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A new sensor for the simultaneous determination of paracetamol and mefenamic acid in a pharmaceutical preparation and biological samples using copper(II) doped zeolite modified carbon paste electrode

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Abstract A new chemically modified electrode is constructed based on a copper(II) doped zeolite modified carbon paste electrode ($Cu^{2+}Y/ZMCPE$). It is demonstrated that this novel sensor could be used for the simultaneous determination of the pharmaceutically important compounds paracetamol (PAR) and mefenamic acid (MEF). The measurements were carried out using the differential pulse voltammetry (DPV) method. The prepared modified electrode shows voltammetric responses of high sensitivity, selectivity and stability for PAR and MEF under optimal conditions, which makes it a suitable sensor for simultaneous submicromolar detection of PAR and MEF in solution. The oxidation peak current for PAR in Briton Robinson buffer (pH = 10) was measured at various concentrations between 0.25 and 900 μM. (The detection limit was 0.1 μM and S/N was 3.) It proved linear (the correlation coefficient was 0.9987). For the MEF a linear correlation between oxidation peak current and concentration of MEF over the range 0.3–100 μM, with a correlation coefficient of 0.9991 and a detection limit of 0.04 μM, was obtained. The analytical performance of this sensor has been evaluated for the detection of PAR and MEF in human serum, human urine and a pharmaceutical preparation.

Keywords Paracetamol · Mefenamic acid · Copper(II) doped zeolite · Modified carbon paste electrode · Differential pulse voltammetry

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1 Introduction

Paracetamol (PAR) is an important medicine and it extensively is used both in pure form and in pharmaceutical preparations [1]. A non-narcotic analgesic, it is mainly used as an analgesic and antipyretic agent as an effective alternative to aspirin in which the secondary effects of the salicylates on the gastric mucosa are absent [2]. It is often self-prescribed for the relief of moderate pain, fever, lumbar pain, migraine or for non-specific indications [3]. It has been reported as a useful drug in osteoarthritis therapy [4]. However an overdose of PAR can lead to the accumulation of toxic metabolites, which may cause severe and some times fatal hepatotoxicity [5–7]. It can also cause liver disorders, skin rashes and inflammation of the pancreas [8]. Several analytical techniques such as titrimetry [4], spectrophotometry [9], spectrofluorometry [10], voltammetry [11], HPLC [12], TLC [13], colorimetry [14] and FTIR [15] have been proposed for the determination of PAR in pharmaceutical formulations and biological samples. Mefenamic acid (MEF) is also a nonsteroidal antiinflammatory drug with analgesic and antipyretic properties. It is used to relieve the symptoms of conditions such as rheumatoid arthritis, osteoarthritis, nonarticular rheumatism and sports injuries [16, 17]. Overdoses of MEF can lead to toxic metabolite accumulation that causes acute hepatic necrosis, and can result in morbidity and mortality in humans [18]. For this drug analytical methods including spectrophotometry [19], chromatography [20], chemiluminescence [21], capillary electrophoresis [22], potentiometry [23], polarography [24], and voltammetry [25] have been proposed for the determination.

Combinations of MEF with PAR are frequently prescribed as analgesics and anti-inflammatory agents in rheumatoid arthritis and overdoses of these can lead to

toxic effects. Most of the proposed methods for simultaneous determination of these compounds are based on UV–VIS spectrophotometry [26], NMR [27] and HPLC [28] techniques. However, in the case of spectrophotometry the absorption peaks of PAR and MEF overlap, so for the simultaneous determination of these compounds complicated techniques involving chemometric methods or first derivative of the ratio spectra are necessary. The other proposed methods all suffer from some disadvantages, such as high costs, long analysis times and requirement for sample pretreatment. In addition, in some cases, low sensitivity and selectivity makes them unsuitable for routine analysis. Consequently, the development of a simple, inexpensive, sensitive and accurate analytical method for simultaneous determination of PAR and MEF is of considerable importance.

Both PAR and MEF are electroactive compounds that can be oxidized electrochemically. To the best of our knowledge there has been no report of the use of an electrochemical sensor for the simultaneous determination of PAR and MEF. Copper(II) shows a tendency towards complex formation with both PAR[29] and MEF [30]. In this work we present for the first time the use of a copper(II) doped zeolite modified carbon paste electrode (Cu^{2+}Y/ZMCPE) as a sensor for simultaneous determination of PAR and MEF. The preparation of the electrode is outlined. The analytical performance of this sensor for the determination of PAR and MEF in typical tablets, human urine and human serum samples is then evaluated using the differential pulse voltammetry (DPV) method.

2 Experimental

2.1 Reagents and solutions

All chemicals were analytical grade and used without further purification. PAR (MW 151.16 g mol^{-1}) and MEF (MW 241.3 g mol^{-1}) were obtained from Merck and Sigma chemical companies, respectively. Stock standard solutions of 10 mM PAR and 10 mM MEF were freshly prepared in triply distilled water and ethanol respectively. All PAR and MEF solutions were prepared by diluting the stock standard solutions with triply distilled water. Briton Robinson buffers were prepared by initially dissolving 10.1 mL concentrated orthophosphoric acid, 8.7 mL concentrated acetic acid and 9.27 g boric acid in water and diluting to 1.0 L in a volumetric flask. This solution was subsequently used to prepare appropriate buffers by addition of 7.5 M sodium to reach the desired pH value. Voltammetric experiments on PAR and MEF were carried out in 0.15 M Briton Robinson buffer of pH 10. Zeolite NaY

was synthesized in our laboratory using the previously reported method [31].

Fresh human serum samples were obtained from from Razi Institute of Vaccine and Serum Company (Tehran, Iran). Before being used for spiking with PAR and MEF this serum was filtered, and diluted 500 times with a 0.15 M Briton Robinson buffer solution of pH 10. Ten tablets of Tylenol (McNeil-PPC Inc., USA) (labeled as 500 mg PAR content) were accurately weighed and powdered in a mortar. An amount equivalent to one tablet was initially dissolved in 70 mL of distilled water. After 10 min sonication, the solution was filtered and the residue washed three times with 10 mL of distilled water. This was added to the solution and the total volume adjusted to 100 mL by the addition of more water. This solution was diluted 800 times using a 0.15 M Briton Robinson buffer solution of pH 10 before being used for the determination of the recovery in spiking of PAR and MEF.

2.2 Instrumentation

All the voltammetric measurements were carried out using modified carbon-paste (Cu^{2+}Y/ZMCPE) as the working electrode, Ag/AgCl/3 M KCl as the reference electrode, and platinum wire as the auxiliary one. Differential pulse voltammetry (DPV) experiments were carried out with a pulse amplitude of 50 mV, a scan rate of 20 mV s^{-1} and a pulse interval of 0.3 s, using an Autolab PGSTAT 30 Potentiostat Galvanostat (EcoChemie, The Netherlands) coupled with a 663 VA stand (Metrohm Switzerland). All potentials given are with respect to the potential of the reference electrode. The pH measurements were performed with a Metrohm 744 pH meter using a combination glass electrode.

2.3 Preparation of the copper(II) doped zeolite-modified carbon paste electrode

One gram of NaY zeolite was lightly ground, immersed in 250 mL of 0.01 M CuCl$_2$ solution and stirred for 48 h. The Cu^{2+} exchanged zeolite was carefully washed with HCl solution (pH = 2) to remove any occluded material and surface-adherent salt, with triply distilled water to remove chloride ion and then dried in air.

The zeolite-modified electrode was prepared by mixing (by weight) 60% of graphite, 10% of zeolite powders and 30% of mineral oil. To obtain better homogeneity the resulting composite was suspended in diethyl ether and the mixture stirred by a magnetic stirrer until the solvent evaporated. The prepared modified electrode composite was then air-dried for 24 h. The paste obtained was packed into the end of an insulin syringe (i.d. 2 mm) and arranged with copper wire serving as external electrical contact. The

unmodified carbon paste electrode (CPE) used for comparison purposes, was prepared in the same way as the $Cu^{2+}Y/ZMCPE$ one above, with the copper(II) doped zeolite omitted. The surface was smoothed on a piece of weighing paper.

2.4 General procedure

Solutions (10 mL) containing appropriate amounts of PAR and MEF in 0.15 M Briton Robinson buffer at pH 10 were transferred into the voltammetric cell. The differential pulse voltammograms were recorded by applying positive-going potentials from 0.0 to 0.8 V. The voltammograms showed anodic peaks around 0.3 and 0.5 V corresponding to PAR and MEF of heights proportional to their concentrations in solution. The calibration curves were obtained by plotting anodic peak currents of PAR and MEF versus the corresponding concentrations. All experiments were carried out under open circuit conditions.

After each measurement, the $Cu^{2+}Y/ZMCPE$ was regenerated by pushing an excess of paste out of the tube, removing the excess, and mechanically polishing the electrode surface.

3 Results and discussion

3.1 Characterization of the copper(II) doped zeolite

The FTIR spectrum of the copper(II) doped NaY zeolite (not shown) was obtained. There were three significant peaks at about 1010, 688 and 457 cm^{-1}, which were assigned to internal the internal vibrations of the TO_4 (T = Si, Al) tetrahedral moiety. A broad peak around 3,489 cm^{-1} was related to the OH stretching vibration of of the T-OH groups. A small peak at 826 cm^{-1} was assigned to an interaction between a Cu(II) ion and the zeolite frame work. We have previously reported the presence of similar peaks in Fe(III) doped zeolite modified carbon paste electrodes [32]. The amount of copper ion present in the doped zeolite was calculated to be 10.25% (w/w) based on atomic absorption spectroscopy determination of the residual amount of copper ion in the solution after copper(II) doped zeolite preparation procedure.

3.2 Voltammetric characteristics of paracetamol and mefenamic acid

The differential pulse voltammograms recorded for paracetamol and mefenamic acid at bare carbon paste (CPE), zeolite modified carbon paste (ZMCPE) and Cu(II) doped modified carbon paste ($Cu^{2+}Y/ZMCPE$) electrodes, are shown in Fig. 1. Voltammogram **a** is that for a solution
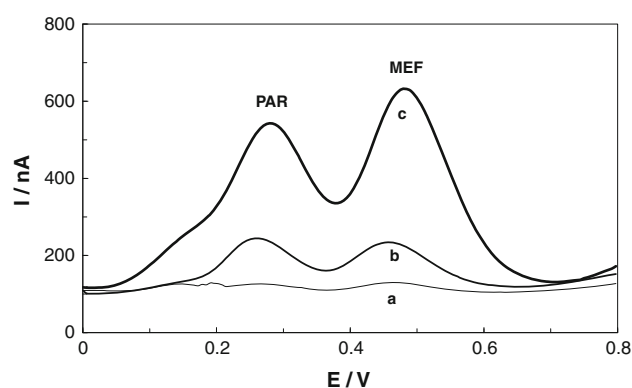
Fig. 1 Differential pulse voltammograms for 50 μM of PAR and 25 μM MEF at (*a*) bare carbon paste; (*b*) zeolite modified carbon paste and (*c*) Cu(II) doped modified carbon paste electrodes in Briton Robinson buffer (pH 10). Other conditions: open circuit, $t_{acc} = 15$ s; electrode modifier percent = 10% (w/w); pulse amplitude = 50 mV and scan rate = 20 mV s^{-1}

50 μM in PAR and 25 μM in MEF in Briton Robinson buffer (pH of 10) at CPE, while **b** and **c** display are those for PAR and MEF under the same at the ZMCPE and the $Cu^{2+}Y/ZMCPE$ respectively. As can be seen from the CPE, a very small oxidation peak is observed for both PAR and MEF. At the ZMCPE slight enhancements of the oxidation peak currents for PAR and MEF were observed. The DPV **c** for PAR and MEF at $Cu^{2+}Y/ZMCPE$ showed excellent improvement in oxidation peak currents for PAR and MEF oxidations. There have been reports of a tendency for complex formation between copper(II) and PAR [29] and MEF [30]. Therefore it is possible that more of the PAR and MEF could be accumulated on the electrode surface due to their interaction with copper(II).

Consequently, the use of $Cu^{2+}Y/ZMCPE$ leads to enhancement of the current sensitivity and selectivity in simultaneous determinations of PAR and MEF.

3.3 Effect of operational parameters

Any variation of the accumulation potential has no significant effect on the proposed electrochemical sensor response, so all measurements were carried out at open circuit condition.

3.3.1 Effect of pH

The effect of solution pH on the electrochemical response of the $Cu^{2+}Y/ZMCPE$ in the simultaneous determination of 50 μM PAR and 25 μM MEF was investigated. The variations of peak current with the pH of the electrolyte in the 8–12 range are shown in Fig. 2. The anodic peak current of the PAR increases with pH until it reaches 10. In this region, as the pH rose PAR (pK_a 9.5) would become increasingly deprotonated to form an anion. This anion
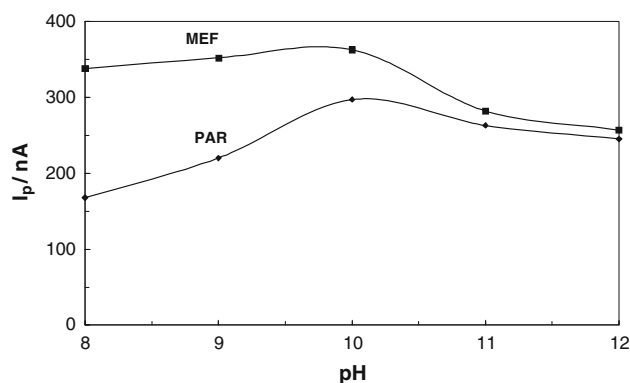
Fig. 2 Effect of pH on the peak currents of oxidations of PAR and MEF at a Cu(II) doped modified carbon paste electrode in Briton Robinson buffer solutions. Concentrations: PAR: 50 μM and MEF: 25 μM. Other conditions are as for Fig. 1

would be attracted to the positively charged electrode surface and complex with the copper(II). The oxidation peak current for MEF remains relatively unchanged over the same range, This is not unexpected as, with a pK_a of 4.25 MEF is completely deprotonated under the conditions. At higher pH values (>10) the anodic peak currents for both PAR and MEF start to diminish. These phenomena were assigned to competition between the anionic structures of PAR and MEF and hydroxide ions to accumulate on the electrode surface. For this reason the optimum solution pH of 10 was chosen for further experiments.

3.3.2 Effect of accumulation time

Figure 3 shows plots of the differential pulse anodic peak currents against accumulation time for 50 μM PAR and 25 μM MEF. Initially, peak currents for these compounds increase with accumulation time up to 15 s. However after 15 s the peak current increase slows and then plateaus. As a consequence, the accumulation time of 15 s was chosen as an optimum time for further experiments.
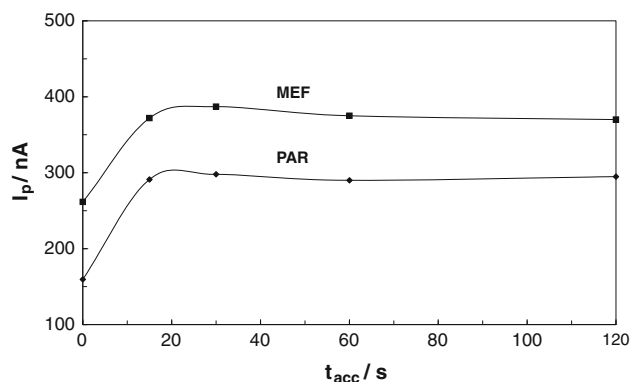
Fig. 3 Effect of accumulation time on the peak currents of 50 μM PAR and 25 μM MEF in Briton Robinson buffer (pH 10) solution. Other conditions are as for Fig. 1
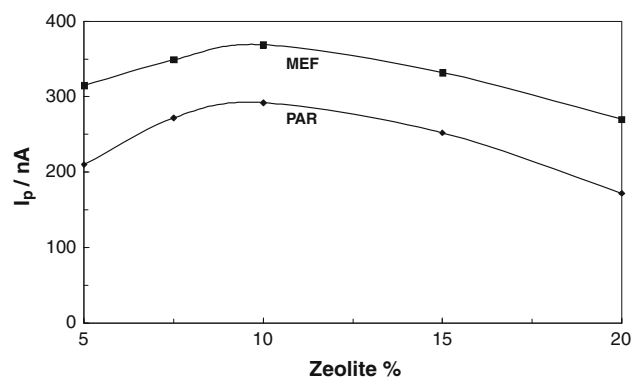

Fig. 4 Effect of modifier percent on the peak current of 50 μM PAR and 25 μM MEF at accumulation time of 15 s. Other conditions are as for Fig. 1

3.3.3 Effect of modifier concentration

The effect of Cu^{2+} doped zeolite as a modifier in the composition of Cu^{2+}Y/ZMCPE is shown in Fig. 4. The results show that the anodic peak current of PAR and MEF reach their highest values at 10% modifier. Higher concentrations of the modifier lead to a decrease in peak current. This is presumably due to a reduction in the conductivity of the electrode resulting from the decrease in graphite powder concentration. For this reason a carbon paste composition of 10% modifier zeolite, 60% graphite and 30% mineral oil was chosen in further studies.

3.4 Linear range, detection limit and reproducibility of the method

In order to verify the linear relationship between the anodic peak currents and PAR and MEF concentrations several calibration curves were constructed using the selected optimum conditions in 0.15 M of Briton Robinson buffer (pH 10). Figures 5 and 6 show differential pulse voltammograms and their corresponding calibration curves obtained at Cu^{2+}Y/ZMCPE for various concentrations of PAR and MEF, respectively. Figure 5 shows the DPV and corresponding calibration curve (inset) for various concentrations of PAR in the presence of 15 μM MEF. Over a linear dynamic range from 0.25 to 900 μM, a calibration equation of Ip (nA) = 5.1762c (μM) + 104.9 (R^2 = 0.9987) was obtained with a detection limit of 0.1 μM (S/N = 3) were obtained. For MEF a similar linear relationship was observed over the range of 0.3 to 100 μM containing 50 μM PAR. Here a calibration equation of Ip (nA) = 13.78c (μM) + 43.2 (R^2 = 0.9991) was obtained with a detection limit of 0.04 μM (Fig. 6). Similar calibration graphs for determination of PAR or MEF in the presence of different concentrations of MEF or PAR were obtained, indicating that they do not interfere in the determination of each other.
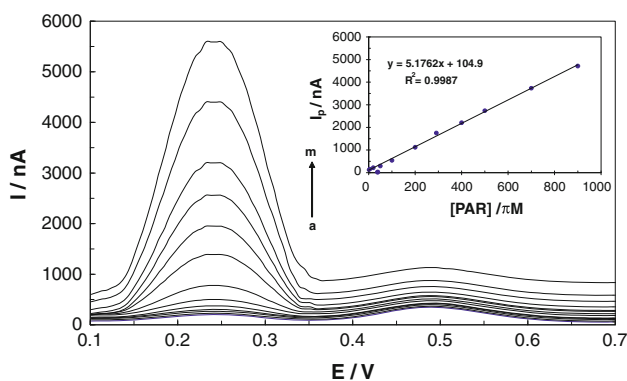
Fig. 5 Differential pulse voltammograms for (*a*) 0.25, (*b*) 0.5, (*c*) 1.0, (*d*) 5.0, (*e*) 20.0, (*f*) 50.0, (*g*) 100.0, (*h*) 200.0, (*i*) 300.0, (*j*) 400.0, (*k*) 500.0, (*l*) 700.0 and (*m*) 900.0 μM of PAR in the presence of 15.0 μM MEF at optimum conditions
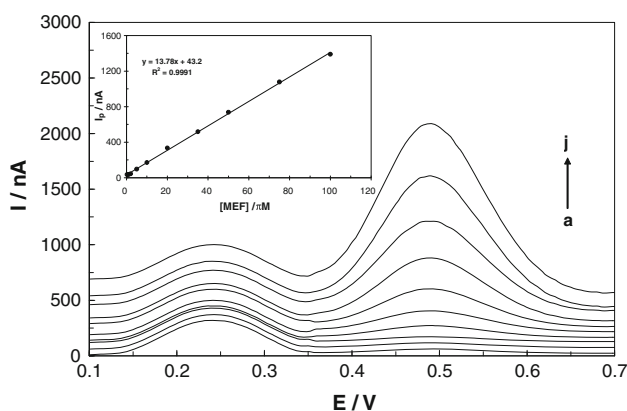
Fig. 6 Differential pulse voltammograms for (*a*) 0.3, (*b*) 1.0, (*c*) 2.0, (*d*) 5.0, (*e*) 10.0, (*f*) 20.0, (*g*) 35.0, (*h*) 50.0, (*i*) 75.0, and (*j*) 100.0 μM of MEF in the presence of 50.0 μM PAR at optimum conditions

3.5 Effect of interferences

The influences of common interfering species were investigated for solutions of 50 μM PAR and 25 μM MEF under optimum conditions. The results showed that concentrations of tyrosine (80), uric acid (800), ascorbic acid (200), dopamine (70), D-glucose (600), L-glutamic Acid (1,600) and phenol (500) did not significantly affect the height of the peak currents. (The data in the brackets are concentrations of the interfering species in μM.) The tolerance limit was defined as the concentrations that give an error of ≤10% in the determination of the two compounds.

3.6 Analytical applications

The applicability of the $Cu^{2+}Y/ZMCPE$ to the determination of PAR and MEF in human serum, human urine and drug samples was examined. The differential pulse voltammograms were obtained by spiking appropriate samples

Table 1 Determination of PAR and MEF in human serum with $Cu^{2+}Y/ZMCPE$

Analyte	Added (μM)	Found[a] (μM)	RSD (%)	Recovery (%)
PAR	20	19.5 (19.8)[b]	3.2 (1.8)[b]	97.5 (99.0)[b]
	40	39.3 (39.7)[b]	2.9 (1.9)[b]	98.2 (99.2)[b]
	60	61.0 (59.6)[b]	3.5 (1.5)[b]	101.6 (99.3)[b]
MEF	10	10.3 (10.2)[b]	2.5 (2.0)[b]	103.0 (102.0)[b]
	30	29.0 (29.7)[b]	3.1 (1.8)[b]	96.7 (99.0)[b]
	50	51.0 (49.9)[b]	3.3 (1.9)[b]	102.0 (99.8)[b]

[a] Average of five determinations at optimum conditions

[b] The amounts in the parenthesis were obtained using spectrophotometric method

Table 2 Determination of PAR and MEF in urine sample with $Cu^{2+}Y/ZMCPE$

Analyte	Added (μM)	Found[a] (μM)	RSD (%)	Recovery (%)
PAR	20	19.8 (20.1)[b]	3.9 (1.9)[b]	99.0 (100.5)[b]
	40	39.0 (40.4)[b]	3.5 (1.7)[b]	97.5 (101.0)[b]
	60	61.3 (59.8)[b]	2.5 (1.8)[b]	102.1 (99.6)[b]
MEF	10	10.2 (9.9)[b]	3.0 (2.0)[b]	102.0 (99.0)[b]
	30	29.6 (30.3)[b]	2.8 (1.7)[b]	98.7 (101.0)[b]
	50	50.5 (50.2)[b]	3.6 (1.8)[b]	101.0 (100.4)[b]

[a] Average of five determinations at optimum conditions

[b] The amounts in the parenthesis were obtained using spectrophotometric method

in the prepared solutions using $Cu^{2+}Y/ZMCPE$ at optimum conditions as described earlier. The concentrations were obtained by applying calibration plot. The results are shown in Tables 1, 2, 3. The amounts shown in the parenthesis were obtained using UV–Vis spectroscopy method, similar to previously reported [33], for comparison with our proposed method. The results obtained by the currently developed method are very close to the spectroscopy method, which prove its validity for determination of PAR and MEF by this method. Even though the RSD%

Table 3 Determination of PAR and MEF in Tylenol tablet with $Cu^{2+}Y/ZMCPE$

Analyte	Added (μM)	Found[a] (μM)	RSD (%)	Recovery (%)
PAR	0	41.1[b] (41.0)[c]	3.1 (1.8)[c]	99.2 (99.1)[c]
	10	50.9 (51.2)[c]	2.8 (1.9)[c]	98.0 (101.0)[c]
	20	61.5 (61.4)[c]	2.9 (1.6)[c]	102.0 (101.5)[c]
MEF	10	10.3 (9.8)[c]	2.8 (2.0)[c]	103.0 (98.0)[c]
	20	19.7 (20.2)[c]	3.2 (1.8)[c]	98.5 (101.0)[c]
	30	30.4 (30.2)[c]	2.7 (1.9)[c]	101.3 (100.6)[c]

[a] Average of five determinations at optimum conditions

[b] This amount is equal to 496.1 mg per tablet

[c] The amounts in the parenthesis were obtained using spectrophotometric method

obtained from spectroscopy method were slightly smaller, however this method has disadvantage of overlapped spectra, when mixture of PAR and MEF were used, as mentioned earlier. The recoveries for the proposed method were acceptable, showing that the method could be efficiently used for the determination of trace amounts of these compounds in biological systems and pharmaceutical preparations.

3.7 Repeatability and long-term stability of the electrode

The main advantage of using the $Cu^{2+}Y/ZMCPE$ is the ease and speed with which the surface can be renewed after each use. For this reason the repeatability of the analytical signal was studied. A relative standard deviation (RSD) of 3.14 and 2.23% for 75 μM PAR and 50 μM MEF respectively in ten consecutive determinations was obtained.

Another attraction of the proposed modified electrode is that the resulting carbon paste electrode has good long-term stability both for measurements in solution and for storage in air. The first was tested by measuring the decrease in voltammetric current during repeated DPV measurements on solutions containing 50 μM PAR and 25 μM MEF in 0.15 M Briton Robinson buffer solution (pH 10), Subjecting the modified electrode to an experiment every 30 min for up to 24 h led to no significant changes in the voltammetric currents. For the second, storage of the electrode in air for 1 month left its current response almost unchanged. This high stability of the zeolite-modified carbon paste electrode could be related to the strong affinity of zeolite Y for Cu(II) ion [34] and insolubility of the zeolite in water.

4 Conclusion

In this paper we introduced a new electrode based on a copper(II) doped zeolite modified carbon paste. Copper(II) loaded zeolite can increase anodic peak currents probably by adsorption of the paracetamol and mefenamic acid on the electrode surface. The results indicate that $Cu^{2+}Y/ZMCPE$ allows the simultaneous determination of PAR and MEF with good sensitivity and selectivity. The electrode showed high stability in repetitive experiments due to the high affinity of zeolite Y for copper(II) and the low solubility of the zeolite in water. The effects of potential interfering ions were studied, and it was found that the proposed procedure is free from interference from most common interfering ions and organic compounds. The proposed sensor was used in determination of PAR and MEF in some real samples like human serum, urine and

some drugs, without the necessity of sample pretreatments or time-consuming extraction or overlapped data analysis, with satisfactory results. The simple fabrication procedure, high speed, reproducibility, high stability, wide linear dynamic range, low detection limit, high sensitivity and a distinct advantage of polishing in the event of surface fouling, suggest that the proposed sensor is an attractive candidate for practical applications.

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