Pencil Graphite Electrodes: A Versatile Tool in Electroanalysis

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Received 22 August 2016; Revised 19 December 2016; Accepted 4 January 2017; Published 31 January 2017

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Due to their electrochemical and economical characteristics, pencil graphite electrodes (PGEs) gained in recent years a large applicability to the analysis of various types of inorganic and organic compounds from very different matrices. The electrode material of this type of working electrodes is constituted by the well-known and easy commercially available graphite pencil leads. Thus, PGEs are cheap and user-friendly and can be employed as disposable electrodes avoiding the time-consuming step of solid electrodes surface cleaning between measurements. When compared to other working electrodes PGEs present lower background currents, higher sensitivity, good reproducibility, and an adjustable electroactive surface area, permitting the analysis of low concentrations and small sample volumes without any deposition/preconcentration step. Therefore, this paper presents a detailed overview of the PGEs characteristics, designs and applications of bare, and electrochemically pretreated and chemically modified PGEs along with the corresponding performance characteristics like linear range and detection limit. Techniques used for bare or modified PGEs surface characterization are also reviewed.

1. Introduction

Graphite has both metallic and nonmetallic properties being thus useful as electrode material. According to Chehreh Chelgani et al. [1] 4% of the world graphite is used to produce pencils consisting of fine graphite powder in an inorganic (resin) or organic matrix (clay or a high polymer, e.g., cellulose). The pencil graphite leads are composite materials containing graphite (∼65%), clay (∼30%), and a binder (wax, resins, or high polymer) [2]. According to the European Letter Scale graphite pencils are marked with letters H (hardness) and B (blackness) and numbers indicating the degree of hardness or blackness from 9H (the hardest) to 8B (the softest). B type leads contain more graphite and are softer, and the harder H-type leads have more lead, whereas HB type pencil leads contain equal portions of graphite and clay [3–7]. Kariuki [5] showed that the added clay has an important influence on the chemical (e.g., ion exchange) and structural properties (e.g., degree of disorder and surface morphology) of the pencil graphite leads.

Aoki et al. [8] reported for the first time about the application of graphite reinforcement carbon (GRC), commonly employed as mechanical pencil leads, as voltammetric electrodes. The large commercial availability of GRC as graphite leads for mechanical pencils having low content of heavy metals impurities and high quality, controlled by the producer, along with all the other electrochemical features of the carbon-based electrodes led to the development of this type of disposable sensors.

Pencil graphite leads used as working electrodes are currently known as pencil graphite electrodes (PGEs). Besides the fact that they are cheap, PGEs are also easy to use and more convenient and there is no time-consuming electrode surface cleaning/polishing step. Applying different types of voltammetric techniques in order to quantify a variety of analytes from a wide range of samples, the used PGEs showed reproducible signals, yielding well-defined voltammetric peaks. These electrodes have proven to provide good sensitivity and reproducibility, being a viable, renewable, and economical tool.

Tavares and Barbeira [6] determined that most pencil leads, independent of the producer and hardness, have electrical resistance lower than 5 ohm, being thus suitable as electrode material. As a result of cyclic voltammetry (CV) studies,
these authors also concluded that harder pencil leads present higher voltammetric signals and separation of the peak potentials are closer to the theoretical value for reversible systems. Despite the fact that Aoki et al. [8] reported that there were no differences between voltammograms of the [Fe(CN)₆]⁢⁢³⁻/⁴⁻ and [Ru(NH₃)₅SO₄]³⁺/²⁺ redox couples recorded on GRC with different hardness, the nature of the pencil lead type influences the voltammetric response of the investigated analyte; for example, B pencil leads exhibited the best signal for the indirect determination of boron in the presence of tiron [4] and 6B leads were optimum for phenol and m-cresol differential pulse voltammetry (DPV) [9], whereas HB pencil leads were chosen for polyphenolic acids determination [10, 11]. Based on CV studies on K₃[Fe(CN)₆], Gong et al. [3] concluded that soft B type PGEs with large diameter enable an easy electron transfer generating thus higher signals and are proper for quantitative determinations, whereas small diameter H-type pencil leads provide better reversibility, being more adequate for qualitative investigations. According to Kariuki et al. [12] HB#2 graphite leads have electron transfer rates similar to glassy carbon electrodes (GCE).

Due to different interactions between an analyte and the common components of a graphite pencil lead, it is possible that electroactive species exhibit different voltammetric behavior on graphite pencil leads of the same hardness but are produced by various manufacturers [6].

As it was already mentioned, nowadays PGEs gain even more applicability in the electroanalysis of very different types of analytes from various matrices and not only. A careful literature search revealed that there are some reviews related to different types of carbon-based electrodes and different application areas of these electrodes and some of them mention also the PGEs [13]. A very recent review presented a history of the use of graphite pencils as electrodes and highlighted the application of PGEs in the analysis of environmental samples [14], but, to the best of our knowledge, there is no paper presenting an overview of general PGEs developments and applications. Therefore, this work is intended to review mainly the analytical applications of bare and modified PGEs along with their performance characteristics. A brief review of the methodologies of electrode surface modification in order to improve the sensitivity and selectivity of the detection method is also included. Moreover, practical examples of the most used techniques for surface characterization are given. It must be mentioned that a huge amount of literature data is related to PGE based biosensors and DNA-modified PGEs, but these types of sensors will constitute the topic of another review paper.

2. Discussions

2.1. PGE Characteristics and Comparison to Other Carbon-Based Electrodes. The electrode material of the PGE is represented by a general purpose writing pencil offering the advantages of being user- and environmental-friendly (it is nontoxic), largely commercially available, and simple to purchase at low costs (e.g., in Romania the graphite pencil lead used for one PGE costs less than 0.04€), being thus a disposable and readily renewable electrode. According to Kariuki et al. [12] the cost per electrode is approximately at least 190$ for GCE and 0.13$ for PGE.

The GRC contained in pencil leads is not as rigid as glassy carbon (GC) but it is more rigid than carbon paste (CP) or pyrolytic carbon (PC) [6, 8].

Like the other carbon-based working electrodes (GC, PC, CP, or CF (carbon fiber)) the PGE presents high (chemical and mechanical) stability, a large working potentials window (e.g., −0.8 to 0.8, −1.0 to 0.8, and −0.8 to 0.6 V versus SCE in H₂SO₄, KCl, and NaOH solutions, resp.), which could be extended to more negative values in comparison to metallic (Au or Pt) electrodes [8]. Perdicakis et al. [15] investigated the accessible electroactivity ranges of PGE in different media and the electron transfer rates of model redox couples [Fe(CN)₆]⁢³⁻/⁴⁻ and [Ru(NH₃)₅SO₄]³⁺/²⁺.

The reproducibility of the voltammetric determinations on solid electrodes is highly dependent on the reproducibility of the electrode active surface, usually ensured by cleaning/polishing/pretreatment of the surface before each recording. These are time-consuming steps which also may destroy the crystalline structure of the graphite. These drawbacks can be eliminated by using disposable graphite pencil leads which can be easily and rapidly replaced, shortening thus the analysis time. Due to the strictly controlled quality of the pencil leads during their manufacturing, uniform composition and surface are provided and the analytes voltammetric signals recorded on individual PGEs of the same type are very similar resulting in a good electrode-to-electrode reproducibility [8]. Therefore, PGEs provide a convenient surface renewal which leads to a good reproducibility of the voltammetric determinations [16]. Even in the early period of use, PGEs represented by GRC proved a good reproducibility, durability, and stability [8, 17].

According to Kariuki et al. [12] more reproducible results (as indicated by the percent relative standard deviations (RSD%) of the peak potentials and areas) were obtained in electrochemical studies on ferricyanide and gallic acid and for the DPV determination of antioxidants in various samples when a disposable wooden PGE was used instead of a CGE or a mechanical PGE, because all the measurements performed during the entire experiment were made on the same HB#2 pencil lead. Vestergaard et al. [18] presented RSD% for the peak potentials and peak heights of <5.0% and <10.0% obtained for eight flavonoids and of 1.7% and 3.2% for a copper solution, respectively.

The reproducibility and stability of the signals showed by the PGEs in correlation with the lead length (until 4 mm) were studied, obtaining very good results for all the lengths [19].

Recently, a study related to the voltammetric determination of strontium ranelate using an unmodified PGE indicated a good reproducibility of the results, similar or even better to those for a CPE and a GCE [20].

Özcan and Şahin [21] reported good fabrication reproducibility (RSD 2%) for the electrochemically treated PGEs (ETPGEs). Intra- and interday precision of the chlorpromazine DPV analysis using an ETPGE were expressed as percentage relative standard deviation of 2.2 and 4.8%, respectively [22].
Bond et al. [23] reported that PGEs give small background currents generated by the clays and polymers contained in the pencil lead but, nevertheless, these currents are lower than those presented by the conventional solid electrodes, like glassy carbon, gold, and platinum [24], but higher than those of boron doped diamond electrodes [25]. Several authors enumerate among others the low background current as an important feature of the PGEs [19, 26–33]. According to Wang et al. [16], the nongraphitic components of PGEs do not give any background signal, but the different types of pencil leads with different compositions of polymers and clays, besides graphite, and roughness have different response characteristics, the most advantageous being HB pencil leads, generating a high analyte (i.e., guanine) signal and relatively low noise. Thus, even if PGEs present background currents, they can be corrected by the advanced data processing programs of the computerized instruments leading to good signal-to-noise ratios [25].

Due to their large active electrode surface area (e.g., 0.255 cm² for PGE compared to 0.0951 cm² for CPE [26]), the PGEs can be used to analyse low concentrations and small volume samples without any preconcentration/deposition step, reducing thus the analysis time [18]. They can also be miniaturized and easily modified [34].

The high electrochemical reactivity of PGEs may be due to the irregular pencil graphite surface morphology which may enhance the active surface area of the electrode, whereas the edge plane sites on the surface result in a better electron transfer and a higher resistance to surface passivation [35]. Comparing voltammograms recorded on PGE with those obtained on GCE some authors attributed the higher peak intensities obtained on PGE to the clay [5] that generates a porous structure and a high specific surface area of the pencil graphite and to a good electrocatalytic effect of the pencil graphite on the electrode process of some analytes (e.g., acyclovir [27], eugenol [36], and niclosamide [37]).

Different papers reported comparisons between the performances of PGEs and other electrodes related to the electroanalysis of different compounds. The lead of a mechanical pencil, that is, GRC electrode, exhibited a well-defined reduction peak of ozone in acidic media, presenting better performances than GC, Au, or Pt for the detection of this analyte [38], whereas the boron voltammetric signal is six times higher and has a lower oxidation potential on PGE than on GCE [4]. Using square wave voltammetry (SWV), Kawde [39] reported that a Bi-GCE presents better sensitivity than Bi-PGE for the simultaneous determination of Pb(II), Cd(II), and Zn(II) from water samples, but Bond et al. [23] demonstrated the better performance of the “low tech” renewable PGE with respect to the “high tech” GCE by comparing the data obtained for cadmium and lead (ng mL⁻¹ range) stripping voltammetric analysis on in situ mercury film coated electrodes, whereas 5H pencil leads are used as working electrode for the acetalophenon detection in a home-made flow-through electrochemical cell performed similarly with the GCE [40]. Rubianes and Rivas [41] compared the performances of different carbon-based electrode materials, among them being graphite as PGE, as support for a melanin type polymer sensor developed for the dopamine amperometric determination. The proper electrode material was GC, whereas electrodes based on graphite (i.e., pencil graphite and graphite paste) were not suitable for this task, probably due to their inherent high electroactivity. CV studies performed on a ferricyanide solution using GCE, mechanical PGE (M-PGE), and wooden PGE (W-PGE) emphasized that W-PGE behaves similar to GCE and superior to M-PGE in terms of electron transfer kinetics. With respect to SWV analysis of gallic acid (GA) all electrodes demonstrated similar linearity, but the W-PGE exhibited a higher sensitivity. Despite the fact that the limits of detection (LD) obtained with the investigated electrodes are of the same order of magnitude, the lowest LD, 2.93 · 10⁻⁴ M GA, was obtained using M-PGE. The applicability of W-PGE as an antioxidant sensor was tested on fruit and vegetable extracts, hot beverages, dopamine, and uric acid, presenting in all cases more intense peaks than GCE [12]. CV measurements of ascorbic acid emphasized that PGE gives similar results with those obtained with more expensive carbon electrodes [42].

Adenine and adenine-copper complexes present higher signals on PGE than on CPE along with a peak shift towards lower potentials and the electrolyte discharge appearing at higher positive potentials enabling thus more sensitive determinations and indicating an easier electrode process and a larger potential range for voltammetric measurements, respectively [43].

Cyclic voltammetric peaks of vitamin B1 and B6 were more intense when recorded on PGE than on GC and Pt electrodes [44] and those of famotidine have about 1.4 times higher sensitivities on PGE compared with GCE [45]. Our studies revealed that polyphenolic acids presented the best shaped and most intense oxidation peaks on PGE in comparison to GC and Pt electrodes. The high sensitivity of the DPV on the PGE determination of these antioxidants was also emphasized by the attained LD (i.e., 8.83 · 10⁻⁸, 7.93 · 10⁻⁹, and 7.14 · 10⁻⁹ M for caffeic [10], rosmarinic [11], and chlorogenic acid [46], resp.), which are among the lowest LDs reported in the literature for other similar studies. α-Naphthol gave a high, well-defined peak at PGE, whereas it did not respond well at GC, CP, Pt, and Au electrodes. Electrochemical treatment of PGE increased the sensitivity of the determination resulting in a very low LD of 1.5 nM [47].

The higher sensitivity of PGE in comparison to CPE and GCE was also demonstrated by the LDs obtained for strontium ranelate of 0.17, 0.24, and 0.39 µg mL⁻¹ for peak 1 and 0.19, 0.27, and 0.51 µg mL⁻¹ for peak 2, respectively [20]. The LD and limit of quantification (LQ) of dantrolene sodium obtained at PGE (0.052 and 0.158 µg mL⁻¹) and GCE (0.095 and 0.289 µg/mL) [48] indicate a more sensitive determination on PGE. Other proofs of the high sensitivity of the voltammetric determinations using PGE as working electrode are the low LDs and LQs values recorded for flutamide (1.55 · 10⁻⁸ M and 5.16 · 10⁻⁸ M), irinotecan (1.68 · 10⁻⁹ and 5.69 · 10⁻⁹ M) [49], capsaicin (3.7 · 10⁻⁹ M and 1.2 · 10⁻⁸ M), dihydrocapsaicin (9.1 · 10⁻¹⁰ M and 3.0 · 10⁻⁹ M) [25], and paclitaxel (2.46 · 10⁻⁹ M and 8.23 · 10⁻⁹ M) [26], respectively.
2.2. Designs of PGE. The most commonly used design of a PGE consists in a pencil lead introduced in a commercially available mechanical pencil acting as holder. A certain length of the lead remains outside the pencil. In order to maintain a constant electroactive surface area the pencil holder is kept in upright position and always a constant length of the pencil rod is introduced in the solution to be analysed [10, 11, 21, 24, 25, 43–45, 49–61]. Other authors reported the direct connection of the PGE to the potentiostat cable [62] or the mounting of the PGE on an improvised electrode clip [63]. One paper describes the sealing with epoxy of the graphite lead into a syringe acting as holder. 1 cm of one lead end remained outside the holder, whereas at the other end a copper wire was attached [28]. In other studies a pencil lead graphite disc electrode is used, being prepared by introducing the pencil lead into a Teflon tube [29, 64–67], a PVC tube [68], and a tip of a micropipette [35] or by covering its outside surface with Teflon band [2, 69] or with a nonconductive parafilm [9] so that only the cross-sectional surface remains free. The electrical contact between the electrode and the instrument was realized through a metal wire wrapped at the other end of the pencil lead. Bund et al. [70] described a PGE developed by connecting a silver wire to the graphite lead and the whole system was introduced through a silicon rubber into a glass tube so that the lead can be pushed out and its surface renewed by polishing before each recording. For clozapine analysis in human plasma a microsystem consisting of a micropipette tip was obtained by inserting the electrodes, with PGE as working electrode, through a septum [71]. Graphite pencil lead microelectrodes (diameter ∼12 μm) employed for cell dielectrophoresis were obtained by electrochemical etching of 0.5 mm HB leads in 1M NaOH. The obtained microelectrode was insulated by an electrogenerated o-phenylenediamine polymer or it was embedded in a micropipette tip by melting [72].

More recently, flexible paper based analytical electrochemical devices (PADs) were developed. Paper is the substrate on which the electrodes are drawn with graphite pencils [30, 73–84]. This strategy is simpler and cheaper than lithography [85].

2.3. Applications of PGE. Due to their inherent electrochemical and economical characteristics PGEs found in recent years a widespread application in various fields. In the field of electroanalysis, bare (Table 1) or modified PGEs (Tables 2–4) have been applied to the determination of both organic and inorganic compounds from different samples ranging from quite simple matrices like water till complex biological fluids like human urine or serum.

In 1996, pencil leads were used as new electrodes in abrasive stripping voltammetry [86]. Two years later a vibrating electrode based on a mechanical graphite pencil was reported to be used for the simultaneous potentiometric stripping determination of Cu(II), Cd(II), and Zn(II) traces in small samples [87]. Perdicakis et al. [15] proposed the use of pencil graphite electrodes for the immobilization and characterization of different types of electroactive species using voltammetry on microparticles. Later on, this principle was applied to get information about lead corrosion in archeological samples [88] and the composition and the degradation products of archeological lead. The electrochemical authentication was based on the observation of stripping peaks for patination products metals present in ancient lead, the potential shift of the reduction peaks, and signals due to the PbO2 reduction [89].

GRC existing as mechanical pencil leads constituted the working electrode for a dopamine determination in the range 5–120 μM in the presence of 5 to 20 times higher ascorbic acid concentrations [17].

A bare PGE was employed for the rapid DPV determination of total polyphenolic content of Sea Buckthorn leaves extract [191] and also for the electrochemical study of flavonoids and their interaction with copper ions. The obtained results could be useful for understanding the flavonoids role in decreasing the copper-induced oxidation of the substrate [18].

2.3.1. Electrochemical Pretreatment of PGE. The electrochemical characteristics of a PGE, which depend on its surface properties, can be changed/improved either by pretreatment or by chemical modification of the electrode active surface. The electrochemical pretreatment of a PGE, which consists in the electrooxidation or electroreduction of the PGE in the selected conditions, is the most rapid, simplest, cheapest, and eco-friendly (no use of toxic reagents) approach in comparison to other surface modification strategies [54, 106]. It was shown that electrochemical pretreatment activates the electrode surface by modifying its surface and redox characteristics [2, 21, 57, 106]. In comparison to non-treated PGE, the electrochemically pretreated PGE (ETPGE) presented improved electrocatalytic activity (e.g., for uric acid and ascorbic acid [2], methamphetamine [101], sulfide [192]), higher sensitivity (e.g., a 2–5 times higher sensitivity for monophenols [9] and a 40-fold increase of uric acid voltammetric signal [91]), higher selectivity by increasing the peaks separation [2, 21], and better adsorption capacity of organic compounds [57, 106, 192, 193]. This properties strongly depend on the activation conditions, that is, electrochemical procedure, electrolyte (type and concentration), applied potential or potential range [54], number of scans, and scan rate [21, 54, 106].

PGEs were pretreated potentiostatically by maintaining the electrode in an electrolyte for more than 30 s at a selected potential higher than 1.3 V [9, 53, 55, 56, 60, 70, 99–101, 105, 192, 193] or by scanning the potential at a given scan rate, for a certain number of cycles within a large potential range [2, 57, 58, 61, 69, 103, 106, 188, 194]. Some papers report a comparison between the two mentioned activation procedures and depending on the electrochemical performances obtained for the investigated analyte one of them was selected; for example, chronoamperometric activation of PGE was used for alkylphenols [50] and tannic acid [51] analysis and cyclic voltammetric activation of PGE for dopamine [21] and bisphenol A [54] detection. A precharged PGE developed by charging the electrode surface using CV in a NaOH solution was applied to phenols sampling and determination [104].

The performances of ETPGE depend on the supporting electrolyte used during the electroactivation and on the
Table 1: Electroanalytical applications of unmodified PGEs.

| Compound                  | Technique | Linear range (µM) | LD (µM) | Sample                  | Ref.  |
|---------------------------|-----------|-------------------|---------|-------------------------|-------|
| Acebutolol                | DPV       | 1–15              | 0.0126  | Urine                   | [90]  |
| Acetaminophen             | CV; FI    | 100–5000          |         | Pharmaceuticals          | [40]  |
| Acetylsalicylic acid      | SWV       | 35–300**          | 167*    | Pharmaceuticals          | [91]  |
| Acyclovir                 | DPV       | 1–100             | 0.3     | Pharmaceuticals          | [27]  |
| Caffeic acid/TPC          | FIA-Amp   | 1–20**            |         | Tea infusion             | [19]  |
| Caffeine                  | SWASV     | <500**            | 9.2**   | Tea                      | [92]  |
| Chlorogenic acid          | DPV       | 0.1–500           | 0.0714  | Dietary supplements      | [46]  |
| Dantrolene sodium         | DPV       | 0.395–2.955**     | 0.09    | Pharmaceuticals, human  | [48]  |
|                           | SWV       | 0.395–1.9**       | 0.052   | mother milk, urine       |       |
| Eugenol                   | DPV       | 0.3–50            | 0.085   | Pharmaceuticals          | [36]  |
| Famotidine                | DPV       | 0.472–495         | 0.151   | Pharmaceuticals          | [45]  |
| Flutamide                 | SWASV     | 0.398–6.36        | 0.0155  | Bulk form, human urine, | [49]  |
|                           |           | 0.0794–0.403      | 0.00168 | serum                    |       |
| Itraconazole              | SWASV     | 10.6–127*         | 8.7*    | Pharmaceuticals, biological fluids | [31] |
| Methylergometrine maleate| DPV       | 0.10–1.00**       | 0.02**  | Pharmaceuticals          | [52]  |
|                           | SWV       | 0.05–10.0         | 0.015   | Pharmaceuticals          | [37]  |
| Niclosamide               | DPV       | 0.01–10           | 0.00793 | Tea infusion             | [11]  |
| Paclitaxel                | DPV       | 0.4–3.0           | 0.00246 | Pharmaceuticals, biological fluids | [26] |
| Rosmarinic acid           | DPV       | 0.1–80**          | 1.7*    | Willow barks and branches | [94] |
| Salicylic acid            | SWV       | 0.015–0.25        | 0.01    | Waters, tobacco cells,  | [95]  |
|                           |           | 30–400            | 0.6     | fish tissues             |       |
| Strontium ranelate        | SWV       | 1–10**            | 0.17**  | Pharmaceuticals          | [20]  |
| Trepibutone                | SWV       | 0.24–10**         | 20*     | Pharmaceuticals          | [96]  |
| Uranium                   | SWASV     | <0.00008*         | 0.000007*| Rocks, earthworm        | [97]  |
| Vitamin B1                | DPV       | 10.0–1000         | 5.34    | Pharmaceuticals          | [44]  |
| Vitamin B6                | DPV       | 5.00–1000         | 2.81    | Pharmaceuticals          |       |

*a ng mL<sup>-1</sup>; ** µg mL<sup>-1</sup>; DPV: differential pulse voltammetry; SWV: square wave voltammetry; CV: cyclic voltammetry; FI(A): flow injection (analysis); Amp: amperometry; SWASV: square wave anodic stripping voltammetry; SWCASV: square wave cathodic adsorptive stripping voltammetry; TPC: total polyphenolic content.

analyte; for example, PGE pretreated in H<sub>3</sub>PO<sub>4</sub> had higher sensitivity towards dopamine and ascorbic acid, whereas the same electrode activation performed in a mixture of LiClO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> led to the best sensitivity and selectivity for uric acid [106] and PGE electroactivated in a mixture of LiClO<sub>4</sub> and NaOH presented the best performances for bisphenol A detection [54].

All these electrochemical improvements of ETPGE may be due to their increased surface area by formation of carbon nanoparticles and of oxygenated functionalities [25, 106] (phenolic, carbonyl and carboxyl [105], quinone [21], or graphite oxide films [2]) during the oxidation of the graphite layer of the PGE accomplished also by an oxidative surface cleaning during the treatment [53, 100]. The oxygen containing groups increase the hydrophilic characteristics of the ETPGE surface [193] and mediate the electron transfer processes [2].

The electrochemical oxidation of aminopurines [43], xanthine, and adenine [194] and of xanthine and its N-methyl-derivatives [195] in the absence and presence of copper ions was investigated by CV, LSV, eliminatory voltammetry with linear scan, DPV, and chronopotentiometric stripping analysis on ETPGE. Similarly, it was shown that using the same working electrode 6-benzylaminopurine (BAP) exhibited, like other aminopurines, an increased oxidation signal in the presence of copper ions. From the electrochemical data a possible stoichiometry and the electrode reaction mechanism of the BPA-Cu complex were established [55]. Other examples of ETPGEs applications along with their analytical performances reported in the literature are listed in Table 2.

2.3.2. PGE Surface Modification. Electrode surface modification is performed in order to enhance the sensitivity and selectivity of the voltammetric determination; for example,
Table 2: Electroanalytical applications of ETPGEs.

| Compound                        | Technique | Linear range (µM) | LD (µM)         | Sample                  | Ref.   |
|---------------------------------|-----------|-------------------|-----------------|-------------------------|--------|
| **Alkylphenols**                |           |                   |                 |                         |        |
| 4-Nonylphenol                   | DPV       | 1.20–94           | 0.420           | Water                   | [50]   |
| 4-Octylphenol                   | DPV       | 0.6–78            | 0.250           |                         |        |
| 4-tert-Octylphenol              | DPV       | 2.38–243          | 0.770           |                         |        |
| **4-Aminophenazone**            |           |                   |                 |                         |        |
| **Caffeine**                    |           |                   |                 |                         |        |
| 4-Nonylphenol                   | DPV       | 1–11              | 0.0796          | Real samples            | [98]   |
| 4-Octylphenol                   | DPV       | 1–9               | 0.00981         |                         |        |
| **Boron**                       |           |                   |                 |                         |        |
| **Capsaicin, dihydrocapsaicin** |           |                   |                 |                         |        |
| 4-Nonylphenol                   | DPV       | 0.016–0.32        | 0.0037          | Turkish pepper          | [25]   |
| 4-Octylphenol                   | DPV       | 0.0033–0.33       | 0.00091         |                         |        |
| **Chlorpromazine**              |           |                   |                 |                         |        |
| **Cinchocaine hydrochloride**   |           |                   |                 |                         |        |
| Dopamine                        | ATSDPV    | 0.01–5.0          | 0.00031         | Blood serum             | [21]   |
| Dopamine                        |           |                   |                 |                         |        |
| Uric acid                       | DPV       | 0.15–15           | 0.033           | Pharmaceuticals, body fluids | [2] |
| **Gluten**                      |           |                   |                 |                         |        |
| **Indole-3-acetic acid**        |           |                   |                 |                         |        |
| **Kinetin**                     |           |                   |                 |                         |        |
| Methamphetamine                 | DPV       | 0.074–54          | 0.05            | Human serum, urine       | [101]  |
| Morphine                        | DPV, Amp  | 1–100             | 0.26            | Human urine, street drug samples | [102] |
| Nalbuphine hydrochloride        |           |                   |                 |                         |        |
| α-Naphthol                      | LSASV     | 0.01–2.0          | 0.0015          | Water                   | [47]   |
| Nicotine                        | SWV       | 7.6–107.5         | 2.0             | Cigarettes              | [53]   |
| Paracetamol                     | ATSDPV    | 0.05–2.5          | 0.0025          | Blood serum             | [57]   |
| Phenol                          | SWV       | 0.05–1            | 0.00417         | Water                   | [104]  |
| Phenol, m-cresol                | DPV       | 40–320            | 0.120           | Insulin formulations     | [9]    |
| Quercetin                       | DPASV     | 0.0001–1.5        | 0.0003          | Cranberry, blackcurrant juices | [105] |
| Tannic acid                     | DPASV     | 0.005–0.5         | 0.0015          | Beverages               | [51]   |
| Uric acid                       | DPV       | 0.05–10           | 0.0015          | Body fluids             | [106]  |
| Uric acid                       | DPV       | 1–160             | 0.19            | Human serum, urine       | [107]  |
| Vitamin C                       | Amp       | 1–100             | 1.18            | Human plasma            | [69]   |

In solution: SDS (sodium dodecyl sulphate) < critical micellar concentration; *ng mL$^{-1}$; **µg mL$^{-1}$; SWSV: square wave stripping voltammetry; AdDPSV: adsorptive differential pulse stripping voltammetry; AdSWSV: adsorptive square wave stripping voltammetry; ox: oxidation; red: reduction; ATSDPV: adsorptive transfer stripping voltammetry differential pulse voltammetry; LSASV: linear sweep anodic stripping voltammetry; DPASV: differential pulse anodic stripping voltammetry. All the other abbreviations are like those in Table 1.

Kawde and Aziz reported the improved electrocatalytic activity of a porous Cu-modified PGE in comparison to bare PGE, with respect to the redox behavior of 4-nitrophenol leading to a three-order magnitude lower amperometric detection limit [165].

The PGE active surface can be modified with nanomaterials, polymers, a combination of both, or using other type of modifiers.

There are many different ways to change the surface characteristics of an electrode. Usually one or more compounds (modifiers) are attached to the electrode surface by coating, casting, or dispersion within a conductive matrix in order to combine the chemical/ electrochemical/ optical or catalytic properties of the modifier(s) with those of the electrode, generating a modified electrode with enhanced figures of merit. A fluorine doped PGE applied to Cr(VI) detection in tap water and smoker urine was obtained by CV in HF solution when fluorinated graphite structures were formed. In SWV the electrode presented two linear ranges, namely, 0.051–0.45 mg L$^{-1}$ and 0.05–0.4 µg L$^{-1}$, and a LD of 0.008 µg L$^{-1}$.
Table 3: Electroanalytical applications of modified PGE.

| Compound                  | Modifier                        | Technique | Linear range (µM) | LD (µM) | Sample                          | Ref.  |
|---------------------------|---------------------------------|-----------|-------------------|---------|---------------------------------|-------|
| Acetaminophen             | Poly(2,5-di(2-hydroxyphenyl)-1-p-(tolyl)Pyrrole) | DPV       | 0.025–5          | 0.00194 | Pharmaceuticals                  | [108] |
| Acyclovir                 | ET β-cyclodextrin polymer       | SWAdSV    | 0.05–0.6         | 0.00759 | Dosage forms, urine pharmacokinetic studies | [109] |
| 2-Amino-benzimidazole     | MI-PPy                          | DPV       | 0.001–30000      | 0.0001  | Biological model samples        | [110] |
| γ-Aminobutyric acid       | MI-FUAA/MWCNTs-COOH             | DPASV     | 0.75–205.19*     | 0.28*   | Cerebrospinal fluid, human serum, aqueous | [111] |
| Arsenic(V)                | PPy-AsO$_4^{3-}$                 | Pot       | 50–1000000       | 28      | Water                           | [112] |
| Arsenic(III)              | Au-NDs/CNTs                      | ASV       | 0.5–80*          | 0.4     | Tap water                       | [113] |
| Ascorbic acid             | MI-PPy                          | DPV       | 250–700000       | 74      | Pharmaceuticals                  | [114] |
| D-,L-Ascorbic acid        | MI-PPy                          | DPV       | 0.006–0.155      | 0.000002 | Pharmaceuticals, human plasma   | [115] |
| D-,L-Aspartic acid        | MI-P3AA/MWCNTs                  | DPASV     | 0.15–74          | 0.025   | Pharmaceuticals, blood serum    | [116] |
| D-,L-Aspartic acid        | MI-NAPD/MWCNTs-TiO$_2$-NPs-CHPA | DPASV     | 9.98–516.25*     | 1.71*   | Cerebrospinal fluid, blood serum, pharmaceuticals | [117] |
| Benzimidazole             | MI-PPy                          | DPV       | 3–50000          | 0.7     | Biological                      | [118] |
| Bisphenol A               | Au-NPs/PVP                      | SWAdSV    | 0.03–1.1         | 0.001   | Bottled drinking water          | [119] |
| Bisphenol A               | PANI-NRs/MWCNTs                 | Amp       | 1–400            | 0.01    | Spiked boiling water            | [120] |
| Cadmium                   | P4VP                            | Pot       | 0.1–1000000      | 0.0251  | Environmental, food, biological | [121] |
| Cadmium                   | Poly(4V-P-co-ANI)               | Pot       | 1–10000          | 0.794   | Sea water, tomato, rice, ayurvedic medicine | [122] |
| Caffeine                  | Au-NPs/MIP-sol-gel              | SWV       | 0.002–0.05       | 0.0009  | Urine, plasma, tablets, tea, energy and soda drink | [60] |
| Carminic acid             | Pd-Au-NPs/PPr                   | SWV       | 0.01–1           | 0.0059  | Popping candy                   | [123] |
| Ceftriaxone sodium        | Copper hexacyanoferrate         | CV, chron-amp | 2–72            | 0.54    | Pharmaceuticals                  | [124] |
| Ciprofloxacin             | MI-PPy and o-PD                 | SWV       | 0.001–10000      | 0.0000758 | Tablets                        | [125] |
| Chlorogenic acid          | MI-PPy                          | Pot       | 1–10000          | 1       | Coffee                          | [126] |
| Chlorpyrifos              | MI-PPy                          | EIS       | 20–300*          | 4.5*    | Soil                            | [127] |
| Copper                    | Alga-OMNiIIP                     | DPASV     | 0.008–7.807*     | 0.0018* | Environmental, pharmaceuticals, blood serum | [128] |
| Copper                    | Cu-carboximine/PANI             | Pot       | 5–100000         | 2       | Tea leaves, black currants, sour cherry juice | [129] |
| Copper                    | PPy-SSA                         | Pot       | 10–100000        | 5.42    | Electrical copper wire          | [130] |
| Copper                    | PPy-P4R                         | Pot       | 10–50000         | 6.7     | Electrical copper wire, tap water | [131] |
| Compound                  | Modifier                      | Technique | Linear range (μM) | LD (μM) | Sample                                      | Ref.   |
|---------------------------|-------------------------------|-----------|-------------------|---------|---------------------------------------------|--------|
| Copper                    | PSS–CnP                       | DPASV     | <1000             | 0.00173 | Mineral, river and sea water                | [68]   |
| L-Cysteine                | Copper hexa-cyanoferrate      | chrono-amp| 1–13              | 0.13    | Urine                                       | [132]  |
| Dextromethorphan          | Poly(diallyl-dimethyl-        | DPV       | 2–600             | 0.2     | Cough syrups, human urine, plasma           | [133]  |
|                           | ammonium chloride)/MWCNT/CQDs |           |                   |         |                                             |        |
| Diazepam                  | ET Bi                         | DPV       | 1.4–16.7          | 11      | Tablets, urine                              | [134]  |
| Diclofenac sodium         | MWCNTs                        | DPV       | 0.047–12.95       | 0.017   | Biological samples, pharmaceuticals         | [135]  |
| 1,4-Dihydroxy-            | MI-PPy/MWCNTs-COOH            | DPV       | 0.01–100          | 0.00415 | Serum, plasma                               | [136]  |
| anthraquinone             |                               |           |                   |         |                                             |        |
| Dipyrone                  | PPy-dipyrone                  | Pot       | 100–400000        | 86.2    | Spiked human urine, Pharmaceuticals          | [62]   |
| Dopamine                  | Poly(xylenol orange)          | DPV       | 2–9               | 0.091   | Injections                                  | [137]  |
| Dopamine                  | Poly(amaranth)                | DPV       | 0–250             | 0.05    | Injections                                  | [138]  |
| Dopamine                  | Poly(Naphthol Green B)        | DPV       | —                 | 0.2     | Injections                                  | [139]  |
| Dopamine                  |                                |           |                   |         |                                             |        |
| L-Dopa                    | Au                            | DPV       | 20–100            | 1.54    | Mucuna pruriens                             | [140]  |
| Epinephrine               | MI-poly(NHPM-MWCNTs)          | DPASV     | 0.09–5.90*        | 0.02*   | Pharmaceuticals, blood serum                 | [141]  |
| Estradiol                 | Au-NPs/MWCNTs                 | LSV       | 0.07–42           | 0.01    | Blood serum                                 | [142]  |
| Ferritin                  | Imprinted Ag@CDs              | DPV       | 1.99–23.43*       | 0.65**  | Blood serum                                 | [143]  |
| Fluoxetine                |                                |           |                   |         |                                             |        |
| Citalopram                | PVC/PEDOT-Ch4                 | ITSV      | 0.1–1.0           | 0.035   | Tap and river water                         | [144]  |
| Sertraline                |                               |           |                   |         |                                             |        |
| Folic acid                | MI-pTAT/sol-gel               | DPCSV     | 0.007–0.156**     | 0.0021**| Blood serum, pharmaceuticals                | [29]   |
| Glucose                   | OxPPyNFs-CoPcTS               | DPV       | 250–200000        | 100     | Serum samples                               | [34]   |
| Glucose                   | Cu-NPs                        | Amp       | 1–100             |         |                                              |        |
|                           |                               |           | 100–100000        | 0.44    | Blood serum                                 | [145]  |
| Glyphosate                | MI-pMAC/AuNPs                 | DPASV     | 3.98–176.23*      | 0.35*   | Aqueous, soil, human serum                  | [146]  |
| Glufosinate               |                                |           | 0.54–3.96*        | 0.19*   |                                              |        |
| Heavy metals              | Bi-film                       | SWASV     | 0.01–0.12         | Pb: 0.0024 | Simultaneous in situ, aqueous solutions    | [64]   |
|                           |                               |           |                   | Cd: 0.0029 |                                              |        |
|                           |                               |           |                   | Zn: 0.012  |                                              |        |
| Heavy metals              | Nafion-graphene nanocomposite | SWASV     | 2–20**            | Pb: 0.13** | Tap water                                   | [147]  |
|                           | Bi-film                       |           | 10–100**          | Cd: 0.09** |                                              |        |
|                           |                               |           |                   | Zn: 0.17**  |                                              |        |
| Compound       | Modifier          | Technique | Linear range (μM) | LD (μM)       | Sample                     | Ref.     |
|---------------|-------------------|-----------|-------------------|---------------|----------------------------|---------|
| Heavy metals  | ERGO-Bi-film      | SWASV     | 2–100 *           | Pb: 0.12 **   | Tap water                  | [28]    |
|               |                   |           |                   | Cd: 0.09 **   |                            |         |
|               |                   |           |                   | Zn: 0.19      |                            |         |
| Hemoglobin    | MI-pNMGA/QDs-MWCNTs | DPCSV    | 27.8–444.0 *      | 6.73 *        |                            | [148]   |
| L-Histidine   | CIP/MWCNTs        | DPASV     | 9.990–323.572 *   | 1.980 *       | Pharmaceuticals, blood serum | [67]    |
| Hydrazine     | Au-NPs            | SWV Amp   | 0.05–1000         | 0.042         | Drinking water             | [32]    |
|               |                   |           | 25–1000           | 3.07          |                            |         |
| Hydrazine     | Cu-NS/MWCNT       | SWV Amp   | 0.1–800           | 0.07          | River, waste, well waters  | [149]   |
|               |                   |           | 50–800            | 4.3           |                            |         |
| Hydrochlorothiazide | MI-PPy/MWCNTs-COOH | DPV     | 0.0009–10         | 0.0001        | Pharmaceuticals, serum     | [150]   |
|               |                   |           | 10–10000          |               |                            |         |
| Hydrogen peroxide | Ag/FeOOH nano-composites | Amp | 30–15000         | 22.8          | Disinfectant               | [151]   |
| Hydrogen peroxide | Pd-NPs         | Amp      | 30–140            | 0.045         | —                          | [24]    |
| Hydrogen peroxide | Pt-NPs          | Amp      | 30–110            | 3.6           | —                          | [152]   |
| Insulin       | MI-pAEP-MWCNTs    | DPASV     | 0.000088–0.005647 | 0.0000186     | Pharmaceuticals, blood serum | [65]    |
| Iodide        | PPy-iodide        | Pot       | 10–80000          | 9.3           | Pharmaceuticals             | [353]   |
| K+, Na+       | PB Pot            | CV        | 1000–500000       | 600–120000    | 600–21000                  | [63]    |
| Lorasepam     | MI-PPy/sol-gel/AuNPs | SWV     | 0.0002–0.002      | 0.00009       | Pharmaceuticals, plasma, urine | [154] |
|               |                   |           | 0.002–0.020       |               |                            |         |
| Lomustine     | MF                 | SWCASV    | 0.192–13.6        | 0.0813        | Human blood, urine         | [155]   |
| Magnesium     | PPy-Titan yellow Pot | 10–50000 | 6.28             |               | Tap and mineral water      | [156]   |
| Mancozeb      | SPIONs/MISP       | —         | 5.96–2570 **      | 0.96 **       | Soil, vegetable            | [157]   |
| Methadone     | MWCNTs            | DPV       | 0.1–15            | 0.087         | Human serum, urine         | [158]   |
| D-, L-Methionine | MI-polyBz/MWCNTs-COOH | DPV | II.7–188.7 **     | 3 **          | Pharmaceuticals, blood serum | [159] |
|               |                   |           | II.7–206.3 **     | 3 **          |                            |         |
| Metoprolol    | MI-PPy/MWCNTs-COOH| DPV       | 0.06–490          | 0.00288       | Pharmaceuticals, serum      | [160]   |
| Morphine      | Au-NPs/MIP/MWCNT  | SWV       | 0.008–5           | 0.0029        | Human urine, serum         | [161]   |
| Nitrate       | PPy-NO3                                 | Pot       | 100–100000        | 50            | Water                      | [162]   |
| Nitrite       | Polypyronin Y Amp | 1–100     | 0.5               |               | Food                       | [163]   |
| Nitrite       | PVF+/MWCNTs       | DPV       | 1–400             | 0.1           | Mineral water               | [164]   |
| 4-Nitrophenol | MWCNTs            | FL-Amp    | 5–300 *           | 1.5 *         | Water                      | [35]    |
| 4-Nitrophenol | Cu Amp            | 50–850    | 1.91              |               |                            | [165]   |
| 2-Nitrophenol | Bi DPV            | 2–200     | 5.42              |               |                            | [166]   |
| 4-Nitrophenol |                   | 4–400     | 7.48              |               |                            |         |
| Pantoprazole  | PPy-PTZ Pot       | 10–100000 | 6.9             |               | Pharmaceuticals             | [167]   |
| Paracetamol   | MI-PPy DPV        | 5–500     | 0.79              |               | Pharmaceuticals             | [168]   |
### Table 3: Continued.

| Compound                  | Modifier        | Technique | Linear range (µM) | LD (µM) | Sample                          | Ref.   |
|---------------------------|-----------------|-----------|-------------------|---------|---------------------------------|--------|
| Phenothiazine             | MI-PPy          | DPV       | 1–300             | 0.3     | Model and real biological      | [169]  |
| D-, L-Pyrog glutamic acid| MI-poly[5-MTCA–Cu(II)] | DPASV    | 2.8–70.0*         | 0.77**  | Cerebrospinal fluid, blood plasma, urine | [66]   |
| Quercetin                 | p-AMT           | DPV       | 0.1–6*            | 2.2     |                                 | [170]  |
| Ranitidine                | Au-NP/MIP-sol–gel/MWCNTs-COOH | SWV    | 0.05–2.0         | 0.02    | Human urine                     | [61]   |
| Sildenafil citrate        | PPy-citrate     | Pot       | 34–1700           | 30      | Pharmaceuticals                  | [62]   |
| Sulfanilamide             | MI-PPy          | DPV       | 0.05–1.1          | 1.1–48  | Spiked human serum, ground water | [173]  |
| Sulfamethoxazole          | MI-OxPPy        | DPV       | 25–750            | 0.359   | Pharmaceuticals                  | [59]   |
| Thiocarbamide             | MI-PPy          | DPV       | 500–6000          | 50      | Biological                      | [174]  |
| 6-Thioguanine             | MI-polyneutial red/ERGO | DPASV | 0.124–78.0*       | 0.02*   | Pharmaceuticals, urine, serum    | [175]  |
| Triamterene               | MI-PPy/MWCNTs-COOH | DPV | 0.08–265         | 0.00335 | Serum, pharmaceuticals          | [176]  |
| L-Tyrosine                | graphene        | SWV       | 0.8–60            | 0.07    | Urine                           | [177]  |
| Uranium(VI)               | PPy-ZnUO₂(CH₃COO)₄ | Pot     | 1–10000           | 0.63    | Mineral and tap water           | [178]  |
| Uric acid                 | Ox-PEDOT-nf     | DPV       | 0.01–20.0         | 0.0013  | Blood serum, urine              | [179]  |
| Valacyclovir              | CuMPs           | AdSWV     | 0.002–0.08        | 0.000178| Pharmaceuticals                  | [180]  |
| Vitamin B12               | PNT             | SWV       | 0.2–9.5           | 0.093   | Tablets                         | [181]  |
| Vitamin B12               | SWCNTs-chitosan | SWV       | 0.005–0.1         | 0.00089 | Pharmaceuticals                  | [182]  |
| Zinc                      | Tartrazine-PPy  | Pot       | 10–100000         | 8       | Barley flakes, rice dry milk    | [183]  |

*ng.mL⁻¹; **µg.mL⁻¹; ET: electrochemically treated; MI: molecularly imprinted; PPy: polypyrrole; FUAA: 5-fluorouracil-N-acetyl acrylamide; NDs: nanodendrites; CNT: carbon nanotubes; ASV: anodic stripping voltammetry; FSA: ferrocene sulfonic acid; P3AA: poly(indole-3-acetic acid); NAPD: N-acryloyl-pyrrolidine-2,5-dione; NPs: nanoparticles; CHPA: 2-chloro-N-(4-hydroxyphenyl)-acetamide; PVP: polyvinylpyrrolidone; SWAdSV: square wave adsorptive stripping voltammetry; PANI: polyaniline; NPs: nanoparticles; CNT: carbon nanotubes; CHPA: 2-chloro-N-(4-hydroxyphenyl)-acetamide; PVAdSV: polyaniline; CoPcTS: cobalt(II) phthalocyanine tetrasulfonate; Bz: benzidine; PVF: poly(vinylferrocene); PTZ: pantoprazole; MTCA: methyl-2-thiophene carboxylic acid; p-AMT: polymerized 5-amino-2-mercapto-1,3,4-thiadiazole; p(P3CA): poly(pyrrole-3-carboxylic acid); Ox-PEDOT-nf: overoxidized poly(3,4-ethylene-dioxythiophene) nanofibers; CuMPs: copper microparticles; PNTs: peptide nanotubes; copper microparticles; SWCNTs: single-wall carbon nanotubes. All the other abbreviations are like those in the previous tables.
Cr(VI) [196], whereas a PGE modified by adsorption of quercetin [192] or hematoxylin [197] exhibited improved electrocatalytic response for sulfide with linear ranges of 1–20 μM and 20–800 μM and a LD of 0.3 μM and 1–200 μM and 0.4 μM sulfide, respectively. An ETPGE modified by adsorption of quercetin was sensitive to reduced β-nicotinamide adenine dinucleotide (NADH) in the range 0.5–100 μM with a LD of 0.15 μM. Based on CV data an ECE mechanism was proposed for the electrocatalytic oxidation of NADH [193].

Cibacron Blue (CB) F3GA modified PGE obtained by both CV and passive adsorption was developed to investigate the CB dye affinity to serum albumin. Using CV, the CB current peak decreased linearly with increased bovine serum albumin concentrations in the range 0.25–2.5 mg mL−1 and the obtained LD was 0.15 mg mL−1 [198].

Different metals or metal containing compounds can be attached to bare or already modified PGEs surface either as thin films [28, 64] or as different nanostructures (NS). For example, in situ generated Hg-film PGEs were used for the potentiometric stripping analysis of Cu(II), Pb(II), Cd(II), and Zn(II) from river sediments with comparable results with those obtained by atomic absorption spectrometry [70] or for anodic stripping voltammetric monitoring of Cu(II) levels in the Prut-river during a period of three years [199].

Due to their large surface area, their excellent conductivity, and electrocatalytic properties, nanomaterials enhance the electrodes sensitivity (by high signal-to-background ratio) [33] (e.g., a Pd-nanoparticles modified PGE was able to detect H2O2 with a LD of 45 nM compared to the LD of 0.58 mM H2O2 obtained at a bare PGE under the same experimental conditions [24]) and selectivity by improving peak separation [14].

The methodologies for PGE modification with nanomaterials (precious metals nanoparticles (NPs), metal oxide NPs, metal complex nanostructures (NS), and carbon nanotubes) and nanomaterials-conducting polymers composites and the electrochemical applications of such modified PGEs were recently reviewed [33].

Galvanostatic double-pulse technique [200] and CV [201] were applied to obtain NS multilayers thin Cu films and Cu particles modified PGEs, respectively, which exhibited electrocatalytic activity towards nitrate reduction. Copper hexacyanoferrate modified PGE for L-cysteine detection was obtained by cooper electrodeposition on PGE and subsequent immersion in a K3[Fe(CN)6] solution [132]. PGE modified with MWCNTs (multiwall carbon nanotubes) and Bi-NS obtained by microwave-assisted polyl method were used for Pb(II) determination with a LD of 1.7 nM [202]. A sensitive composite sensor for hydrazine was developed by CV deposition of Cu-NS on MWCNTs modified PGE [149].

Nanoparticles (NP) immobilized on electrodes surfaces improve the electrodes electrochemical characteristics by mediating the electron transfer reactions of electroactive species. NP-modified electrodes can be obtained by electrodeposition [140, 161, 203] or by simply immersion of the pencil lead into the NP solution [25, 32, 188]. Tl2O3-NS obtained by a sonochemical method were used to develop a Tl2O3-NS/MWCNTs modified PGE for Cu2+ trace sensing with a LD of 4.63 nM Cu2+. The developed modified PGE was able to detect three oxidation states of copper [204].

Carbon nanomaterials, as carbon nanotubes (CNTs) [120, 135, 158, 204, 205], nanofibers [206], nanopowders [68], or graphene [28, 147, 175, 177], are largely used for the development of electrochemical sensors. CNTs are NS very suitable for PGEs surface modification due to their nanometer dimensions, high stability, large specific area, good conductivity, electronic properties, and topological defects conferring them excellent catalytic characteristics which

| Compound          | PGE modifier | Technique      | Linear range (μM) | LD (μM)      | Sample                  | Ref. |
|-------------------|--------------|----------------|-------------------|-------------|-------------------------|-----|
| D-, L- Aspartic acid | MIP          | MIP-SPME-DPASV | 0.6–10*           | 0.180*      | Blood serum, cerebrospinal fluid | [184] |
| Buprenorphine     | MWCNTs       | PTFE-LPME-DPV  | 0.0000001–0.000109 | 0.0000006   | Human urine and plasma   | [185] |
| Clozapine         | —            | EME-DPV        | 3–1500*           | 0.9*        | Human plasma            | [71] |
| Epinephrine       | MIP/MWCNTs-NHMP | MI-MSPE-DPASV | 0.005–8*         | 0.002*      | Cerebrospinal fluid, plasma, pharmaceutics | [186] |
| Flutamide         | SDS-modified silica film | DPV       | 0.0000–0.02       | 0.000034    | Human urine and plasma   | [187] |
| Insulin           | RuO2-GO nanocomposite | DPV       | 0.0008–0.02       | 0.000024    | Blood, urine             | [188] |
| D-, L- Methionine | EC-MIP/MWCNTs-COOH | MI-MSPE-DPCSv | 0.03–30.00*       | 0.0098*     | Pharmaceuticals, human blood plasma | [189] |
| Tramadol          | RGO          | EM-SPME-LSV    | 0.01–0.50**       | 0.003**     | Urine                    | [190] |

* ng mL−1; ** μg mL−1; MI(P): molecularly imprinted (polymer); SPME: solid phase microextraction; PTFE: polytetrafluorethylene; LPME: liquid three-phase microextraction; EM(E): electromembrane (extraction); MI-MSPE: MI-micro-solid-phase extraction; SDS: sodium dodecyl sulphate; (R)GO; (reduced) graphene oxide; EC-MIP: electrochemically synthesized-MIP. All the other abbreviations are like those in the previous tables.
enable the promotion of redox reactions at the electrode surface (improvement of electron transfer rate and redox reversibility), and the ability to reduce the electrode surface fouling and the electrolyte impedance [3, 120, 158, 161, 205].

Particularly selectivity but also the sensitivity of the voltammetric determinations can be improved by covering the electrode (PGE) surface with a polymer bearing chemical groups able to interact differently with various compounds or with molecularly imprinted polymers (MIP) whose interaction with diverse species is restricted by both its functional groups and the shape and size of the cavity resulted after template removal from the polymer.

Recently, polymer modified electrodes gained great interest due to their good stability, reproducibility, more active sites, homogeneity in electrochemical deposition [138], and improved response characteristics [156]. One of the most used technique for covering the electrode surfaces with polymeric films is electropolymerization; it can be realized by cyclic voltammetry [34, 59, 66, 114, 118, 121, 122, 130, 138, 156, 168, 170, 173, 175, 207, 208], by applying a constant potential [41, 112, 183] or a constant current [62, 153, 172, 178] to the bare or previously modified PGE immersed in the solution containing monomer and eventually other components. A dip-coating method was applied to modify a PGE from a casting solution containing carmoisine/polyaniline or copper-carmoisine complex/polyaniline [129]. To enhance the polymers ability to recognize and bind selective the analyte, they can be molecularly imprinted with the target/analyte molecule (template) by chemical grafting, soft lithography, molecular self-assembly, electropolymerization (galvanostatic, potentiostatic, and cyclic voltammetric methods), irradiation, or heating [118, 168, 169, 173], followed by the template extraction from this polymer resulting a tailor made receptor that can recognize and rebind the analyte according to its shape and functionality. Besides their increased selectivity, molecularly imprinted polymers- (MIP-) modified PGEs have also other advantages like ease of preparation and low-cost and high chemical stability under various circumstances [111, 125–127, 148, 161, 175], but they also have some possible drawbacks as incomplete template removal, embedding of binding sites, analyte constraint accessibility to the template cavities, and electroinsulating [111, 141, 175]. Hybrid nanocomposites combining the advantages of their constituents (e.g., MIP and nanomaterials) have been used for electrode surface modification in order to overcome the above-mentioned disadvantages of MIPs and to improve the electrochemical and sensing characteristics of the PGE through a synergistic effect. Therefore, the chemical stable polymer acts as a “recognition element” which reduces interferences and responds quickly by selective recognition of the analyte molecules via ion exchange and electrostatic and/or hydrophilic/hydrophobic interactions whereas the nanomaterials, due to their unique and specific electroanalytical characteristics, increase the conductivity and improve the analyte mass transport and charge transfer, enhancing the electrochemical activity towards the compound of interest [14, 33, 68]. On the other hand, molecular imprinting on nanomaterials, after template removal, will improve the analyte targeted accessibility to the electron transfer site at the electrode surface reducing the mass transfer resistance [148]. Rezaei et al. [61] explain the role of each component in the stepwise development of modified Au nanoparticles-imprinted sol-gel-MWCNTs-PGE sensitive to ranitidine.

Hybrid nanocomposite PGEs have a high surface to volume ratio, more functional groups that constitute specific binding sites, higher adsorption capacity, excellent recognition ability, and thus very good sensitivity and selectivity, but also good reproducibility and stability due to the three-dimensional nanocomposite MIP structure. So a nanocomposite MIP-Au-NPs-PGE used for sensitive (LD 0.9 nM) and selective caffeine determination from real samples without interference of compounds with similar structure displayed good construction reproducibility (RSD 4.4%), repeatability (RSD 3.7%), and stability of over two weeks [60]. The immobilization of a MIP onto a functionalized MWCNTs modified PGE resulted in a very sensitive (LD 0.28 ng mL\(^{-1}\)) electrode for γ-aminobutyric acid detection at ultra-trace levels in a wide concentration range (0.75–205.19 ng mL\(^{-1}\)) from biological samples without any cross-reactivity and false positives. The electrode presented good preparation reproducibility (RSD 3.3%), regeneration ability, and stability (one month) [111]. A MI-polyaniline ferricene-sulfonic acid–carbon dots PGE could be used for over 40 days (when stored at room temperature) for chiral sensitive (LD at 10\(^{-12}\) M level), accurate (RSD 3.4%), and selective recognition of L- and D-ascorbic acid from biological fluids in the presence of structurally close chiral or nonchiral molecules [115]. It is worth mentioning that the modified electrode surface was easy regenerated either by analyte elution using an adequate electrolyte [60] or by electrochemical dedoping [115].

Materials of the MWCNTs-MIP-template adduct type were usually obtained by molecular imprinting on nanosstructures and can be easily covered onto PGEs [61, 65, 67, 111, 116, 137, 148, 150, 159–161]. Applications and performance characteristics of the above-mentioned and also other modified PGEs are listed in Table 3.

Stability and reproducibility are important parameters for the electrode performance; the modification can improve the properties of substrates, the stability, and reproducibility of the electrode response.

The tested room temperature and long-term stabilities of modified PGEs from several days to more than 100 days showed good stability. Thus, ETPG electrodes conserved their activity for a long time (i.e., 30 days) when they are stored in a vacuum desiccator [21, 57, 106]. The results obtained for the working stability of some modified PGEs investigated by monitoring the analyte peak after more consecutive runs on a single modified electrode indicated a decrease of the peak current less than 5%. A single electrode could be used after regeneration for 30 [25, 116] to 90–100 consecutive runs [66, 67, 159] with quantitative recoveries. The response of some modified electrodes, especially modified with conducting polymers evaluated for a long period of time, showed that the sensor kept 98% of the initial performance after 70 days and 81% even after 140 days [34] or 96% of its initial response after 105 days [169].
The good reproducibility of the modified PGEs is correlated with the electrode stability. The fabrication reproducibility of more than five different electrodes, prepared under the same conditions, showed acceptable reproducibility with a RSD value between 0.95% and 4.9% [21, 57, 60, 62, 67, 106, 117, 125, 133, 160, 175]. Similar results for the reproducibility were obtained in the case of the insulin determination with a RuO$_2$-graphene oxide PGE [188], the phenol detection using a precharged disposable PGE [104], and the sulfide quantitation with a PGE modified with hematoxylin [197], namely, RSD% values of 3.7, 3.76, and 4.1%, respectively. Repetitive measurements carried out for 10 successive runs showed a RSD between 0.87% and 1.36% [65–67, 116, 117, 204]. So the reproducible current response with a single electrode proves the stability of the electrode.

2.3.3. Other Applications. A microfluidic chip containing an N-doped carbon nanofiber modified PGE as working electrode was recently described for the simple electrochemical detection of hydroxyl radicals in cigarette smoke with a detection limit of $10^{-6}$ M [206]. A PANI-film modified PGE acting as a pH sensor was connected between the tips of the working and counter electrodes coupled to a potentiostat generating thus an amperometric pH-controllable molecular switch that forms a measuring system together with a suited reference electrode immersed in the analysed solution [207, 208].

Due to a complex matrix of the sample to be analysed or in order to improve the selectivity and sensitivity, the electrochemical detection methods are often coupled to separation methods. Amperometric oxidation of phenols and chlorophenols at disposable GRC was used as detection mean in liquid chromatography [209]. Ensafi et al. [187] reported the use of a PGE modified with a thiol-functionalized silica film incorporating SDS (sodium dodecyl sulphate) which extracts and preconcentrates the reduced form of flavimide due to the applied potential. Subsequently, the accumulated analyte was stripped from the electrode surface and determined by DPV. Insulin was preconcentrated by extraction into a SDS supported liquid membrane by formation of a SDS-insulin complex which was further reextracted into a small volume of acceptor phase and was analysed by DPV on a modified PGE [188]. Other examples of PGEs used in combination with separation techniques are presented in Table 4.

PGE modified by electrodeposition of tartrate-doped polypyrrole [210], different aniline [211–213], or thiophene [214–216] derivatives based polymers were investigated in order to obtain electrode active materials for supercapacitors application. In recent years, graphite pencils were used for the development of interesting electronic applications like bilayer chemiresistor [217], photoconductive PbS photodetector realized by pencil graphite electrodes drawn on stone paper acting as substrate, or a hand drawn pencil electrode for determination of lead traces in water [73], dopamine [74], or p-nitrophenol [30]. It was demonstrated that pencil drawn electrodes present the best reversibility and the highest signal if they were drawn 10 times with a 6B pencil [75]. Dipped pencil leads for paper based analytical devices with chemical modified electrodes have been also reported [76]. Pencil leads doped with Ag and AgCl were used to draw carbon-based Ag/AgCl reference electrodes [77]. A paper based potentiometric electronic tongue comprising three pencil drawn sensors sensitive to Cl$^-$, Na$^+$/K$^+$, and Ca$^{2+}$/Mg$^{2+}$ was able to make the difference between different types of mineral water and between tap and mineral water [78]. Pencil-on-paper devices can be employed as analytical tools [79–81] or as electronic devices [82–85].

2.4. Techniques Used for Surface Characterization of Bare or Modified PGEs. In order to demonstrate the modification of a surface, different techniques are used to investigate and to compare the morphology and/or the electrochemical characteristics of the respective surface and/or of the modifier, before, during, or after the modification process. For surface morphology of bare or modified PGE investigations, different techniques of electron [3, 15, 24, 28, 29, 32, 34, 35, 54, 60, 65–67, 85, 111, 118–122, 126–128, 130, 135, 141–143, 145–148, 158, 161, 170, 173, 175, 178, 181–183, 189, 198, 200, 204, 205, 210, 216, 218, 219] and atomic force microscopy [28, 29, 60, 65–67, 112, 126, 172, 198, 205] are widely used. Sometimes, scanning electron microscopy (SEM) was coupled with energy-dispersive X-ray spectroscopy analysis [130, 143, 149, 152, 156, 172, 187, 188, 203–205]. X-ray diffraction was applied to investigate the chemical composition and/or crystal structure [143, 145, 203, 204, 206]. Fourier transform-infrared (FT-IR) investigations were performed to emphasize the presence of certain functional groups indicating the chemical structure modification during the chemical reactions, like polymerization [3, 29, 65, 117, 121, 122, 128, 130, 141, 143, 146, 148, 156, 170, 175, 189, 205, 210]. FT-IR and Raman spectroscopy were also applied to determine the structure modification from graphite to graphene oxide [28, 147, 194].

Electrochemical impedance spectroscopy (EIS) provided information on impedance changes at the electrode surface and therefore on the appearance of surface modifications enabling thus the differentiation between unmodified and modified electrodes [3, 54, 60, 61, 104, 119, 127, 140, 149, 161, 170, 173, 182, 198, 205, 210, 216], while CV is useful to characterize an electrode from electrochemical point of view or to investigate the electroactivity of conducting polymers, providing information about the formation, the potential, and the anodic/cathodic peak potentials of the polymer [3, 15, 24, 28, 32, 43, 54, 60–63, 66, 67, 72, 104, 111, 114, 117, 118, 120–122, 125, 127, 135, 140, 144, 145, 149, 152, 158, 161, 168, 170, 175, 177, 181, 183, 192, 193, 203–205, 208, 210].

Some examples of these techniques used in the development of modified PGEs are listed below. Thus, SEM images of bare 2B-type PGE showed a smooth surface [29, 140] and for H-type pencil leads they revealed a porous, dense surface due to the homogeneous dispersion of graphite powder in the organic binder [158], while for the modified PGE they indicate a homogeneous distribution of the MWCNTs on the electrode surface [158], spindle-like Au-nanostructures [140], or different structures for sol-gel modified PGE, MIP-folic acid layer and MIP-layer on the sol-gel modified PGE [29]. SEM investigations revealed that the density of copper nanostructures on PGE is higher than on GCE or pyrolytic graphite.
electrodes and this fact is due to the PGE higher active surface area [201].

Metals electrodeposition is of high technological importance, for example, in the electronic industry as coatings. Thus, the mechanism of copper electrodeposition on PGE was investigated by CV and chronoamperometry, while SEM was used to observe the morphology of copper nuclei obtained in different experimental conditions [218]. Pd electrocrystallization mechanism on PGE was established based on the current transient curves. SEM micrographs indicate a homogeneous distribution of hemispherical Pd clusters on the PGE [219].

Raman spectroscopic examinations of the PGE carbon structure and SEM micrographs of the PGE surface before and after DPV oxidation of acyclovir emphasized no modifications during acyclovir electrochemical measurement, confirming thereby the stability of the PGE surface [27]. In the case of the Cu-microparticles modified PGE, SEM analysis showed that the surface morphology of the Cu-microparticles changed during the electroanalysis of valacyclovir due to the adsorption of the Cu-valacyclovir complex [180].

3. Conclusions

The data included in this paper were compiled after carefully studying, comparing, and correlating the information found in over two hundred articles that appeared in the last two and a half decades approaching this topic. The review pointed out the most important features of PGE as working electrode in comparison to other graphite based electrodes, emphasizing its even better electrochemical performances in some cases, but most of all its simplicity and high cost-effectiveness ratio. Due to the graphite pencil leads widespread availability (they can be purchased in local market at low costs) they constitute an important single-use electrode material. Therefore, PGEs are cheap and easy disposable, having also an adjustable area of the working surface, enabling shorter analysis times, and offering the possibility of determining low concentrations in small sample volumes. PGEs can be also readily miniaturized or modified. Thus, they can be employed as working electrodes as such or by modifying their surface either by electrochemical pretreatment or by covering it with different types of materials, ranging from simple compounds to various imprinted or nonimprinted polymers, nanomaterials, or combinations of these (nanocomposites), leading to improved selectivities and sensitivities. The techniques used to characterize the bare or modified PGEs are also listed together with some practical examples. Electroanalysis using PGEs include potentiometric, amperometric, or different voltammetric techniques and proved to reach wide linear ranges and low detection limits. All these resulted in the widespread applicability of PGEs to the determination of different inorganic and organic species from environmental, archeological, food, pharmaceutical, and clinical samples. It is worth mentioning the development, in recent years, of flexible paper based analytical electrochemical devices which use pencil drawn electrodes. Consequently, pencil graphite electrodes have proven to be a viable and economical electroanalytical tool.

Besides the various analytical applications, graphite pencils also found interesting uses in electronics.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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