ABSTRACT. The electrochemical behaviour of solutions containing metal complexes was treated theoretically in order to describe the distortion of "free metal ion" anodic stripping voltammetric signals by reduction of the complex present in a large excess. The treatment was based on the model of complete reversibility as the "worst case". The derived equations allow the calculation of polarographic as well as "pseudo polarographic" curves which are useful to characterize electrochemical metal deposition processes in solutions containing "free metal ions" or "free ligand molecules", as well as strong complexes in different ratios. The calculation procedure proved useful for interpretation of results in complexometric titration with anodic stripping end point determination.

INTRODUCTION

In most of the existing polarographic textbooks, the question of voltammetric reduction of complex species is treated in a rather restricted manner. Attention is directed toward the reduction of a complex in the presence of a large ligand excess. This case is important if complex stability constants have to be determined via the shift of half wave potentials (1), (2), (3).

During the last few years, new voltammetric methods like anodic stripping complexometric titration or speciation of complexation state by anodic stripping voltammetry (ASV) have attracted attention. In these cases the voltammetric behaviour of strong complexes without ligand excess or even in the presence of "free metal ion" has to be investigated. In ASV, the reduction process is additionally complicated by metal accumulation during electrolysis time. To solve the problem, a first step is the calculation of instantaneous reduction current without metal accumulation, but for presence of complex species. In a second step, the effect of accumulated metal can be considered.

Theoretical treatment is often referred to kinetic considerations. It seems to be better, however, to discuss the problem on the basis of the "reversible case", i.e. if all reactions including complex dissociation are in equilibrium. This is the "worst case", in which distortion of the voltammetric wave of the "free metal ion" by the complex reduction wave and vice versa would be a maximum. For the special case that a complex alone is reversibly reduced under polarographic conditions, Butler and Kaye (4) derived an equation. Later Macovschi (5) has given an extended treatment. Both of these treatments are not very well suited to form the basis of a more general theoretical understanding.

The problem is much more complicated if anodic stripping is used. Accumulation of metal will change electrode properties in the course of deposition. Consequently, one additional parameter has to be taken into consideration, namely

the deposition time. Behaviour of species electrolyzed under such conditions can be well represented by "pseudo polarograms", i.e. the plots of stripping signal versus deposition potential. Since the "half wave potential" of such curves is shifted by complex formation in the same manner as with ordinary polarograms, they are often used to determine stability constants of complexes in dilute solution (6)-(11). For the simple case of "free metal ion" deposition, equations for pseudo polarograms have been derived, mostly for simplified conditions (12),(13),(14). For the most interesting case, i.e. anodic stripping voltammetry of "free metal ion" in the presence of strong complexes of the same metal, the theoretical treatment of pseudo polarograms known from the literature seems to be simplified too much (15).

It is tried in this paper to reconsider the problem of complex reduction without arbitrary assumptions. The treatment is restricted to solutions which contain a strong 1:1 complex (of the EDTA type) in presence of either the ligand or the "free metal ion". As an electrode material, only mercury is considered. All considerations are based on the "reversible case", i.e. the assumption that all reactions are in equilibrium. Kinetic behaviour may be discussed on the basis of this model in the form of a distortion. Conclusions for "anodic stripping indicated titration" may be drawn.

INSTANTANEOUS REDUCTION CURRENT OF SOLUTIONS CONTAINING A STRONG 1:1 COMPLEX

We consider a solution which contains a strong complex MY composed of the metal M and the ligand Y (e.g. anion of EDTA). As the "free metal ion" concentration we define all species derived from the metal ion which are not complex of Y, e.g. aquo complexes, hydroxo complexes and so on. The sum of all these concentrations is given the symbol $|M'|$. No further strong complexes except MY shall exist in the solution. Electrolysis current i for a given potential E will be composed of $i_{M'}$ (the reduction current of "free metal ion") and of i_{MY} (the reduction current of MY):

$$i = i_{M'} + i_{MY} \quad (1)$$

Using the "diffusion current constants" κ_{MY} and $\kappa_{M'}$, for the species MY and M' respectively, κ_Y for all ligand containing species except MY, and $\kappa_{M(Hg)}$ for the metal dissolved in mercury, we write, with the assumption of constant average diffusion layer thickness:

$$i_{MY} = \kappa_{MY} (|MY| - |MY|_0); \quad i_{M'} = \kappa_{M'} (|M'| - |M'|_0)$$

$$i_Y = \kappa_Y (|Y|_0 - |Y'|); \quad i_{MY} + i_{M'} = \kappa_{M(Hg)} \cdot |M|_{(Hg)0}$$

Index 0 is used throughout to characterize surface concentrations. Further we use the following equation:

$$E(MY) = E_{1/2}(M') + 0.059/z \cdot \log \pi$$

with
$$\pi = |M'|_0 / |M|_{(Hg)0}$$

This is the Nernst equation for our special case. For the total concentrations we set:

$$c_Y = |MY| + |Y'| \quad \text{and} \quad c_M = |MY| + |M'|$$

Substituting and rearranging the expression for Π we get:

$$i/\kappa \cdot \Pi \cdot K' \{c_Y - c_M + i/\kappa \cdot (\Pi + 1)\} = c_M - i/\kappa \cdot (\Pi + 1) \quad (2)$$

By rearrangement we obtain a quadratic equation

$$i^2/\kappa^2 + i/\kappa \left\{ \frac{c_Y - c_M}{\Pi + 1} + \frac{1}{K' \cdot \Pi} \right\} - \frac{c_M}{K' \cdot \Pi \cdot (\Pi + 1)} = 0 \quad (3)$$

where $K' = |MY| / |M'| \cdot |Y'|$ is the conditional stability constant of MY under given conditions.

Equation (3) can be used to calculate polarographic curves in different ways. One way would be to rearrange the Nernst equation given above, by introducing the potential E instead of Π , using the relationship

$$\Pi = \exp(\Delta E \cdot zF/RT) \quad (4)$$

with $\Delta E = E(MY) - E_{1/2}(M')$

This would result in very complicated expressions. In the practical application, we preferred a simpler calculation procedure. In a first step, a value for Π was calculated for every given potential value. In a second step i was then calculated following equation (3).

In the same way as above we may express the partial current i_{MY} (which is drawn by reduction of the complex species MY) in terms of Π :

$$i^2/\kappa^2 + i_{MY}/\kappa \cdot \left(|Y'| + |M'| + \frac{\Pi + 1}{\Pi \cdot K'} \right) - \frac{|MY|}{\Pi \cdot K'} = 0 \quad (5)$$

Using eq. (5) we are able to calculate the polarogram of the species MY. In this case, it is assumed that the initial concentration of metal M in mercury for every newly formed drop is approximately zero. The plot of instantaneous current i_{MY} versus applied potential thereby reflects the form of the polarographic wave.

Further, we may use eq. (5) to derive an expression which allows the calculation of the half wave potential of species MY. At the half wave potential, the current i_{MY} is just half of the diffusion limited current $i_D(MY) = \kappa \cdot |MY|$. We get an expression $\Pi_{E(1/2)}$ for Π at the half wave potential:

$$\Pi_{E(1/2)} = \frac{|M'| / (K' \cdot |M'| + 2)}{0.5 |MY| + |M'| - |M'| / (K' \cdot |M'| + 2)} \quad (6)$$

The homogeneous concentrations $|M'|$ and $|MY|$ may be expressed, alternatively, in terms of total concentrations c_M and c_Y . With the above equation, it can be shown that the half wave potential of the complex with increasing dilution will shift more and more toward positive values. For infinite dilution, it becomes identical to that of the "free metal ion".

By means of the derived equations, polarographic curves for a model case with the conditional stability constant $\log K' = 10$ were calculated (Fig. 1).

In Fig. 1, the i axis is denumbered in terms of i/i_D for every corresponding species. The zero point of the abscissa is identical to the half wave potential of the "free metal ion", i.e. the potential axis is denumbered in terms of the difference $\Delta E = E(MY) - E_{1/2}(M')$. At the upper part, curves for two different solutions, containing either $|M'| = 10^{-4} \text{ mol/l}$ or $|MY| = 10^{-4} \text{ mol/l}$ are shown. The central part gives a curve for the mixture of both, and in the lower part the curve for a complex solution in presence of excess ligand is shown. The calculated

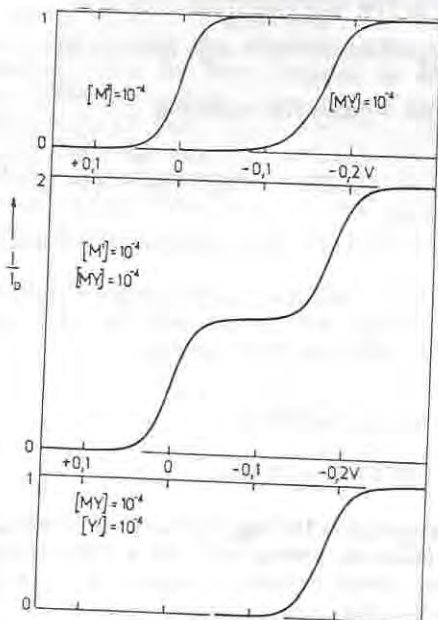


Fig. 1 Calculated polarographic waves of a complex MY with $\log K' = 10$

polarogram of the pure complex solution has a somewhat different appearance, as if there were some degree of irreversibility. The same effect has been stated by Macovski (5).

LONG TERM REDUCTION CURRENT OF THE "FREE METAL ION"

In ASV, the electrolysis time is generally much longer than in voltammetric experiments. As a consequence of metal accumulation in the electrode, electrolysis current will decrease with time. Such systems can be characterized very well by means of the above mentioned "pseudo polarograms" which give a normalized description independent of the actual deposition time. In the theoretical treatment known from the literature, a constant average reduction current for every corresponding deposition potential is often assumed (12). This assumption does not hold true when "free metal" is deposited at a potential close to the half wave potential of a complex which is present in large excess.

During electrolysis, in a stationary mercury electrode of volume v , metal concentration in mercury will increase with time following the relationship

$$M(\text{Hg}) = \frac{1}{z F v} \int_0^t i dt = \frac{Q}{z F v} \quad (7)$$

For the concentration dependent term of the Nernst equation we write

$$\Pi = \frac{i_D - i}{i + \frac{\kappa \cdot Q}{z F v}} \quad (8)$$

Rearrangement with $i = \frac{dQ}{dt}$ gives the differential equation

$$\frac{dQ}{dt} + \frac{\kappa \cdot Q}{(1+1/\pi) \cdot z \cdot F \cdot v} - \frac{i_D}{1+\pi} = 0 \quad (9)$$

Solution of this equation yields

$$Q = \frac{i_D \cdot z \cdot F \cdot v}{\pi \cdot \kappa} [1 - \exp(-t \cdot \kappa / zFv(1+1/\pi))] \quad (10)$$

A similar expression has been derived by Lee (14).

For a fresh electrode, which is free from deposited metal, at the start of polarization (i.e. for $t = 0$), deposition current will possess its maximum value i_0 which is referred to diffusion current i_D : $i_0 = i_D/(1+\pi)$. After a very long time, if the applied potential is not negative enough to cause limiting diffusion current, the electrode will become enriched with metal so much that it is in equilibrium with solution. Deposition current approaches zero. We have then, for the corresponding potential, the maximum possible charge Q_{lim} accumulated in the electrode in the form of deposited metal. With the relation $Q_{lim} = i_D \cdot z \cdot f \cdot v / \kappa \cdot \pi$ we get

$$Q = Q_{lim} \{1 - \exp(-i_0 \cdot t / Q_{lim})\} \quad (11)$$

If much more negative potentials are applied the deposition current will become equal to the diffusion limited current i_D . Consequently, instead of reaching the finite value Q_{lim} , the amount of metal at the electrode is increasing linearly with time in terms of the value Q_D according to $Q = i_D \cdot t$. Q_D in pseudo polarograms plays the same role as i_D in ordinary polarographic curves.

An appropriate form for a graphical representation of pseudo polarograms is to plot the "relative charge" Q_{rel} versus potential:

$$Q_{rel} = Q/Q_D = Q/i_{d,t} = f(E) \quad (12)$$

Thus, with pseudo polarograms, the deposition time has to be considered as a parameter. For the "half wave potential" of the curve, of course Q_{rel} has the value 1/2.

For the case that the mercury electrode in the course of deposition will become saturated with metal (e.g. in very thin mercury films) somewhat different equations have been derived which will not be discussed here (16).

REDUCTION CURRENT WITH METAL ACCUMULATION IN COMPLEX CONTAINING MEDIA

If, at a stationary mercury electrode, a solution containing the complex MY is electrolyzed, two different accumulation processes will occur. The first one is deposition of metal in the electrode, the second one consists in accumulation of free ligand molecules at the electrode surface. Thus, we have to consider two surface concentrations $|M|_{(Hg)0}$ and $|Y|_0$ both changing with deposition time t . For the special case that the solution contains a huge excess of free ligand, surface concentration of the latter may be considered as constant. Then a simplified mathematical treatment becomes possible (15). For the case of a complexometric titration with anodic stripping detection, however, as well as for other practically interesting conditions, neither $|M|_{(Hg)0}$ nor $|Y|_0$ will be kept constant. A more general theoretical treatment is necessary under these conditions.

As a basis for further considerations, we use again the concentration dependent term of the Nernst equation, $\Pi = |M'|_0 / |M|_{(Hg)0}$. This term is modified by introducing the following relationships:

$$K' = \frac{|MY|_0}{|M'|_0 |Y'|_0} \quad ; \quad i/\kappa = |MY| - |MY|_0 + |M'| - |M'|_0$$

$$i/\kappa = |M|_{(Hg)0} - |M|_{Hg} \quad ; \quad c_M = |MY| + |M'| \quad ; \quad c_Y = |MY| + |Y'|$$

The resulting expression,

$$\Pi (i/\kappa + |M|_{(Hg)}) = \{ c_M^{-\Pi} \cdot |M|_{(Hg)}^{-i/\kappa \cdot (\Pi+1)} \} / K' \{ c_Y - c_M + \Pi \cdot |M|_{(Hg)}^{i/\kappa \cdot (\Pi+1)} \} \quad (13)$$

after rearrangement, yields the following fundamental equation:

$$i^2/\kappa^2 + i/\kappa \cdot \{ (c_Y - c_M) / (\Pi+1) + 1/K' \Pi + |M|_{(Hg)} / (\Pi+1) \} + |M|_{(Hg)}^2 / (\Pi+1) + |M|_{(Hg)} \cdot \{ (c_Y - c_M) / (\Pi+1) + 1/K'(\Pi+1) \} - c_M / K' \Pi (\Pi+1) = 0 \quad (14)$$

This important equation can now be used to calculate all possible cases in the system considered here, namely,

"free metal ion" with and without accumulation,

complex solution with excess of "free metal ion" with and without accumulation,

complex solution with excess of free ligand with and without accumulation,

complex solution with and without accumulation.

There are two interesting conditions under which equation (14) can be simplified.

The first one is to consider a deposition time of zero. For this case the concentration of metal in the electrode is zero, i.e. $|M|_{(Hg)} = 0$, and deposition current is identical to the starting current after application of a potential to a freshly formed mercury drop. Equation (14) then simplifies to

$$i_0^2/\kappa^2 + i_0/\kappa \cdot \{ (c_Y - c_M) / (\Pi+1) + 1/(K' \Pi) \} - c_M / K' \Pi (\Pi+1) = 0 \quad (15)$$

The resulting expression is identical to the equation of the polarogram for a complex containing solution.

The second boundary condition would correspond to infinite deposition time, when the current has ceased to zero for the corresponding potential. Then we get

$$|M|_{(Hg)}^2 \lim^+ |M|_{(Hg)} \lim \cdot (c_Y - c_M) \Pi + 1/K' \Pi - c_M / K' \Pi^2 = 0 \quad (16)$$

The latter equation is of less practical importance.

If we want to evaluate eq. (14) for calculation of pseudo polarograms in complex containing media, we have to solve it for finite deposition time. Eq. (14) is, however, a differential equation (because of $i = dQ/dt$), which does not contain explicitly the time dependence of accumulated charge Q . An analytical solution of the equation cannot be given. It has to be solved by numerical or graphical approximation. Computing can be done easily by means of the existing standard methods. An example will be given in the following.

We found that consecutive anodic stripping determination of "free metal ion concentration" in the course of a complexometric titration can be used to localize the endpoint of such a titration very precisely (17). Among the investigated examples was titration of bismuth(III) ion with EDTA

Electrochemical reduction of complex species

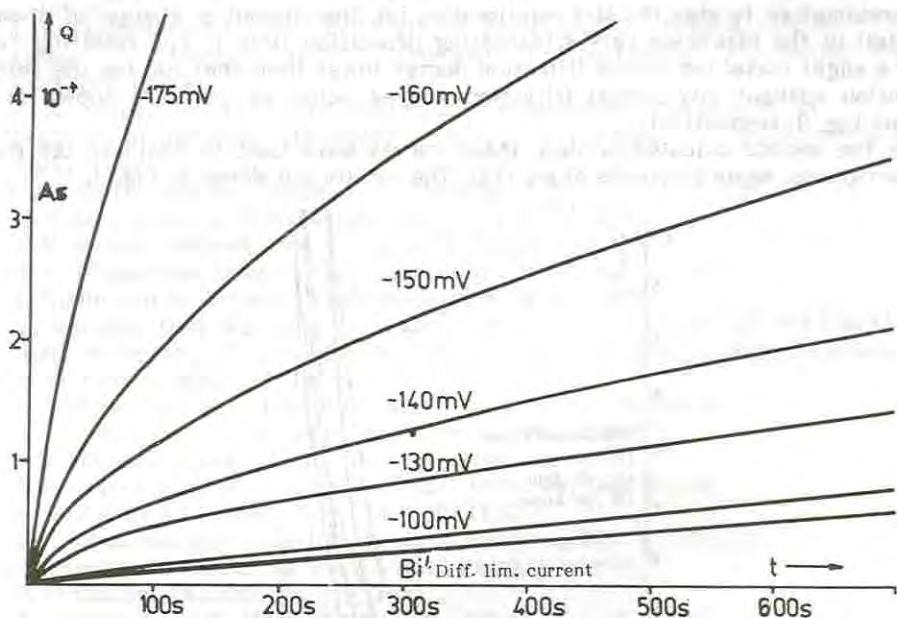


Fig. 2 Electric charge Q equivalent to accumulated metal amount vers. deposition time for anodic stripping of bismuth in 0.05 M solution which had been titrated with EDTA to a degree of 0.99985. Stat mercury drop electrode, volume $v = 5.23 \cdot 10^{-7} l$. Additional data see Fig. 4.

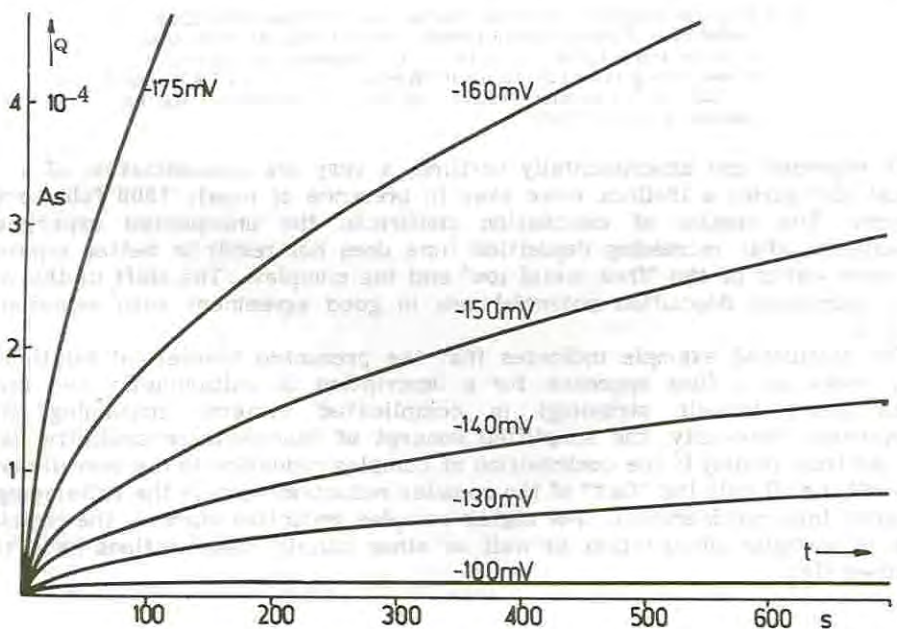


Fig. 3 as Fig. 2, but titration degree 1.0000

(16). For a better understanding, the pseudo polarograms of the system used were calculated for titration conditions very close to the endpoint. A two step calculation procedure was used. In the first step eq. (14) was solved by numerical approximation to give the $Q-t$ relationship, i.e. the amount of charge (of dissolved metal) in the electrode versus increasing deposition time t . The resulting curves for a slight metal ion excess (titration degree lower than one) and for the complex solution without any excess (titration degree equal to one) are shown in Fig. 2 and Fig. 3, respectively.

In the second calculation step, these curves were used to compute the pseudo polarograms, again by means of eq. (14). The results are shown in Fig. 4.

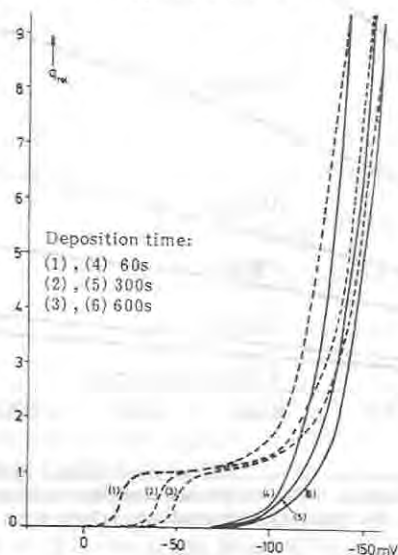


Fig. 4 Pseudo polarograms for bismuth solution 0.05 M titrated with EDTA. Dotted lines: Titration degree 0.99985, curves (1), (2), (3). Solid lines: Titration degree 1.0000, curves (4), (5), (6). Potential axis referred to half wave potential of bismuth(III) at pH 2. $\kappa = 1.21 \cdot 10^{-2}$ A. l. mol⁻¹; $\nu = 5.23 \cdot 10^{-7}$ l (mercury electrode); $\lg K' = 13.75$ (conditional stability constant of bismuth-EDTA).

As expected and experimentally verified, a very low concentration of a "free metal ion" forms a distinct wave even in presence of nearly 7000 fold complex excess. The results of calculation confirmed the unexpected experimental experience, that increasing deposition time does not result in better separation between waves of the "free metal ion" and the complex. The shift of the waves with increasing deposition potential was in good agreement with experimental results.

The calculated example indicates that the presented theoretical relationships may serve as a first approach for a description of voltammetry and inverse voltammetry (anodic stripping) in complicated systems containing strong complexes. Obviously, the simplified concept of "complete reversibility" is not too far from reality if the contribution of complex reduction to the overall current is small, i.e. if only the "foot" of the complex reduction wave in the voltammogram is taken into consideration. For higher complex reduction current, the restricted rate of complex dissociation as well as other kinetic complications have to be included (16).

REFERENCES

1. J. Heyrovsky and J.Kuta, "Principles of Polarography", Prague, (1965).
2. Proszk, V. Cielezsky and K. Gyorbiró, "Polarographie", Akademiai Kiado, Budapest, (1967).
3. A.A. Vlcek, "Polarographic behaviour of coordination compounds", in "Progress in inorganic chemistry", Vol.5, F.A. Cotton, Ed., Interscience, New York, (1963).
4. C.G. Butler and R.C. Kaye, *J. Electroanal. Chem.*, **8**, 463 (1964).
5. M.E Macovschi, *J. Electroanal. Chem.*, **16**, 457 (1968).
6. W.R Matson, Dissertation, Cambridge, Mass., USA (1968).
7. W.F. Fitzgerald, Dissertation, Cambridge, Mass., USA, (1969).
8. S. Bubic and M. Branica, *Thalassia Jugosl.*, **9**, 47 (1973).
9. M. Branica, D.M. Novak and S. Bubic, *Croatica Chem. Acta*, **49**, 539 (1977).
10. H.W. Nurnberg, P. Valenta, L. Mart, B. Raspor and L. Sipos, *Fresen. Z. Anal. Chem.*, **282**, 357 (1976).
11. S.D. Brown and B.R. Kowalski, *Anal. Chem.*, **51**, 2133 (1979).
12. A. Zirino and S.P. Kounaves, *Anal. Chem.*, **49**, 56 (1977).
Correction in *Anal. Chem.*, **51**, 592 (1979).
13. M.S. Shuman and J.L. Cromer, *Anal. Chem.*, **51**, 1546 (1979).
14. T.S. Lee, *J. Am. Chem. Soc.*, **74**, 5001 (1952).
15. S.P. Kounaves and A. Zirino, *Anal. Chim. Acta*, **109**, 327 (1979).
16. P.Grundler, Dissertation Dr. sc. nat., Leipzig, (1984).
17. P. Grundler, *Talanta*, **30**, 870 (1983).
18. P. Grundler and E. Marx, *Acta Chim. Hung.*, **115**, 397 (1984).