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Evaluation of antioxidant properties of dermo-cosmetic creams by direct electrochemical measurements

C. Guitton, P. Gros, M. Comtat

Laboratoire de Génie Chimique, UMR 5503, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

R. Tarroux, P. Bordat

Centre de Recherche Dermo-cosmétique Pierre Fabre, allée Camille Soula, BP 74-Vigoulet, 31322 Castanet Tolosan

Abstract:

Cyclic voltammetry and linear sweep voltammetry were preliminarily used in order to evaluate the global antioxidant properties of dermo-cosmetic creams. Experiments were performed by introducing electrodes directly in the creams without any pre-treatment of the samples. Current-potential curves showed significant anodic current depending on the antioxidant containing cream studied. In comparison, little amperometric response was recorded with an antioxidant free cream base. Aqueous solutions of the corresponding antioxidants showed analogous anodic waves and similar peak potentials. A correlation between the global anodic peak and the presence of the antioxidant species in the cream was made with eleven skin creams, attesting the reliability of the method. Among electrode materials tested, platinum gave the best results in term of electrochemical kinetics and measurement precision (current peak standard deviation less than 5%). Exposure of the depilatory cream to oxidizing agents, e.g. hydrogen peroxide, air or light caused decrease in peak current as expected. This methodology enabled to evaluate the evolution of the total antioxidant capacity under oxidative stress and gives encouragement to further develop a voltammetric method to quantify cream antioxidant power.

Key words: cyclic voltammetry, dermo-cosmetic creams, antioxidants, oxidative stress.

Introduction

Among the greatest medical problems to be solved in the 21st century, aging is considered as one of the most important challenges. Aging process not only induces change in physical appearance but is also the cause of numerous diseases: cataract, atherosclerosis, Parkinson, Alzheimer, cancers (1-2). Among body tissues particularly involved in aging, skin constitutes one of the major targets, since it is the most exposed to external oxidant agents: U.V. light, chemical pollutants, oxygen, etc. The symptoms are quite different, ranging from early appearance of wrinkles to possible skin cancer caused by excessive exposure to sun light, including numerous diseases like psoriasis, etc. This process and its consequences represent a crucial health problem as much as an exponentially grown commercial market for cosmetic industry, since an increasingly ageing population takes care of healthy appearance, trying to “turn back the clock”: more than 30 % of the personal care market in 1999 concerned skin care segment, with almost \$20 billion in the world (3).

One of the main causes of aging is a deregulation of the cell respiratory metabolism involving the incomplete oxygen reduction (4-5). This natural process induces a continuous production of free radicals and reactive oxygen species like superoxide anion O_2° , hydroxyl radical OH° , hydrogen peroxide H_2O_2 , etc. (6). Skin has different antiradical defence systems to regulate these reactive species (7). These include several enzymatic reactions catalysed by catalase, superoxide dismutase or peroxidase which consume reactive oxygen species, and low molecular weight antioxidants (vitamins C and E, glutathione...) which reduce them during oxido-reduction reactions (8-9). Defection of these preventing mechanisms or excessive production of reactive oxygen species induce the so-called oxidative stress, leading to the oxidation of polyunsaturated fat acids and resulting in lipid peroxidation (10). These oxygen-

induced oxidative chain reactions are very implicated in cellular membrane defaults, DNA damages, etc (11).

It is obvious that cosmetic (creams, lotions, etc.) and pharmaceutical products containing vitamins and others antioxidants are efficient in slowing or even preventing skin ageing (12). However little is known about their efficiency life. Moreover, to our knowledge no study has been yet devoted to the evolution of their properties in real conditions, i.e. when the product is left in contact with air or U.V. light. An analytical method would be useful to control redox properties of creams in situ in order to improve their composition. This control process is all the more important as one specie can show pro-oxidant or antioxidant activity depending on its concentration (13-14).

Numerous methods are available to determine total antioxidant capacity. Most of them are based on inhibition reactions in solution involving a specific oxidant reagent like Fe^{3+} (FRAP assay) or ABTS (TEAC assay) (15) and used chromatography, chemiluminescence or spectroscopy as detection method (16-18). These methods need expensive materials and involve sometimes complex chemical protocols including dilutions, extractions, etc. Moreover the composition of the assayed sample is modified; these techniques cannot therefore be used on-line during fabrication of the cosmetic products. In this field, electrochemistry appears to be a convenient approach to evaluate the overall antioxidant properties of cosmetics. Recently cyclic voltammetry has shown to be a suitable electrochemical method to evaluate the global antioxidant capacity of real samples like edible plants, plasma or wine (19-21). A few electrochemical techniques have also been devoted to detect antioxidants in dermo-cosmetic products (22-23). For instance sensors and biosensors were developed to the assay of one species like kojic acid (24), hydroquinone (25) or arbutin (26). However quantify specific antioxidant species suffered from two major drawbacks. Firstly, although specific analyses can present some interest in a few cases, the great number

of species introduced in formulations as well as the possible interaction among the different antioxidants makes the assay of only one of them less representative of the global antioxidant capacity of cosmetics. Secondly, all the measurements were realised with diluted samples in solution and not directly in the cream or in the lotion. This paper presents preliminary work allowing the evaluation of the total antioxidant properties of dermo-cosmetic product from electrochemical techniques performed directly in the bulk of the cream, without any pre-treatment of the sample. Cyclic and linear sweep voltammetry were used to show the overall antioxidant capacity of the product. Comparison of the voltammograms with those recorded with antioxidants containing aqueous solutions allowed to correlate the electrochemical characteristics of the samples with the redox species properties. Finally, the influence of irradiations and oxygen as well as the addition of hydrogen peroxide as a strong oxidant on the global redox status of the creams was highlighted.

Principles of voltammetry

Cyclic voltammetry is one of the most frequently used electrochemical methods for more than three decades. The reason is its relative simplicity and its high information content. Cyclic voltammetry is performed using potentiostatic equipment in experimental conditions such as the only mass transport phenomenon to be taken into account is semi infinite diffusion. Generally, the working electrode on which the oxidation and reduction reactions are studied is flat so that the mass transport may be considered as unidirectional. The solution contains an electrolyte in large excess compared to the concentration of the electroactive species; these ions are not involved in the electron transfer reaction at the electrode. This electrolyte decreases the internal cell resistance and enables to neglect migration phenomena of the charged electroactive species. There is no forced convection because the electrodes are fixed and the solution is not stirred. Furthermore the relatively short experimental time scales allow

neglecting the natural convection. The electrode surface area, the volume of solution and the concentrations of the electroactive species are such that the experimental determination of the oxidation and reduction current (proportional to the heterogeneous electron transfer rate) change the electroactive species concentration in a negligible way. The waveform of the voltage applied to the working electrode versus reference electrode is triangular. The voltage varies linearly with time and the slope is referred to as the scan rate. In a few seconds, a current density - potential curve can be obtained, giving information about the energy level necessary to perform the electrode reactions and the rate of these reactions. If the heterogeneous electron transfer rate is high compared to the diffusion rate, this curve presents a peak, the intensity of which is namely proportional to the concentration of the electroactive species present in solution and to the square root of the scan rate (27). Another important criterion to characterize the electrode reaction is the value of the peak potential which is independent of the scan rate if the electron transfer is fast versus diffusion. If the product of an electrochemical reduction reaction may be reoxidized during the reverse scan rate, the reduction peak is accompanied by an oxidation one and the difference between the peak potentials is an indication of the reversibility of the heterogeneous electron exchange reaction. Cyclic voltammetry is a very useful method to elucidate mechanism of electrode reactions in the case where the heterogeneous electron transfer is accompanied by chemical reactions occurring before or after the electrode reaction.

Material and methods

H₂SO₄, NaOH and thiolactic acid were purchased from Acros, K₂SO₄ and H₂O₂ from Sigma and KH₂PO₄ and K₂HPO₄ from Merck. Unless otherwise indicated, all solutions were prepared in potassium sulphate solution 0.4 mol.L⁻¹, pH=11.0.

Creams were either commercially available or made in Pierre Fabre's laboratory. In the later case the samples were gels containing PEG 600, carbopol 980, paraffin, cremophor RH40,

sorbic acid, nipagin, sodium hydroxide and water. Three gels were made: one with pH = 4.86, one with pH = 6.88 and one containing BHT, with pH = 6.95. A hair removal cream from Klorane (pH=11.0, ingredients: water, strontium hydroxide, glycerin, cetearyl alcohol, guanidine carbonate, thiolactic acid, cetareth-33, silica, titanium dioxide, BHA, EDTA, parfum, potassium hydroxide, squalane) was chosen as an example. Others creams were studied : a restructuring care from Nivea Vital (pH=6.0, ingredients : water, glycerin, cyclomethicone, dicaprylyl carbonate, ascorbic acid, butyrospermum parkii, alcohol cetearyl, octocrylene, glyceryl stearate, C12-15 alkyl-benzoate, cera microcristallina, tocopheryl acetate, vitis vinifera, PEG-40 stearate, sodium carbomer, paraffinum liquidum, tetrasodium iminodisuccinate, BHT, phenoxyethanol, methyl paraben, propyl paraben, diazolidinyl urea, parfum), a corrective dermatological care for wrinkles Active C from Laroche-Posay (ingredients : aqua, glycerin, cyclopentasiloxane, ascorbic acid, propylene glycol, nylon-12, sodium citrate, dimethicone copolyol, acrylates copolymer, disodium EDTA, methyl paraben, propylparaben, parfum), a depigmenting emulsion Trio D from Laboratoires d'Evolution Dermatologique (pH=4.8, ingredients : Aqua, ammonium lactate, aluminium starch octenylsuccinate, C12-15 alkyl benzoate, isopropyl palmitate, polymethyl methacrylate, glycereth-26, isostearyl isostearate, titanium dioxide, arachidyl alcohol, ascorbic acid polypeptide, citric acid, dimethicone, behenyl alcohol, glyceryl stearate, PEG-100 stearate, cetyl alcohol, arachidyl glucoside, disodium EDTA, sodium metabisulfite, PEG-15 hydroxystearate, PEG-54 hydrogenated castor oil, imidazolidinyl urea, parfum, xanthan gum, methylparaben, propylparaben, tocopherol, trimethoxycaprylylsilane, glycyrrhiza glabra (licorice extract), a whitening day cream Decleor from (pH=6.8, ingredients : ethyl hexyl methoxycinnamate, benzophenone-3, water, propylene glycol, C12-15 alkyl benzoate, titanium dioxide, glyceryl stearate, sunflower (helianthus annuus) seed oil, beeswax (cera alba), jojoba (buxus chinensis) oil, glycerin, methyl gluceth 20, sorbitan stearate, stearic acid, steareth 100, grapefruit (citrus grandis) extract, cetyl alcohol, wheat (triticum vulgare) germ oil, carob (cetonia siliqua) extract, mulberry (morus alba) extract, mica, magnesium aluminium silicate, cellulose gum, fragrance, triethanolamine, bisabolol, tocopheryl acetate, magnesium ascorbyl phosphate, butylene glycol, polyhydroxystearic acid, alumina, silica, xanthan gum, phenoxyethanol, methylparaben, ethylparaben, propylparaben, buthylparaben, isobuthylparaben, sodium dehydroacetate, sorbic acid), an emulsion Ystheal + from Laboratoires dermatologiques Avène (Pierre Fabre) (pH=6.65, ingrédients : aqua, caprylic/capric triglyceride, Avène aqua, paraffinum liquidum, propylene glycol, glyceryl stearate, PEG-100 stearate, squalane, BHT, butyl paraben, C13-14 isoparaffin, carbomer,

disodium EDTA, laureth-7, phenoxyethanol, polyacrylamide, propylparaben, CI 17200, retinal, tocopheryl glucoside, triethanolamine, epithelial cream A Derma from Laboratoires dermatologiques Ducray (pH=6.46, ingredients : water, butyrospermum parkii (shea butter) fruit, glyceryl stearate, glycerin, ethoxydiglycol, squalane, cyclomethicone, avena sativa (oat), kernel oil, batyl alcohol, cetearyl alcohol, cetearyl glucoside, dimethiconol, methylparaben, propylparaben, retinol, tocopheryl acetate, triethanol amine) and after sun repair balm Uriage from Laboratoires dermatologiques Uriage (pH=5.34, ingredients : water, uriage thermal spring water, paraffinum liquidum (mineral oil), butyrospermum parkii (shea butter) fruit, polysorbate 60, glycerine, sorbitan stearate, hydrogenated polydecene, cetyl palmitate, glyceryl stearate, PEG 100 stearate, phenoxyethanol, triethanolamine, acrylates/C10-30 alkyl acrylate cross polymer, glucose, parfum, glycyrrhetic acid, methylparaben, dimethicone, tocopheryl acetate, propylparaben, trehalose, ascorbyl tetraisopalmitate).

All the electrochemical experiments were carried out in a single compartment cell at room temperature. An air-tight cell was used to study the influence of oxidative stress. An air or a nitrogen flux was introduced when necessary and the flow was controlled with a flow-meter Brooks (tube R-2-15-AAA P-072, float: sapphire, scale: 0-5 L/h). The electrochemical manipulations were performed with an Autolab Metrohm potentiostat interfaced to a HP omni-book XE 4500 microcomputer and using the GPES software. The working electrodes were platinum (0.03 cm²), gold (0.07 cm²) or vitreous carbon (0.07 cm²) rotating-disc electrodes. A large surface area platinum grid was used as counter-electrode. All potentials were measured and expressed versus a saturated mercurous sulphate electrode (MSE) connected to the cell by a Luggin capillary. Before each experiment, the working electrode surface was polished with abrasive paper (262X imperial lapping film sheets) and rinsed with distilled water. For vitreous carbon, anodic polarization was then imposed at 1 V during one minute in sulphuric acid H₂SO₄ 0.1 mol L⁻¹. For platinum (respectively gold) electrode, cyclic voltammograms were performed in H₂SO₄ 0.5 mol L⁻¹ (resp. 0.1 mol L⁻¹) at 50 mV s⁻¹ between -0.65 V and 0.75 V (resp. between -0.25 V and 1.1 V) until obtaining reproducible current density-potential curves (28).

Results and discussion

Cyclic voltammogram in the creams

Figure 1 shows the experimental device used. Experiments were performed by simply introducing the working, counter and reference electrodes directly into the creams. A few grams (about 5 to 7 grams, depending on the cream density) were necessary, in order the electrodes to be in contact with the cream. Figure 2 shows cyclic voltammograms obtained with a platinum electrode introduced directly in two samples, e.g. a hair removal cream from Klorane pH=11 containing BHA and thiolactic acid as antioxidants (solid line) and an antioxidant free base made in Pierre Fabre's laboratory (dashed line). In both cases, the curve presented a conventional shape with essentially no resistive or capacitive current. In the former case a significant anodic current was recorded with a peak potential close to 0.31 V. Comparatively only a little amperometric response was obtained with the other cream. The difference can therefore be attributed to the presence of antioxidant species in the hair removal cream. Figure 3 shows linear sweep voltammograms performed with the same electrodes immersed in a potassium sulphate solution pH=11 containing BHA $5.5 \cdot 10^{-5} \text{ mol L}^{-1}$ or thiolactic acid $5 \cdot 10^{-4} \text{ mol L}^{-1}$. The pH was chosen to be in accordance with that of the depilatory cream. Both curves presented an anodic wave. Although the nature and the physico-chemical properties of a cream and an electrolytic solution were quite different, comparison of potentials obtained in the two medium clearly demonstrated that antioxidant species like thiolactic acid and BHA could be detected in a dermocosmetic cream by a simple electrochemical method. Cyclic voltammetry appeared therefore suitable to evaluate antioxidant global capacity of creams similarly to what was concluded by Chevion et al. (19-21) from experiments performed in plasma or plants.

The voltammograms recorded in the hair removal cream (Figure 2, solid line) showed no cathodic current, excepted that corresponding to the reduction of water appearing at potential below -1.2 V. Consequently the cream did not contain any oxidant species that could be detected electrochemically with the operational conditions adopted. On the contrary the curve obtained with the antioxidant free base (Figure 2, dashed line) revealed several cathodic peaks. In particular an amperometric response was recorded with a half-wave potential near -0.3 V corresponding to the reduction of oxygen. Korotkova et al. (20) demonstrated the diminution of the oxygen reduction current on a platinum electrode immersed in aqueous solution containing antioxidant species. Actually dissolved oxygen was contained in the cream sample prepared without antioxidant species since upper potential boundary, i.e. 1.1 V, was chosen in order to avoid oxidation of water into oxygen at the electrode surface during experiments. These last results confirm that cyclic voltammetry is a suitable method to reveal directly the presence of antioxidant species in the cream and to evaluate its antioxidant properties without any pre-treatment of the sample.

Table 1 shows the electrochemical characteristics of cyclic voltammograms obtained in the hair removal cream by using different electrode materials. Although antioxidants species are generally studied with carbon electrode (29-30), best results were obtained in our case with platinum. Not only the peak current was higher but also the peak potential presented the lowest value, indicating that the electron transfer kinetics between platinum and the electroactive species was faster. For each electrode, the experiment was repeated at least six times. Between each experiment, the electrode surface was regenerated (see § material and methods) and a new cream sample was used. In all cases the standard deviation was at most 10 % for the peak current and 70 mV for the peak potential.

Adopting this protocol eleven creams were studied. The conductivity of the samples, the peak potential and current density and the amount of charge consumed in the anodic part of the

curve were measured. Results are listed in Table 2. Firstly electrochemical measurements were possible provided the conductivity differed from zero. Secondly an anodic peak current was recorded with most of the samples. If yes, the corresponding peak potential was correlated to the presence of one or several antioxidant species. Furthermore the amount of charge recorded with the antioxidant containing creams (e.g. 0.11 C for the depilatory cream) compared to that obtained with the free bases (less than $2 \cdot 10^{-4}$ C) makes evidence in the first case of a global antioxidant power. Finally the protocol gave a good reproducibility, with a standard deviation of the peak current density less than 15% in most cases. All these results consequently attest the reliability of the method.

The influence of the potential scan rate on the electrochemical data was also investigated. Figure 4.a shows the evolution of the peak current density recorded with the hair removal cream as a function of the square root of the scan rate. The variation was linear suggesting that the electrochemical reaction is mass transport controlled (27). Likewise a direct proportionality was established between the peak potential and the logarithm of the scan rate (Figure 4.b). These results were in accordance with Randles, Sevcik, Nicholson and Shain equation (27) in the case of irreversible electrochemical system and were analogous to those commonly observed in electrolytic solution. It might therefore be concluded that the electrochemical response recorded in the cream were not disturbed by subsequent ohmic drop.

Addition of hydrogen peroxide as oxidant

Different volumes of a hydrogen peroxide H_2O_2 solution were manually mixed with a sample of the hair removal cream until the mixture appeared homogeneous. This species was added in order to simulate the action of a strong oxidant on the redox properties of the cosmetic product. Schöberl and Wiesner (31) showed that hydrogen peroxide oxidized thiolactic acid with kinetics depending on the concentration of H_2O_2 . Figure 5 shows the evolution of the

cyclic voltammogram recorded in the cream as a function of the amount of hydrogen peroxide added. Cyclic voltammograms were recorded immediately after the addition of hydrogen peroxide. When the concentration of H_2O_2 was less than $25 \mu\text{mol per gram of cream}$, the cyclic voltammogram of the cream was roughly unchanged. In this case, the whole quantity of hydrogen peroxide was consumed by antioxidants. For concentrations of H_2O_2 ranging from 25 to $500 \mu\text{mol.g}^{-1}$, the anodic peak current at 0.31V gradually decreased, indicating a consumption of the antioxidants. In the same time, a second anodic peak appeared at potential close to 0.9 V . This new current cannot be attributed to the presence of an excess of hydrogen peroxide in the cream. As a matter of fact the peak potential did not correspond to that classically recorded for the oxidation of H_2O_2 on platinum electrode. Figure 3 clearly shows that H_2O_2 oxidation began at around -0.4 V . Moreover figure 5 revealed no current corresponding to the reduction of H_2O_2 . This new anodic response can rather be attributed to the presence of one or several products resulting from the previous electrochemical and/or chemical oxidation of the antioxidant species. Finally for concentrations of H_2O_2 more than $1000 \mu\text{mol g}^{-1}$, the cyclic voltammogram presented the electrochemical characteristics of hydrogen peroxide, i.e. an anodic current with peak potential close to -0.25 V and a cathodic wave appearing from -0.5 V . The whole antioxidant species were then oxidized and hydrogen peroxide was no more consumed. It was verified that both amperometric responses increased with further successive additions of hydrogen peroxide. All these results highlight the cream efficiency to scavenge significant amounts of hydrogen peroxide as a reactive oxygen species. They give also the possibility to further develop the method in a way to quantitatively measure the amount of reduced species which show efficient antioxidant activity, expressed by an equivalent of hydrogen peroxide added to consume them.

Influence of oxygen and natural light

In order to evaluate the stability of the cream, the influence of two sources of “natural” oxidative stress – oxygen of air and natural light – on its antioxidant properties was studied. An air or a nitrogen flux was maintained in the electrochemical cell containing the cream sample and the experiment was performed in the dark or in daylight. Cyclic voltammograms were performed at the surface of the cream and the anodic peak current was recorded as a function of time. Figure 6 represents the evolution of the anodic peak current i_p compared to the initial peak current i_{p0} for the different experimental conditions.

Firstly, results revealed in all cases a general decrease of the ratio i_p/i_{p0} with time. This evolution was observed even when the cream was protected from light and oxygen. In this latter case, the decrease of 20 % of the peak current density after 500 min cannot be due to oxidative stress. It can better be assumed that the surface of the cream dried, resulting in the modification of the diffusion properties and a decrease in the electrochemical reaction rate. However, this phenomenon if right remained the same for all the conditions studied because the flux was controlled by a flow-meter (flow: 1 L/h). Secondly, the comparison of the different curves highlights an influence of oxygen and light on the antioxidant properties. An important decrease of the antioxidant properties was observed when the cream was exposed to oxidative stress; the fastest decrease was recorded for the creams exposed to daylight. The loss of the antioxidant properties of the cream exposed to light and nitrogen was 30 %; in the case where the cream was exposed to oxygen only, it was 25% (compared to 20% when the cream was protected from oxidative stress). Consequently, daylight and oxygen played an important role in the loss of the antioxidant properties but the influence of daylight appeared more significant. Anyway, the most important decrease was observed when the cream was exposed to both factors (air and daylight) simultaneously: 40% of its antioxidant properties was lost after 500 min. Otherwise, the modification of the cream properties was mainly situated at the surface of the cream (data not shown).

Conclusion

Cyclic voltammetry and linear sweep voltammetry are reliable methods to evaluate the effective global antioxidant power of dermocosmetic creams. The protocol allowed a simple, rapid, precise and direct determination of the redox properties of eleven antioxidant containing or antioxidant free creams without any pre-treatment of the sample. The method made it also possible to highlight the evolution of the antioxidant capacity under oxidative stress. This preliminary study gives opportunity to further develop the method in a way to quantitatively determine the cream antioxidant titer.

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Abbreviations :

BHA : tert-butyl-4-methoxyphenol

EDTA : ethylenediamine-tetraacetic acid

BHT : butyl-hydroxy-toluene

PEG : polyethyleneglycol

MSE : mercurous sulphate electrode

FRAP : Ferric-Reducing Ability of Plasma

ABTS : 2,2'-azinobis(3-éthylbenzothiazolinesulfonate)

TEAC : Trolox-Equivalent Antioxidant Capacity

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electrode material	i_{peak} (mA cm ⁻²)	E_{peak} (V/MSE)	number of measurements
platinum	6.0 ± 0.3	0.29 ± 0.04	6
vitreous carbon	5.2 ± 0.3	0.38 ± 0.06	10
gold	5.4 ± 0.6	0.42 ± 0.07	7

Table 1.

Influence of the electrode material on the anodic peak current density and potential of the cyclic voltammogram obtained in the hair removal cream. All electrodes were cleaned as described in section material and method.

cream	antioxidant species	conductivity ($10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$)	reproducibility	
			potential (V/ESM)	current density i_p ($\text{mA} \cdot \text{cm}^{-2}$)
cream, pH=4.86 ¹	no	1.5	0.71 +/- 0.02	0.78 (4%)
cream, pH=6.88 ¹	no	3.1	0.59 +/- 0.02	0.81 (4%)
cream, pH=6.95 ¹	BHT	3.3	0.60 +/- 0.02	0.95 (13%)
depilatory cream Klorane	thiolactic acid, BHA	3.4	0.29 +/- 0.04	6.0 (5%)
anti-aging cream Nivea Vital	ascorbic acid, BHT tocopheryl acetate,	1.6	0.34 +/- 0.07	3.1 (13%)
Corrective dermatological care for wrinkles Active C	Ascorbic acid	0.0	<i>no voltammogram recorded</i>	
Depigmenting emulsion Trio D (LED)	ascorbic acid polypeptide, tocopherol	8.6	0.70 ²	0.6 (30%)
whitening day cream Decleor	tocopheryl acetate	0.4	0.93 +/- 0.07	0.49 (15%)
Ysthéal emulsion	BHT, retinal, tocopheryl glucoside	0.9	0.87 +/- 0.03	0.8 (22%)
Epithelial cream A Derma	retinol, tocopheryl acetate	0.1	1.20 ²	0.25 (4%)
After sun repair balm Uriage	no	3.7	0.66 +/- 0.02	0.83 (3%)

¹ : Creams made in Pierre Fabre Laboratory (see § material and methods)

² : No peak potential was observed. The standard deviation was calculated from the current at the indicated potential, where a significant anodic wave was observed.

Table 2.

Values of the conductivity and the anodic peak current density and potential recorded with 11 antioxidant containing creams or free bases.

Figure 1: Experimental device used. The three electrode system was introduced directly in the cream.

Figure 2: Cyclic voltammograms obtained with platinum electrode introduced in the bulk of the cream: hair removal cream (—), cream containing no antioxidants (⋯⋯). Potential scan rate: 50 mV.s⁻¹.

Figure 3: Linear sweep voltammograms obtained with platinum electrode immersed in potassium sulphate solution 0.4 mol.L⁻¹, pH=11.0 (⋯⋯) containing: H₂O₂ 1.96 10⁻³ mol.L⁻¹ (— · —), thiolactic acid 5.00 10⁻⁴ mol.L⁻¹ (— —), BHA 5.55 10⁻⁵ mol.L⁻¹ (—). Potential scan rate: 50 mV.s⁻¹.

Figure 4.a: Evolution of the peak current density i_p as a function of the potential scan rate r in hair removal cream (working electrode: platinum disk)

Figures 4.b: Variation of the peak potential E_p as a function of the scan rate r in hair removal cream (working electrode: platinum disk)

Figure 5: Linear sweep voltammograms obtained with platinum electrode introduced in the bulk of the hair removal cream containing: 0 (—), 10 (—), 361 (— · —), 1246(- - -) μ mole of H₂O₂ per gram of cream. Potential scan rate: 50 mV.s⁻¹.

Figure 6: Influence of natural light and/or air on the global antioxidant capacity of an hair removal cream. Evolution of the ratio (peak current density)/(initial peak current density) as a function of time (working electrode: platinum disk, potential scan rate : 50 mV/s): — \diamond

exposed to nitrogen and protected from light, \cdot — \cdot Δ exposed to air and protected from light,
...□ exposed to nitrogen and light, — — x exposed to air and light.

Figure 1.

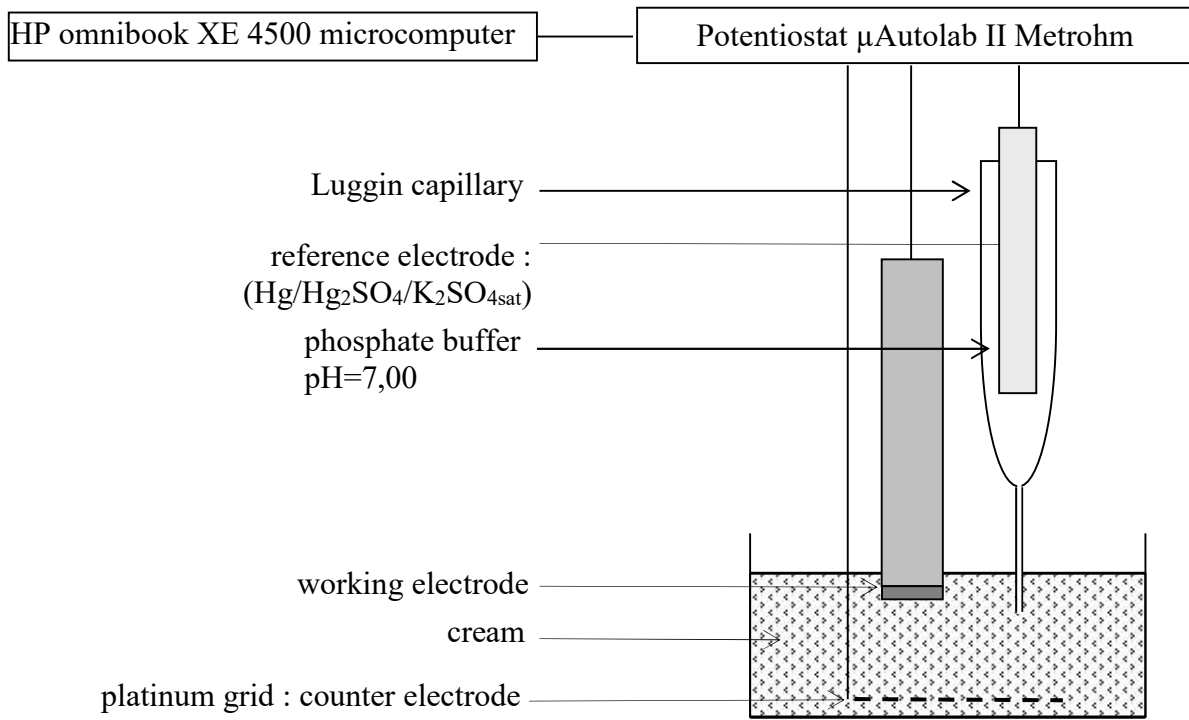


Figure 2.

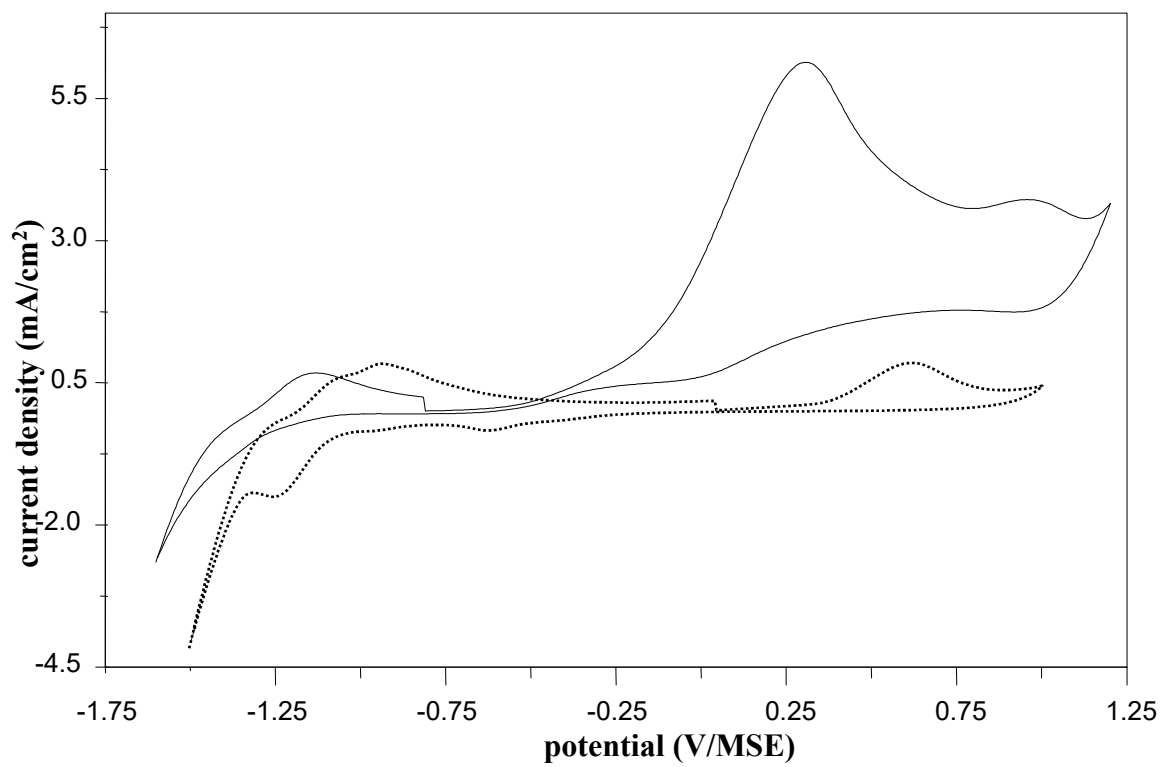
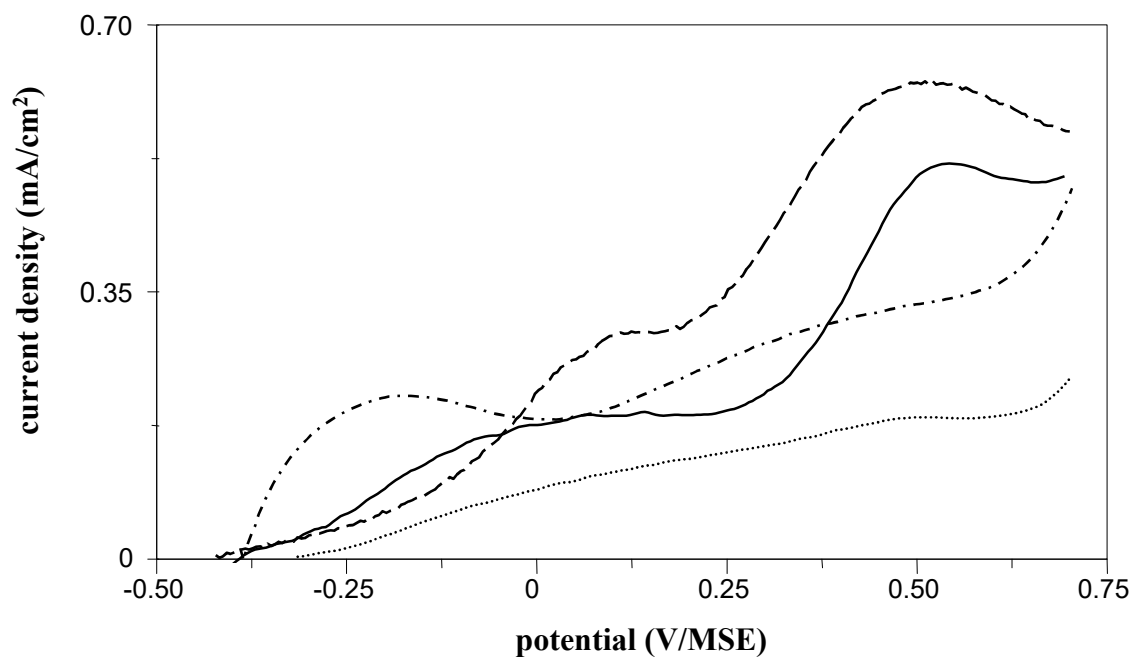
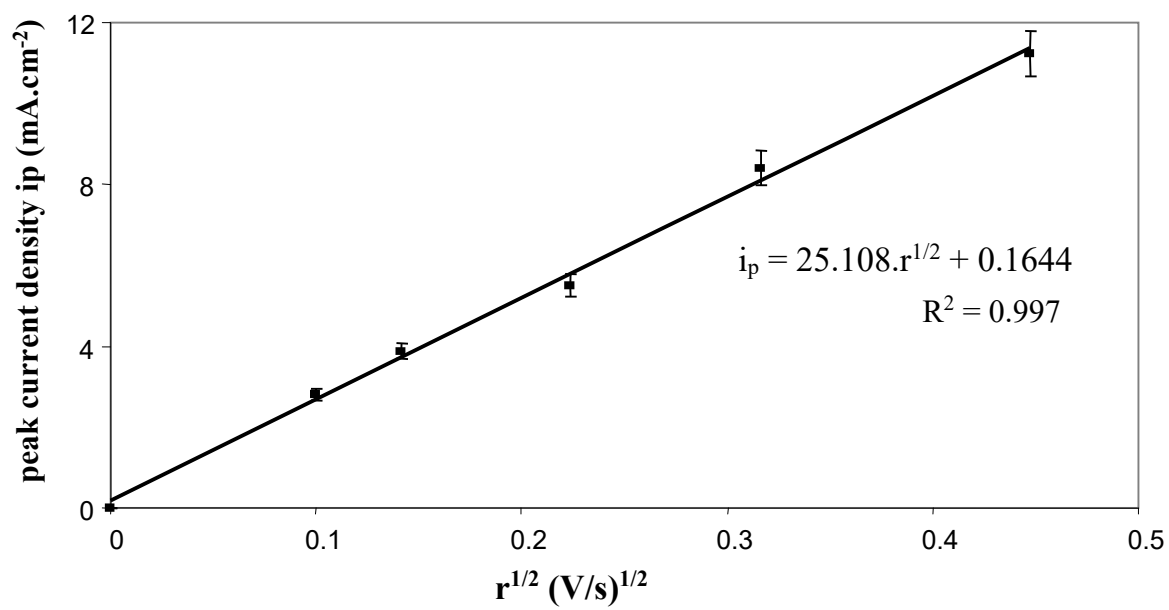


Figure 3:



Figures 4.a:



Figures 4.b:

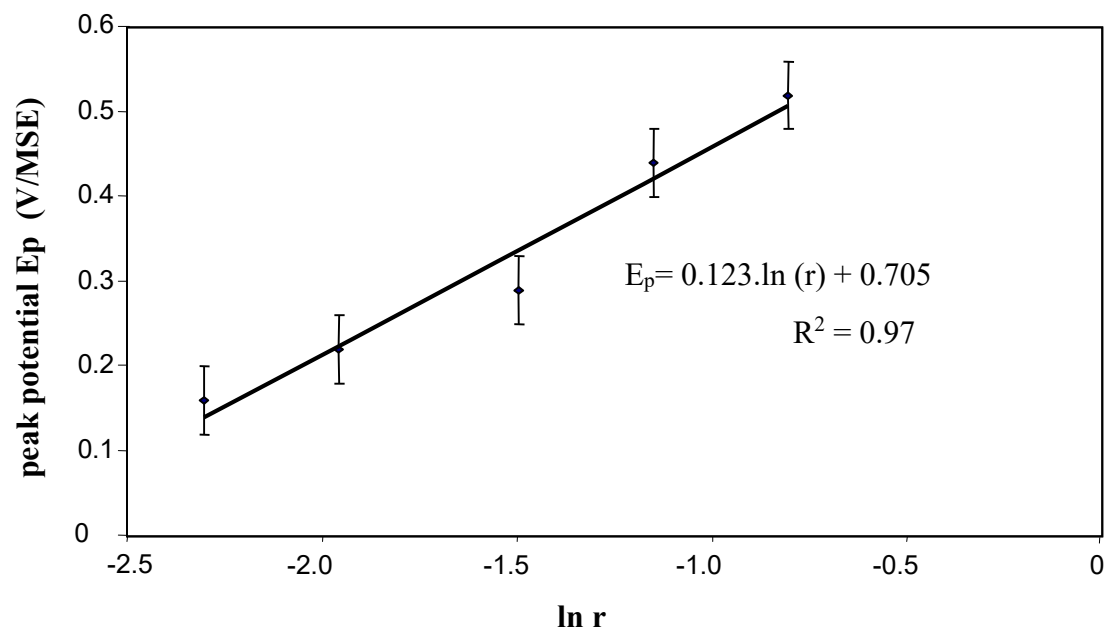


Figure 5.

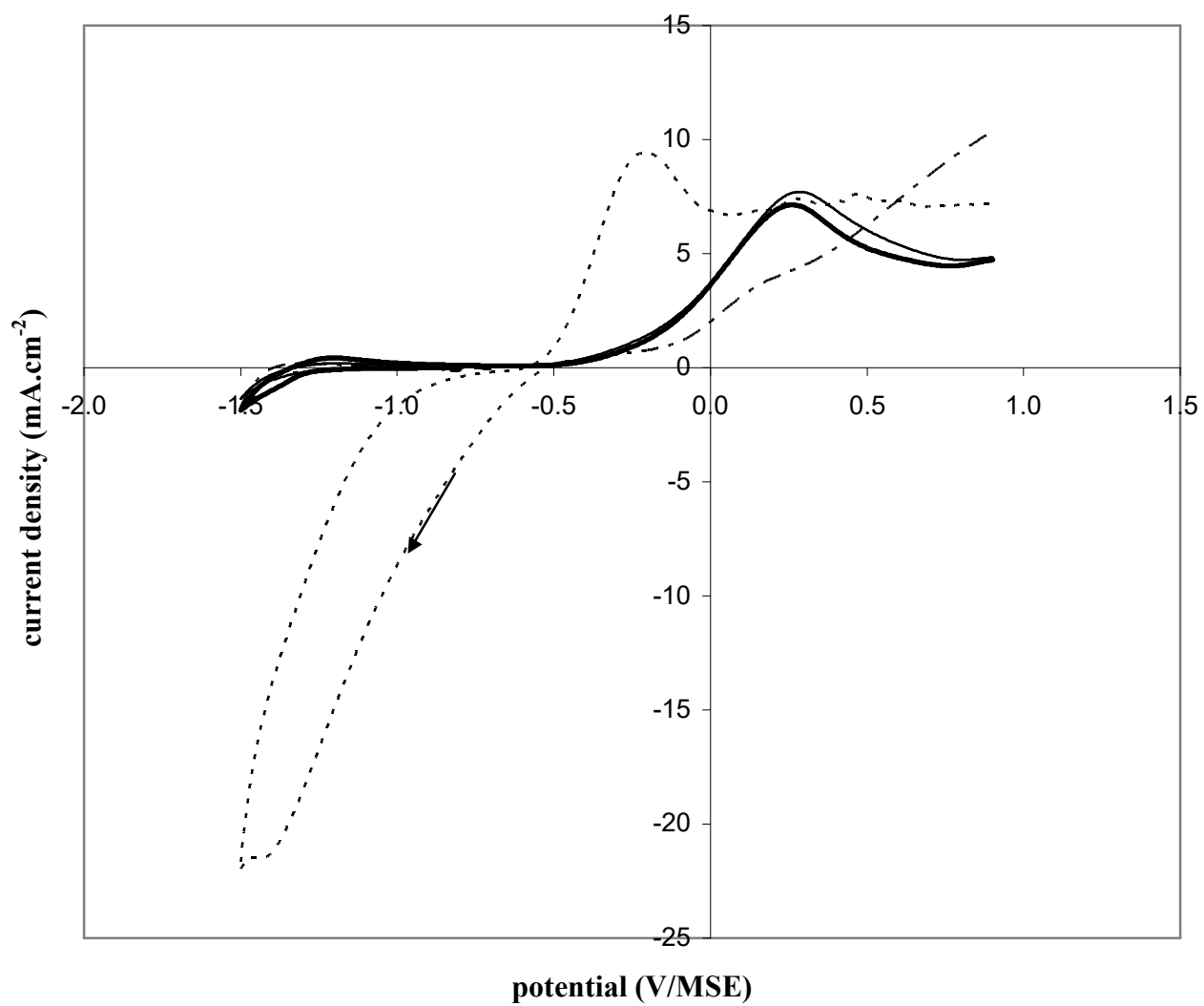


Figure 6.

