ANKARA ÜNİVERSİTESİ
BİLİMSEL ARAŞTIRMA PROJELERİ
KOORDİNASYON BİRİMİ KOORDİNATÖRLÜĞÜNE

Proje Türü : Lisansüstü Tez Projesi (Yüksek Lisans)
Proje No : 16L0430002
Proje Yürütücüsü : Prof. Dr. Zehra YAZAN

Proje Başlığı : Askorbik asit ve/veya Kafein'in nano malzemelerle modifiye edilmiş karbon
elektrot yüzeylerinde voltametrik analizi

Yukarıda bilgileri yazılı olan projemin sonuç raporunun e-kitüphanede yayınlanmasını;

İSTİYORUM ✗
İSTEMİYORUM ☐ GEREKÇESİ:

17.05.2017
Prof. Dr. Zehra YAZAN

İmza
ANKARA ÜNIVERSITESİ

BİLİMSEL ARAŞTIRMA PROJESİ
SONUC RAPORU

Proje Başlığı
Askorbik asit ve / veya Kafein’in nano malzemelerle modifiye edilmiş karbon elektrot yüzeylerinde voltametrik analizi

Proje Yürütücününün İsmi
Prof. Dr. Zehra YAZAN

Araştırmacılarnın İsmi
Melike PEKİN
Dilek ESKİKOY BAYRAKTEPE

Proje Numarası

Başlama Tarihi
26.02.2016

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26.02.2017

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17.05.2017

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[Signature]
Projenin Türkçe ve İngilizce Adı ve Özetleri

**Özet:** Bu çalışmada sepiyolit kili (SC) ile modifiye edilmiş karbon pasta elektrot (SC/KPE) hazırlanan olup bu elektrot asidik asidin (AA) diferansiyel puls adsorptif sinyalvolatmetrisi (AdsDPV) yöntemi ile tayininde kullanılmıştır. pH, elektrot bileşimi, birikirme potansiyeli ve birikirme süresinin etkilerini araştırarak AA tayini için en uygun ortam ve yöntem şartları belirlenmiştir. Belirlenen optimum koşullarla AA için AdsDPV yöntemi ile oluşturululan kalibrasyon grafiğine ait doğrusal çalışma aralığı 1,4×10⁸ - 9,0×10⁷ mol L⁻¹'dir. Gözlenebileme sınırı (LOD) ve kantitatif tayin sınırı (LOQ) ise sırasıyla, 0,0042 µmol L⁻¹, 0,014 µmol L⁻¹ olarak bulunmuştur. Geliştirilen yöntemin seçiciliği ise Na⁺, Cl⁻, Ca²⁺, Mg²⁺, NO₃⁻, sütik asit ve glikoz içeren ortamlarda AA tayini yapılaraq araştırılmış ve bu türlerin AA tayinine herhangi bir girişim etkisi yapılmadığı görülmüştür. AA tayini için geliştirilmiş olan SC/KPE elektrodunun ömrü çalışmaları yapılmış ve en az bir ay kararlı olduğunu sonucuna varılmıştır. Ayrıca geliştirilmiş olan bu elektrot sistemini ve yöntemi ile ilaç preparatlarında, piyasada bulunan C vitaminli soda ve doğal Kuşburnu örneklerinde AA tayini yapılması ve oldukça iyi sonuçlar elde edilmiştir.

**İngilizce özet:** A new electrode composed of sepiolite clay (SC) carbon paste (CP) was developed and used for the adsorptive stripping differential puls voltammetric quantification of ascorbic acid (AA). The effects of pH, the ratios of the electrode ingredients, accumulation potential and accumulation time were investigated. The SC/CP electrode (SC/CPE) was found to have a good linear working range (1.4×10⁸ - 9.0×10⁷ mol L⁻¹) and the detection limit of 4.2×10⁻⁸ mol L⁻¹. The sensitivity is fairly good with LOQ of 0.014 µmol L⁻¹ and LOD of 0.0042 µmol L⁻¹. The selectivity in the presence of some common species i.e. Na⁺, Cl⁻, Ca²⁺, Mg²⁺, NO₃⁻, citric acid, and glucose at concentrations well above those encountered in body fluids was found to be satisfactory. The SC/CPE system has a lifetime not shorter than a month and proved to be practical for the analysis of not only pharmaceutical formulations but also natural products such as vitamin C, rich fruit rosa canina and mineral waters.

I. **Amaç ve Kapsam**

Önerilmiş olan projede yapılması amaçlananlar aşağıdaki gibidir:

- Sepiyolit kili ile modifiye edilmiş karbon pasta elektrotların hazırlanması
- Hazırlanan elektrotların yüzey özelliklerinin elektrokimyasal empedans spektroskopisi ve dönüştürülmü voltametri yöntemleri ile incelenmesi
- Askorbik asidin elektrokimyasal davranışının incelenmesi
- Askorbik asidin duyarlı bir şekilde analiz edilebilmesi için voltametrik adsorptif sinyal yöntem geliştirilmesi
II. **Materyal ve Yöntem**

Projeden üretilmiş olan yayın ekte verilmiştir.

III. ** ANALIZ ve Bulgular**

Proje kapsamında yapılması öngörülen çalışmalar arasında askorbik asit ve kafein ile ilgili voltametriik yöntem geliştirilmesi ve gerçek numunelere uygulanması amaçlanmıştır. Ancak Kafein ile ilgili olarak yapılan çalışmalar neticesinde, tekrarlanabilir ve keskin bir pike sahip olmadığı görülmuş olup uygun bir kalibrasyon eğrisi elde edilememiştir. Bu nedenle çalışmalar askorbik asit üzerinde yoğunlaştırılmıştır.

Projeden üretilmiş olan yayın ekte verilmiştir.

IV. **Sonuç ve Öneriler**

- Bu proje çalışması ile AA tayini için yeni olan, karbon pasta ve sepiyolit kiline dayanan sensör geliştirilmiştir.
- Geliştirilen sensör ile AA tayini için voltametrik bir yöntem geliştirilmiş olup geliştirilen bu yöntemin gözlenebilme sürü literatürde AA tayini için yapılmış olan diğer voltametrik çalışmalarla karşılaştırılabilecektir.
- Ayrıca, geliştirilmiş olduğumuz bu yeni yöntem ile AA‘ın piyasada yer alan ilaç preparatlarından biri olan Redoxan adlı C vitamin tabletinden, C vitaminii içeren soda örneğinde ve Nallihan ilcesinden temin edilen kusburnu örneklerinden tayini başarıyla gerçekleştirmiştir. Elde edilen sonuçlar aşağıdaki çizelgede sunulmuştur.

Çizelge 1. Askorbik asidin farklı gerçek numunelerden tayininden elde edilen sonuçlar (4)

<table>
<thead>
<tr>
<th>Örnek</th>
<th>Eklenen AA miktarı (µmol/L)</th>
<th>Bulunan AA miktarı (µmol/L)</th>
<th>Geri Kazanım (%)</th>
<th>t-testi, tₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redoxan tablet</td>
<td>0,100</td>
<td>0,098</td>
<td>98,0±3.0</td>
<td>1,86</td>
</tr>
<tr>
<td>Vitamin C içeren soda</td>
<td>0,100</td>
<td>0,104</td>
<td>104,0±6.0</td>
<td>1,85</td>
</tr>
<tr>
<td>Kuşburnu örnek</td>
<td></td>
<td></td>
<td>0,44</td>
<td></td>
</tr>
<tr>
<td>(g AA/100 g numune)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(95% güven seviyesinde tₐ: 2,78 (N=5)
Çizelge 1'de görüldüğü üzere, geliştirmiş olduğumuz yeni yöntem ve elektrotla soda ve tablet örneklerinden oldukça yüksek geri kazanın değerleri ile AA tayini yapılmış.

- Nallihan ilçesinden elde edilmiş olan Kuşburnu örneklerinde yer alan AA miktarı da yine geliştirilen bu yöntemle 0,44 g/100 g olarak bulunmuştur. Elde edilen bu sonuç ise literatürlerde, farklı bölgelerden alınan (Türkiye dışında) kuşburnunda yapılmış olan AA tayini çalışmalarından elde edilen sonuçlarla karşılaştırılabilir niteliktedir (1-3).

V. Geleceğe İlişkin Öngörullen Katkılar

- Hem ilaç endüstrisinde hem de AR-GE çalışmalarında, bu çalışma ile önerilen modifiye elektrot sensörü ve voltametrik yöntemler kalite kontrol amacı ve rutin analizlere başlarıyla uygulanmıştır.
- Bu projede bilinen voltametrik yöntemlerin Türkiye'de yetiştirilen Kuşburnu örneklerine uygulanmasına yeni bir modifiye elektrot sensörü kullanılmıştır. Bu kapsamda bilime yenilik getirmiştir.
- Ilerleyen yıllarda AA üzerinde yapılacak olan analiz çalışmalarında bu projede geliştirilmiş olan yöntem ile elde edilen bulgular bir kaynak oluşturacaktır.

VI. Sağlanan Altyapı Olanakları ile Varsa Gerçekleştirilen Projeler

Bu projeden sadece sırf malzemeler temin edilmştir.

VII. Sağlanan Altyapı Olanaklarının Varsa Bilim/Hizmet ve Eğitim Alanlarındaki Katkıları

Laboratuvarımızda, projeden temin edilen sırf malzeme olanakları ile üç yüksek lisans ve bir doktora tez çalışması kullanılmıştır. Doktora çalışması tamamlanmış olup yüksek lisans çalışması ise tamamlanmak üzereidir.

Ayrıca bu proje ile yapılmış olan çalışmalar 2017 yılında SCIE kapsamında bir dergide yayınlanmış olup, 2016 yılında ise Çanakkale'de gerçekleştirilen uluslararası bir Analitik Kimya kongresinde poster bildirisi olarak sunulmuştur.

VIII. Kaynaklar


Ekler

a. Mali Bilanço ve Açıklamaları
Projemiz 14.000 TL ile desteklenmiştir. Bu tutarın tamamı kimyasal madde ve sarf malzemeler için harcanmıştır. Harcama listesi ekte sunulmuştur.

b. Makine ve Teçhizatın Konumu ve İlerideki Kullanımına Dair Açıklamalar

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c. Teknik ve Bilimsel Ayrıntılar

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d. Sunumlar (bildiriler ve teknik raporlar) (Altyapı ve Yönlendirilmiş Projeler için uygulanmaz)

Ekte verilmiştir.

e. Yayınlar (hakemli bilimsel dergiler) ve tezler (Altyapı ve Yönlendirilmiş Projeler için uygulanmaz)

Ekte verilmiştir.

NOT: Verilen sonuç raporu bir (1) nüsha olarak cilt siz şekilde verilecek, sonuç raporu Komisyon onayından sonra ciltlenerek bir kopyasını yer aldığı CD ile birlikte sunulacaktır. Sonuç raporunda proje sonuçlarını içeren, ISP'nin SCI veya SSCI veya AHCI dizinleri kapsamında ve diğer uluslararası dergilerde yayınlanılmış makaleler, III. Materyal ve Yöntem ve IV. Analiz ve Bulgular bölümleri yerine kabul edilir.
<table>
<thead>
<tr>
<th>Bütçe Yılı</th>
<th>Bütçe Kodu</th>
<th>Açıklama</th>
<th>Önceki Yıllan Devir</th>
<th>Başlangıç Ödeneği</th>
<th>Eklenen Akışma</th>
<th>Düşülen Akışma</th>
<th>Eklenen Ödenek</th>
<th>Net Ödenek</th>
<th>Harcanan</th>
<th>Bloke Edilen (Avans)</th>
<th>Bloke Edilen (Dışarı)</th>
<th>Kalan</th>
</tr>
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<tr>
<td>2016</td>
<td>03.2</td>
<td>TÜKETIME YÖNELİK MAL VE MALZEME ALIMLARI</td>
<td>0,00</td>
<td>14.000,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>14.000,00</td>
<td>7.601,56</td>
<td>0,00</td>
<td>0,00</td>
<td>6.398,44</td>
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<td></td>
<td>0,00</td>
<td>14.000,00</td>
<td>0,00</td>
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<td>0,00</td>
<td>14.000,00</td>
<td>7.601,56</td>
<td>0,00</td>
<td>0,00</td>
<td>6.398,44</td>
</tr>
</tbody>
</table>

Ek Ödenekler ve Akıtmalar (Bu bölüm BAP Koordinatörlüğü tarafından doldurulacaktır)
<table>
<thead>
<tr>
<th>Hayır</th>
<th>Ag/AgCl Referans elektrot</th>
<th>1 paket</th>
<th>1</th>
<th>0</th>
<th>882,15</th>
<th>882,15</th>
<th>882,15</th>
<th>0</th>
<th>0</th>
<th>882,15</th>
<th>882,15</th>
<th>882,15</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hayır</td>
<td>platin tel kärst elektrot</td>
<td>1 Adet</td>
<td>1</td>
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<td>1.040,94</td>
<td>1.040,94</td>
<td>1.040,94</td>
<td>0</td>
<td>0</td>
<td>1.040,94</td>
<td>1.040,94</td>
<td>1.040,94</td>
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<tr>
<td>Hayır</td>
<td>peek elektrot gövdesi</td>
<td>10 Adet</td>
<td>10</td>
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<td>68,3</td>
<td>682,98</td>
<td>682,98</td>
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<td>0</td>
<td>68,3</td>
<td>682,98</td>
<td>682,98</td>
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<tr>
<td>Hayır</td>
<td>Metanol</td>
<td>2,5 litre</td>
<td>2,5</td>
<td>0</td>
<td>33,04</td>
<td>82,6</td>
<td>82,6</td>
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<td>0</td>
<td>33,04</td>
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<tr>
<td>Hayır</td>
<td>Kitosan</td>
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<td>638,38</td>
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<td>0</td>
<td>12,77</td>
<td>638,38</td>
<td>638,38</td>
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<tr>
<td>Hayır</td>
<td>urlik asit</td>
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<td>25</td>
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<td>0</td>
<td>13,88</td>
<td>346,92</td>
<td>346,92</td>
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</tr>
<tr>
<td>Hayır</td>
<td>Askorbik asit</td>
<td>100 gram</td>
<td>100</td>
<td>0</td>
<td>2,5</td>
<td>250,16</td>
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<td>0</td>
<td>0</td>
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<td>250,16</td>
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<td>0</td>
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<tr>
<td>Hayır</td>
<td>L-sistein</td>
<td>25 gram</td>
<td>25</td>
<td>0</td>
<td>9,44</td>
<td>236</td>
<td>236</td>
<td>0</td>
<td>0</td>
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<td>236</td>
<td>236</td>
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<tr>
<td>Hayır</td>
<td>magnezyum klorür</td>
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<td>1</td>
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<td>167,56</td>
<td>167,56</td>
<td>167,56</td>
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<tr>
<td>Hayır</td>
<td>sodyum klorür</td>
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<td>64,9</td>
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<tr>
<td>Hayır</td>
<td>çinko nitrat</td>
<td>500 gram</td>
<td>500</td>
<td>0</td>
<td>0,65</td>
<td>325,68</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>Hayır</td>
<td>dopamin hidroklorür</td>
<td>5 gr</td>
<td>5</td>
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<td>43,42</td>
<td>217,12</td>
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<td>43,42</td>
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<td>Hayır</td>
<td>glikoz</td>
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<td>Hayır</td>
<td>kalsiyum klorür</td>
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<td>potasyum klorür</td>
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<tr>
<td>Hayır</td>
<td>sitrik asit</td>
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<td>0</td>
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<td>77,88</td>
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<tr>
<td>Hayır</td>
<td>mikro pipet (10-100 mikrolitre)</td>
<td>1 Adet</td>
<td>1</td>
<td>0</td>
<td>749,3</td>
<td>749,3</td>
<td>749,3</td>
<td>0</td>
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<tr>
<td>Hayır</td>
<td>mikropipet (100-1000 mikrolitre)</td>
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<td>0</td>
<td>749,3</td>
<td>749,3</td>
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</tr>
<tr>
<td>Hayır</td>
<td>1-Butyl-3-methylimidazolium</td>
<td>5 gram</td>
<td>5</td>
<td>0</td>
<td>100,3</td>
<td>501,5</td>
<td>501,5</td>
<td>0</td>
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</tr>
<tr>
<td>Hayır</td>
<td>hidroklorik asit</td>
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<td>30,68</td>
<td>76,7</td>
<td>76,7</td>
<td>0</td>
<td>0</td>
<td>30,68</td>
<td>76,7</td>
<td>76,7</td>
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<tr>
<td>Hayır</td>
<td>L-glutamik asit</td>
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<td>250</td>
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<td>292,64</td>
<td>292,64</td>
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<td>0</td>
<td>1,17</td>
<td>292,64</td>
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<tr>
<td>Hayır</td>
<td>okzalik asit</td>
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<td>0</td>
<td>0,3</td>
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<td>152,22</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hayır</td>
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Novel Electrochemical Sensor Based on Sepiolite Clay Modified Carbon Paste Electrode for Ascorbic Acid Detection

Melike Pekin*, Dilek Eskiköy Bayraktepe, Zehra Yazar

Ankara University Faculty of Science, Department of Chemistry, Tandogan, Ankara, TURKEY, 06560

*E-mail: melikep0@gmail.com

Ascorbic acid and its sodium, potassium, and calcium salts are commonly used as antioxidant food additives. These compounds are water-soluble and, thus, cannot protect fats from oxidation: For this purpose, the fat-soluble esters of ascorbic acid with long-chain fatty acids (ascorbyl palmitate or ascorbyl stearate) can be used as food antioxidants. Eighty percent of the world’s supply of ascorbic acid is produced in China [1]. By virtue of its biological importance, it is vital to develop a sensitive and selective method for quick and reliable determination of AA in various samples like drug, beverage and biological matrices. To meet this need, we have focused on to develop voltammetric method by using novel clay modified carbon paste sensor (SC/CPE). Therefore, differential puls adsorptive stripping voltammetry (AdsDPV) technique was developed for determination of AA on proposed sensor.

Electrochemical stripping methods have some advantages of being relatively less expensive, highly sensitive and they provide low limit of detection (LOD). Therefore, electrochemical stripping methods are becoming more popular as alternative methods in pharmaceutical formulations and biological samples [2-3]. Electrochemical oxidation behavior of AA was examined by using cyclic voltammetry on SC/CPE and other experimental parameters such as pH, composition of sepiolite clay, deposition time and deposition potential were optimized. Under optimized conditions the calibration graph was established and linear working range was identified with in the range of 0.014-0.9 μM and also limit of detection (LOD) and limit of quantification (LOQ) values were calculated as 0.0042 μM and 0.014 μM, respectively. These results are comparable with literature data’s. The method was applied successfully to different real samples. The recovery results are very close to 100%.

![Molecular structure of ascorbic acid](image)

Fig1. Molecular structure of ascorbic acid

Keywords: Ascorbic acid, rosehip, sepiolite clay, carbon paste electrode, voltammetry

References:
Electrochemical sensor based on a sepiolite clay nanoparticle-based electrochemical sensor for ascorbic acid detection in real-life samples

Melike Pekin, Dilek Eskiköy Bayraktepe, Zehra Yazan

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Abstract A new electrode composed of sepiolite clay (SC) carbon paste (CP) was developed and used for the adsorptive stripping differential pulse voltammetric quantification of ascorbic acid (AA). The effects of pH, the ratios of the electrode ingredients, accumulation potential, and accumulation time were investigated. The SC/CP electrode (SC/CPE) was found to have a good linear working range (1.4 × 10^{-3} - 9.0 × 10^{-7} mol L^{-1}) and the detection limit of 4.2 × 10^{-9} mol L^{-1}. The sensitivity is fairly good with a LOD of 0.014 μmol L^{-1} and a LOD of 0.0042 μmol L^{-1}. The selectivity in the presence of some common species, i.e., Na⁺, Cl⁻, Ca^{2+}, Mg^{2+}, NO₃⁻, citric acid, and glucose, at concentrations well above those encountered in body fluids was found to be satisfactory. The SC/CPE system has a lifetime not shorter than a month and proved to be practical for the analysis of not only pharmaceutical formulations but also natural products such as vitamin C-rich fruit Rosa canina and mineral waters.

Keywords Modified carbon paste electrode · Ascorbic acid · Stripping voltammetry · Rosa canina · Sepiolite clay

Introduction

Ascorbic acid (AA) is a water-soluble vitamin, lack of which has been shown to cause a disease called scurvy. Unlike many animals, the human body is not able to produce ascorbic acid itself. So, vitamin C has to be a part of the diet [1]. Apart from its role as a vitamin, AA is widely used as an antioxidant food additive [2]. It has also been used as a biological response modifying agent [3].

Due to its increasing clinical and industrial applications, new procedures for the determination of AA are being developed. Here, we focus on the development of a voltammetric method based on the anodic oxidation of AA on a sepiolite clay-modified carbon paste electrode (SC/CPE).

Numerous analytical methods are based on the determination of AA. These include high-performance liquid chromatography (HPLC) [4, 5], liquid chromatography–mass spectrometry (LC–MS) [6], spectrophotometry [7, 8], and voltammetric methods [9–11]. Many of these methods already established are time consuming or based on the use of large volumes of organic liquids. The existing voltammetric methods are based on the oxidation of AA on various electrode systems. All of them are reported to suit the quantitative analysis of AA in a wide range of pharmaceutical, industrial, and domestic products [12–14]. Many reports indicate that these voltammetric procedures do not require any derivatization and very little matrix effects are involved compared to other analytical techniques [15, 16].

Among other electroanalytical sensors, CPE are in common use in the determination of AA and some other organic species in a host of products. The choice of CPE is mainly due to short analysis time, high analytical sensitivity, and wide potential windows. For example, the residual currents on carbon paste electrodes are ten times lower than those on the glassy carbon electrodes or noble metals [17]. The carbon paste can easily be modified by combining with several materials so as to improve the signal quality (selectivity and the sensitivity) [18]. Among these, sepiolite (Si₃O₁₀Mg₂(OH)₆(1/2H₂O)·8H₂O) [19], a special type of clay, can be used as a modifier for CPEs. Sepiolite structure comprises octahedral magnesium oxide planes
sandwiched between tetrahedral silicate sheets [20]. The anionic and cationic sites on and between the sheets provide an ease of adsorption for the polar organic species and ions; so is the reason it is used as an electrode modifier. The use of this mineral as an electrode modifier dates back to 1983 [20]. The material also imparts changes into the electrical conductivity of the carbon paste and thereby may have a catalytic contribution to the electrochemical processes. Furthermore, the intercalation and ion exchange capacity of the mineral is likely to improve the sorption capacity and conductivity properties of the electrode [21]. Another positive effect of the clay mineral to the electrode characteristics is to provide a greater specific surface area which could lead to new patterns of reactivity and selectivity. Clay minerals other than sepiolite were also reported to have been used to improve the electrochemical characteristics of the carbon paste electrodes [22–24]. In our previous studies, we have tried the sepiolite mineral along with other modifiers in carbon paste electrodes [25, 26].

In this work, we first focus on the optimum proportion of the SC to be added to the carbon paste to obtain the best voltammetric signals. The carbon paste electrode with the best characteristics was used to develop a sensitive and reliable electroanalytical method for the determination of AA. The voltammetric method thus developed was applied to the analysis of AA in real-life samples. We have also conducted studies to evaluate the working range, sensitivity, stability, and the selectivity of the electrode.

**Experimental**

**Reagents, solutions, and apparatus**

AA, graphite powder, SC, and paraffin oil were purchased from Sigma-Aldrich, St. Louis MO, USA.

In our work, 1.00 mM aqueous AA standard solution was kept at +4 °C when not in use. A secondary standard stock solution was prepared for the analytical procedures by diluting 1.00 mL of this solution to 1000 mL. The secondary stock solution has a concentration (1.00 µM) that is close to the analytical working range.

In our work, a 0.02 M Britton Robinon buffer solution (BR) was prepared by mixing boric acid, acetic acid, and phosphoric acid. The pH of the buffer was adjusted by adding 0.1 M NaOH solution. Double distilled and deionized water supplied from Human Power I® Ultra-Pure Water System was used throughout in this work.

Electrochemical experiments were performed on a CHI 660c workstaton with a C4 cell stand that accommodates a three-electrode system. Bare and modified carbon paste electrodes (BCPE and SC/CPE, respectively) were prepared as working electrodes by packing the respective material in an electrode body (BAS MF-2010). Ag AgCl (in 0.1 M NaCl) electrode was used as the reference electrode (BAS MF-2052). A platinum wire (BAS MW-1032) served as the auxiliary electrode.

The pH measurements were carried out on a HANNA Instruments HI2211 pH/ORP-meter. All measurements were performed at room temperature.

**Preparation of the sensors**

The BCPE was prepared by hand mixing graphite powder (30 mg) and mineral oil (10 µL) in a petri dish with a spatula. The mixture was transferred to the hole at the tip of an electrode body. This wave then polished using a piece of sandpaper. This electrode was then used as a sensor.

The SC/CPE mixtures of six different proportions were prepared by hand-mixing known masses (0.5; 1.0; 1.5; 2.0; 2.5; and 3.0 mg) of sepiolite with proper masses of graphite powder to make up to final weight to 30 mg. The mixture was mixed well with mineral oil (10 µL) as described above. The electrode surface was formed in the same way as in the BCPE. A copper wire imbedded in the paste provided the electrical contact. Before all experiments, CPE sensor surfaces were rinsed using water.

**Surface characterization of CPE sensors**

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were employed to characterize the sensors. All CV and EIS measurements were carried out in 0.1 M KCl containing 5.0 mM [Fe(CN)₆]³⁻/⁴⁻. The EIS measurements have been recorded at the open circuit potential (OCP) within the frequency range of 0.05–10⁴ Hz.

The surface areas of CPEs were estimated using CV. The potential scan rate was changed in the range 5.0–100 mV s⁻¹ and the voltammetric data were then processed based on Randles-Sevcik equation, [27], to estimate the surface area.

**Analytical procedure**

The voltammetric cell used in electrochemical measurements CV, differential pulse voltammetry (DPV) was of 10 mL capacity. The analytic solution of known volume and concentration was mixed with the required volume of BR buffer of a known pH to make up the final volume of 10 mL. The solution in the cell was purged with ultra-pure nitrogen (99.999%) for 60 s to expel the dissolved oxygen. After 2-s quiet time, the voltammograms were recorded in the potential range, −0.8 to 1.3 V. The ultra-pure nitrogen was supplied by Oksan Gaz A.S.
Preparation of the real sample solutions

In this work, three real-life samples were analyzed. The products used as the samples are described in the following paragraphs.

1. Pharmaceutical: A tablet of Redoxon (BAYER) with a nominal AA content of 1000 mg (plus 10 mg zinc) was dissolved in 1000 mL of water to serve as the stock solution. In the analytical part of the voltammetric studies, the stock solution was diluted 10^4 times and used as the secondary stock solution. This was necessary because the linear working range was below 1.0 µmol L\(^{-1}\) level. The test solutions were prepared by mixing the proper volume of the stock solution and the BR buffer of the desired pH so as to make up the final volume 10 mL.

2. A regional brand of mineral water (Beypažar) enriched with 300 mg L\(^{-1}\) vitamin C. In the analysis procedure, the product was regarded as the substitute for the stock solution. The secondary stock solution was obtained in the same way.

3. Dried hips of the plant Rosa canina: The dried fruits of the plant collected at Nallıhan/Ankara/Turkey and packed for domestic use in the form of hot infusions was sampled. The stock solution of the hips was prepared after cutting them into pieces of 2-5 mm size. A 10-g sample so prepared was mixed with 250 mL of boiling water and the mixture was put into an ultrasonic bath with the thermostat adjusted to 95 °C. Trial experiments with extraction periods of 5, 15, 30, and 60 min showed that 30 min was a good choice. After 30 min, the peak current of AA was decreased. As AA is oxidized by the atmospheric oxygen, longer extraction periods were avoided. As the AA level in these solutions was similar to that of the AA stock solution, they were all diluted in a similar manner during the preparation steps of the voltammetric analysis procedures.

Adsortive differential pulse voltammograms were recorded by using these experimental parameters: 0.05 V pulse height; 0.05 s pulse width; 0.0167 s sample width; 0.5 s pulse period; 2 s quiet time; \(1 \times 10^{-5}\) A/V sensitivity; \(-0.1\) V deposition potential; 0 s deposition time.

Results and discussion

The BCPE and SC/CPE electrodes were prepared as described in the “Experimental” section. The modifier content of the modified plattorms was kept at 0.5/30 (1.67%), 1/30 (3.33%), 1.5/30(5%), 2/30 (6.67%), 2.5/30 (8.33%), and 3/30 (10%). The performance parameters of each electrode were tested by evaluating the CV data of the 3.0 × 10^{-4} mol L\(^{-1}\) AA at each electrode. The experiments were carried out at a scan rate of 100 mV s\(^{-1}\). The voltammograms and the change of peak current with the sepilite content (inset) are shown in Fig. 1.

It can be seen that, among the anodic peaks, the one corresponding to 6.67% sepilite is the sharpest. Consequently, we have chosen this electrode as the working electrode.

The cyclic voltammograms of 5.0 × 10^{-3} mol L\(^{-1}\) \(\text{K}_2\text{Fe(CN)}_6\) (a standard redox couple) on the bare- and 2/30 (6.67%) SC-modified CPE are shown in the Fig. 2.a. Evidently, the modified electrode gave rise to a voltammogram with about 5.0% larger \(\text{Fe(CN)}_6^{3-}\) oxidation current than that obtained at a bare electrode. The reverse scan with the modified electrode does not show a betterment in the peak height rather, the reduction peak remains almost the same as the one with the bare electrode. This observation strongly

![Fig. 1 Cyclic voltammograms of 3.0 × 10^{-4} M ascorbic acid on the bare and modified CPEs at pH 3.0 with a scan rate of 0.1 V s^{-1}](image)
Fig. 2 Nyquist plots of $1.0 \times 10^{-3}$ mol L$^{-1}$ $K_2Fe(CN)_6$ on the CPE and SC/CPE

suggests that the oxidized species of the redox couple is not adsorbed as strongly as the reduced form.

Theory of impedance spectroscopy states that, on the
Nyquist plots, the radius of the circular part of the graph is
equal to the charge transfer resistance of the electrode surface
for the electrochemical reaction concerned [28]. Indeed the
two sensors we used in this context displayed well-defined
semi-circular parts (Fig. 2b). The circular part of Nyquist plot
corresponding to the bare electrode (~16,000 Ω) is about five
times larger than that of the modified counterpart (~84,000Ω).

That the electrical resistance of the modified electrode is no-
tably smaller explains partly why this platform gives rise to
relatively sharper CV peaks.

For the comparison of the specific area of the two elec-
trodes, CVs of $5.0 \times 10^{-3}$ mol L$^{-1}$ $K_2Fe(CN)_6$ on the both
electrodes were conducted at various scan rate ($\nu$). A plot of the
anodic peak current ($i_p^a$) versus $\nu^0.5$ was then prepared. Based
on the Randles-Sevcik equation [27], the active surface area of
each electrode was then estimated from the slope of the $i_p^a$
versus $\nu^{0.5}$ plot based on a known diffusion coefficient of
4.76 $\times$ 10$^{-6}$ cm$^2$ s$^{-1}$ [29]. In this way, the surface area of the
bare electrode was evaluated to be 0.066 cm$^2$ and that of the
SC/CPE was 0.0904 cm$^2$. This means a nearly 1.5-fold in-
crease in the electrode surface area. The modifying effect of
the sepilite material is obviously related to this finding.

Electrochemical behavior of AA

In order to investigate the effect of scan rate on the peak
currents of AA at the working electrode, cyclic voltam-
mograms of AA in 0.02 M BR buffer solution (pH 3.0) were
recorded at various scan rates (Fig. 3). The scan rate was
changed over the 5–500 mV s$^{-1}$ range. The plots indicate that,
with increasing scan rate, the peak currents constantly increase

Fig. 3 Cyclic voltammograms of AA at different scan rates.
Electrode: SC/CPE (insert a: the plot of $i_p^a$ vs $\nu$; insert b: log $i_p^a$ vs log $\nu$) ($C_{Fe(CN)_6}$: $3.0 \times 10^{-3}$ mol L$^{-1}$ in
BR buffer, pH 3.0)
and the peak potential moves to more positive values. This state represents the irreversibility of oxidation process. As indicated in Fig. 3 (inset a), there is a good linear relationship between the peak current and the scan rate, which indicates that the electrochemical reaction is adsorption-controlled [30].

The linear equation is as follows:

$$i_p = 90.79v + 2.25 (R^2 = 0.988)$$

If the electrochemical reaction proceeds under normal diffusion conditions, the relation between $i_p$ and $v^{1/2}$ is given by the Randles-Sevcik equation [27]:

$$i_p = 2.69 \times 10^{5} n^{3/2} D a^{1/2} C_{eq} v^{1/2}$$

According to this equation, the slope of the log $i_p$ vs log $v$ graph should be close to 0.5 if the process is diffusion-controlled. On the other hand, wherever a pre-adsorption step prevails in the kinetics of the electrochemical reaction, the relation between $i_p$ and $v^{1/2}$ takes the following form [26]:

$$i_p = \frac{nFQ}{4RT}$$

This equation shows that for a strictly adsorption-controlled reaction, the slope of the log $i_p$ vs log $v$ graph should be close to unity.

In our experiments, the slope of log $i_p$ vs log $v$ graph (Fig. 3 inset b) was read to be (0.62 ± 0.06). This value is obviously reflecting a process which is adsorption-controlled under diffusion conditions [31].

The influence of pH on the oxidation peak currents and on the peak potentials was examined by running the CVs at media of different pH values (2.0–6.0; with one unit increments). As seen in Fig. 4(a), up to pH 3.0 the peak current increases with increasing pH but the curve declines at pH 4.0. Thus, pH 3.0 was decided to be the optimum pH for voltammetric quantitative work SC. Figure 4 (inset b) also depicts the relationship between the peak potential and the pH. Apparently, with increasing pH, peak potentials shift to more negative values. Presumably, a deprotonation reaction is involved in the process and the oxidation becomes easier as the medium gets more basic (deprotonation is much likely). There are literature reports supporting this approach [32].

**Optimization of accumulation potential and accumulation time**

The effects of accumulation time and accumulation potential on the peak current obtained with the same concentration of AA were also investigated. To this end, differential pulse adsorptive stripping voltammograms (AdsDPV) were obtained at different potentials (from -0.30 to +0.40 V) range: 0.1 V increments and the peak currents were plotted against potentials (Fig. 5a). A similar graph showing the effect of accumulation time (from 0 to 75 s; 15 s increments) was also obtained to optimize the accumulation time (Fig. 5b). The optimum values for the accumulation potential and the accumulation time were chosen to be -0.1 V and 15 s, respectively.

**Voltammetric determination of AA**

Standard series of AA in the concentration range of $1.0 \times 10^{-8}$–$7.0 \times 10^{-6}$ mol L$^{-1}$ were prepared and AdsDPV voltammograms were recorded using optimum pH, accumulation potential, and accumulation time and they are shown in Fig. 6a. A peak current against AA concentration calibration
Fig. 5 Peak currents obtained from AdsDPV voltamograms to analyze the effect of accumulation potential (a) and accumulation time (b) ($C_{AA}$: 1.0 × 10^{-5} mol L^{-1}, SC/CPE).

![Graphs showing peak currents vs. time and deposition potential](image)

To test the reproducibility of the analytical procedure, three different electrodes were prepared from different batches, but the same proportions, of SC/CPE composite. Using these electrodes, AdsDPV voltamograms of a 7.0 × 10^{-7} mol L^{-1} AA solution were run to measure the peak currents. The averages of three replicate readings with the three electrodes were employed for the statistical analysis. The statistical parameters based on these measurements are listed in Table 1.

From the parameters given in Table 1, the reproducibility (percent RSD) of the peak current and of the peak potential was found to be 2.1 and 0.46%, respectively. The limit of detection (LOD) and limit of quantification (LOQ) values were calculated using the relations LOD = 3σ/m and LOQ = 10σ/m. Here, σ stands for the standard deviation and m, the slope of the calibration curve. LOD and LOQ values were found to be 0.0042 and 0.014 μmol L^{-1}, respectively.

The working range and the LOD of the quantitative volumetric method developed here were compared with the electrochemical literature concerning the quantitative analysis of AA. The comparison is given in Table 2. The table indicates that the measurements done with the electrode system developed are among the best ones (the lowest LOD values). The linear working range is also among the widest ones.

Repeatability and stability

The repeatability of the SC/CPE was evaluated by measuring the volumetric signals of 5.0 × 10^{-6} mol L^{-1} AA solution, 10 times under identical optimum conditions. The RSD of the repeatability was found to be below 4.0%.

The stability of the sensor made up of SC/CPE composite was evaluated by comparing current responses obtained weakly on 7.0 × 10^{-6} mol L^{-1} AA solution for a period of 30 days.
### Table 1  The statistical results of regression analysis

| Method | AdsDPV |  
|---|---|---|---|---|
| Peak potential, V | 0.24 |  
| Slope, mol L⁻¹ (A/L/mol) | 1.35 |  
| Regression coefficient, R² | 0.9980 |  
| Working range, µmol L⁻¹ | 0.014-0.90 |  
| LOD, µmol L⁻¹ | 0.0042 |  
| LOQ, µmol L⁻¹ | 0.014 |  
| Reproducibility of peak current, RSD % (n=5) | 2.1 |  
| Reproducibility of peak potential, RSD % (n=5) | 0.46 |  

RSD is the relative standard deviation of five replications. 

In the confidence limit of 95%, i = 2.57 for N = 5 for all experiments.

### Interference studies

Possible interferences were explored by adding common chemical agents into the BR buffer (pH 3.0) containing 1.0 × 10⁻⁵ mol L⁻¹ AA. These include 1000-fold concentration of Na⁺, Cl⁻, Ca²⁺, Mg²⁺, NO₃⁻, citric acid, and glucose. At these levels, all the chemical species were found to have statistically insignificant effect on the intensity of the peak currents (relative errors <5.0%).

### Analytical application

Using the electrode developed, two different commercial samples (Redoxon tablet and local brand mineral water enriched with AA) were analyzed in relation to AA contents. The AA contents were found by taking the average of five replicate determinations. For each replicate, the AA concentration was calculated.

### Table 2  Comparison of the performances of different electrochemical sensors for the determination of AA

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<td>PBG/GCE</td>
<td>5-300</td>
<td>0.12</td>
<td>Fetid bovine serum</td>
<td>[37]</td>
</tr>
<tr>
<td>DPV</td>
<td>Fe₃O₄/CPE</td>
<td>0.5-1000</td>
<td>0.17</td>
<td>Human serum, tablets</td>
<td>[38]</td>
</tr>
<tr>
<td>DPV</td>
<td>Fe₃O₄/CPE</td>
<td>1-500</td>
<td>0.2</td>
<td>Vc medicine</td>
<td>[39]</td>
</tr>
<tr>
<td>DPV</td>
<td>Fe₃O₄/CPE</td>
<td>0.009-4700</td>
<td>0.251</td>
<td>Pharmaceutical preparations</td>
<td>[12]</td>
</tr>
<tr>
<td>DPV</td>
<td>PNNP/CMP/CPE</td>
<td>3.266-40.51</td>
<td>0.53</td>
<td>Human serum</td>
<td>[40]</td>
</tr>
<tr>
<td>DPV</td>
<td>IL-SWCNT</td>
<td>3.0-4200</td>
<td>1.0</td>
<td>Fruit drink, vegetable extract drinks, tea extract drinks</td>
<td>[2]</td>
</tr>
<tr>
<td>DPV</td>
<td>GNP/GCE</td>
<td>210-1010</td>
<td>2.0</td>
<td>Dopamine Injection Tablets, Human serum, Human urine</td>
<td>[13]</td>
</tr>
</tbody>
</table>

erGO/ImAS/GCE electroreduced graphene oxide imidazolium alloxysilane modified glassy carbon electrode, poly-Tyran/GCE poly-trypan blue modified glassy carbon electrode, ERGO/PLL/GCE electrodeposited reduced graphene oxide poly L-lysine modified glassy carbon electrode, MgO/Gr/Ta MgO nanohell-modified graphene-tantalum wire electrode, PDDA@HCNTs/GCE poly(diallyl dimethyl ammonium chloride) helical carbon nanotubes modified glassy carbon electrode, PBG/GCE poly(bromoresol green) modified glassy carbon electrode, Fe₃O₄/CPE ferric-acetyl acetone chloroquinone self-assembled supramolecular film modified electrode, Fe₃O₄/CPE Fe₃O₄ nanoparticles modified carbon paste electrode, PNNP/CMP/CPE palladium nanoparticles deposited on carbon monolith modified carbon paste electrode, IL-SWCNT ionic liquid and single-walled carbon nanotube modified composite electrode, GNP/GCE gold nanoparticles/oxidized-polyimidazole composite modified glassy carbon electrode, p-A_TD/GCE electropolymerized film of 2-amino-1,3,4-thiadiazole modified glassy carbon electrode, AlA/GCE 3-alanine modified glassy carbon electrode, SC/CPE sepiolite clay-modified carbon paste electrode.
read from the calibration curve. The accuracy of the method was estimated by comparing the results found with the nominal AA contents of the samples. The mean recovery results and the relative standard deviations are listed in Table 3. The recovery data and t test results indicate that the method proposed can be used safely in real-life samples.

The voltammetric method was also applied to AA analysis in dried fruit of R. canina collected from around the town of Nallithan (Ankara). Aqueous extract of fruits was prepared as described in the section “Experimental.” The average of five replicates indicates an AA content of 0.44 g/100 g. AA contents in various samples of R. canina are reported in the range 0.26/100–0.42/100 g [42, 44, 45], which is comparable with our average value.

Conclusion

A simple sensor made up of SC/CPE has been developed for the voltammetric (AdsDPV) determination of AA in beverages and pharmaceutical samples. The sensor has the advantages of ease of preparation, good stability, practical surface regeneration, high precision, low cost, wide linear range, and low detection limit. The electrode proved to be applicable to ascorbic acid assay in real-life samples.

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References