CHAPTER III

RESULTS AND DISCUSSION

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Although many ion-selective electrodes are found in literature for the direct potentiometric determination of surfactants [29, 52-56, 159-161, 241, 241-245, 268-273], deviation from the linearity at the lower concentration levels (< 1×10^{-5} M) is caused by gradual dissolution of the ion pair complex from the electrode matrix and at the higher concentration (> 1×10^{-3} M) due to the micelle formation. In contrast to the direct potentiometric measurements requiring careful calibrations of the measuring cells, the potentiometric titration technique offers the advantage of high accuracy and precision although the cost of increased time and consumption of reagents used as titrants. Another advantage is that the potential break at the titration end-point must be well defined, but the slope of the sensing electrode response need to be either reproducible or Nernstian and the actual potential values are of secondary interest. This allows the use of sensors of more simplified construction.

Potentiometric titrations of surfactants are often based on the formation of ion pairs between the determinand and the titrant which has an opposite charge and involve precipitation of an ion pair of limited solubility in water:

$$Q^+ + X^- \longrightarrow QX_{ppt}$$

As the result of the precipitate formation, the concentration of the ions in the solution decreases and hence the electrode potential decreases. A sharp potential break takes place at the end point as the concentration of the analyte is sharply decreased giving the S shape titration curve as in Figure 6:

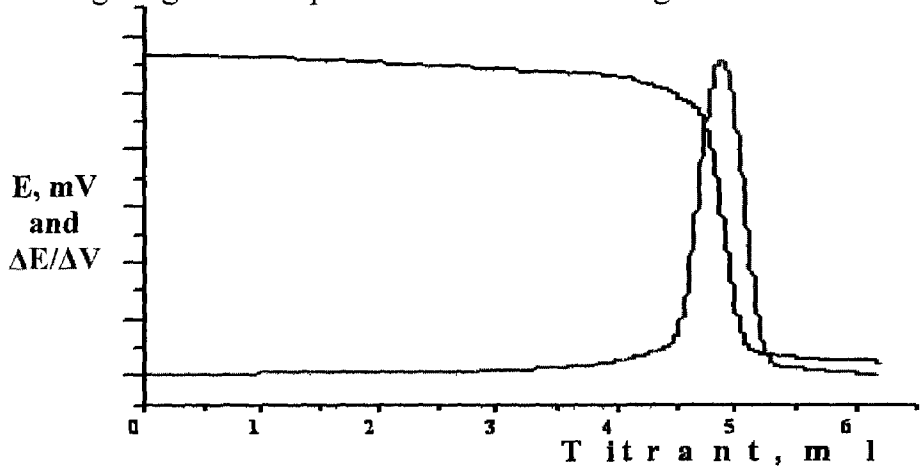


Figure 6: Typical potentiometric titration curve of CPCl with NaTPB

Vytras group used simple and inexpensive CPEs prepared without direct addition of the ion-exchanger in the electrode matrix for monitoring the potentiometric titration of different surfactants [65, 67, 246]. A quantitative expression for the precipitation equilibrium is given by the solubility product, K_s (QX), which is defined by:

$$K_s (QX) = [Q^+] [X^-] \quad (1)$$

In the presence of another, immiscible organic solvent, another equilibrium is attained because the two ions will form an associated ion-pair in a phase of lower polarity,

$$Q^+_{aq} + X^-_{aq} = QX_{org} \quad (2)$$

Which is characterized by the extraction constant, K_{ex} (QX),

$$K_{ex} (QX) = [QX]_{org} [Q^+]^{-1}_{aq} [X^-]^{-1}_{aq} \quad (3)$$

The distribution ratio of Q^+ ion, D (Q^+), could be expressed by

$$D (Q^+) = [QX]_{org} [Q^+]^{-1}_{aq} = K_{ex} (QX) [X^-]_{aq} \quad (4)$$

It is expected that during electrode conditioning in the aqueous suspension of the ion in air, an organic solvent (a plasticizer in CWEs or pasting liquid in CPEs) becomes gradually saturated with the ion-pair QX. In the absence of side reactions, the ion-pair concentration in the organic phase which is in contact with an aqueous suspension of the same ion-pair is determined by the two above constants,

$$[QX]_{org} = K_{ex} (QX) \cdot K_s (QX) \quad (5)$$

This concentration could be considered as that of ion-exchanging sites in the membrane of such a Q^+ (or X^-) selective electrode. It follows that this concentration increases with increasing values of both the extraction constant and the solubility product of the ion-pair formed [47]. Consequently, it is expected that when ion selective electrodes are immersed in a stirred aqueous suspension of the ion pair formed during a titration, their organic solvents (plasticizers) becomes gradually saturated with the ion pairs and there is no need for the addition of the electroactive material to the electrode matrix.

Although the carbon paste electrodes still play an important role in the electrochemical analysis, the prepared pastes are soft and non-compactable and have to be packed into a special piston shaped holder with definite shape and size. However, designs and shapes of such electrodes are not suitable for every purpose as in the case of measurements in flowing streams or field monitoring with portable analyzers where the respective detection units require electrodes of special constructions.

Screen printing seems to be the most suitable technique for the mass production of small size, simple, rapid and disposable sensors. Commercially available carbon inks used for the fabrication of the carbon working electrodes are usually composed of graphite particles, polymer binders and other proprietary additives for the promotion of dispersion, printing and adhesion [130, 249]. It is well known that such differences in the ink compositions as well as the printing and curing processes greatly affect the electrochemical properties of the fabricated sensor, so the selection and use of a particular ink is not a simple task as its exact composition may not be available. Also, some of these printing inks need high curing temperature which may destroy the ink components, especially organic ionophores, and require special ceramic substrates. The above mentioned consideration devoted the present work to the preparation of home made printing inks, with known formula, enables deposition of the films containing organic components under mild conditions which is not destructive for ionophores, plasticizers and support.

III.1. Optimization of the printing ink composition and printing process

The first part of the present work is oriented to the optimization of the printing inks formulations containing carbon particles, suitable binder and plasticizer, where the performance of the printed electrodes is tested in the potentiometric titration of CPCl with NaTPB.

The primary investigations on the manual screen printing are also done to optimize the electrical resistance, mechanical properties, thickness of the printed strips as well as the performance of the manual printing process.

III.1.1. Effect of plasticizer content

Addition of plasticizer to the printing ink will produce electrodes having similar properties to the carbon paste where the carbon particle within the electrodes matrix will be surrounded with a very thin film of the plasticizer [66]. Optimization of the plasticizer content within the printing ink is an important factor as it will affect the printing process (viscosity of the printing ink, adhesion of the printed electrodes on the substrate and the electrical resistance of the printed electrodes) as well as the performance of the printed electrodes in the potentiometric titration of CPCl with NaTPB. The thickness of the printed electrodes is decreased by increasing the plasticizer content to reach ≈ 50% of its original value at 37% plasticizer content (from 70 μm to 40μm). Also the adhesion of the printed electrodes decreases with increasing the plasticizer content from 5C to 3C with plasticizer content of 37% [274]. On the other side, the electrical resistance greatly increased from 200 Ω to about 2000 Ω by increasing the plasticizer content from 0 to 37%.

With respect to the potentiometric titration using printed electrodes fabricated using printing inks with different DOP content; it is found that both the total potential change and the potential break at the end point increase by increasing the plasticizer content in the printing ink. The effect of the plasticizer content on the titration of CPCl with NaTPB is listed in Table (1) and represented graphically as shown in Figure (7).

It is obvious that, no sharp end points are obtained when the plasticizer content is below 26%, while by increasing the plasticizer content, the total potential change and the potential break at the end point increase to reach its maximum value at 34.6%. Further increase in the plasticizer content do not improve the performance of the electrode but increase the electrical resistance and decrease the adhesion of the printed electrodes onto the substrate, so 34.6% will be applied in the further studies.

Table (1): Effect of the plasticizer content on the SPCPEs performance* in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Plasticizer content %	Total potential change, mV	Potential break at the end point, mV	ΔE/ΔV
0.0%	0	0	0
5.0%	20	0	10
10.5 %	52	10	23
15.0 %	50	14	30
20.0 %	53	14	35
26.0 %	201	70	275
30.0 %	350	165	488
32.0 %	385	170	495
34.6 %	438	253	730
37.0 %	433	240	675

*Average of five fabricated electrodes.

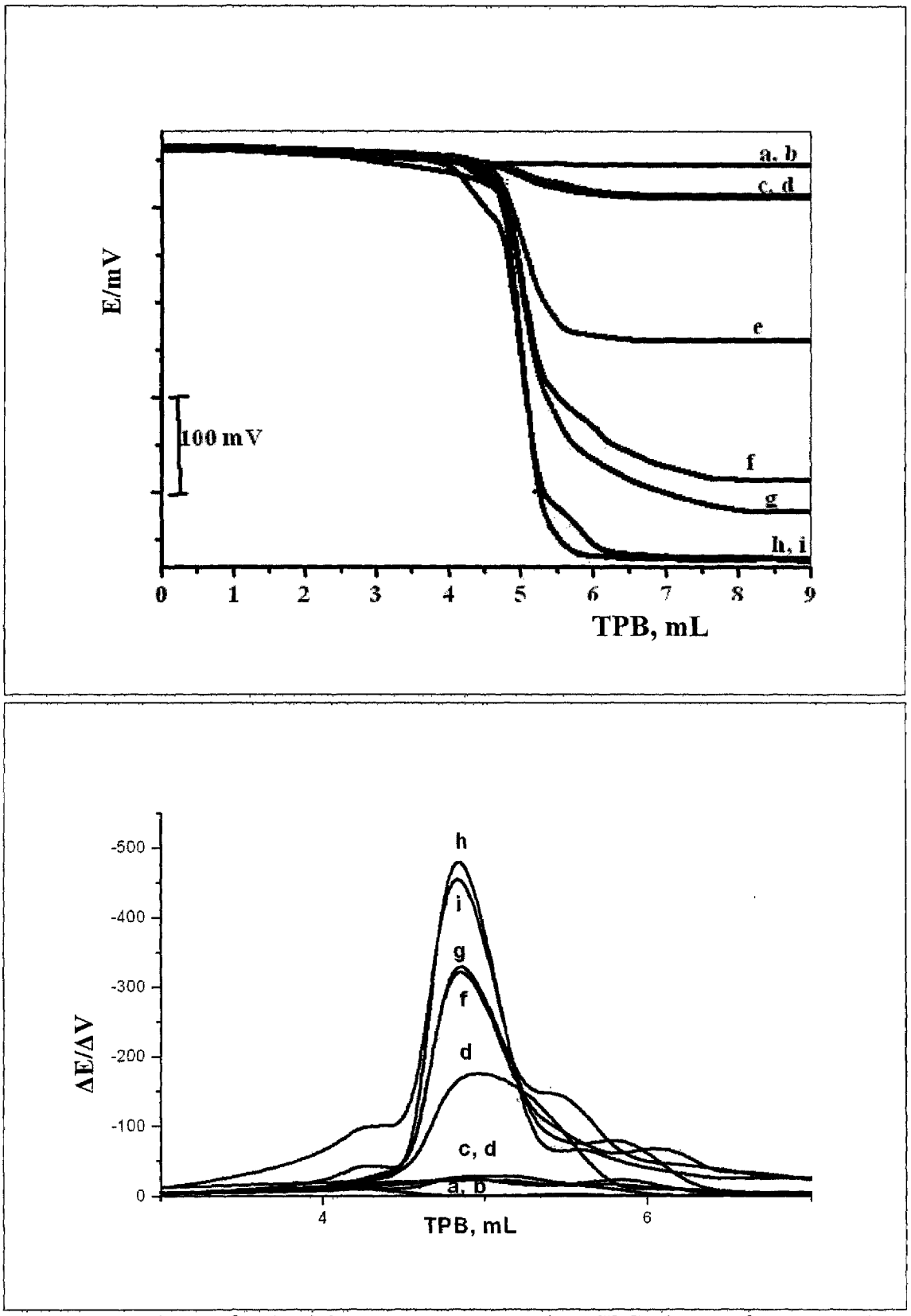


Figure 7:: Effect of plasticizer content on the SPCPEs performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB: (a) 0%; (b) 5%, (c) 10.5%; (d) 15%; (e) 26%; (f) 30%; (g) 32%; (h) 34.6% and (i) 37% plasticizer.

III.1.2. Effect of plasticizer type

The role of plasticizer may be considered analogous to that of the organic solvent in liquid membrane electrodes and it influences both the selectivity and sensitivity of the electrode. When these electrodes are used to monitor the potentiometric titration based on ion-pair formation, the magnitude of both the potential break and sharpness at the inflexion point of the titration curve is predetermined by the plasticizer polarity (dielecterical constants, ε) as a result of higher extractability of the ion-pair into the plasticizer [47].

The influence of the plasticizer choice on the electrode performances has been studied as the electrode plasticized with *o*-NPOE is compared with those plasticized with DBP, DOP, DOS, or TCP (Figure 8 and Table 2) from the all tested plasticizer. *o*-NPOE shows the highest total potential change (469 mV) and the highest potential break at the end point ($\Delta E/\Delta V$ = 1000 mV) which may be attributed to the high dielecterical constant of *o*-NPOE and the high extractability of the formed CP-TPB ion pair into the electrode matrix compared with other tested plasticizers (ε values are 24, 3.88, 5.2, 4.7 and 17.6, for *o*-NPOE, DOS, DOP, DBP and TCP, respectively). Due to the high extractability of the formed ion pair in the electrode materix, no electrode preconditioning is needed before applying in the potentiometric titration and excellent titration curves can be achieved from the second titration process, while electrodes fabricated using other plasticizers need either to operate the titration process at least 5-7 times or to soak the electrode in the aqueous solution of the ion pair for 1hr before using these electrodes in the titration process.

Also the electrode plasticized with *o*-NPOE showed the shortest response time compared with other electrodes plasticized with the rest of plasticizers which is reflected on the total time required to achieve stable potential readings and the titration time.

III.1.3. Effect of binding materials

Hand made carbon paste (made of carbon powder and a liquid binder) is a soft and non-compactable paste which can not be printed on the PVC substrate and need to be packed in a special electrode holder. Carbon based printing are usually

Table (2): Effect of the plasticizer type on the SPCPEs performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Plasticizer	Total potential change , mV	Potential break at the end point, mV	ΔE/ΔV
o-NPOE	469	375	1000
TCP	407	301	858
DOP	360	253	730
DBP	280	180	528
DOS	301	160	463

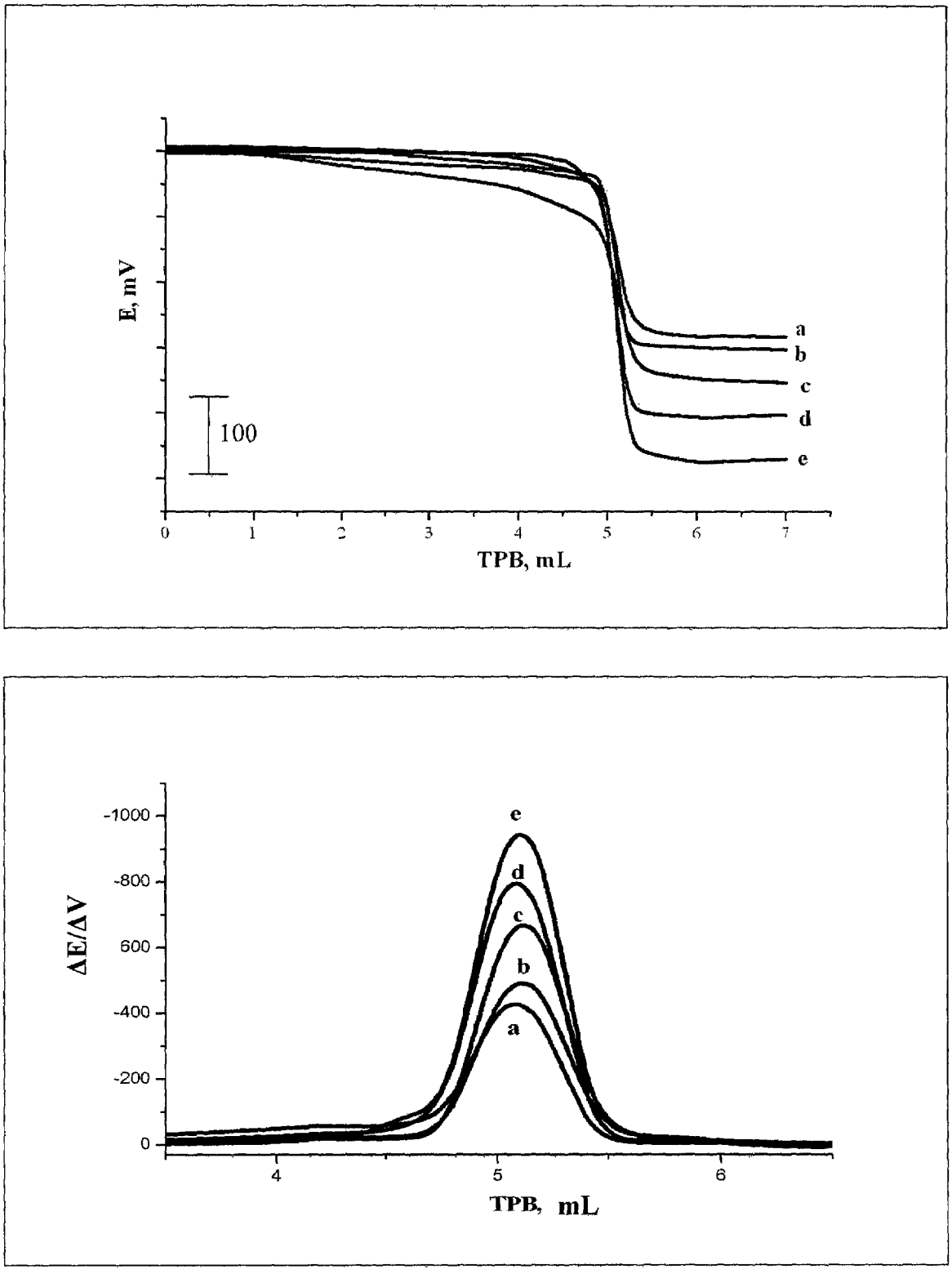


Figure 8: The effect of plasticizer type on the SPCPEs performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB, (a) DOS, (b) DBP, (c) DOP, (d) TCP, (e) *o*-NPOE.

composed of carbon particles dispersed with the binder in a suitable volatile organic solvent. After printing and curing processes, the binder solidified and adhere the printed carbon onto the substrate.

Different polymer binders are usually applied for the preparation of ink matrixes such as cellulose acetate (CA), polyacrylic acid, polyvinyl chloride (PVC) and epoxy resins dissolved in the proper organic solvents [130, 249]. In the present work, different inks containing the aforementioned binding polymers are used for printing of the working electrodes.

It is found that the printed electrodes containing CA as binding material showed the lowest electerical resistance (210, 1000, 2200 & 2800Ω for CA, PVC, polyacrylic and epoxy resin, respectively). The concentration of CA is then optimized as the CA content in (acetone/cyclohexanone 1:1 mixture) is changed from 0.5-7%. The resistance and the thickness of the printed electrodes increase by increasing the CA content and the concentration of 2% CA is selected as it gives the best printing quality with a good electerical resistance. It is also noticed that CA concentration more than 7% will give a very viscous ink that can not pass through the mesh while lower concentrations give a poor printing quality. Primary potentiometric measurements using such electrodes show a serious interference from some metal cations, which may arises from the complexation of CA through its hydroxyl groups, which makes its application as a binding material unsuitable in the presence of metal cations.

On the other side, PVC is known to be inert and usually used for fabrication of PVC membranes. Different PVC solutions in (cyclohexanone / acetone 1:1 mixture) are prepared with a concentration range from 2-14% and it is found that the 8% is the most suitable as it give better printing quality with a moderate electrode resistance (1100 Ω).

With regard to the potentiometric titration of CPCl with NaTPB, the electrodes prepared using the PVC as polymeric binder show the best titration curve (Figure 9 and Table 3) when compared with other binders which may be attributed to the high computability of the PVC matrix with the plasticizer used and other ink components.

Table (3): Effect of the binding materials on the SPCPEs performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Binder	Total potential change, mV	Potential break at the end point, mV	ΔE/ΔV
PVC	564	475	1203
Polyacrylic	180	125	330
CA	259	122	318
Epoxy	165	131	345

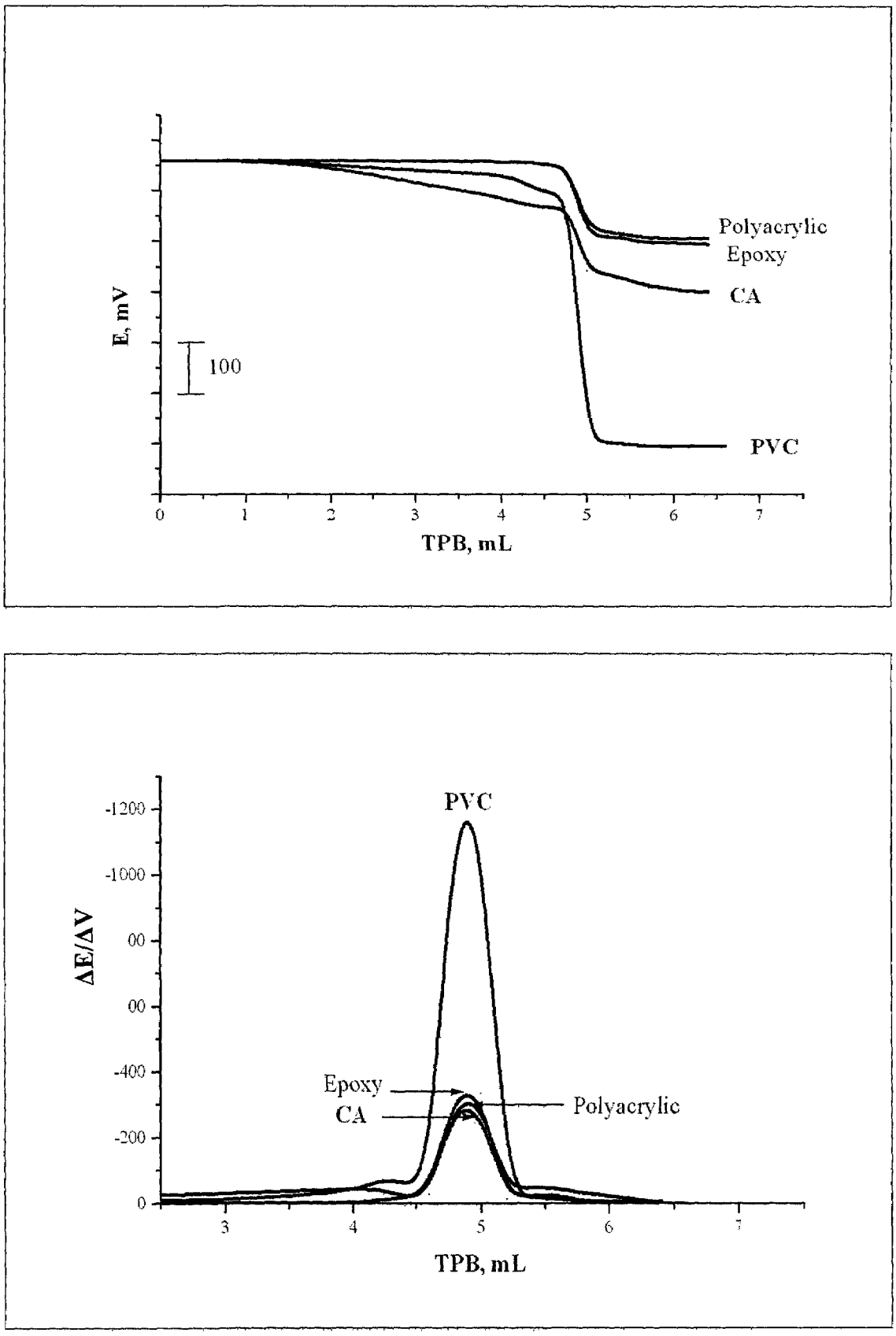


Figure 9: The effect of the binding materials on the SPCPEs performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

III.1.4. Effect of carbon content

The carbon content within the printing ink is varied from 15 to 65 % and the carbon ratio of 57.7% is selected as the printed electrodes are found to have a moderate electrical resistance with good adhesion to the PVC substrate.

The performance of the SPCPEs is also tested, by increasing the electrode thickness from 13 to 55 μm with increasing the carbon content from 15 to 65%. It is found that the electrode resistance is decreased from 2000 to 800 Ω with increasing the carbon content from 15 to 65%.

Printing ink is prepared using carbon powder with different particle sizes and it is found that increasing particle size reduces the height of the potential jump. Therefore the particle size of 1-2μm is applied in the preparation of the printing ink as it gives homogenous ink and printed electrodes with the best performance. The printed electrodes prepared with the present home made ink show similar electrical resistance and adhesion compared with that of the commercially available carbon ink and no significant difference in the performance of the electrodes fabricated using either home made or commercial ink is observed.

Owing to the quite low electrode resistance, there is no need to print a conductive silver track underneath the carbon layer which is usually subjected to oxidative corrosion and in addition, it is chemically/potentiometrically sensitive to various substances present in the analyzed solution; such procedures simplifies the printing of the working electrodes to one-step process.

III.1.5. Effect of ink solvents

The traditional THF solvent used in hand cast PVC membranes cannot be used for screen-printing because of its high evaporation rate which rapidly change the viscosity of the ink during the printing process and causing heterogeneity of the ink composition. Also, it is noticed that when using THF as ink solvent and due to its high evaporation rate, the silk screen is blocked with the ink and need to be reconstructed after approximately 5 printing process.

Several relative high boiling point solvents (e.g. cyclohexanone, cyclohexanone-acetone mixture, commercial thinner, ethylene glycol, acetone, ethyl cellulose, terpineol) are used as subsistents for THF and it is found that the mixture

of cyclohexanone-acetone 1:1 (v/v) is the most suitable solvent for the printing process and appropriate curing time.

III.1.6. Selection of the screen materials

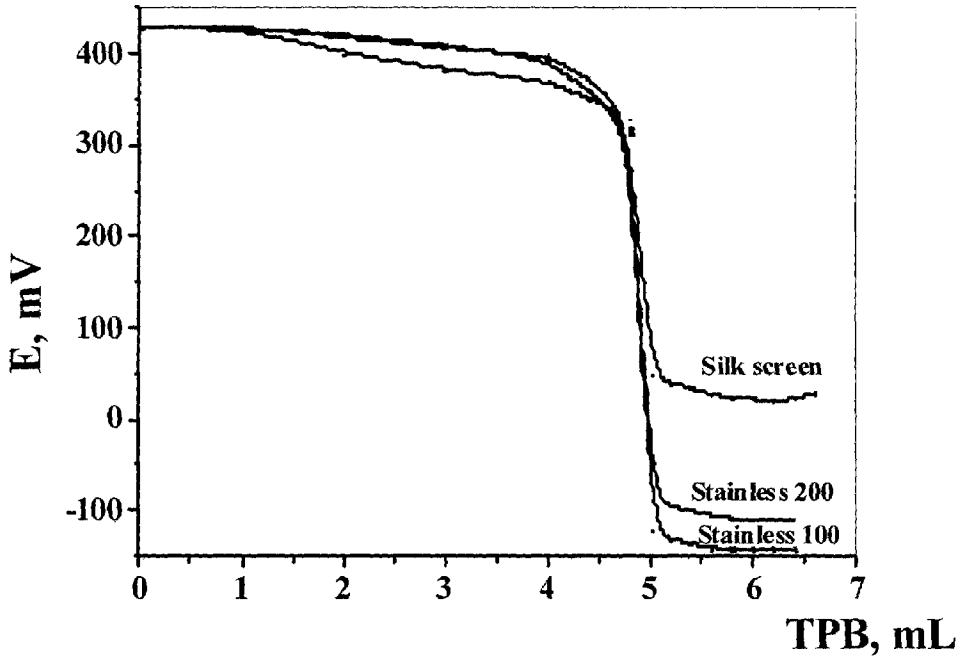
Polyester fabrics are considered to be one of the best all round materials for screen printing as they are dimensionally stable and resistant to the organic solvents used for ink preparation. Selection of the mish count of the polyester fabric (which indicates the number of threads per centimeter) is also important as the larger the mesh count the smaller is the pore size and hence the smaller the amount of ink that pass through the screen during the printing process. By changing of the mesh count from 36 to 90, both the electrode thickness and resistance are changed (the resistance increased from 1000 to 4500 Ω and the electrode thicknesses decreased from 48 to 14μm).

The SPCPEs printed using silk screens with different meshes are tested in the potentiometric titration of CPCl with NaTPB, and it is found that the electrode printed using a silk screen with mesh count 36 is the best with regard to the total potential change and potential break at the end point.

Also the stainless steel screen, with the same electrode shapes and dimensions, is tested as an alternative to the silk screen. From different sheet thicknesses (50-300μm), the screen with 100 μm thickness is selected as it gave printed electrodes with a moderate thickness and resistance with the best performance in the titration process (Figure 10).

The printing process using the stainless steel screen is much easier than silk screen regarding to the cleaning of the screen after each printing process and the life time of the screen (after about 15 printing processes, the silk screen must be removed from the wooden frame and reconstructed again according to the procedures in (II.5) while the main disadvantages of the stainless steel screen arises from the corrosion after long period exposure to the ink components.

Even the printing process is a manual, the reproducibility within the batch is quite good (the thickness is 50±8.0μm with a resistance of 1120±35 Ω). For three different batches the average electrode thickness is found to be 52.9±6.8 μm



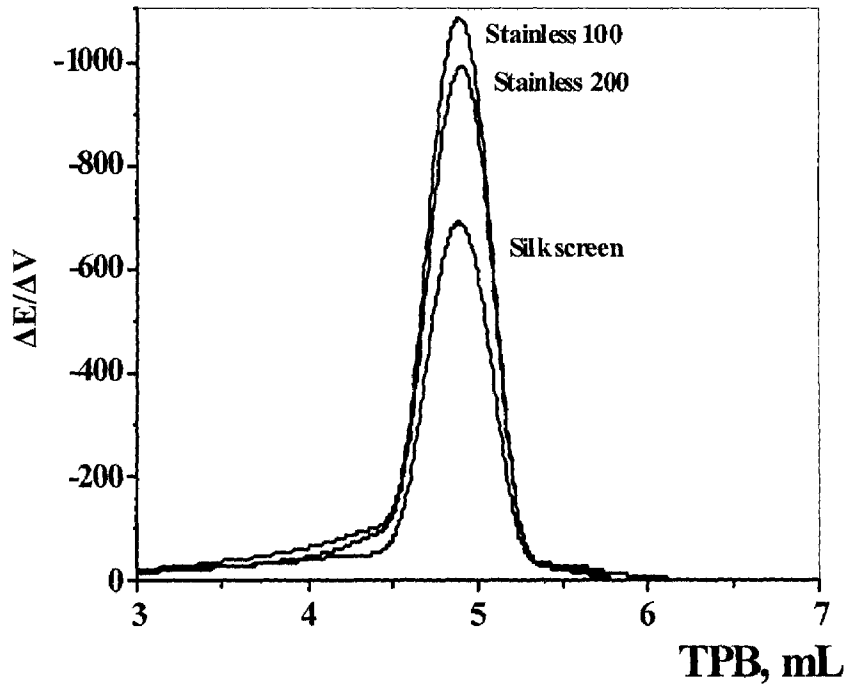


Figure 10: Effect of the screen materials on the SPCPEs performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

and the average resistance is 1110±10 Ω.

III.1.7. Selection of the substrate materials

The substrate is in most cases an insulator onto which the working electrode (optionally with other electrodes and/or layers) is printed. The used substrate material must fulfill at least two requirements: it must fit to the concepts of the sensing assay (flexibility, rigidity, mechanical and chemical stability, etc.) and it must guarantee that the printed layers are adhered strongly enough to it to provide the necessary mechanical stability.

In the present work, PVC sheet, polycarbonate sheet, X-ray film sheet (polyacetate sheet) and sheets for overhead projectors are tested as substrate for the printing process. From different substrates applied in screen printing, polyacetate (films for X ray) is selected as it gives the highest resistance to the ink solvent used, good adhesion of the printed carbon film as well as the suitability for thermal curing. Other substrates are not suitable as they do not resist the solvent applied or not suitable for the curing temperature.

III.1.8. Effect of the curing temperature and time

After the electrode printing, curing is required to evaporate the residual organic solvent and polymerize the binding material. Optimization of the curing temperature and time is an essential factor as high curing temperature will cause fast polymerization of the binder, damage of the substrate and loss of the plasticizer within the printed electrodes. From different curing times and temperatures it is found that 60 °C for 30 min is the most suitable.

III.2. Electrode Performance:

The analytical performance of the fabricated SPCPEs electrodes is compared with the traditional CPEs and PVC, CWE, coated graphite electrodes as well as the commercial surfactant electrode. Among the all tested electrodes (9 electrodes), listed in Table (4), the SPCPEs have the best performance (total potential change, potential break at the end point as well as the response time) in comparison with other electrodes. This will be explained in details as given below.

III.2.1. Comparison between the performances of SPCPEs fabricated using home made ink and the commercial ink.

The data obtained using SPCPEs fabricated using the home made ink are compared with those fabricated with the commercial ink in order to give an idea about the performance of newly home made ink and hence its application in the micro determination of surfactants.

It is obvious from the data listed in Table (4) and shown in Figure (11) that the SPCPEs printed with the home made ink show better performance (total potential change, potential break at the end point as well as the response time) compared with the commercial ink.

In addition, modification of the commercially available carbon ink with the plasticizer is not so easy as in the case of the home made ink which may be attributed to the high viscosity of the commercial ink. Also the commercial ink have a limited shelf life time (6 months) during which the ink must be consumed, while on the other side, the home made ink can be mixed at once and used for fabrication of the working electrodes.

III.2.2. Comparison between the performances of SPCPEs and double layers screen printed electrodes types B& C

In the present work, the three types of the screen printed electrodes A, B, C, electrodes are prepared depending on the method of fabrication. For fabrication of the double layer electrodes, a sensitive membrane can be printed on conductive pads (PVC carbon based ink for type B and PVC silver based ink for type C). After evaporation of the solvent, PVC membrane is obtained and the electrode behaves

Table (4): The performance characteristics of different fabricated electrodes in the potentiometric titration of 5 mL 10^{-2} M CPCl with 10^{-2} M NaTPB.

Electrode	Total potential change (mV)	ΔE/mV titrant at the end point	Response time (s)	Life Time (day)
SPCPEs (A)	564.0 ± 14.4	1202.5 ± 16.7	3	90
SPCPEs with Commercial ink	507.3 ± 32.7	1072.8 ± 45.5	3	40
SPEs (B) PVC /carbon	505.0 ± 14.4	1039.0 ± 70.3	6	30
SPEs (C) PVC/ Silver	455.0 ± 18.2	1002.0 ± 21.0	7	21
Surfactant commercial electrode	512.0 ± 17.5	950.6 ± 22.3	60	----
CPEs	558.0 ± 16.1	1205.3 ± 64.1	3	40
Coated graphite	517.0 ± 21.0	1065.0 ± 33.0	8	30
CWE	433.3 ± 9.5	887.5 ± 67.7	8	21
PVC	480.8 ± 39.7	1077.0 ± 41.0	10	21

* Five different electrodes are fabricated in each case

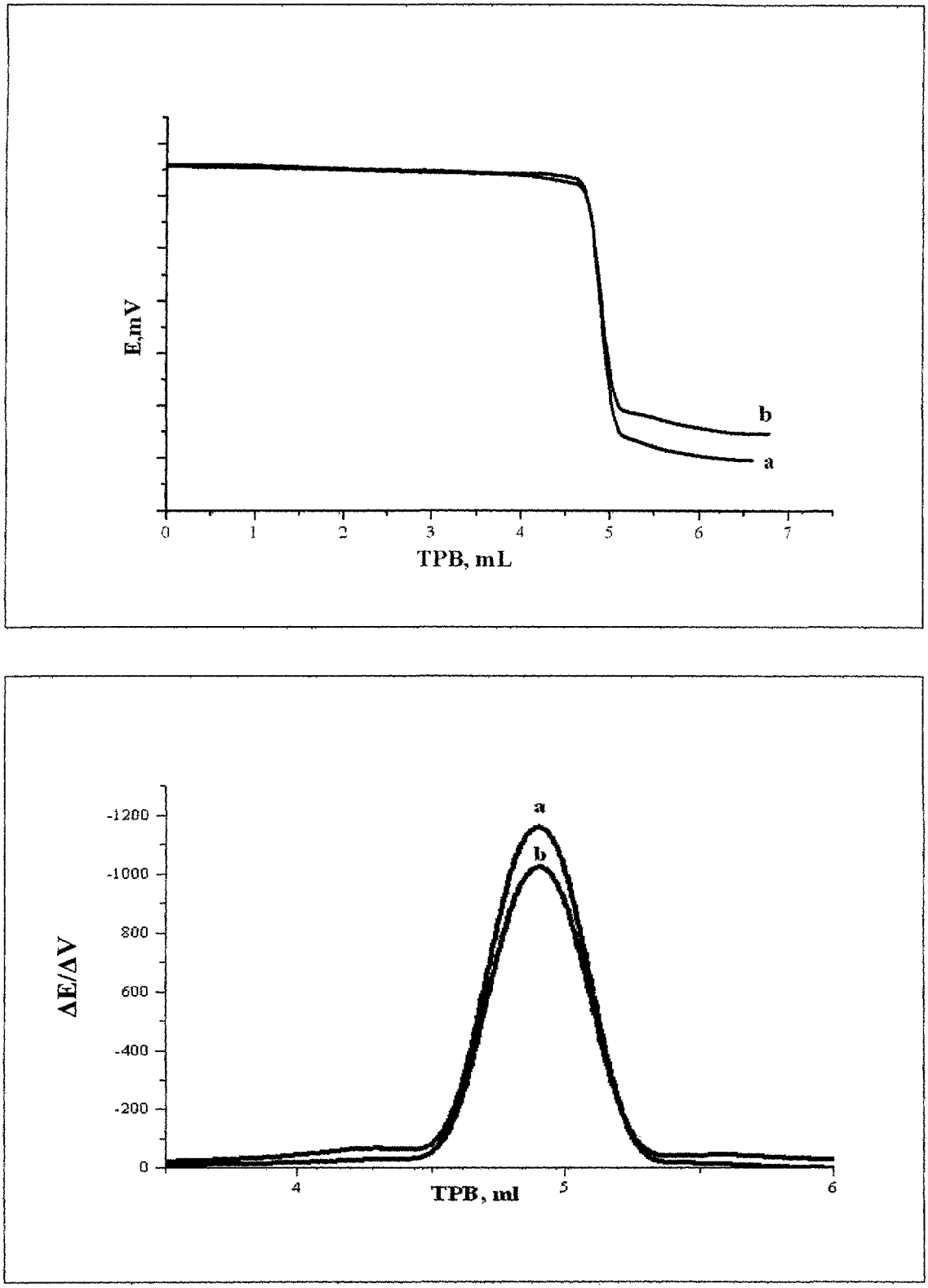


Figure 11: Comparison between the performances of SPCPEs fabricated using home made ink and commercial ink in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB, (a) home made ink, (b) commercial ink.

similar to the coated graphite electrode and CWE type electrodes with improvement of the fabrication reproducibility.

When such electrodes are used in the potentiometric titration of CPCl with NaTPB (Figure (12), the SPCPEs show better performance with regard to the total potential change and the potential break at the end point, longer life time as well as simplifying the printing process in one step printing.

III.2.3. Comparison between SPCPEs and carbon paste electrode

The SPCPEs show similar behavior to the traditional CPEs but with longer life time and better reproducibility, smaller size and lower consumption of the plasticizer needed for the electrode fabrication. From the titration curves shown in Figure (13), it is concluded that the SPCPEs show the identical performance (total potential change, potential break at the end point as well as the response time) compared with CPEs as given in Table (4).

In addition to the identical performances of the investigated electrodes, the SPCPEs have the very important advantages such as small size (5x35 mm for SPCPE and more than 15 cm for CPEs) which will be reflected on the sample needed for titration (1ml for SPCPEs and 10 ml for CPEs) as well as the large saving in chemicals (chemicals needed for fabrication of CPE will be sufficient for production of more than 15 SPCPEs) and high reproducibility with possibility of commercialization.

III.2.4. Comparison between SPCPEs and PVC electrode

According to the data listed in the Table (4), the SPCPEs are found to have the best performance with regard to total potential change, potential break at the end point as well as the response time if compared with PVC electrode. The titration curves obtained with SPCPEs exhibit higher potential jumps than those obtained with PVC electrode (Figure 14).

A drawback in the use of PVC membrane electrodes arises from the time consuming and inconsistent manual fabrication methods, difficult to be manufactured in small size, as well as the shorter life span of the electrode.

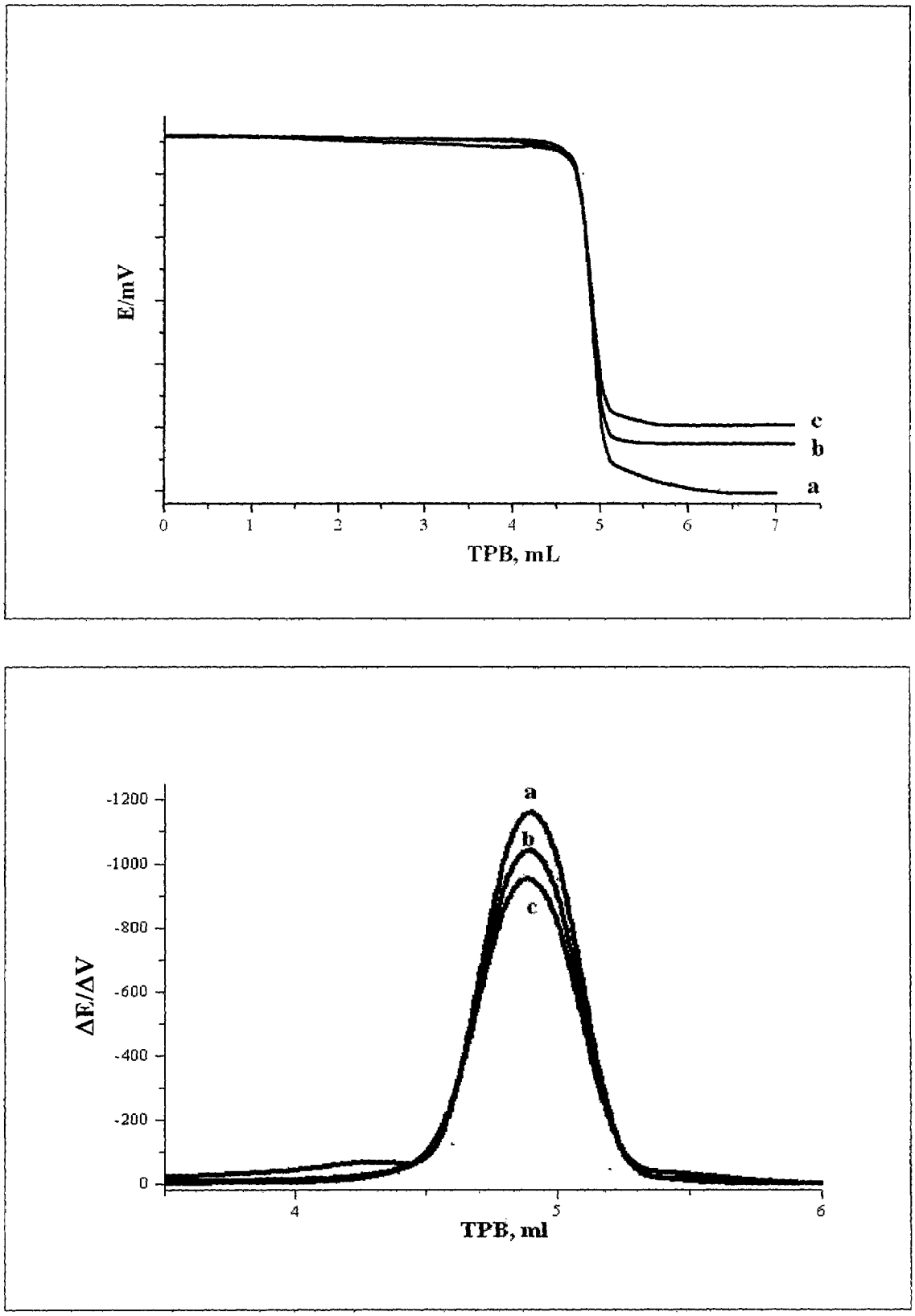


Figure 12: Comparison between the performances of SPCPEs and double layer electrodes for type B, C in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB, (a) SPCPEs type, (b) type (B), (c) type (C).

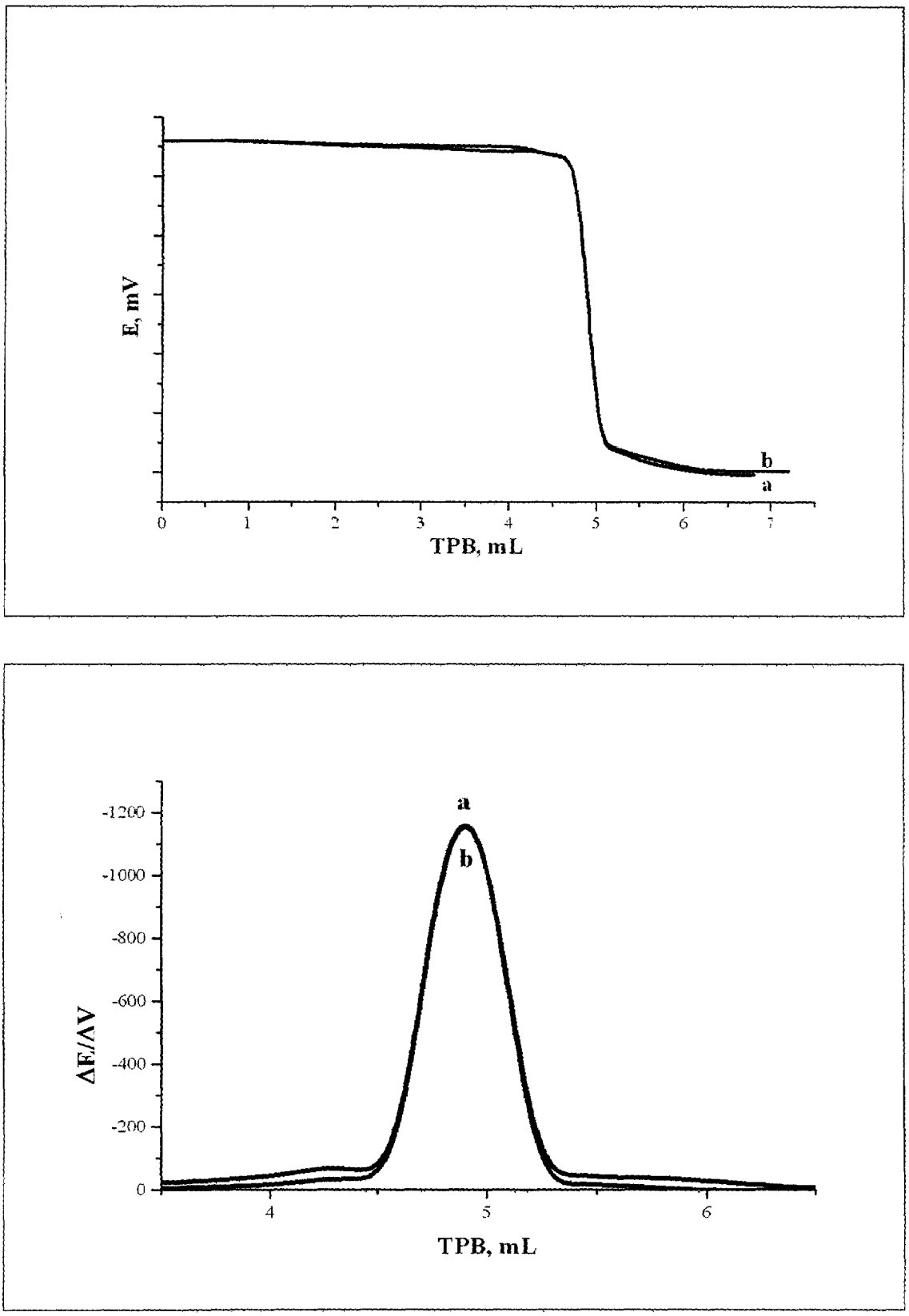


Figure 13: Comparison between the performances of SPCPEs and CPE in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB, of (a) SPCPEs, (b) CPE.

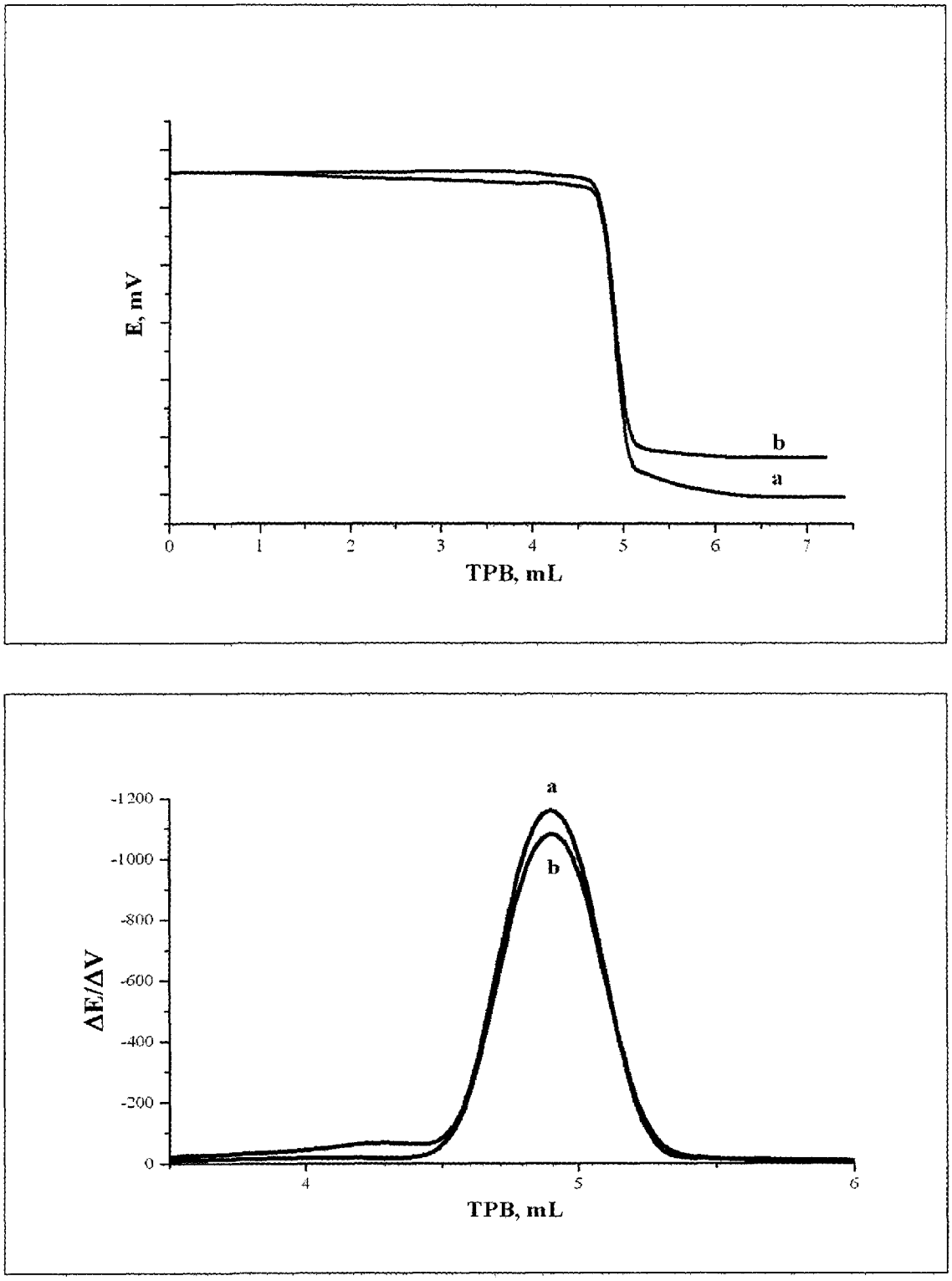


Figure 14: Comparison between the performances of SPCPEs and PVC electrode in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB, with (a) SPCPEs, (b) PVC electrode.

III.2.5. Comparison between SPCPEs and coated graphite electrode

The values of the total potential change, potential break at the end point and the response time of the titration of CPCl with NaTPB using both SPCPEs and coated graphite electrode are listed in Table (4). From the results obtained applying both electrodes under study, one can conclude that the SPCPEs show better performance total potential change, potential break at the end point as well as the response time in comparison with coated graphite electrode (Figure 15).

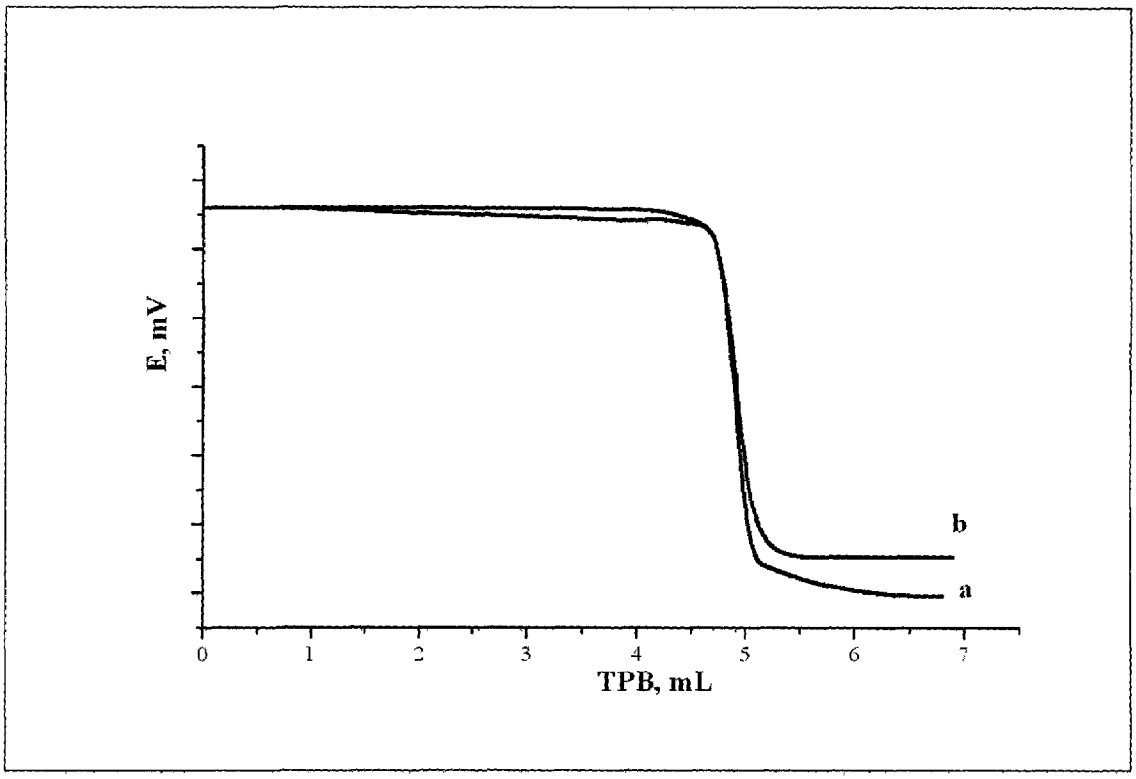
III.2.6. Comparison between SPCPEs and coated wire electrode (CWE)

The performance of SPCPEs and CWE are compared upon using both of them in the titration of CPCl against NaTPB under optimum conditions and the results obtained are given in Table (4) and Figure (16).

On comparison, it is clear that the SPCPEs show the best performance with regard to total potential change, potential break at the end point as well as the response time compared with CWE. The higher potential jump obtained in case SPCPEs compared those obtained with CWE which can be attributed to the longer response time of the CWE compared with SPCPEs.

III.2.7.Comparison between SPCPEs and commercial surfactant electrode

The date given in Table (4) and Figure (17) show that the SPCPEs have better performance with regard to total potential change, potential break at the end point as well as the response time when compared with commercial surfactant electrode (Cationic Surfactant Electrode, Metrohm 6.0507.150). It is clear from the titration curves that the curves obtained with SPCPEs exhibit higher potential jumps than those obtained with commercial surfactant electrode. This can be attributed to the longer response time of the commercial surfactant electrode as shown in Figure (17).



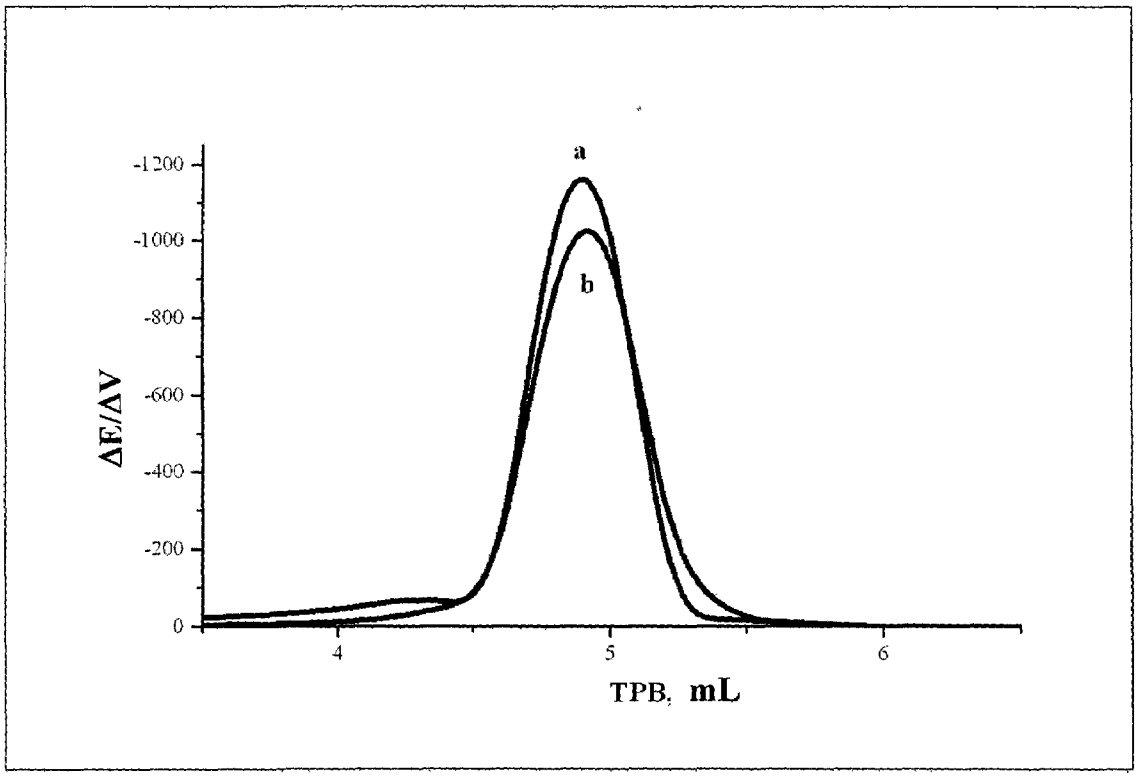


Figure 15: Comparison between the performances of SPCPEs and coated graphite electrode in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB, with (a) SPCPEs, (b) coated graphite electrode.

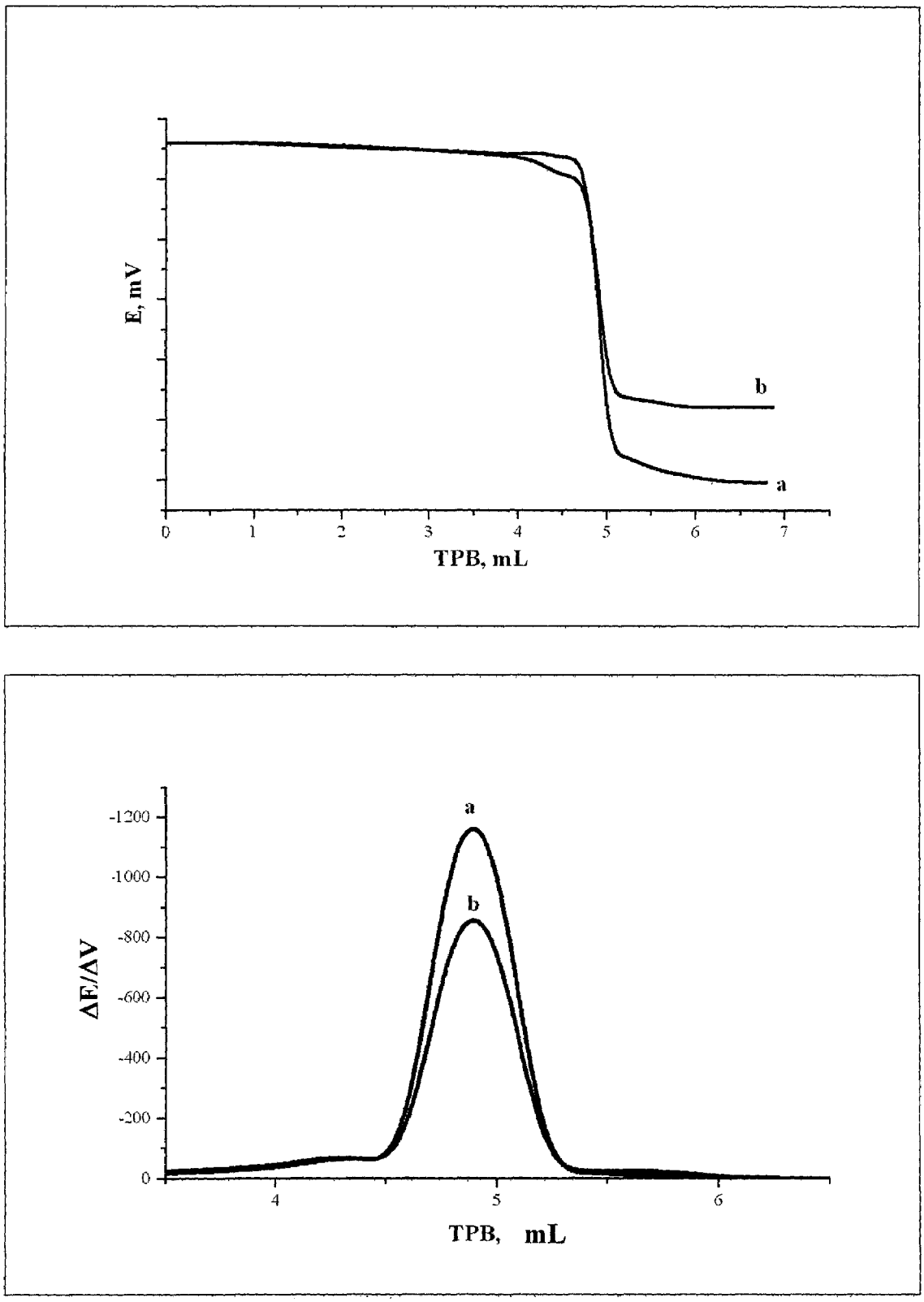
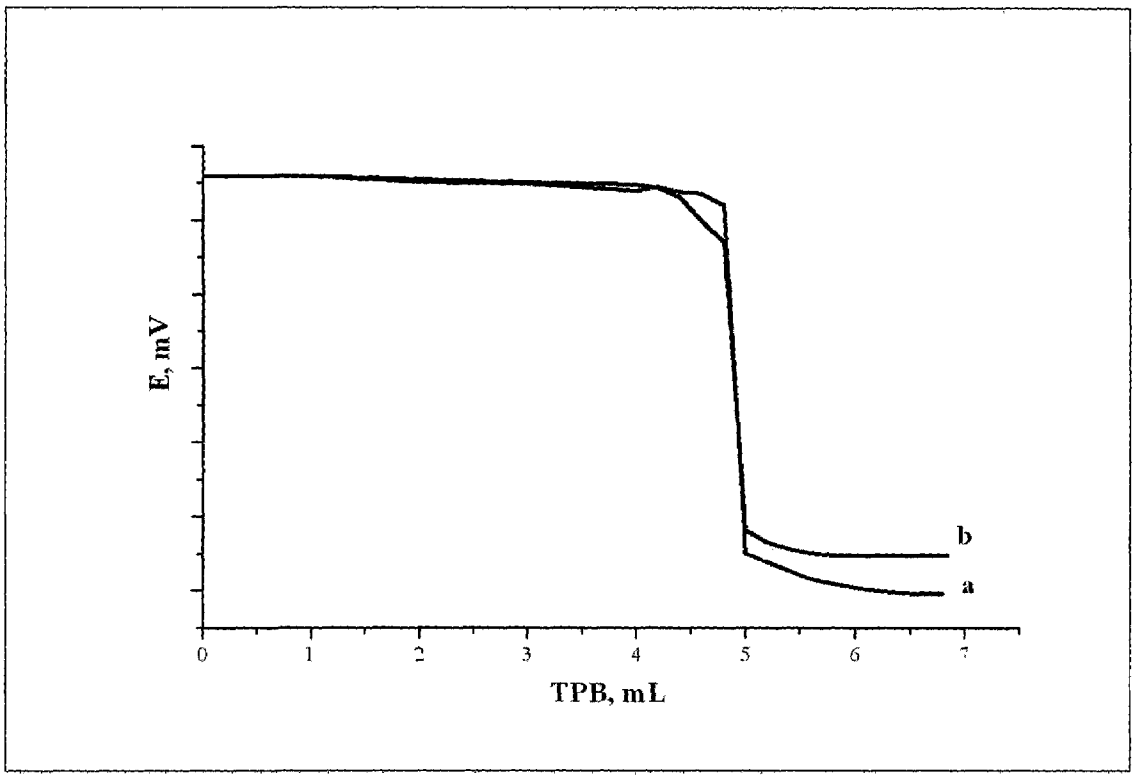


Figure 16: Comparison between the performances of SPCPEs and CWE in the potentiometric titration of 5 mL 10^{-2} M CPCl with 10^{-2} M NaTPB, with (a) SPCPEs, (b) CWE.



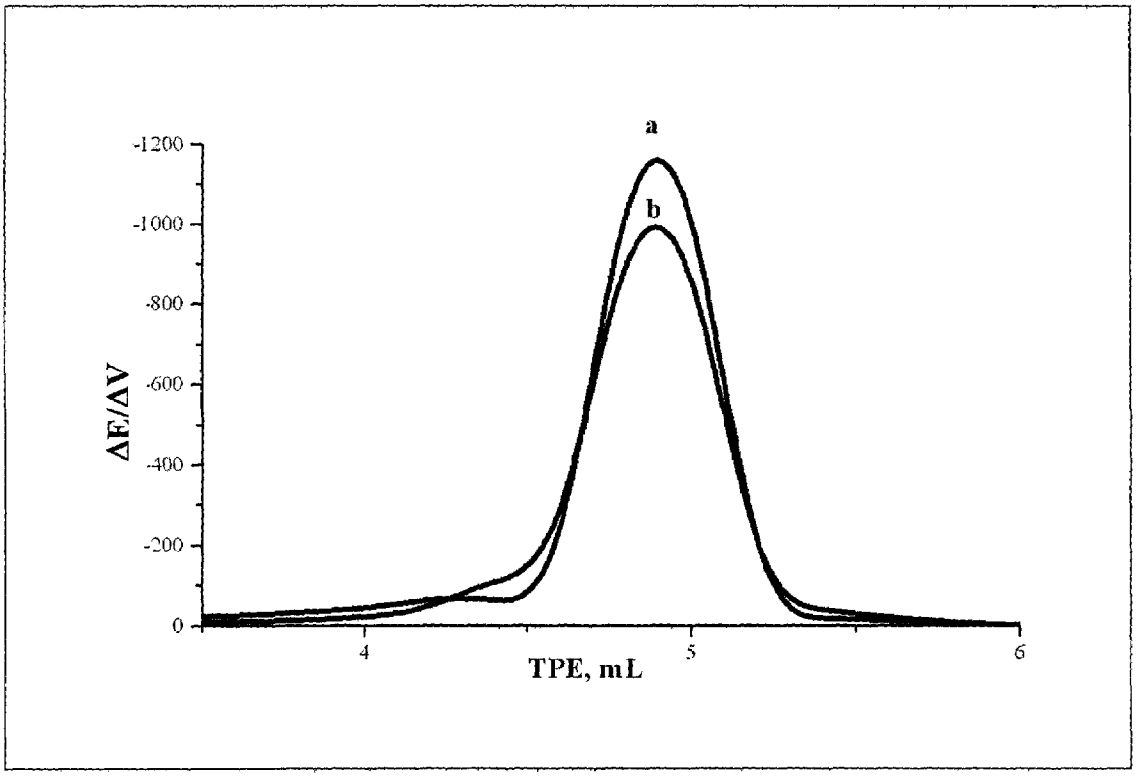


Figure 17: Comparison between the performances of SPCPEs and commercial surfactant electrode in the potentiometric titration of 5 mL 10^{-2} M CPCl with 10^{-2} M NaTPB, with (a) SPCPEs, (b) commercial surfactant electrode.

III.3. Response time

For analytical applications, the response time of a fabricated sensor is of critical importance. The average time required for the electrode to reach a steady potential response within ±1 mV of the final equilibrium value after successive immersion of a series of SDS solutions, each having a 10-fold difference in concentration, is investigated [275]. The electrode response time is found to be 3s (Figure 18) which is much shorter than any previously mentioned surfactant electrode [29, 243-245, 268-271] and the equilibrium potentials essentially remained constant for over 10 min. This fast and stable potential reading is reflected on the time needed for complete titration process as it is only about 3-5 min. The other tested electrodes, except the SPCPEs prepared with the commercial ink and CPEs, showed longer response time than that of SPCPEs.

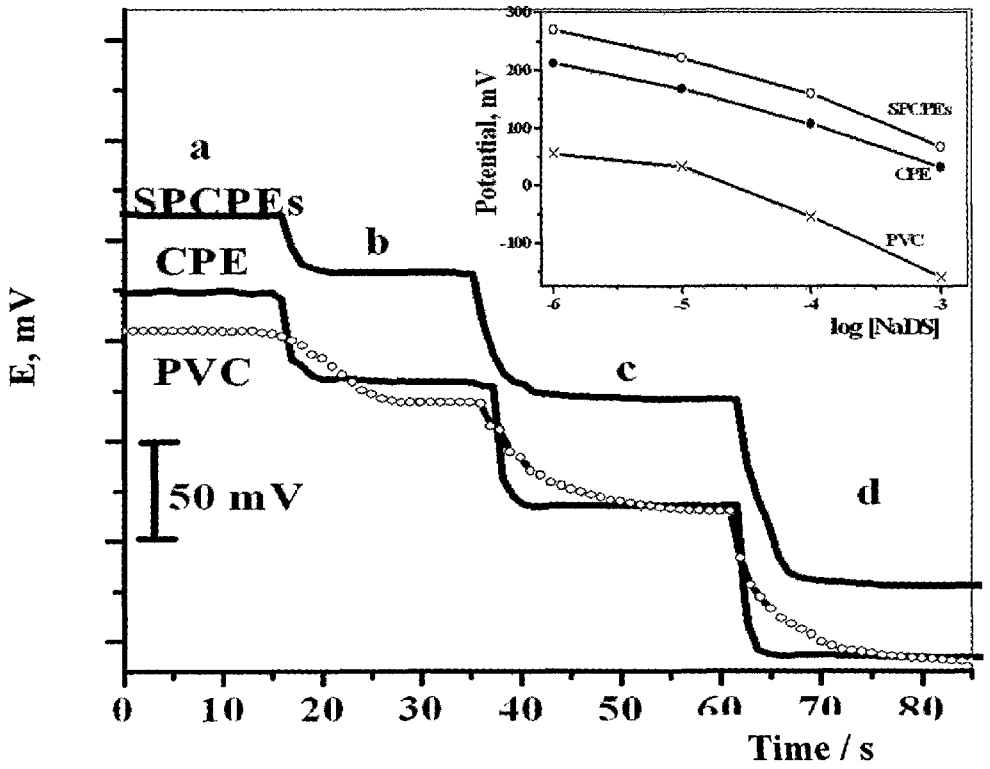


Figure 18: Dynamic response time of different SDS sensors: a) 10^{-6}, b) 10^{-5}, c) 10^{-3} M SDS.

III.4. Life time

All the printed sensors have high mechanical durability and good adherent to the PVC substrate. The method of electrode fabrication (type B and C) applied here has solved the crucial problem of adhesion between the sensitive membrane and the surface of the conductor in case of CWE. Both dry and wet ion-sensitive membranes adhere very tightly to the conductive track and the substrate material. Mechanical separation of these layers is impossible as the consecutive thick-films forming the sensor contain the same polymer matrix material.

For the determination of the storage stability, sensors fabricated in the same production cycle have been used. Every week a new electrode is used in the potentiometric titration of CPCl with NaTPB under optimum conditions.

III.4.1. Home made ink electrode (screen printed electrode).

The present work has successfully demonstrated that the screen-printing technology can be successfully applied for fabrication of simple, rapid, inexpensive and disposable ion-selective electrodes for the potentiometric titration of surfactants. The proposed work is devoted also for the preparation of home made printing inks used for working electrodes fabrication. Bielectrode potentiometric strip including both the working and the references electrodes in the same strip is presented. The fabricated sensor is applied for the ion-pair formation-based on potentiometric titration of surfactants in their authentic solution, pharmaceutical formulations, detergents, as well as water samples.

The performance of the fabricated electrodes has been tested by titration of CPCl with NaTPB on different days ranged from one day to 90 days and every time, the measurement of the total potential change, potential break at the end point and end point are recorded and the data obtained are listed in Table (5) and Figure 19. It is clear that there is a change in the potential break at the end point by 10% after 83 days.

Although the electrode is a disposable device, longer stability tests is also investigated and the electrodes of type A are successfully used for at least 50 consecutive titration processes (in a duration of 3 months) without a significant change in the potential break at the end point ($\Delta E/\Delta V$ = 1200.0 ± 17.2 mV/mL titrant).

Table (5): Life time of the SPCPEs in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Time	End point	Recovery %	Total potential change, mV	Potential break at the end point, mV	ΔE/ΔV
First	4.99	99.80	542	413	1087
1 day	4.98	99.60	540	408	1083
21 days	4.99	99.80	539	408	1083
29 days	4.97	99.40	524	408	1078
49 days	4.97	99.40	522	405	1075
56 days	4.98	99.60	521	405	1075
61 days	4.97	99.40	500	401	1050
68 days	4.96	99.20	499	402	1047
75 days	4.96	99.20	479	395	1045
83 days	4.95	99.00	492	364	1032

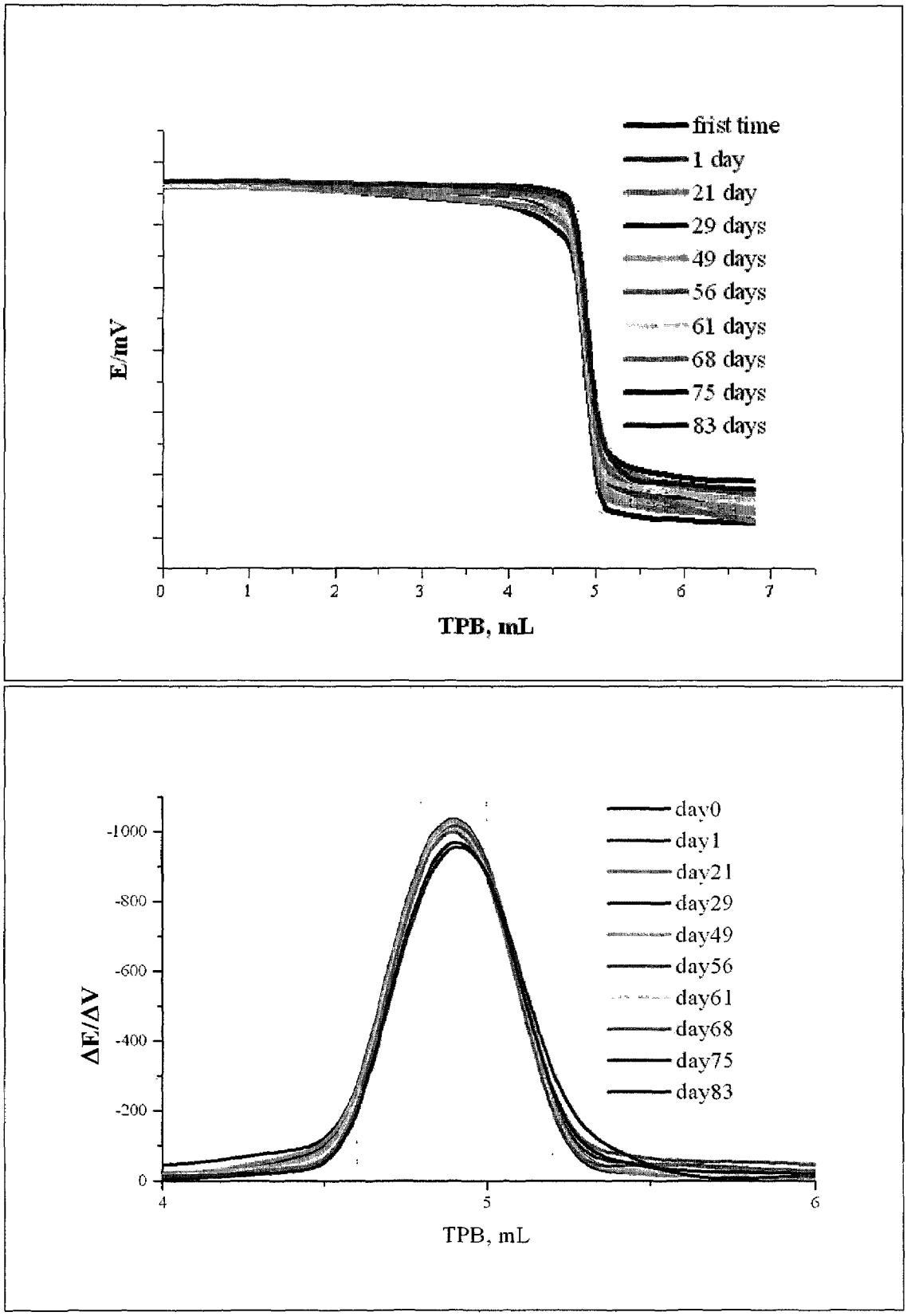


Figure 19: Life time of the SPCPEs in the potentiometric titration of 5 mL 10^{-2} M CPCl with 10^{-2} M NaTPB on different days from one day to 90 days.

III.4.2. The double layer printed electrodes for types B& C

III.4.2.1. The type B

The data listed in Table (6) and presented in Figure (20) show the total potential, potential break at the end point and the $\Delta E/\Delta V$ values which are obtained upon titration of CPCl against NaTPB at different time intervals (1 to 20 days) using the screen printed electrode type B and the results obtained show a decrease in the potential break at the end point by 10% after 20 days.

4.2.2. The type C

The performance of the electrode has been tested by titration of CPCl with NaTPB standard solution on different days ranged from one day to 21days where the total potential change, potential break at the end point and end point are listed in Table (7).

It is obvious from these results that the electrode performance and sensitivity decrease by 20% after 21 days (see Figure 21).

III.4.3. Commercial ink (screen printed electrode).

As mentioned before, the present work is also oriented to the preparation of home made printing carbon ink as an alternative to the commercial ink and using this ink for fabrication of the working electrode.

It is noticed that the electrode fabricated using the commercial ink works within 40 day after which the electrode starts to lose its performance (Table 8 and Figure 22).

Table (6): Life time of the screen printed electrode type B in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Time	End point	Recovery %	Total potential change, mV	Potential break at the end point, mV	ΔE/ΔV
First day	5.01	100.20	559	310	1105
6 days	5.01	100.20	379	282	1095
14 days	5.01	100.20	375	259	983
20 days	5.01	100.20	351	245	887

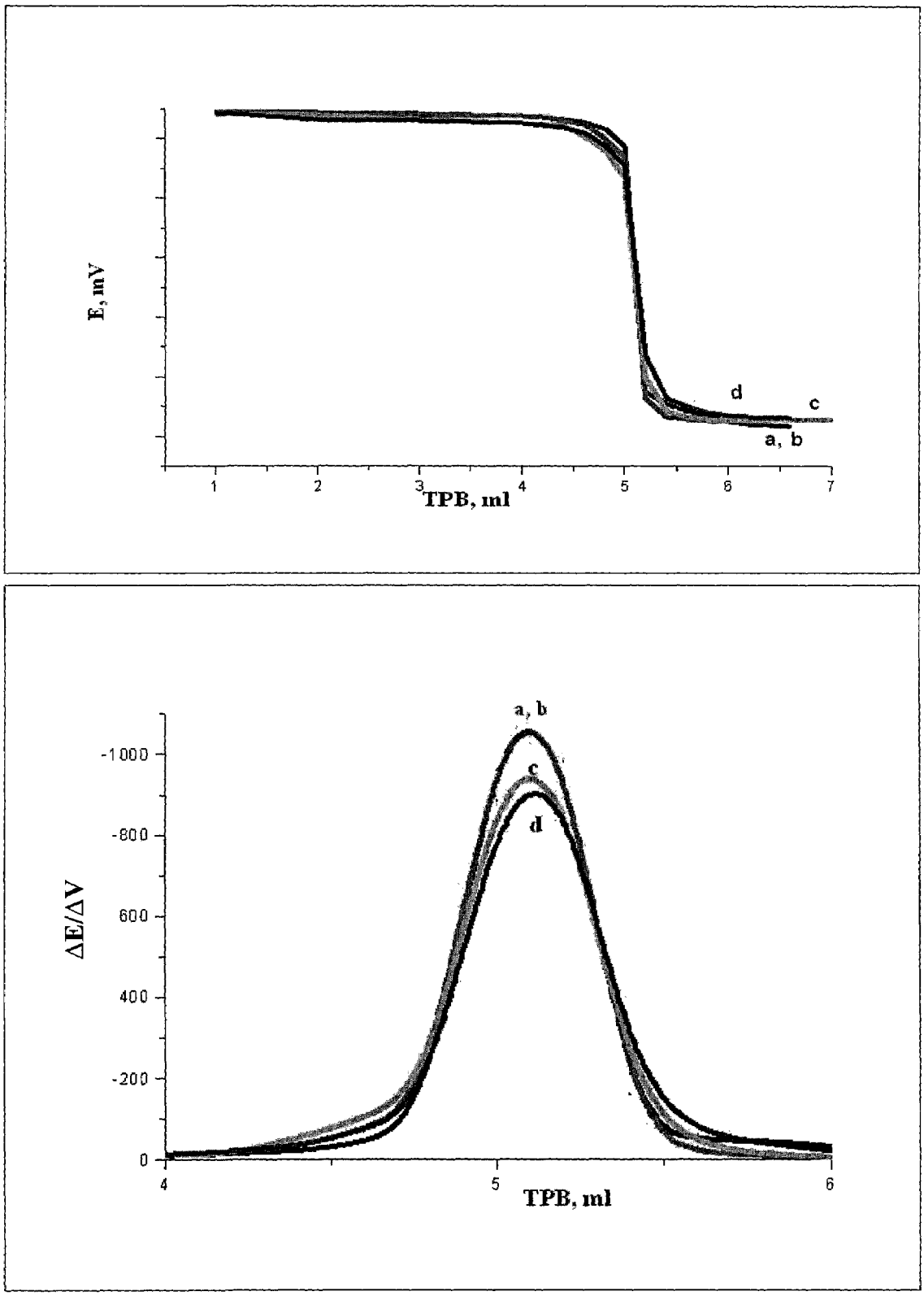


Figure 20: Life time of the screen printed electrode type B in the potentiometric titration of 5 mL 10^{-2} M CPCl with 10^{-2} M NaTPB on different days, a) first day, b) 6 days, c) 14 days, d) 20 days.

Table 7: Life time of the screen printed electrode type C in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Time	End point	Recovery %	Total potential change, mV	Potential break , mV	ΔE/ΔV
First day	4.96	99.20	455	370	1050
3 day	4.96	99.20	425	363	1025
7 days	4.97	99.40	491	361	950
15 days	4.96	99.20	507	349	900
21 days	4.95	99.00	468	365	800

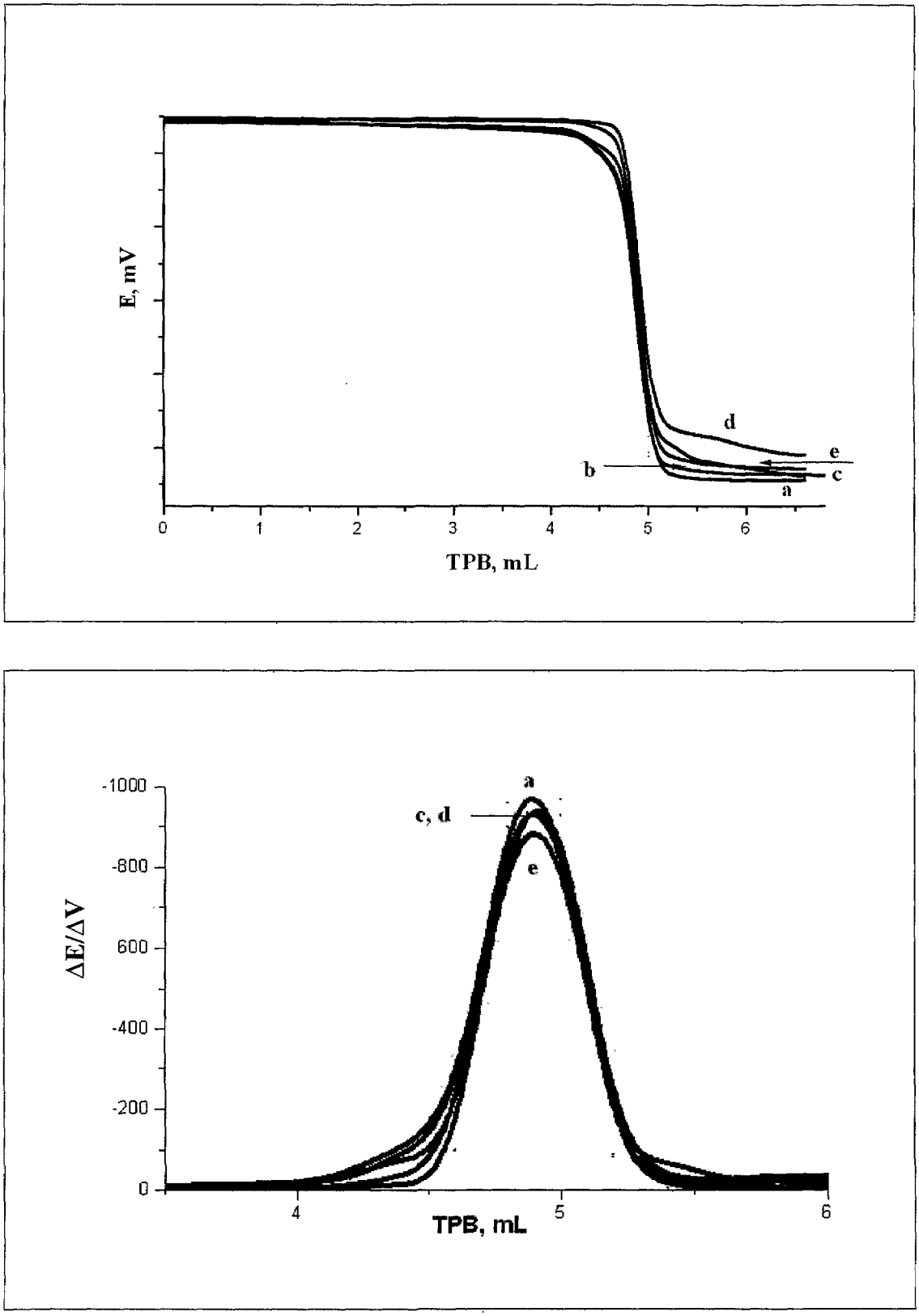


Figure 21: Life time of the SPCPE type C in the potentiometric titration of 5 mL 10^{-2} M CPCl with 10^{-2} M NaTPB on different days, a) first day, b) 3 days, c) 7 days, d) 15 days, e) 21 days.

Table (8): Life time of the SPCPEs fabricated using commercial ink in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Time	End point	Recovery %	Total potential change, mV	Potential break at the end point, mV	ΔE/ΔV
First day	4.97	99.20	507	416	1073
15 days	4.95	990	498	390	1060
22 days	4.95	99.00	490	380	1025
27 days	4.95	99.00	486	380	983
34 days	4.95	99.00	458	354	975
41 days	4.93	98.60	446	340	968

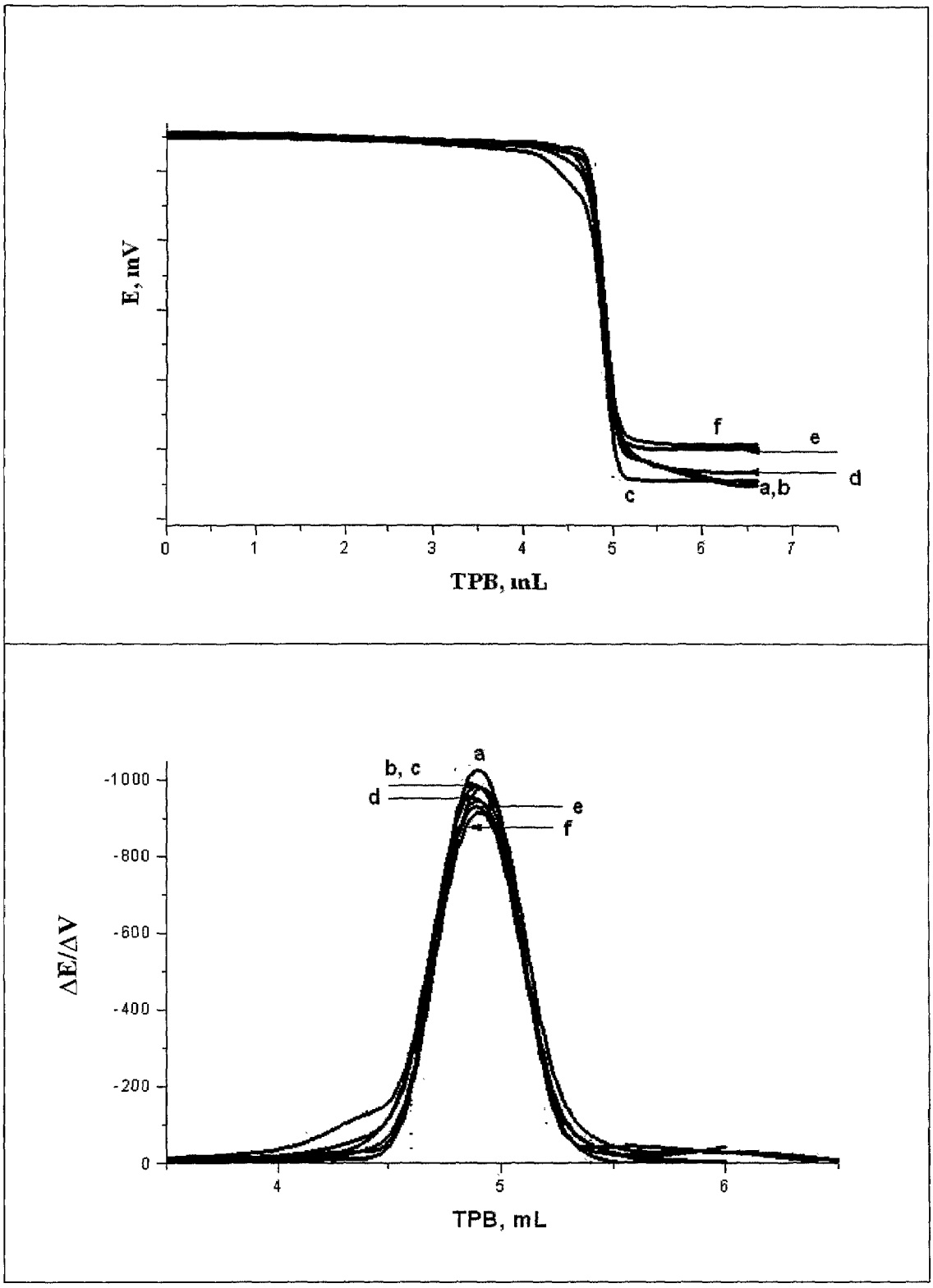


Figure 22: Life time of the SPCPEs fabricated using commercial ink on different days, a) first day, b) 15 days, c) 22 days, d) 27 days, e) 34 days, f) 41 days.

III.4.4. Carbon paste electrode

The performance of the electrode has been tested by titration of CPCl with NaTPB standard solution on different days from one day to 73 days where the total potential change, potential break at the end point and end point, results are listed in Table (9). Also, the titration curves obtained after different time intervals are shown in Figure (23). It is indicated from the Figure that there is a change in the potential break at the end point by 30 % after 30 days.

A new surface for measurement can be achieved daily by simply squeezing out a small amount of the paste and polishing the electrode surface on a smooth filter paper till a shiny surface is obtained.

III.4.5. PVC membrane electrode

The data listed in Table (10) and presented in Figure (24) show the values of the measured total potential change, potential break at the end point and end point, upon titrating CPCl against standard NaTPB using PVC membrane electrode. The results obtained show a decrease in the potential break at the end point by 10% after 21 days of electrode application.

III.4.6. Coated wire electrodes (CWEs)

The performance of the electrode has been tested by carrying out the titration of CPCl against standard solution of NaTPB on different days ranged from one day to 21 days. The measured total potential change, potential break at the end point and end point are given in Table (11) and Figure (25).

The results obtained using CWEs show a decrease in the potential break at the end point by 65 % after 21 days. The decrease of the performance may be attributed to the reaction of the silver with NaTPB as well as infusion of some ions of solution that may react with silver.

Table (9): Life time of the carbon paste electrodes in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Time	End point	Recovery %	Total potential change, mV	Potential break at the end point, mV	ΔE/ΔV
First day	4.96	99.20	567	515	1323
7 day	4.95	99.00	566	510	1312
20 days	4.96	99.20	564	503	1290
30 days	4.96	99.20	540	468	1218
51 days	4.95	99.00	496	447	1113
58 days	4.96	99.20	495	415	1088
73 days	4.95	99.00	445	377	980

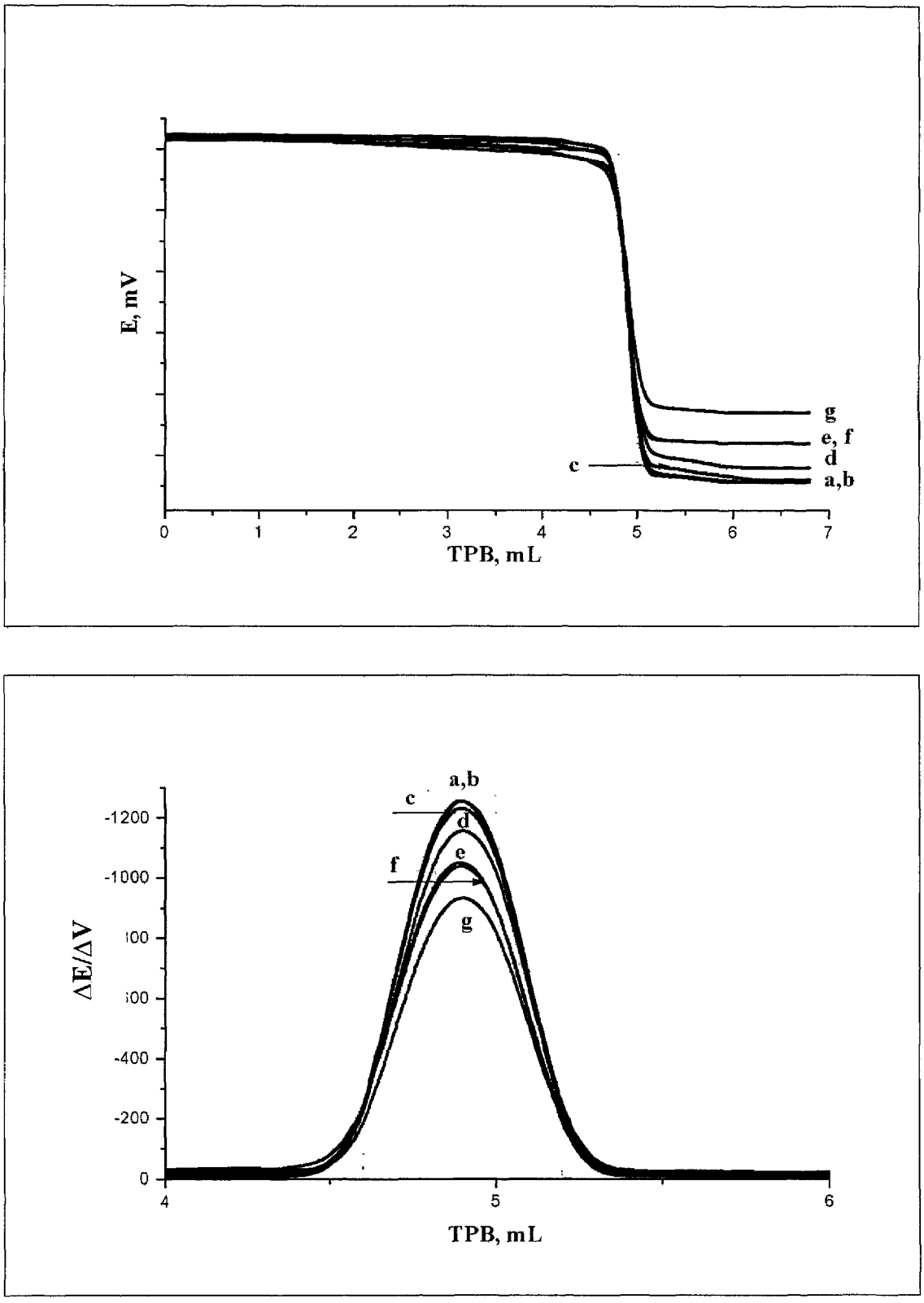


Figure 23: Life time of the carbon paste electrode performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB on different days, a) first day, b) 7 days, c) 20 days, d) 30 days, e) 51 days, f) 58 days, g) 73 days.

Table (10): Life time of the PVC membrane electrode in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Time	End point	Recovery %	Total potential change, mV	Potential break at the end Point, mV	ΔE/ΔV
first day	4.94	98.80	541	397	1135
14 day	4.93	98.60	537	381	1113
21 days	4.94	98.80	512	375	1013
28 days	4.92	98.40	436	366	950

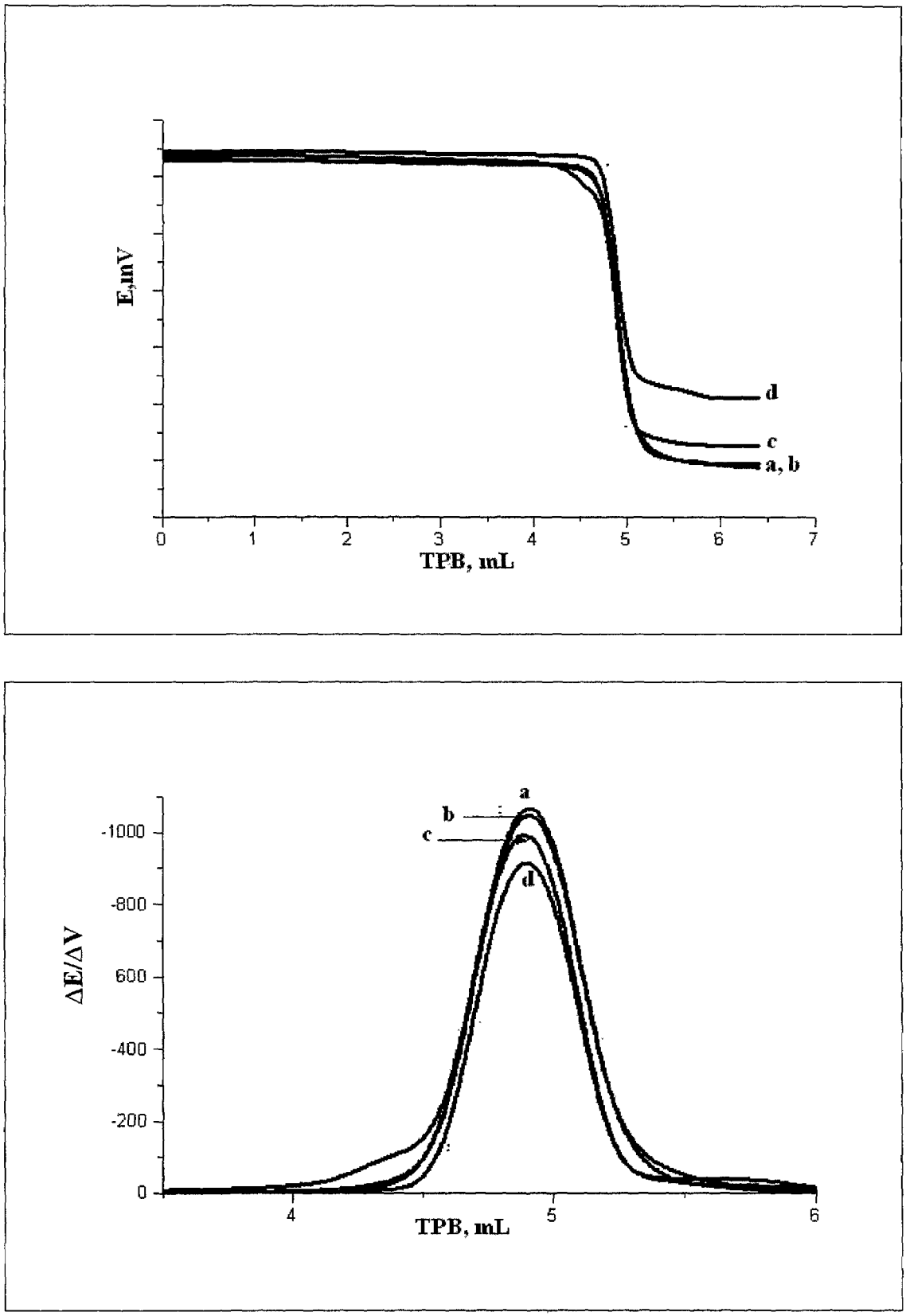


Figure 24: Life time of the PVC membrane electrode performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB on different days, a) first day, b) 14 days, c) 21 days, d) 28 days.

Table (11): Life time of the coated wire electrode (CWEs) in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB

Time	End point	Recovery %	Total Potential change, mV	Potential break at the end point, mV	ΔE/ΔV
First day	4.93	98.60	475	335	983
4 day	4.92	98.40	443	334	893
7 days	4.92	98.40	439	307	843
15 days	4.93	98.60	421	252	755
21 days	4.92	98.40	354	214	633

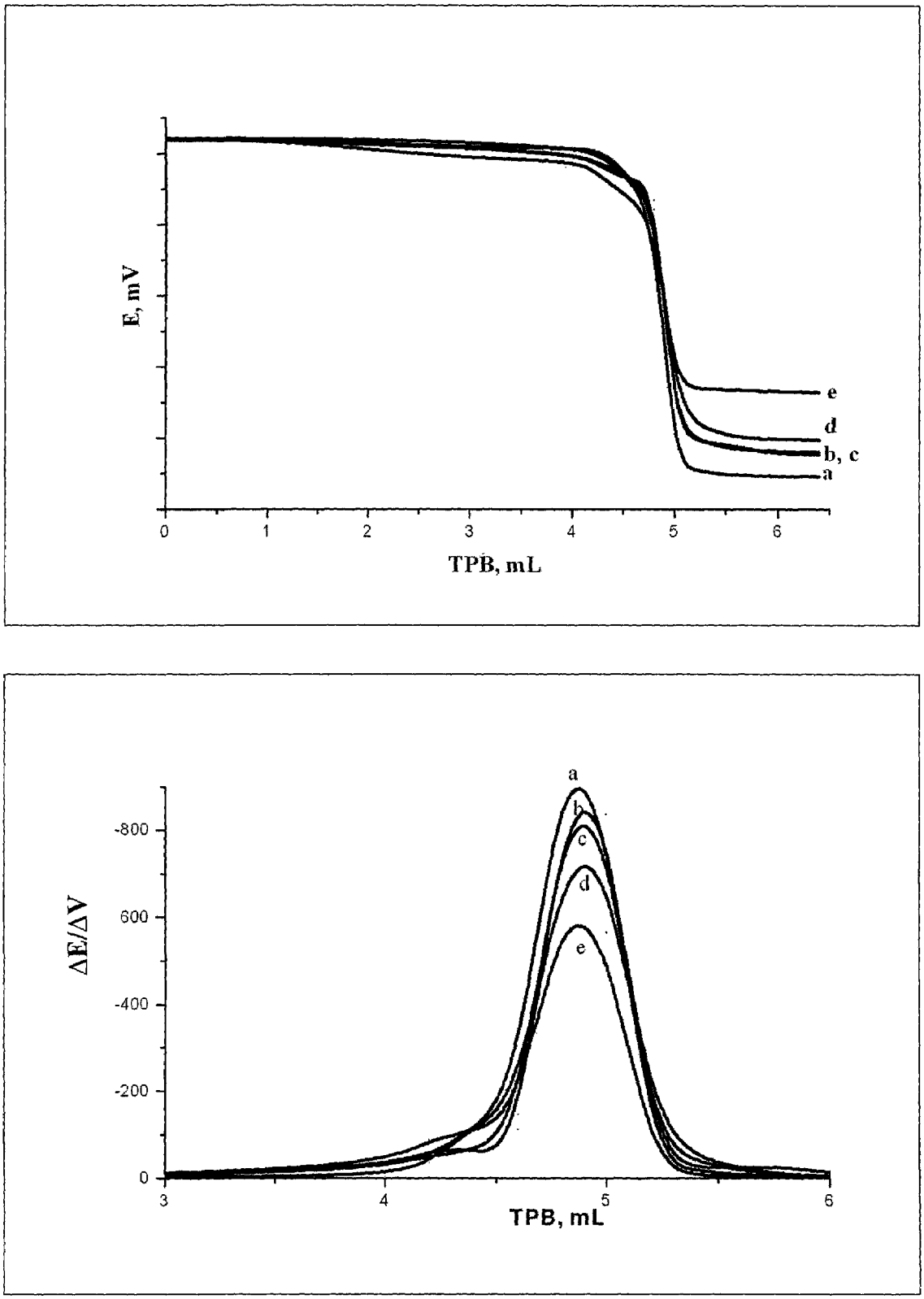


Figure 25: Life time of the coated wire electrode (CWEs) performance in the potentiometric titration of 5 mL 10^{-2} M CPCl with 10^{-2} M NaTPB on different days, a) first day, b) 4 days, c) 7 days, d) 15 days, e) 21 days.

III.4.7. Coated graphite electrode

The life time of the coated graphite is given in Table (12) and Figure (26). It is obvious from the data that the potential break at the end point is decreased by 20 % after 7 days, and the reading are stable for at least 3 weeks.

III.5. Between day assays

For the developed surfactant electrode, four different titration runs of 5 mL of 10^{-2} mol l^{-1} CPCl with 10^{-2} mol l^{-1} NaTPB standard solution are performed on 4 different days, in order to evaluate the reproducibility of the results obtained. Table (13) gives a statistical summary of each of the titration series using the SPCPEs, including the means of the end point volumes and the potential break at the end point. The values for the end-point are highly reproducible within each series compared with either the commercial surfactant electrodes or the official two phase titration method.

Table (12): Life time of the coated graphite electrode performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB

Time	End point	Recovery %	Total potential change, mV	Potential break at the end Point, mV	ΔE/ΔV
first day	4.94	98.80	534	377	1113
7days	4.93	98.60	518	345	1062
15 days	4.94	98.80	512	340	1025
21 days	4.93	98.60	504	340	1000

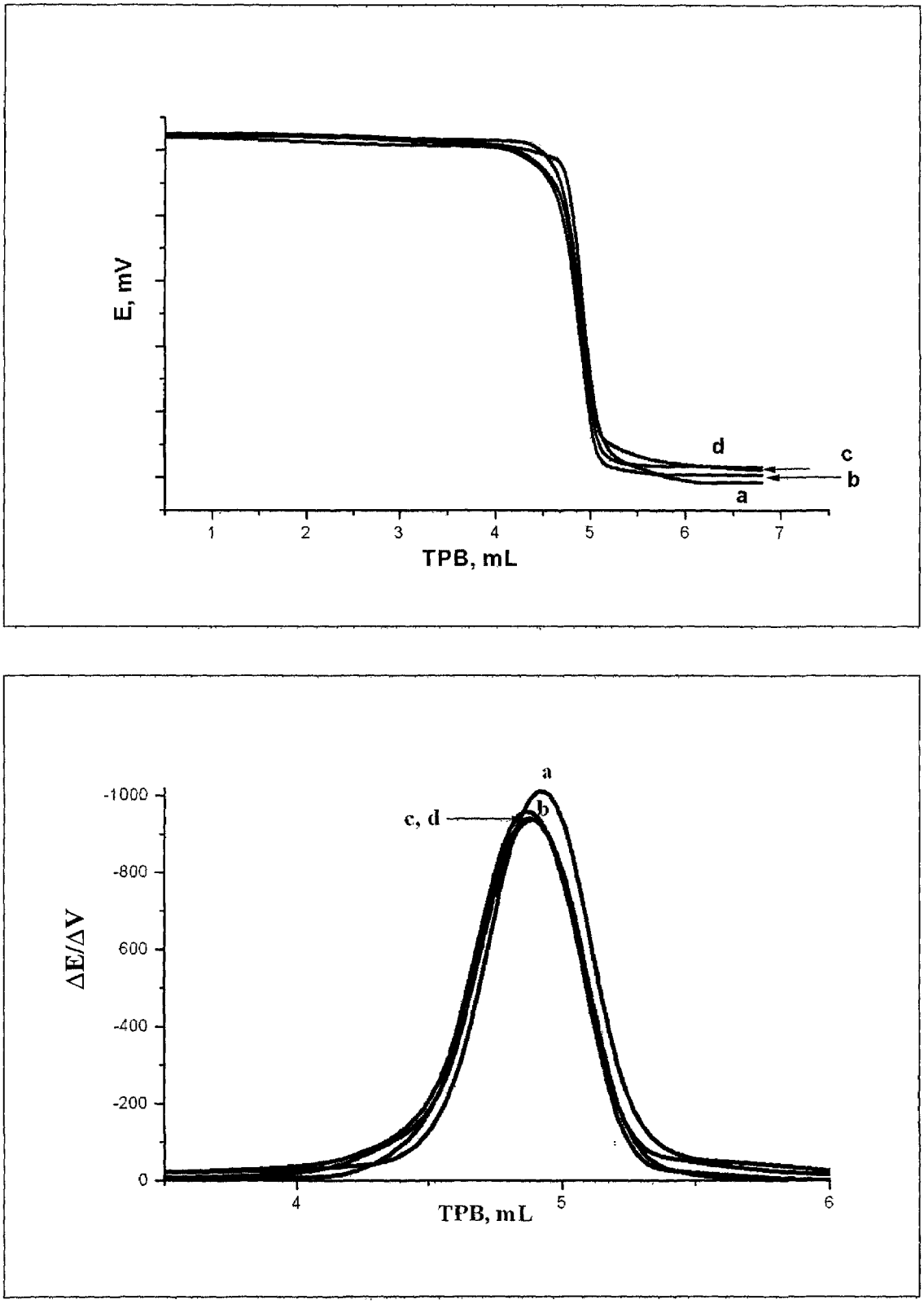


Figure 26: Life time of the coated graphite electrode performance in the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB on different days, a) first day, b) 7 days, c) 15 days, d) 21 days.

Table 13: Between-day precision of the potentiometric titration of 5 mL of 10^{-2} M CPCl with 10^{-2} M NaTPB.

Analytical method	End point			ΔE/ΔV			Total potential change		
	mL	SD [a]	RSD [a]	mV/mL	SD [a]	RSD [a]	mV	SD [a]	RSD [a]
SPCPEs	4.98	0.008	0.18	1203	16.80	1.55	564.0	14.4	2.71
Commercial electrode	4.90	0.015	0.35	951	22.30	2.11	512.0	17.5	2.95
Two phase titration	4.93	0.025	0.64	-	-	-	-	-	-

[a] Mean values for four experiments carried out on four different days.

III.6. Potentiometric titration

III.6.1. Effect of titrant

The effect of titrant on the performance of the potentiometric titration of CPCl is investigated as NaTPB is replaced by ammonium reineckate (RN), phosphotungstic acid (PTA), phosphomolybdic acid (PMA), silicotungestic acid (STA) and SDS. CPCl reacts with PTA and PMA in the molar ratio of 3:1 and with STA in the ratio 4:1 while with NaTPB, RN and SDS the ratios are 1:1. The highest total potential change is obtained using NaTPB and SDS as a titrant with good reproducibility compared with other titrants, (Table 14 and Figure 27).

III.6.2. Effect of pH

The developed electrode permits the titration of CPCl with NaTPB to be carried out in the pH range from 2-8. The pH selected for the titration is found to be acidic to resemble the condition of the official two-phase titration procedures. For this purpose, a pH 3.0 using citrate buffer is selected as it gives the highest potential jump at the end point.

III.6.3. Effect of nonionic surfactants

The nonionic surfactants are very often a component part of anionic surfactants based formulated products. The widely used classes of nonionics are alkoxylated alcohols which under certain circumstances may exhibit anionic character. Therefore, its influence on the potentiometric titration of SDS has been investigated. It can be concluded that no significant change in the shape of the titration curves and the magnitude of the potential break has been observed in the presence of the nonionic surfactant. It is not worthy to mention that the presented electrode can also be used in the potentiometric titration of such nonionic surfactants as they are precipitated by NaTPB in the presence of an excess of Ba(II)[276].

III.6.4. Titration of cationic surfactants

It is quite startling that a little attention is paid to standardization procedures of cationic titrants; these are usually considered to be of 100% purity and their concentrations are calculated from the weighted amount of the substance. However, a titer of freshly prepared titrants is not stable (especially at low concentrations) due to adsorption effects on the inner surface of vessels.

The success in the application of the SPCPEs in the potentiometric titration of CPCl with NaTPB devoted this work to expand the investigation to include other types of cationic surfactants. An aliquot of the investigated compounds containing 90 µg to 15 mg of CPCl, 92 µg to 15 mg of CTABr, 105 µg to 17 mg of septonex, 154 µg to 12.5 mg of DDABr and 464.5 µg to19 mg of DTABr, is transferred into 100 mL titration cell and diluted to 10 mL by distilled water.

From the shape of the titration curves (Figures 28-33 and Tables 15-19), it is clear that the total potential change and the potential break at the end-point is large where the total potential change ranges between 322 to 528 mV for CPCl, 306 to 503 mV for CTABr, 280 to 385 mV for Septonex, 226 to 408 mV for DDABr and 146 to 306 mV for DTABr.

Figure 31 collects the titration data of all cationic surfactants with NaTPB where the total potential change and the potential break at the end point (depending on the nature of surfactants) are found to follow the order CPCl > CTABr > Septonex > DDABr > DTABr.

Table 14: Potentiometric titration of 3 mL of 10^{-2} M CPCl with different titrants a) 1×10^{-2} M NaTPB , b) 1×10^{-2} M RN, c) 3.3×10^{-3} M PTA, d) 3.3×10^{-3} M PMA, e) 2.5×10^{-3} M STA using SPCPES.

Titrants	Total potential change, mV	Potential break at the end point, mV	ΔE/ΔV
NaTPB	419	394	1057
RN	364	251	737
PTA	321	202	567
STA	271	170	495
PMA	194	106	302
SDS	328	166	990

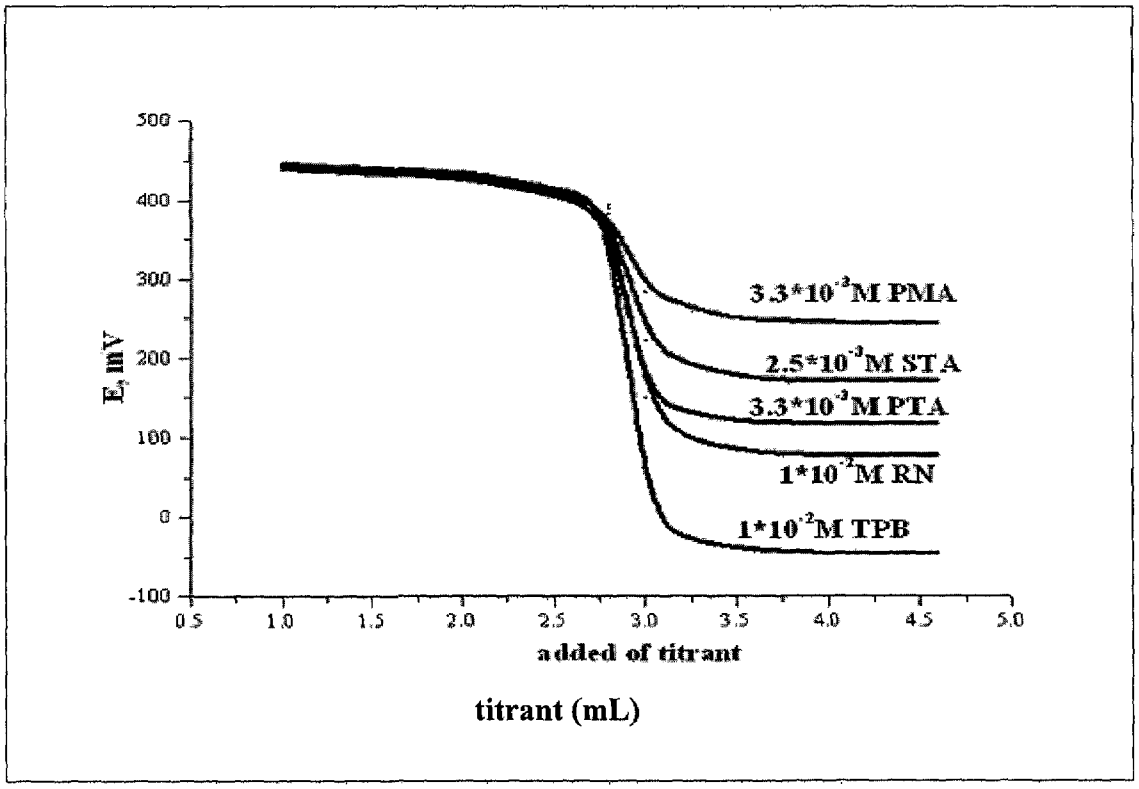


Figure 27: Potentiometric titration of 3 mL of 10^{-2} M CPCl with different titrants using SPCPEs.

Table 15: Determination of CPCl using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Taken, mg	Found, mg	Recovery (%)	Total potential change, mV	ΔE/ΔV
15.00	14.90	99.50	528	2170
11.00	10.80	99.00	511	2090
7.00	6.90	99.00	505	2035
4.00	3.90	99.00	492	1925
2.00.	1.90	98.80	451	1875
0.50	0.490	98.80	366	13150
0.18	0.179	98.80	322	12250
0.09	0.089	98.40	234	19115

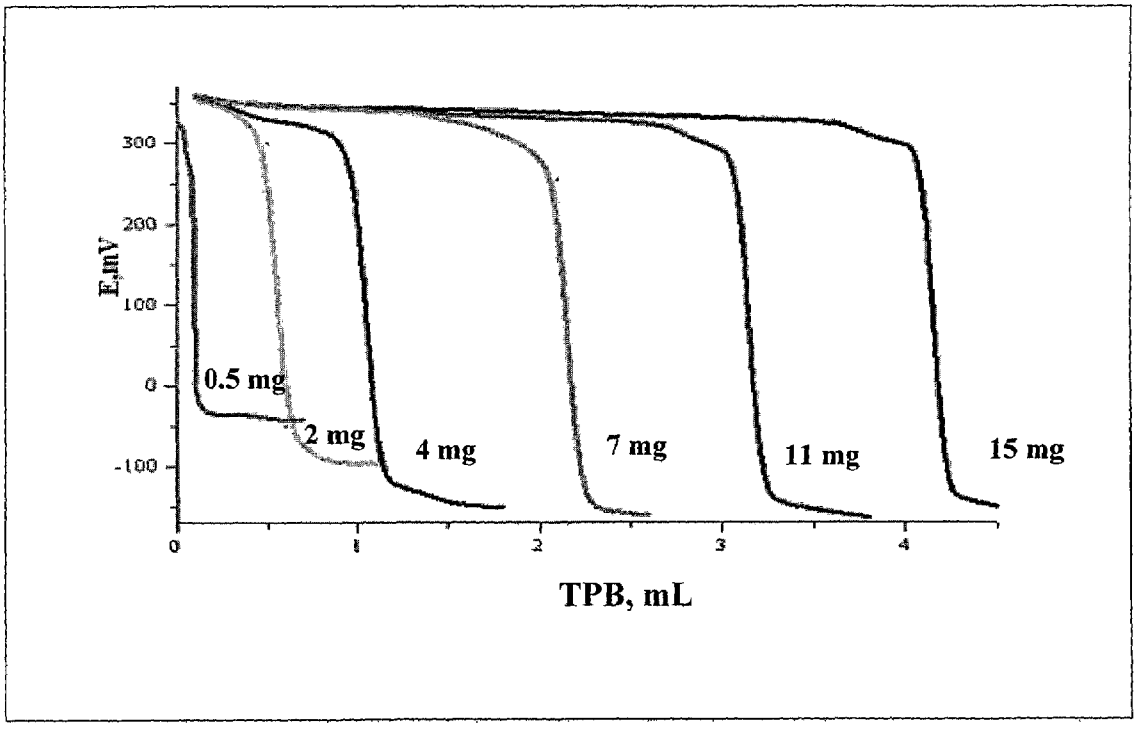


Figure 28: Determination of CPCl using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Table 16: Determination of CTABr using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Taken, mg	Found, mg	Recovery (%)	Total potential change, mV	ΔE/ΔV
15.00	14.90	99.30	503	2010
11.00	10.90	99.00	494	1930
8.00	7.90	99.00	476	1800
4.00	3.90	99.00	450	1740
2.00	1.90	98.80	406	1560
0.50	0.49	98.80	367	12250
0.182	0.18	98.80	327	11450
0.092	0.091	98.40	306	10410

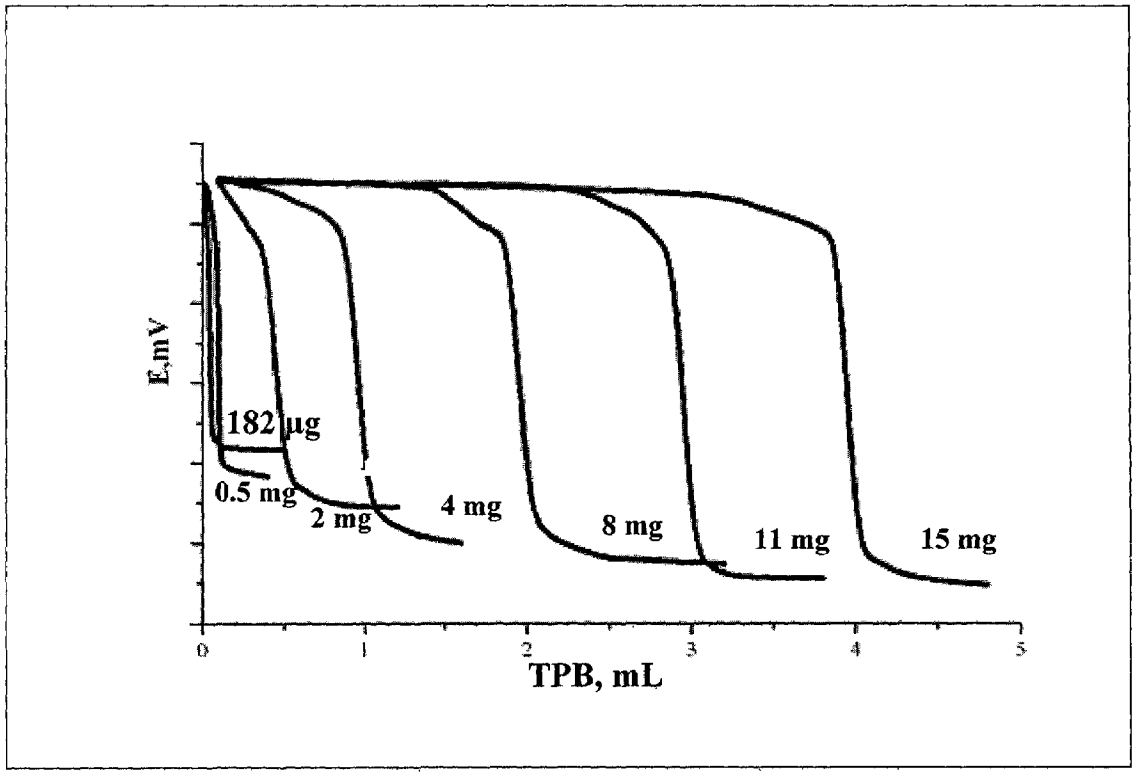


Figure 29: Determination of CTABr using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Table 17: Determination of Septonex using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Taken, mg	Found, mg	Recovery (%)	Total potential change, mV	ΔE/ΔV
17.00	16.90	99.30	385	1650
13.00	12.90	99.30	367	1510
8.50	8.40	99.00	361	1450
4.50	4.40	99.00	353	1420
2.00	1.90	98.80	333	1415
0.50	0.49	98.80	286	10000
0.21	0.208	98.80	280	1700

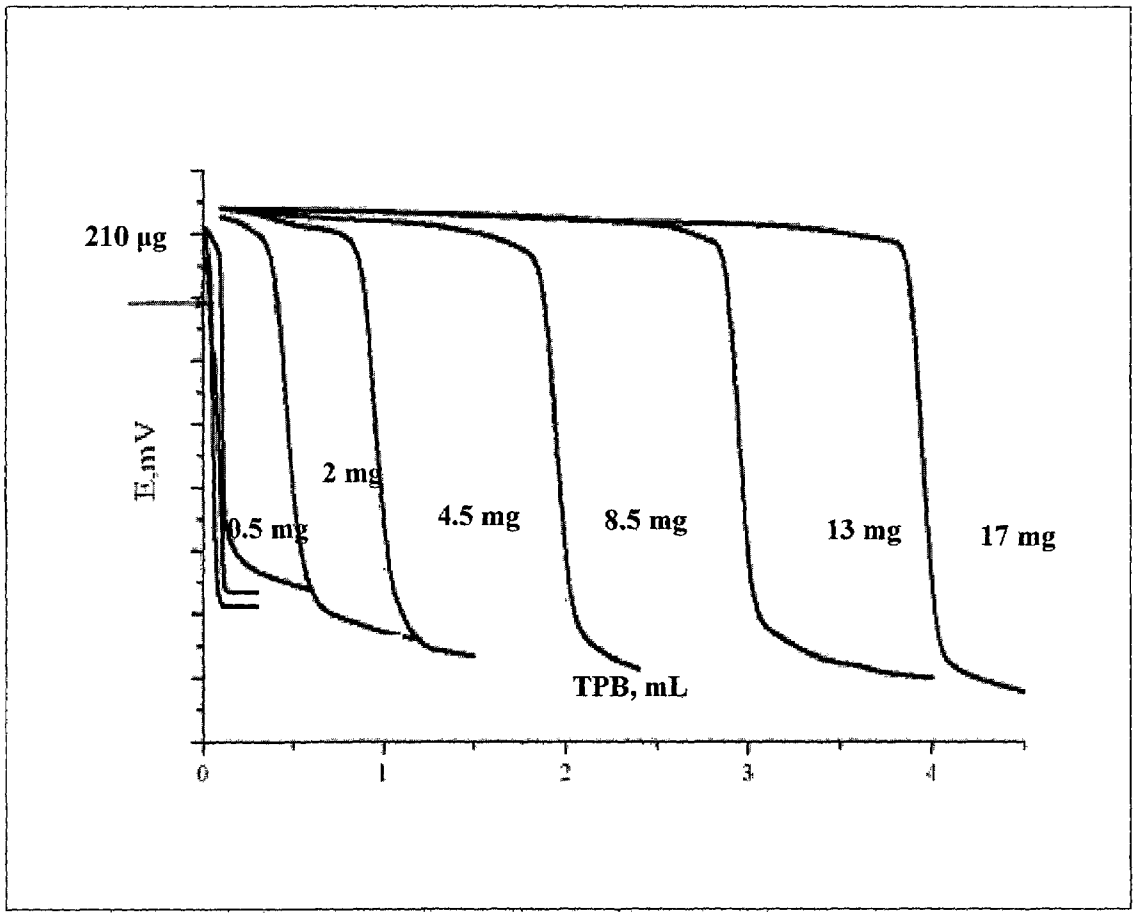


Figure 30: Determination of Septonex using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Table 18: Determination of DDABr using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Taken, mg	Found, mg	Recovery (%)	Total potential change, mV	ΔE/ΔV
12.50	12.40	99.50	408	1345
9.50	9.40	99.30	355	1310
6.50	6.40	99.00	324	1250
3.00	2.90	99.00	302	1235
1.50	1.40	98.80	287	1125
0.30	0.29	98.80	226	7700

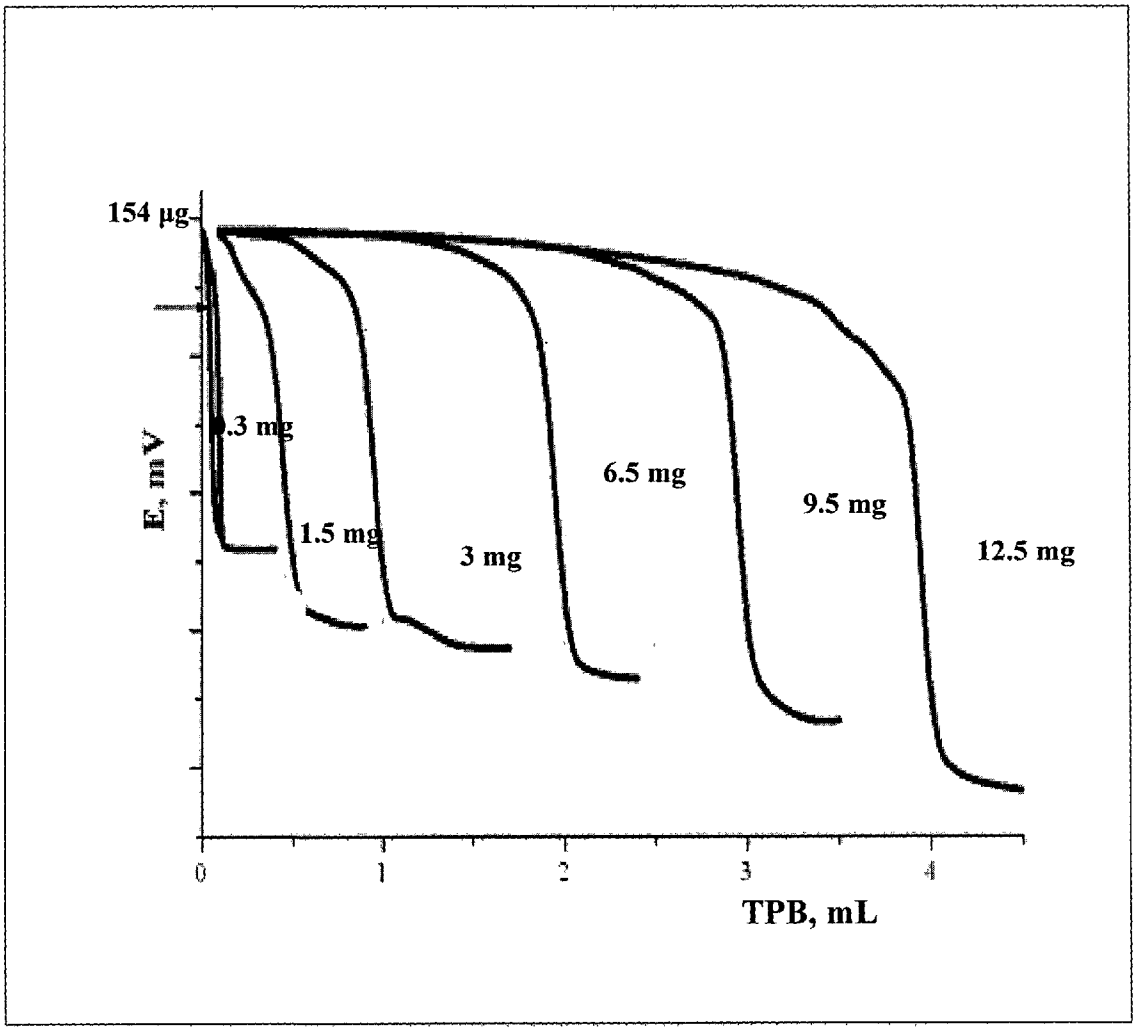


Figure 31: Determination of DDABr using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Table 19: Determination of DTABr using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

Taken, mg	Found, mg	Recovery (%)	Total potential change , mV	ΔE/ΔV
19.00	18.90	99.50	306	1005
14.00	13.80	99.30	251	750
9.50	9.40	99.00	232	650
4.50	4.40	99.00	226	650
2.50	2.40	98.80	206	450
0.50	0.49	98.80	146	2200

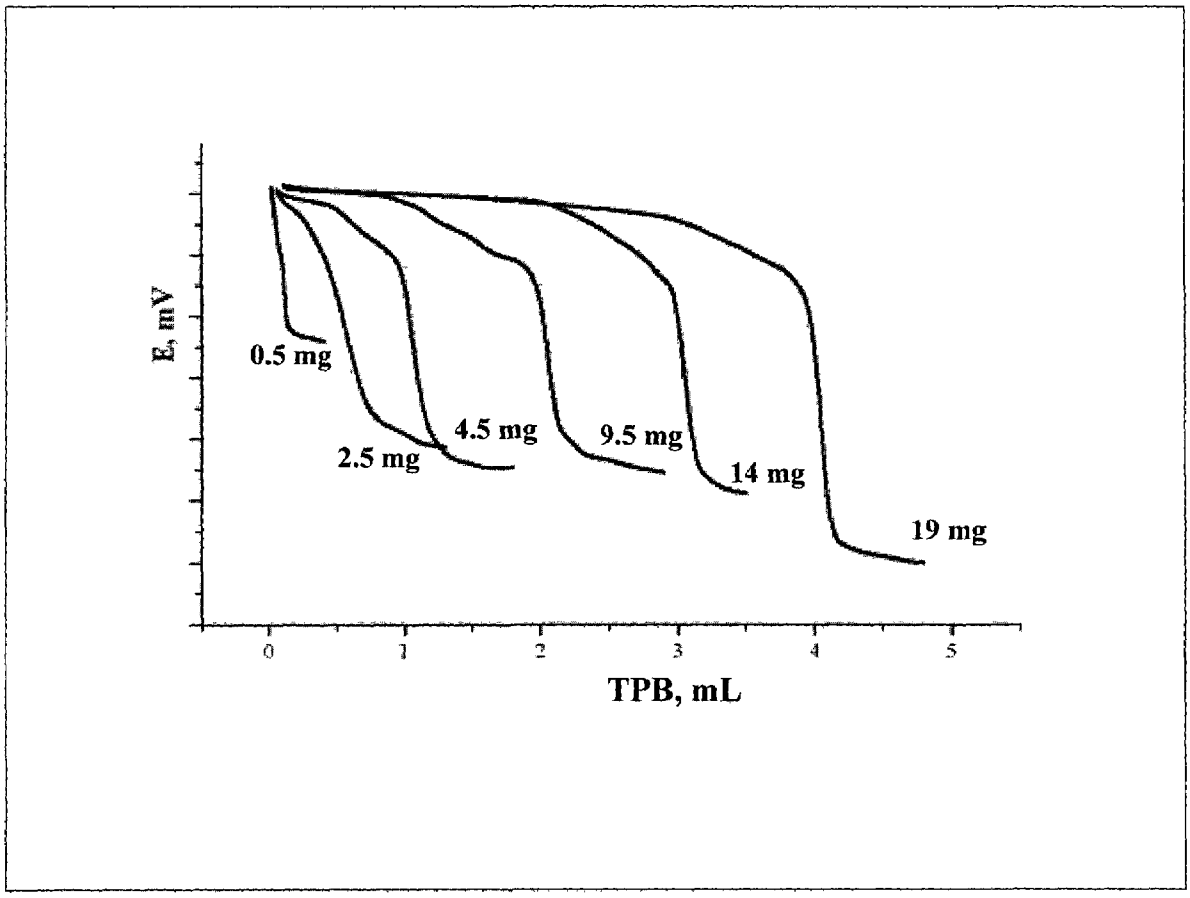


Figure 32: Determination of DTABr using SPCPEs through the potentiometric titration with 10^{-2} M NaTPB.

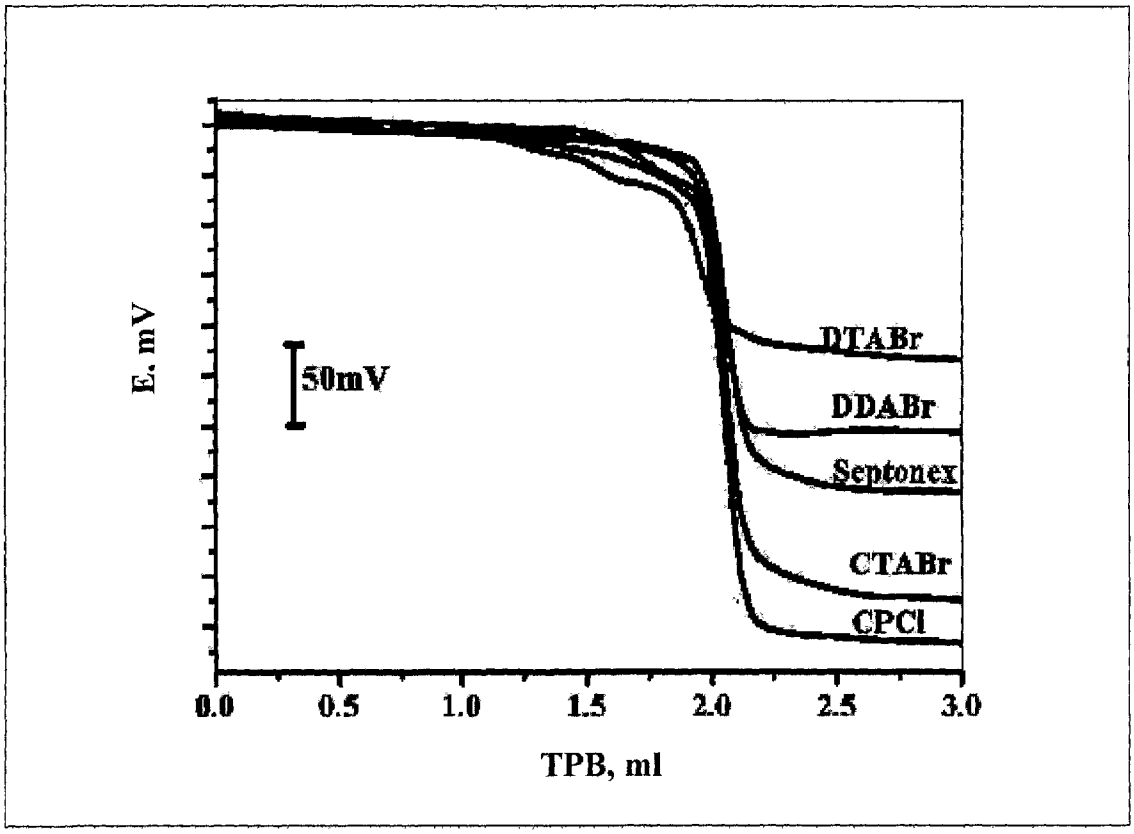


Figure 33: Titration curves of several analytical grad cationic surfactants using SPCPEs as sensor and NaTPB as titrant.

III.6.2. Titration of anionic surfactant using SPCPEs as sensor and CPCl as titrant.

The success of the application of the SPCPEs in the potentiometric titration of different cationic surfactants with SDS encouraged the research team to expand the investigation to titrat SDS using standard solution of CPCl as titrant where the results are shown in Table (20). The shape of the titration curve, the total potential change and the potential break at the end-point is large (total potential change ranges between 322 to 521 mV with potential break ranging from 218 to 424 mV/mL titrant). This may be attributed to the combined electrode response to both the cationic and anionic species and allows the application of the electrode to determine low concentration of such surfactants reaching to 144 μg as shown as in Figure (34).

Table 20: Determination of SDS using SPCPEs through the potentiometric titration with 10^{-2} M CPCl.

Taken, mg	Found, mg	Recovery (%)	Total potential change, mV	ΔE/ΔV
12.00	11.90	99.50	396	1240
9.00	8.90	99.30	316	1020
6.00	5.90	99.00	286	900
3.00	2.40	99.00	267	875
1.50	1.40	99.00	219	790
0.50	0.40	98.80	186	845
0.144	0.142	98.80	155	4300

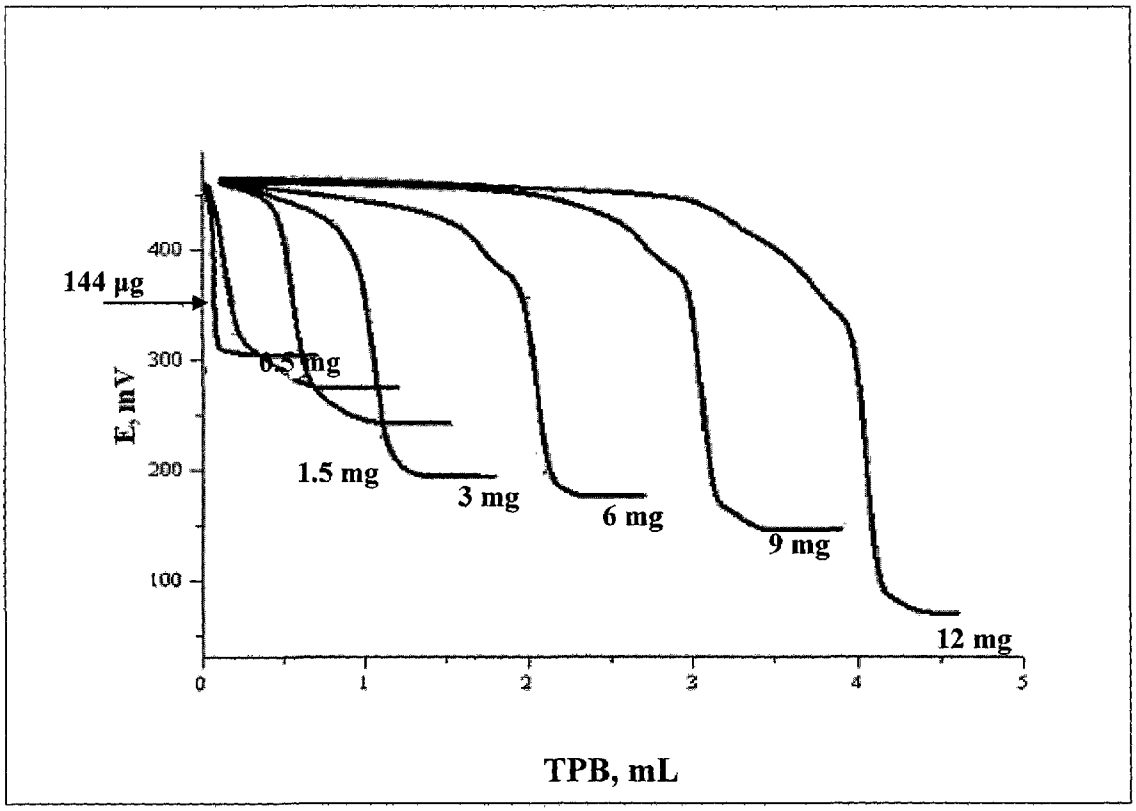


Figure 34: Determination of SDS using SPCPEs through the potentiometric titration with 1×10^{-2} M CPCl.

III.7. Applications

The proposed electrode is successfully employed for the assay of different ionic surfactants in some pharmaceutical formulations, detergents and water samples. The results of the potentiometric methods compared with the commercial surfactant electrode and the official methods are shown in Tables (21 to 23).

III.7.1. Potentiometric determination of surfactants in different pharmaceutical formulations using SPCPEs

III.7.1.1. Determination of CPCl in Ezafluor

In order to assess the validity of the prepared electrodes, the potentiometric titration methods are applied for the determination of CPCl in mouth wash solution (Ezafluor, Kahira Pharmaceutical and Chemical Industries Co.). The application of proposed method for the potentiometric determination of CPCl in Ezafluor mouth wash preparation gave good results as shown in Table 21.

The results are compared with the commercial electrodes and standard methods and has shown that the electrode prepared by SPCPEs method has good efficiency as regard of sensitivity, index of retrieving and repetition.

III.7.1.2. Determination of CTABr in Citrolin

The potentiometric titration methods are applied for determination of CTABr in mouth wash solution (Citrolin, Pharco Pharmaceuticals, Alexandria) and the results obtained are listed in Table (21). The values obtained are in agreement with those obtained by the British Pharmacopoeia method. The values of the percentage recovery obtained using SPCPEs are very close to those obtained by the official and British Pharmacopoeia method [265].

III.7.1.3. Determination of SDS in Femigin B

The proposed electrodes and the potentiometric titration methods are applied for determination of SDS in vaginal powder (Femigin B, Pharco Pharmaceuticals, Alexandria). The results applying the potentiometric titration method (Table 21) reveal that the constructed electrode can be used successfully as indicator electrode in the potentiometric titrations of CPCl, CTABr and SDS in different real samples with very high percentage recovery ranging from 98.10 - 99.00% with relative standard deviations of 0.55- 0.82%.

Table 21: Potentiometric determination* of surfactants in different pharmaceutical formulations using SPCPEs.

Sample	Taken ($\mu g\ mL^{-1}$)	SPCPEs			Commercial electrode			British Pharmacopiea		
		Found ($\mu g\ mL^{-1}$)	Recovery (%)	RSD [a]	Found ($\mu g\ mL^{-1}$)	Recovery (%)	RSD[a]	Found ($\mu g\ mL^{-1}$)	Recovery (%)	RSD [a]
Ezaflour, CPCl	500	495	99.0	0.55	486	97.2	0.9	492	98.40	1.80
Citrolin (CTABr)	250	247	98.80	0.62	244	97.60	0.85	248	99.20	1.55
Femigin B (NaDS)	630	618	98.10	0.82	610	96.80	1.20	620	98.40	2.10

* CPCl in Ezaflour and CTABr in Citrolin are titrated with NaTPB standard solution while NaDS in Femigin B is titrated with CPCl standard solution.

[a] Average of five determination.

III.7.2. Determination of anionic surfactants in commercial household cleaning products by the potentiometric titration with 10^{-2} M CPCl using the proposed SPCPEs.

Potentiometric titration of anionic surfactants (as SDS) with a standard solution of CPCl offers a reliable technique for its measurement in commercial detergents sample by using an appropriate concentration of the titrant. The electrode has been successfully applied for the determination of other anionic surfactant in different detergent samples Arial, Tide (Procter and Gamble, Egypt), Persil (Port Said for Detergents) and OMO (Chemical Industries, Egypt) are obtained from local markets. By potentiometric titration with 10^{-2} M solution of CPCl. Table (22) shows clearly that the results obtained by the proposed method agrees favorably with those obtained by two-phase titration method.

The titration curves are symmetrical but with lower potential jump than that of corresponding analytical grade SDS. Commercially available detergents contain many other constituents rather than SDS, such as bleaching agents (sodium perborate, sodium percarbonate, hydrogen peroxide or sodium hypochlorite), phosphates and silicates which affect the titration process and cause poisoning of the electrode surface. Such detergent structure cause decrease in the sensitivity and life time of the electrode when conducting the process of calibration (3-4 times in both the carbon paste and SPCPEs electrodes) are done. At the time of scraping the carbon paste to get a new surface, there has been no complete recovery of the electrode efficiency and will be necessary to prepare a new electrode, while with the SPCPEs we use a new electrode of the same preparation and has the same properties, which clearly improve the advantages of using the SPCPEs.

Table 22: Determination of anionic surfactants in commercial household cleaning products by the potentiometric titration with 10^{-2} M CPCl using the proposed SPCPEs.

Sample	Found (%) [a]					
	SPCEs		Commercial electrode		Two phase method	
	Found	RSD (%)	Found	RSD (%)	Found	RSD (%)
Arial	19.70	1.13	18.90	1.80	19.40	2.20
Persil	20.17	1.66	19.40	1.90	19.65	1.70
Tide	20.14	1.64	19.10	1.70	19.75	2.30
Omo	19.24	0.79	18.40	1.60	18.80	2.55

[a] Average of five determination

III.7.3. Determination of anionic surfactants in sea water and waste water samples by potentiometric titration with 10^{-3} M CPCl using the proposed SPCPEs.

The content of anionic surfactant is estimated via potentiometric titration with CPCl using SPCPE and commercial surfactant electrode as sensing electrodes in addition to the two-phase titration method [266-267].

Potentiometric titration of anionic surfactants (SDS) with a standard solution of CPCl offers a reliable technique for its measurement in sea water and waste water samples by using an appropriate concentration of the titrant. The electrode has been successfully applied for the determination of anionic surfactant in the sea water (1) (Port Said and Suez, Egypt), sea water (2) (Suez Canal area, Egypt) and waste water samples (Dakahlyia, Egypt).

Table (23) contains the results of analyzing two sea water and waste water samples by the proposed method and the two phase titration method, which are found in close agreement, and this has shown the success of the electrode in estimating such materials in different samples with the same efficiency of the commercial electrode and the two phase titration method [266-267].

The data given clearly indicate satisfactory agreement between the surfactant contents in different samples determined by the proposed sensor and the official method. Lower reproducibility of results are achieved with application of a surfactant electrode; which may be attributed to the slow establishing of equlibria of the commercial surfactant electrode potential after addition of the titrant as it is in the case with SPCPEs. Moreover, the potentiometric procedures require approximately 5 min on the contrary to 15 min in the two phase titration method. Also using of the portable system proposed in the present work allows analysis of surfactant in sample field rather than transferring to the laboratory.

Table 23: Determination of anionic surfactants in sea water and waste water samples by potentiometric titration with 10^{-3} M CPCl using the proposed SPCPEs.

Sample	Found ($\mu g\ mL^{-1}$) [a]					
	SPCEs		Commercial electrode		Two phase method	
	Found	RSD (%)	Found	RSD (%)	Found	RSD (%)
Sea water 1	13.11	1.13	12.21	1.65	12.92	2.20
Sea water 2	16.30	1.40	15.70	1.90	16.10	2.15
Waste water 1	11.52	1.32	11.32	2.10	11.20	2.40

[a] Average of five determinations