

Short Communication

THE GRAPHITE SPRAY ELECTRODE AND ITS APPLICATION IN THE ANODIC STRIPPING VOLTAMMETRY OF BISMUTH

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**Summary.** The surface characteristics of carbon-paste electrodes are greatly improved by spraying the surface with graphite from an aerosol. Significant differences are shown by scanning electron microscopy. The available potential range in different electrolytes is narrower but background currents are decreased and reproducibility is improved, compared to the carbon-paste electrode. With a mercury film and 10-min deposition times, the detection limit for bismuth(III) is  $2 \times 10^{-9}$  M by the differential pulse technique.

Solid electrodes have become widely used in analytical electrochemistry [1, 1a], largely because of the interesting properties of carbon materials compared to platinum and gold surfaces, particularly their low background currents. Modified carbon electrodes have been the subject of many investigations [2, 3]. A very easy and rapid way of preparing a reproducible graphite surface is described in this paper. The graphite spray electrode was prepared on a carbon-paste electrode and on a glassy carbon electrode.

Bismuth determination was made on the mercury-covered graphite surface [4]; this technique was reported by Matson et al. [5] and further studied by Seitz [6].

*Experimental*

**Apparatus.** Voltammetric measurements were made on a Bruker E100 polarograph with a Hewlett-Packard type 7004B recorder. A three-electrode cell was used, with a saturated calomel reference electrode and a platinum auxiliary electrode. Nitrogen was passed over the solutions during all measurements.

Two different working electrodes were tested: (1) a rotating disc electrode which was a Tacussel type EDI electrode with a glassy carbon disk (7.07-mm<sup>2</sup> geometric area); and (2) a stationary carbon-paste electrode (Metrohm EA267; 1.2-cm diameter) prepared from a standard paste (Metrohm EA207C) of spectroscopic-grade carbon powder and Uvasol liquid paraffin.

*Reagents and solutions.* Reagent-grade sulfuric acid and potassium chloride were found to have very low bismuth contents and were used without further purification. Water was demineralized and then distilled twice, first from permanganate, and stored in polyethylene bottles.

Stock solutions of  $5 \times 10^{-3}$  M bismuth chloride in 1 M HCl were diluted with 0.25 M HCl to prepare standard solutions with lower concentrations for use: the solutions were deaerated by bubbling nitrogen for 15 min. Metal solutions were transferred with Eppendorf micropipettes having disposable plastic tips.

*Preparation of the graphite spray electrodes.* Glassy carbon electrodes were cleaned before the graphite spray was applied, by polishing on metallographic paper (Carbinet 600, Buchler, Evanston, IL). A uniform layer of graphite particles was applied to the disc by spraying from a can of Kontakt Chemie Graphite 33 (Rastatt, Germany) available in electronic stores. The spray was applied in short (2 s) spurts from the can held at a distance of approximately 50 cm until complete coating of the disk and teflon ring surrounding it was observed. Then the outer edge of the electrode body was polished to give a graphite spray disk covering only the glassy carbon disk plus the teflon ring surrounding the disk. The total surface area (disk and teflon ring) of the electrode was 95.0 mm<sup>2</sup> (11-mm diameter). After each measurement, the electrode was cleaned and resprayed.

When carbon-paste electrodes were used, the carbon-paste surface was renewed, before the spraying, and before each run, by extruding a small portion of the paste from the electrode followed by polishing on a smooth paper surface.

In both cases, the coated electrodes were heated under ventilation for a short time in order to remove any traces of organic solvents.

*Surface observation of the electrodes.* Comparison of the physical properties of the carbon-paste electrode and the graphite spray electrodes was done by optical and scanning electron microscopy (s.e.m.). The s.e.m. observations were made without prior metallic vapor coating.

### *Results and discussion*

*Surface properties of the electrodes.* Optical microscopy at different magnifications revealed very different granular textures of the carbon-paste and graphite spray electrodes (Fig. 1). With the carbon-paste electrode (Fig. 1a, b), the grain size is non-uniform and the shape is irregular; the grains are separated, with paraffin cementing them together. The surface of the carbon-paste electrode is also characterized by the presence of pits and channels between the grains, associated with the mosaic structure. In contrast, the graphite spray electrode (Fig. 1c) has much more finely divided and uniform, perhaps more amorphous, particles more evenly distributed. There is a notable absence of cavities or canyons between particles. The s.e.m. observations confirm these interpretations (Fig. 2).

*Electrochemical properties of the graphite spray electrode.* Table 1

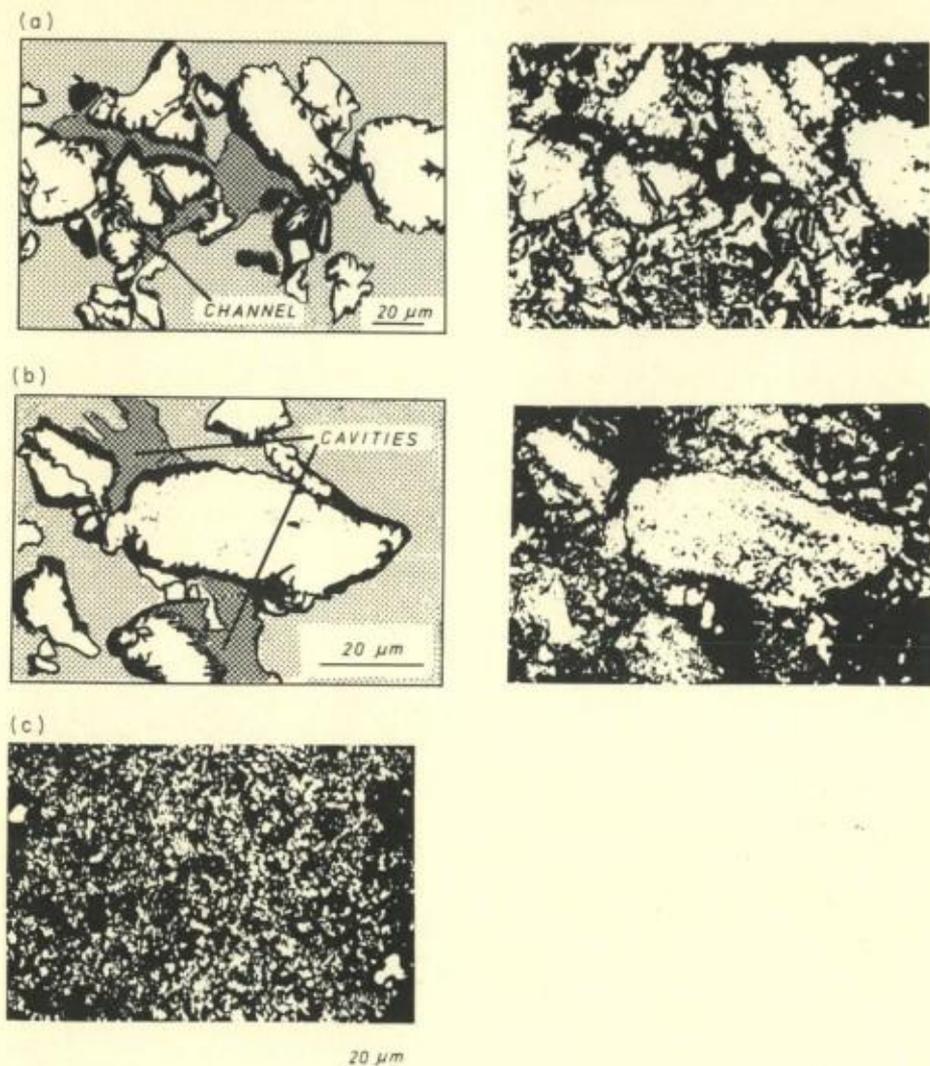


Fig. 1. Optical micrographs of the electrodes: (a) and (b) carbon-paste electrodes; (c) graphite spray electrode.

reports the cathodic and anodic potential limits observed in different media for the carbon-paste and graphite spray electrodes; a  $1\text{-}\mu\text{A}$  deviation from the residual current was used as the cut-off limit under conventional voltammetric conditions.

Differential pulse anodic stripping voltammetry at the graphite-covered carbon-paste electrode was examined. Mercury film electrodes prepared in situ were employed, for which purpose various volumes of the  $5 \times 10^{-3}$  M mercury(II) chloride solution were added to 25 ml of test solution to obtain

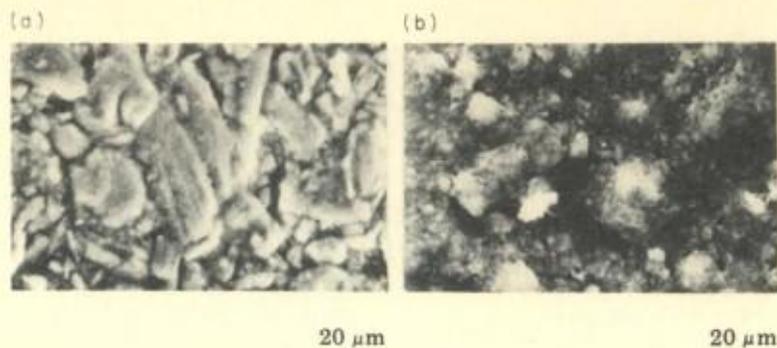


Fig. 2. Scanning electron micrographs: (a) carbon paste (350 $\times$ ); (b) graphite spray (350 $\times$ ).

TABLE 1

Potential limits for the carbon-paste and the graphite spray electrodes

Medium	Cathodic potential (V)		Anodic potential (V)	
	Carbon paste	Graphite spray	Carbon paste	Graphite spray
0.25 M HCl	-0.550	-0.250	+1.100	+0.850
1 M H <sub>2</sub> SO <sub>4</sub>	-0.450	-0.200	+1.250	+0.975
1 M H <sub>2</sub> SO <sub>4</sub> + 0.1 M KCl	-0.520	-0.225	+1.200	+0.900
PO <sub>4</sub> <sup>3-</sup> buffer, pH 2.0	-0.425	-0.300	+1.250	+0.900
PO <sub>4</sub> <sup>3-</sup> buffer, pH 6.5	-0.650	-0.350	+1.200	+0.700

a  $5 \times 10^{-6}$ – $2 \times 10^{-4}$  M mercury(II) ion concentration. The tested ion was bismuth(III) in a 1 M sulfuric acid solution containing potassium chloride [4]; bismuth was chosen because it is toxicologically interesting and is known not to form intermetallic compounds with other metals [7, 8]. The presence of chloride is necessary in order to obtain high sensitivities for bismuth [8]. An electrodeposition potential of  $-0.300$  V vs. SCE was employed for up to 20 min, with a waiting period of 30 s before the stripping scan was initiated. The stripping peak current observed at the graphite-covered electrode became independent of the mercury concentration at about  $10^{-4}$  M mercury(II) and this concentration was employed in subsequent studies. Figure 3 shows the high reproducibility from run-to-run on seven freshly prepared graphite-covered carbon-paste surfaces in 1 M sulfuric acid solutions containing 0.1 M potassium chloride and  $10^{-4}$  M mercury(II) chloride. The coefficient of variation was 2%; the carbon-paste electrode under the same conditions gave a coefficient of variation of 11%.

The peak current for  $2 \times 10^{-8}$  M bismuth at the graphite-covered electrode was a linear function of the electrodeposition time up to at least 15 min.

Differential pulse anodic stripping voltammetry at the graphite-covered

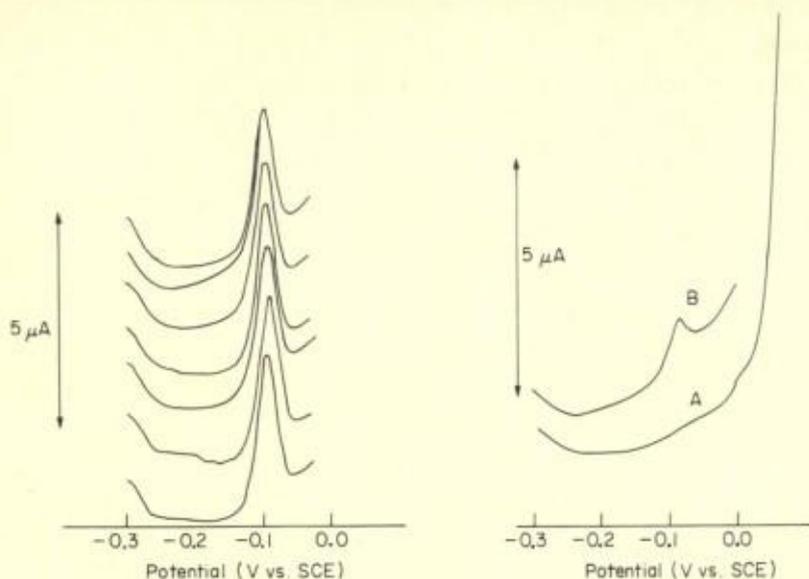


Fig. 3. Anodic stripping peaks of bismuth ( $2 \times 10^{-8}$  M) on seven different graphite spray surfaces from 1 M  $\text{H}_2\text{SO}_4$ -0.1 M KCl, after deposition for 10 min. Scan rate  $2 \text{ mV s}^{-1}$ ; measurements on first scan.

Fig. 4. Differential pulse stripping voltammetry of bismuth(III): (A) background current of the 1 M  $\text{H}_2\text{SO}_4$ -0.1 M KCl supporting electrolyte; (B) detection of  $2 \times 10^{-9}$  M bismuth(III) after deposition for 10 min.

glassy carbon electrode was also tested; the experimental conditions were the same as above. Seven determinations on fresh surfaces for the glassy carbon electrode and the graphite-covered glassy carbon electrode (scan rate  $2 \text{ mV s}^{-1}$ ; rotation speed = 1,500 rpm; deposition time 10 min) gave coefficients of variation of 5% and 4%, respectively. The bismuth peak currents at the graphite-covered glassy carbon electrode were proportional to the square root of the rotation speed up to 3500 rpm. A linear calibration graph was obtained for  $10^{-8}$ - $10^{-7}$  M bismuth. The dependence of the bismuth peak current on the electrodeposition time was linear up to 15 min.

Figure 4 shows the peak current observed with the carbon-paste graphite-covered electrode for a bismuth solution. The detection limits for the different electrodes used in this study, with 10-min deposition times, are reported in Table 2. Further experimental data on copper, selenium, cadmium, thallium, lead and zinc ions will be presented in a future publication.

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TABLE 2

Limits of detection ( $\mu\text{g l}^{-1}$ ) with 10-min deposition times

Carbon paste	Carbon-paste graphite covered	Glassy carbon	Glassy-carbon graphite covered
0.5	0.1	1	1

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