

# Amperometric end-point detection of complexometric titrations with platinum microelectrodes

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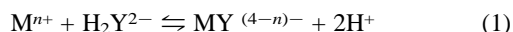
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Received 20th April 1999, Accepted 24th May 1999

An amperometric method is proposed for end-point detection of complexometric titrations of metal ions in unbuffered solutions with disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{H}_2\text{Y}$ ). It is based on the use of a platinum disc microelectrode as a sensor for monitoring the hydrogen ions delivered during the titration. Synthetic solutions containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, each alone or in mixture, are examined. The method is also applied to the determination of the total concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , *i.e.*, the total hardness, in mineral and tap waters. The precision of the method is satisfactory, the relative standard deviation being not greater than 2% for at least three replicates. Comparative measurements performed by the classical procedures using a metallochromic indicator give data agreement within 3.5%.

## 1. Introduction

Many standard procedures for the detection of metal ions in aqueous solutions rely on complexometric titrations using disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{H}_2\text{Y}$ ) salt as the titrant:<sup>1–3</sup>



The end-point detection is usually accomplished by means of metallochromic indicators.<sup>1–6</sup> However, for rapid, automatic and more sensitive end-point detection, instrumental analytical procedures have also been employed.<sup>3</sup> For this purpose, spectroscopic<sup>7–10</sup> and electrochemical<sup>11–15</sup> techniques have been applied to follow either the formation of the complex  $\text{MY}^{(4-n)-}$ , or the decrease of the amount of the metal ion  $\text{M}^{n+}$  in the solution. In a few instances, potentiometry, based on pH detection with a glass electrode, and conductometry have also been employed to monitor the hydrogen ions delivered from reaction (1).<sup>16–18</sup> The concentration of hydrogen ions in a solution could also be detected by exploiting the electrochemical reduction process:



An amperometric approach, based on this process, might be intrinsically very sensitive due to the large diffusivity of  $\text{H}^+$  in water.<sup>19</sup>

In recent years, several papers have appeared concerning the voltammetric behaviour for reduction of several strong and weak acids, alone and in mixture, at platinum microelectrodes.<sup>19–23</sup> The attractive features of microelectrodes, as for instance rapid achievement of steady-state limiting currents, low ohmic drop and simplification of the electrochemical apparatus,<sup>24</sup> make them suitable for many electroanalytical applications.<sup>24,25</sup> Hence, an alternative analytical instrumental route to follow the occurrence of reaction (1) could be based on the reduction process of hydrogen ions at platinum microelectrodes. Obviously, this approach will prove more sensitive if the medium is not buffered. Under this condition, however, during the titration both pH of the medium and the conditional constant of reaction (1) decrease. This may cause reaction (1) to be no longer effective in the bulk solution.<sup>3</sup>

This paper will present a study which shows that voltammetry at microelectrodes, exploiting the reduction process (2), can be employed for end-point detection of complexometric

titrations of metal ions, such as calcium and magnesium, with  $\text{Na}_2\text{H}_2\text{Y}$  in unbuffered solutions.

## 2. Experimental

### 2.1. Reagents and samples

All the chemicals employed were of analytical-reagent grade. Calcium chloride and magnesium chloride (Aldrich) were used to prepare stock solutions of these metal ions. Disodium ethylenediaminetetraacetate, a volumetric standard 0.1 M solution in water (Aldrich, Milwaukee, WI, USA), was used as the titrant. The solutions of the cations studied were standardised daily before the measurements by standard procedures,<sup>2</sup> using Eriochrome Black T (Aldrich) as metallochromic indicator. All the solutions were prepared with water purified with a Milli-Q system (Millipore, Milford, MA, USA). Nitrogen (99.99%) pure from SIAD (Bergamo, Italy) was used for deoxygenation in the voltammetric experiments.

The measurements in synthetic solutions were made in unbuffered conditions and in the presence of 0.1 M KCl. The real samples analysed were commercially available mineral water (natural pH over the range 7.72–7.80), and tap water from the municipal waterworks of Venice (natural pH over the range 7.15–7.30). These real samples were analysed after acidification to about pH = 5.5 with HCl 1 M.

All the measurements were carried out at room temperature ( $21 \pm 0.5^\circ\text{C}$ ) and after deaeration with nitrogen.

### 2.2. Electrodes and instrumentation

Voltammetric experiments were carried out with a two-electrode cell located in a Faraday cage made of sheets of aluminium. The working electrode was a  $12.5\ \mu\text{m}$  radius platinum microdisc, prepared by sealing a  $25\ \mu\text{m}$  diameter platinum wire (Goodfellow Metals, Cambridge, UK) directly into glass. The microelectrode surface was polished mechanically with graded alumina powder of different sizes (1, 0.3, to  $0.05\ \mu\text{m}$ , Buehler, Lake Bluff, IL, USA) on a polishing microcloth. In order to improve the repeatability of the measurements, an electrochemical activation of the electrode

surface was also made by cycling the potential 2–3 times over the range  $-0.1$ – $2$  V at  $200 \text{ mV s}^{-1}$  and then keeping the electrode at  $-0.1$  V for 10–15 s.

The effective electrode radius was determined by recording the steady-state diffusion limiting current,  $I_l$ , from a 1 mM ferrocene solution in acetonitrile and using the following equation:<sup>24,25</sup>

$$I_l = 4 n F D C^b r \quad (3)$$

where  $r$  is the radius of the microdisc,  $C^b$  the bulk concentration,  $D$  the diffusion coefficient [ $2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , ref. (26)] and the other symbols have their usual meanings. The reference electrode used was a saturated calomel electrode (SCE, AMEL, Milano, Italy).

Voltammetric experiments were controlled by a PAR 175 function generator (EG&G, Princeton, NJ, USA). A Keithley 428 picoammeter (Cleveland, OH, USA) was used as current-measurement device, and data were plotted with a Hewlett-Packard 7045 B X-Y recorder (San Diego, CA, USA).

A Metrohm 605 pH-meter (Herisau, Switzerland) was employed for pH measurements.

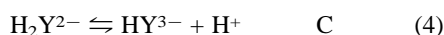
Theoretical concentrations of the chemical species at equilibrium in the bulk solution were calculated by using the MINEQL+ program, A Chemical Equilibrium Model System, Version 4.0 for Windows, from Environmental Research Software (Hallowell, Maine).<sup>27</sup>

### 3. Results and discussion

#### 3.1. Voltammetric titrations in synthetic solutions

This section is concerned with the complexometric titration of synthetic solutions made by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, each alone and in mixtures, over a range of concentrations that can be found experimentally in real matrices such as tap and mineral waters. All the solutions investigated, apart from the specific values, exhibited rather similar voltammetric behaviour. Hence, in order to illustrate the proposed method, we shall discuss thoroughly the case of a solution containing a given concentration of  $\text{CaCl}_2$ .

Fig. 1a shows typical voltammograms recorded at  $5 \text{ mV s}^{-1}$  with a  $12.5 \text{ }\mu\text{m}$  radius platinum disc in a  $0.1 \text{ M}$  KCl aqueous solution containing  $1.25 \text{ mM}$   $\text{CaCl}_2$ , to which increasing amounts of  $\text{Na}_2\text{H}_2\text{Y}$  were added. The voltammetric behaviour can be summarised as follows. Before the addition of the titrant, only the background discharge of water is noticed (see curve 1), in agreement with the fact that  $\text{Ca}^{2+}$  ions are not electroactive over the cathodic potential window available at the platinum microelectrode.<sup>26</sup> Upon addition of  $\text{Na}_2\text{H}_2\text{Y}$ , over a range of concentrations less than the initial concentration of  $\text{CaCl}_2$ , single sigmoidal waves with a half-wave potential ( $E_{1/2}$ ) of about  $-0.480$  V, are observed (see curves 2 or 3). When the concentration of  $\text{Na}_2\text{H}_2\text{Y}$  outweighs that of  $\text{CaCl}_2$ , a second more cathodic wave with  $E_{1/2}$  of about  $-0.590$  V appears (see, for instance, curves 5–7 of Fig. 1). Both shape and position of the less negative cathodic wave are congruent with those found for reduction of aqueous solutions containing a strong acid,<sup>20</sup> while the characteristics of the more negative cathodic wave are similar to those found for the reduction of  $\text{H}_2\text{Y}^{2-}$ , which occurs through the following scheme:<sup>20</sup>

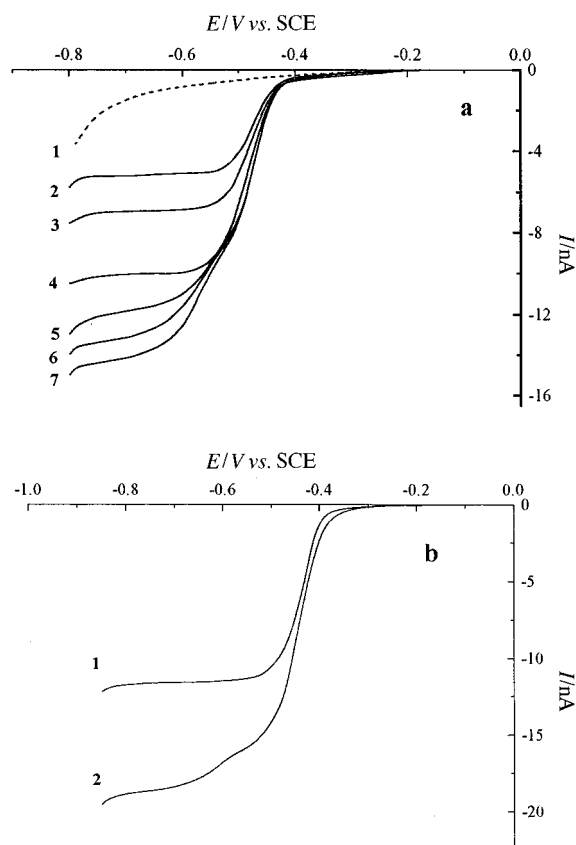


i.e., a homogeneous chemical reaction, C, preceding the heterogeneous electron transfer, E, at the electrode surface.

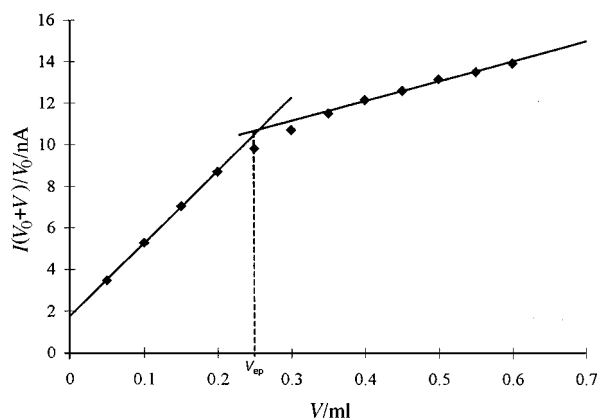
This wave assignment was confirmed by the voltammograms recorded in aqueous solutions containing  $\text{HClO}_4$  alone (see Fig.1b, curve 1) and in a mixture of  $\text{HClO}_4$  and  $\text{Na}_2\text{H}_2\text{Y}$

(Fig.1b, curve 2). In fact, these waves are very similar to those obtained in the first and second part of the titration, respectively.

From an analytical point of view, the appearance of the second wave is relevant, as it would indicate the end-point of the titration. For this purpose, however, it is easier to analyse the plot of the overall steady-state limiting current,  $I$ , against the volume,  $V$ , of the titrant added, i.e., the titration curve. The plot of the overall limiting current corrected for dilution effects, that is  $I(V_0 + V)/V_0$ , where  $V_0$  is the initial volume of the solution, as a function of volume of  $\text{Na}_2\text{H}_2\text{Y}$  added, for  $1.25 \text{ mM}$   $\text{CaCl}_2$  solution, is shown in Fig. 2. From this plot two well-defined linear portions with different slopes can be derived. The linear regression analysis yielded the parameters shown in Table 1



**Fig. 1** Steady-state voltammograms obtained from  $0.1 \text{ M}$  KCl aqueous solutions containing (a)  $1.25 \text{ mM}$   $\text{CaCl}_2$  and varying concentrations of  $\text{Na}_2\text{H}_2\text{Y}$ :  $0.0$  (1),  $0.5$  (2),  $0.75$  (3),  $1.25$  (4),  $1.5$  (5),  $2.0$  (6) and  $2.5 \text{ mM}$  (7); (b)  $0.3 \text{ mM}$   $\text{HClO}_4$  (1) and  $1.0 \text{ mM}$   $\text{HClO}_4$  +  $2.0 \text{ mM}$   $\text{Na}_2\text{H}_2\text{Y}$  (2) Pt microelectrode,  $r = 12.5 \text{ }\mu\text{m}$ , scan rate  $5 \text{ mV s}^{-1}$ .



**Fig. 2** Experimental  $I$  vs.  $V$  plot obtained for the solutions of Fig. 1a.  $\text{Na}_2\text{H}_2\text{Y}$ :  $0.1 \text{ M}$ . Initial volume of solution:  $V_0 = 20 \text{ mL}$ ;  $V_{ep} = V$  at the end point.

(first row). The results can be rationalised as follows. Before the equivalence point, the overall current is mainly related to the concentration of hydrogen ions, which increases up to the point where all  $\text{Ca}^{2+}$  ions have been titrated. After the equivalence point, the overall current is instead related to the concentrations of both  $\text{H}^+$  and  $\text{H}_2\text{Y}^{2-}$ . However,  $\text{H}^+$  is now almost constant, and  $\text{H}_2\text{Y}^{2-}$  increases while the volume of the titrant increases. Since the diffusion coefficient of  $\text{H}_2\text{Y}^{2-}$  is lower than that of  $\text{H}^+$  by more than one order of magnitude,<sup>22</sup> the overall current increases to a lower extent. If this view is correct, then the intersection point of the two straight lines should conceivably be assumed as the end-point of the titration. The concentration value obtained by this procedure is shown in Table 2 (second row). As a comparison, the same solution was titrated by the classical method using Eriochrome Black T as an indicator, and this result is also included in Table 2. The data obtained with the two different approaches agree satisfactorily.

The results presented up to now would indicate that, in spite of the fact that the solution becomes acid during the titration, any addition of  $\text{Na}_2\text{H}_2\text{Y}$  led reaction (1) to proceed to completeness. Actually, under acidic conditions, the conditional constant of the complex  $\text{CaY}^{2-}$  may decrease considerably, so that only a small amount of  $\text{Ca}^{2+}$  would be chelated by  $\text{Y}^{4-}$ . In order to investigate this aspect, the concentrations of the main species at equilibrium in the bulk solution were calculated using both thermodynamic equilibrium constants available from the literature,<sup>28</sup> and the experimental pH monitored during the titration. Table 3 shows the conditional constant ( $K'$ ) values calculated over the pH range 5.5–3.5, which includes most of the ranges observed experimentally. Fig. 3 shows the bulk molar fractions (in percent) and pH dependence on the volume of the titrant added in the solution containing 1.25 mM  $\text{CaCl}_2$ . From the figure it is evident that during the titration the pH of the solution drops, as expected, to rather low values. Accordingly, the conditional constant decreases (see Table 3). Moreover, when the concentration of  $\text{Na}_2\text{H}_2\text{Y}$  is theoretically

equal to that of  $\text{CaCl}_2$  (indicated with a vertical dashed line in Fig. 3), only 10.3% of the total  $\text{Ca}^{2+}$  is converted into  $\text{CaY}^{2-}$ . This means that under the experimental conditions employed here, reaction (1) is no longer effective in the bulk solution.

The latter conclusion clearly contradicts both the voltammetric behaviour observed in Fig. 1, and the data shown in Table 2. In fact, despite the fact that the concentration of  $\text{H}_2\text{Y}^{2-}$ , at any point of the titration, is always in excess (see Fig. 3), the wave due to this species appears only after the end point (see Fig. 1). Also, the concentration value of  $\text{CaCl}_2$  evaluated by the intersection of the straight lines, as shown in Fig. 2, is amazingly in good agreement with the reference value. These seemingly contradictory aspects can be explained considering that, at the electrode surface, the reduction process (2) forces the coupled reaction (1) towards the right hand side. Under the assumption that the complexation equilibrium is fast enough, reaction (1) proceeds to completeness only at the electrode surface, through a CE mechanism.

At the electrode surface reaction (4) may also be shifted towards the right hand side. However, the wave due to  $\text{H}_2\text{Y}^{2-}$  is observed only after the end point. It is likely that, when the bulk concentration of  $\text{H}_2\text{Y}^{2-}$  is less than that of  $\text{CaCl}_2$ , reaction

**Table 3** Conditional constants ( $K'$ ) for  $\text{MY}^{(4-n)-}$  complexes calculated over the pH range 5.5–3.5

$\text{M}^{n+}$	$\log K_T^a$	pH	$\log K'^b$
$\text{Ca}^{2+}$	10.7	5.5	5.2
		5.0	4.2
		4.5	3.2
		4.0	2.2
		3.5	1.2
$\text{Mg}^{2+}$	8.79	5.5	3.3
		5.0	2.3
		4.5	1.3
		4.0	0.3
		3.5	−0.7

<sup>a</sup> Thermodynamic equilibrium constants, at 0.1M ionic strength, from ref. 28. <sup>b</sup>  $K'$  calculated using the following dissociation constants for  $\text{H}_4\text{Y}$ :  $K_1 = 10^{-2.0}$ ;  $K_2 = 10^{-2.7}$ ;  $K_3 = 10^{-6.2}$ ;  $K_4 = 10^{-10.3}$ , from ref. 28.

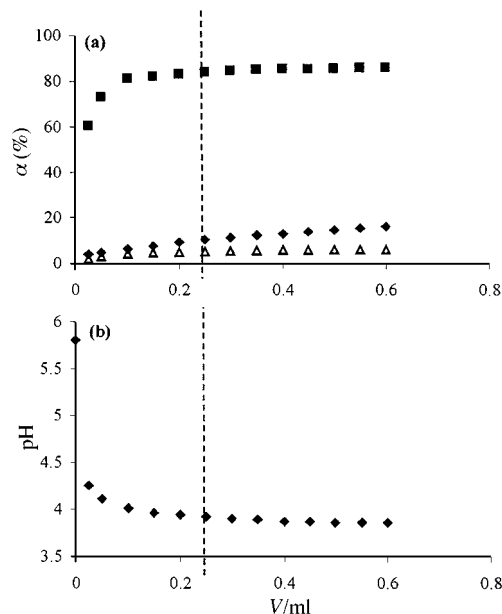
**Table 1** Typical regression parameters of the straight lines derived from the amperometric titration curves of metal ions with  $\text{Na}_2\text{H}_2\text{Y}$

Aqueous solution composition	Linear regression parameters			
	First branch		Second branch	
	Slope/nA ml <sup>−1</sup>	$R^2$	Slope/nA ml <sup>−1</sup>	$R^2$
1.25 mM $\text{Ca}^{2+}$	35.0	0.999	9.70	0.994
2.0 mM $\text{Mg}^{2+}$	21.8	0.999	10.1	0.998
1.25 mM $\text{Ca}^{2+}$ +2.0 mM $\text{Mg}^{2+}$	23.7	0.999	9.85	0.999

**Table 2** Quantitative data for the determination of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in aqueous solutions using the indicated methods

Cation	Concentration/mM		Difference %
	This work <sup>a</sup>	EBT <sup>b</sup>	
$\text{Ca}^{2+}$	1.01 (2.0)	0.99	+2.0
	1.26 (1.6)	1.25	+0.8
	2.57 (1.1)	2.54	+1.2
	3.51 (0.9)	3.48	+0.9
$\text{Mg}^{2+}$	0.98 (1.8)	1.01	−3.0
	1.98 (2.0)	2.05	−3.4
	2.92 (1.7)	3.00	−2.6
	4.05 (1.1)	4.18	−3.1
$\text{Ca}^{2+} + \text{Mg}^{2+}$	1.97 (1.9)	2.02	−2.5
	3.20 (1.5)	3.28	−2.4
	5.45 (0.5)	5.51	−1.1
	7.50 (0.8)	7.65	−2.0

<sup>a</sup> Mean values for three replicates, with RSD (%) in parentheses. <sup>b</sup> EBT = Eriochrome Black T method



**Fig. 3** (a) Bulk molar fraction ( $\alpha$ , %) of the main species present at equilibrium during the titration of  $\text{CaCl}_2$  with  $\text{Na}_2\text{H}_2\text{Y}$ : ( $\blacklozenge$ )  $\alpha_{\text{CaY}^{2-}}$ ; ( $\blacksquare$ )  $\alpha_{\text{H}_2\text{Y}^{2-}}$ ; ( $\blacktriangle$ )  $\alpha_{\text{H}_3\text{Y}^-}$ . (b) Experimental variation of pH during the titration; experimental conditions as in Fig. 2. The vertical dashed lines represent the theoretical equivalence volume.

(1) is prevailing, owing to its greater thermodynamic constant value (see Table 3). Instead, when the bulk concentration of  $\text{H}_2\text{Y}^{2-}$  is larger than that of  $\text{CaCl}_2$ , reaction (4) is also operative, thus providing the second more cathodic wave.

As stated above, a voltammetric behaviour similar to that shown in Fig. 1 was also obtained for solutions containing different concentrations of  $\text{Ca}^{2+}$  ions, for solutions containing  $\text{Mg}^{2+}$  ions, and for mixtures containing both cations. Typical titration curves for the latter instances are shown in Fig. 4, and their linear regression parameters are included in Table 1.

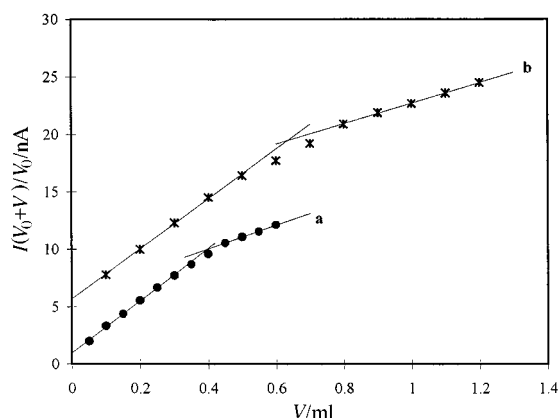
It is interesting to note that the slope of the plot of the first branch of the titration for  $\text{Ca}^{2+}$  is greater than that found for  $\text{Mg}^{2+}$  ions (see Table 1). This is conceivably due to the larger conditional constant of  $\text{CaY}^{2-}$  with respect to  $\text{MgY}^{2-}$ , which leads to a larger concentration of hydrogen ions in the bulk solution during the titration. On the other hand, the slope of the plot of the second branch is almost constant, regardless of both nature and concentration of the cation employed. This result further corroborates the hypothesis on the mechanism occurring in the titration, and that after the equivalence point the total current increases essentially for the increase of the concentration of  $\text{H}_2\text{Y}^{2-}$ .

Table 2 includes the quantitative data obtained for all the solutions examined. Also in this case the values obtained with the voltammetric method proposed here are compared with those found by the Black Eriochrome T procedure. The two sets of data agree satisfactorily, the difference observed being within 3.5%, even if a systematic error, which is positive for  $\text{Ca}^{2+}$  and negative for  $\text{Mg}^{2+}$  ions and the mixture of cations, is found. The reason for these differences is not clear at the moment; it may be due to different kinetics involving the cations in reaction (1) at the electrode surface.

Table 2 shows that the reproducibility of the amperometric method, over the concentration range of metal ions here considered, is good, the relative standard deviation (RSD) being over the range 0.5–2.0% from at least three replicates.

### 3.2. Application to real samples

The procedure described in the previous section was applied to the determination of total  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  content, that is the total hardness, in tap and mineral waters. Both these samples were characterised by a natural pH greater than 7. At this pH, the initial concentration of free hydrogen ions is too low to be detected by linear sweep voltammetry. Thus, in order to follow the entire titration curve with the method proposed here, the real samples were acidified with pure HCl to about pH 5.5. This affects only the conditional constants of the various  $\text{MY}^{(4-n)-}$

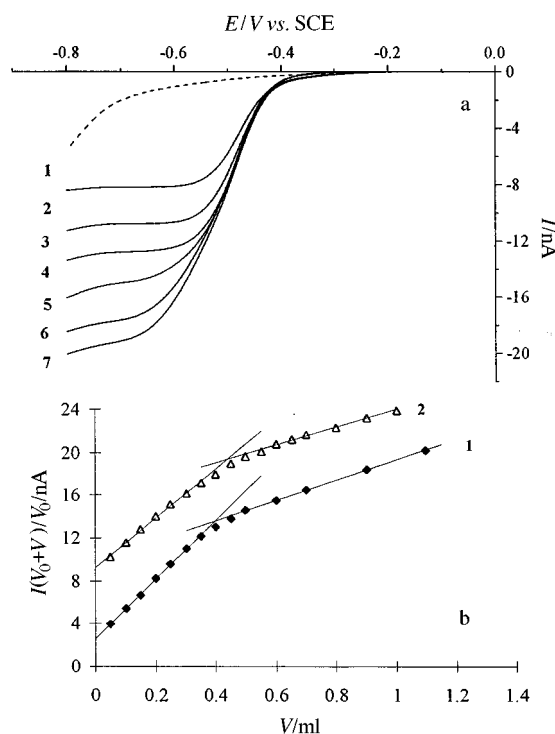


**Fig. 4** Experimental  $I$  vs.  $V$  plots obtained for 0.1 M KCl aqueous solutions containing: (a) 2 mM  $\text{MgCl}_2$  and (b) 2 mM  $\text{MgCl}_2$  + 1.25 mM  $\text{CaCl}_2$ .  $\text{Na}_2\text{H}_2\text{Y}$ : 0.1 M. Initial volume of solution:  $V_0 = 20$  mL.

species, but, as explained above, it does not affect the position of the end point, the titration actually occurring at the electrode surface.

Fig. 5a shows typical steady-state voltammograms obtained in the titration of a sample of an oligomineral water, while Fig. 5b (curve 1) shows the relevant  $I$  vs.  $V$  plot. The similarities between the experimental responses of Fig. 5 and those obtained above in the titration of aqueous synthetic solutions of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , are evident. Similar responses and plots were also found in the titration of tap water samples. In Fig. 5b (curve 2) the  $I$  vs.  $V$  plot relevant to a tap water sample is also shown.

Table 4 collects the total  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  contents found in the real samples analysed with the voltammetric method, along with the certified values reported on the bottle for mineral water, and those found by the metalochromic indicator method for tap water. The different experimental approaches provide data that agree within 3.6%.



**Fig. 5** (a) Steady-state voltammograms obtained for the titration of a mineral water sample with  $\text{Na}_2\text{H}_2\text{Y}$ . Blank (1) and after the addition of 1.0 (2), 1.5 (3), 2.0 (4), 3.0 (5), 4.3 (6) and 5.2 mM (7)  $\text{Na}_2\text{H}_2\text{Y}$ , respectively. Pt microelectrode,  $r = 12.5$   $\mu\text{m}$ . Scan rate  $5$   $\text{mV s}^{-1}$ . (b)  $I$  vs.  $V$  plots obtained from conditions as in Fig. 5a (1), and from the titration of a tap water sample (2). Initial volume of solution:  $V_0 = 20$  mL.

**Table 4** Total  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  determined in mineral and tap waters

Sample	Concentration/mM		Difference (%)
	This work <sup>a</sup>	Reference value <sup>b</sup>	
Mineral water			
1	2.02 (1.9)	2.07	−2.4
2	1.78 (1.6)	1.81	−1.7
3	1.06 (2.1)	1.10	−3.6
Tap water			
1	2.14 (1.5)	2.15	−0.5
2	2.28 (0.9)	2.31	−1.3

<sup>a</sup> Mean values for three replicates, with RSD% in parentheses <sup>b</sup> Mineral water: certified values reported on the bottle. Tap water: determined by titration using Eriochrome Black T method.

## 4. Conclusions

In this paper a voltammetric approach based on the hydrogen ion reduction process at platinum microelectrodes has been employed to detect the end point of complexometric titrations using disodium ethylenediaminetetraacetate salt as the titrant. Two aspects are noteworthy. First, the titrations are carried out under unbuffered conditions, which are rather uncommon for complexometric titrations with  $\text{Na}_2\text{H}_2\text{Y}$  performed with other existing methods.<sup>3</sup> Second, the titration is feasible even if the stability constants of the various  $\text{MY}^{(4-n)-}$  complexes are not very large. Consequently, the procedure proposed here has, in principle, wider applicability for titrating metal ions with  $\text{Na}_2\text{H}_2\text{Y}$ .

## Acknowledgements

This work was supported by the Italian National Council of Research (CNR) and the Ministry of University and Scientific Research (MURST), Rome.

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Paper 9/03144H