

## Carbon Paste Electrode Containing Dispersed Bismuth Powder for pH Measurements

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**Abstract:** The carbon paste electrode containing 17 % (w/w) of dispersed bismuth powder, despite its well-known performance in electroanalytical stripping methods, was also evaluated as a potential pH sensor. Potentiometric response to pH of solutions was ascertained under batch and flow conditions and compared to that of classical glass electrode. Continuous flow or flow injection modes of analysis together with buffers of different pH were employed to study the behavior of modified carbon paste electrode in thin layer cell. Proposed pH sensor exhibited linear, sub-Nernstian response of -41.2 mV per pH unit within the working range of pH 2 – 10 in mode of flow injection analysis. The longest response time registered to sudden change in hydrogen ion activity was 40 s. The sensor works de facto sequentially in two modes of operation, which is rather interesting feature described for an electrochemical sensor.

**Keywords:** Carbon paste electrodes; Bismuth powder; Electrode modification; pH measurements; Flow injection analysis.

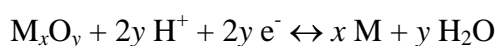
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## Introduction

In 2000, a bismuth film electrode (BiFE) was first reported as an environmentally friendly alternative to mercury electrodes in procedures involving electrometric stripping analysis [1]. However, such electrodes were introduced in potentiometry roughly a half-century ago by Schwabe, who had prepared his BiFEs by electrolytic plating of metal bismuth layers on graphite rods [2-4]. At those times, even glass electrodes for potentiometric pH measurements still belonged to rare instrumentation in some laboratories, and many researchers were interested in so-called metal/metal oxide electrodes serving for the same purpose. In principle, the pH sensing with such electrodes is based on the oxidation-reduction equilibrium between the particular metal and its anti-corrosion oxide layer immersed into an aqueous solution containing hydrogen ions, which can generally be written as



For potential of such a half-cell, noted as  $M | M_xO_y | H^+$ , the corresponding Nernst-Peters equation can be written in the form of

$$E = E^o(M_xO_y/M) + 0.0592/y \log [a(M_xO_y) a(H^+)^{2y} / a(M)^x a(H_2O)^y]$$

Further, taking into account unit activities of both solid substances as well as of water, the above equation is simplified to the form of

$$E = E^o(M_xO_y/M) + 0.0592 \log a(H^+) = E^o(M_xO_y/M) - 0.0592 \text{ pH}$$

Concerning bismuth electrodes for pH measurements as such, they were introduced even sooner (according to the literature in 1935) by Mehta and Jaktar [5], and further studied by others [6-12]; all the history involving also their applications in potentiometric as well as biamperometric titrations was reviewed very recently [13]. Analogously, antimony electrodes ( $Sb | Sb_2O_3 | H^+$ ) were recommended for pH measurements at those times [14,15], followed by other contributors [16,17] and reviewed in [18]; a capillary melt method for antimony oxide pH microelectrode represents one of the recent papers dealing with the matter [19]. It should be mentioned that the era of metal/metal oxide electrodes is still open for research; one can

follow numerous new articles dealing with the matter in the literature. Nowadays, especially pH electrodes based on platinum metals and their oxides stay in the centre of interest (for example, see refs. [20-22]).

As shown in our recent papers oriented to electroanalytical stripping methods [23-29], carbon paste electrode served as a proper material to be either covered by bismuth film or mixed with bismuth powder. It was expected that such a bismuth-dispersed electrode [27] could also be used for pH measurements as indicated above. The study of its possible applications under both batch and flow conditions are presented here.

## **Experimental**

### *Chemicals*

All the chemicals used for the preparation of solutions were of analytical reagent grade and purchased from Lachema (Czech Republic), Lach.Ner (Czech Republic), or Penta (Czech Republic). Phthalate (pH 4.01), phosphate (pH 6.98), and borate (pH 8.95) standard buffer concentrates were from Sevapharma (Czech Republic). All chemicals were dissolved as required with double-distilled water. Bismuth powder used for modification of carbon paste was from Sigma-Aldrich (99.99+%, 100 mesh, product 00914HQ).

### *Apparatus*

The flow injection system consisted of a peristaltic pump (Minipuls 3, Gilson SA., France), an injection valve with a sample loop 100  $\mu$ l (Ventil D, ECOM, Czech Republic), and a thin layer crossflow cell (BASi, USA). The working electrode was fixed via Teflon gasket with thickness 0.6 mm directly to the stainless steel back plate of the thin-layer cell. The reference electrode for flow measurements was Ag/AgCl/3M KCl (RE-6, BASi, USA). The argentchloride reference electrode of classical construction (type 10-25+, Elektrochemické detektory s. r. o., Czech Republic) with saturated KCl as inner electrolyte was used in batch configuration. For potential readings the electrodes were connected to a portable pH-meter (type 208L, Gryf HB s. r. o., Czech Republic). Solution pH was verified with a combined glass pH-electrode (HC 113, Theta '90, Czech Republic) and another

pH-meter (type 158, Gryf HB s. r. o., Czech Republic). The electrode was calibrated against standard buffer solutions [30].

### *Electrodes*

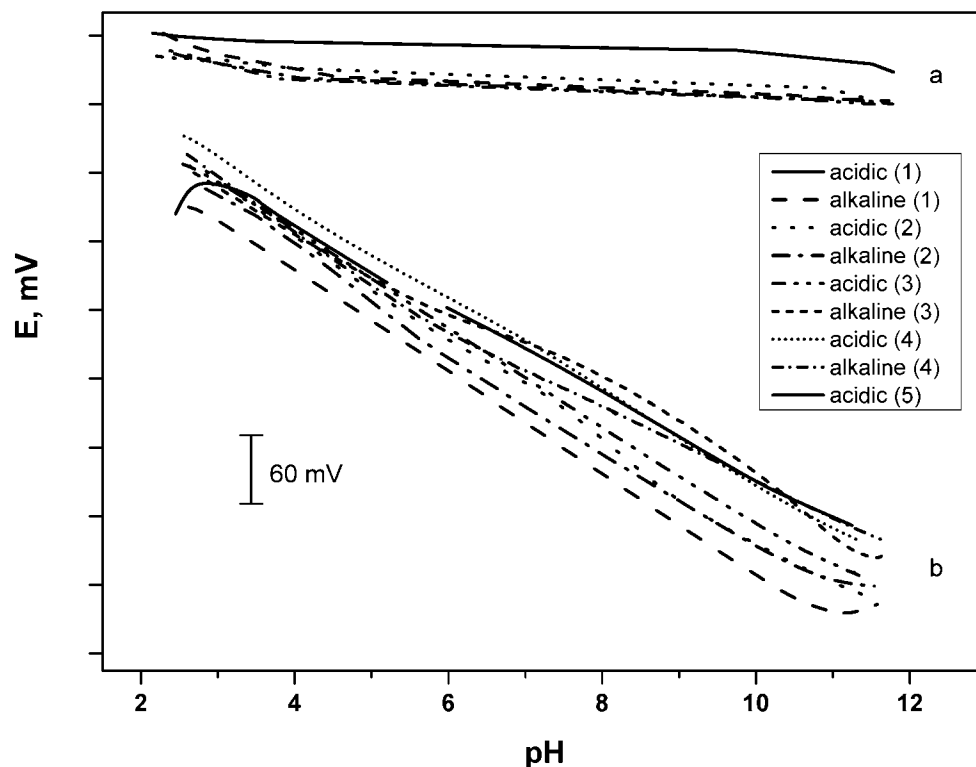
An unmodified bare carbon paste electrode (CPE) was prepared by intimately hand-mixing of 0.5 g spectroscopic graphite powder (CR-5, Maziva Týn, Czech Republic) with approx. 0.15 ml of mineral oil (Nujol, Fluka) using a pestle and mortar. Freshly made carbon paste mixture was packed into specially designed piston-type or groove electrode holder. The electrode surface was renewed by extruding small portion of carbon paste out from the holder with subsequently smoothing on wet filter paper before starting a new set of experiments. Carbon paste in groove electrode holder was just polished in the same way or exchanged completely if needed. Bismuth-modified carbon paste electrode (Bi-CPE) was prepared by mixing of 0.5 g bare carbon paste with 102 mg of bismuth powder to obtain carbon paste electrode containing 17 % (w/w) amount of bismuth.

## **Results and Discussion**

Initial tests were performed to determine the dependence of measured potential on changes in pH of the solution in batch configuration. Concerning the amount of bismuth, used for modification of electrode, the ratio 17 % (w/w) was selected as it was found minimal to achieve the best electroanalytical performance in stripping analysis of heavy metals [27]. The ability to monitor pH even with some limitations could extend functionality of already renowned voltammetric sensor.

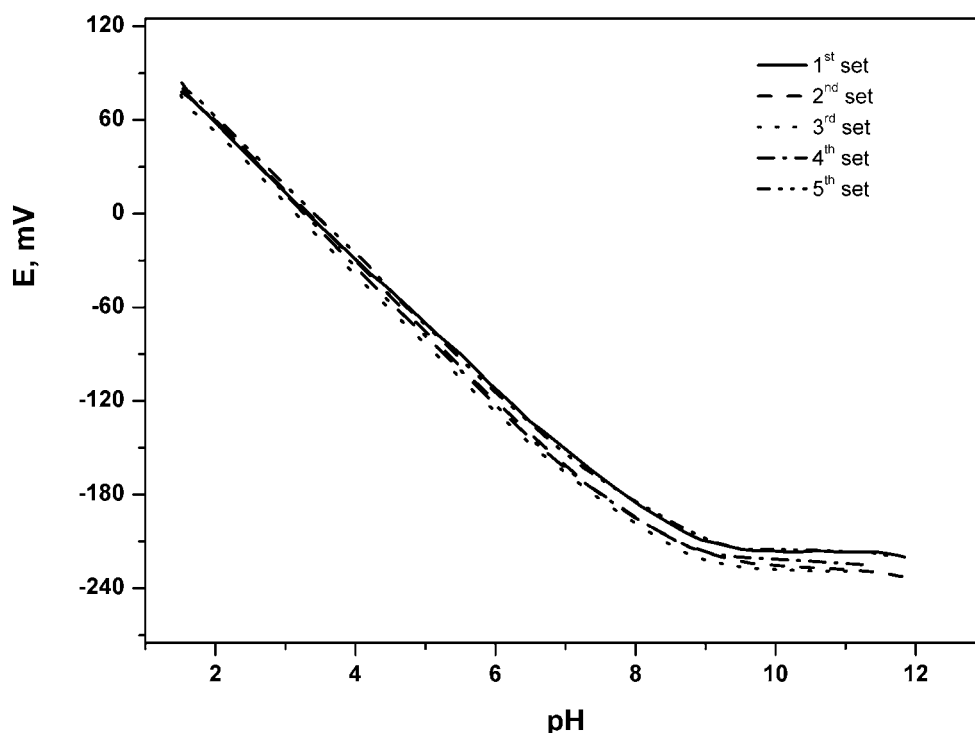
Bare carbon paste or Bi-CPE together with argentchloride reference electrode and a glass electrode for pH control were immersed into the solution agitated by the magnetic stirrer and the pH was altered gradually and repetitively via small additions of H<sub>2</sub>SO<sub>4</sub> or NaOH. Resulting potentiometric responses of both unmodified and Bi-modified CPE are presented in Fig. 1. The firstly mentioned electrode exhibited only weak dependence of potential on the solution pH. The potentiometric activity of carbon substrates for pH sensing due to the presence of adsorbed oxygen or residual functional groups, formed during manufacturing process, was already described [31]; however, the reproducibility, measurable range of pH and calibration slopes were worse to the glass electrode and such sensors demanded proper

activation. In case of CPE, chemically inert and hydrophobic paraffin oil, which is used as a binder of the paste, could also contribute to non-ideal potentiometric behavior of such heterogeneous carbon surface.



**Figure 1.** Potentiometric responses of bare CPE (a) and Bi-CPE (b) during consecutive pH cycling. Legend: direction of pH change (number of cycle).

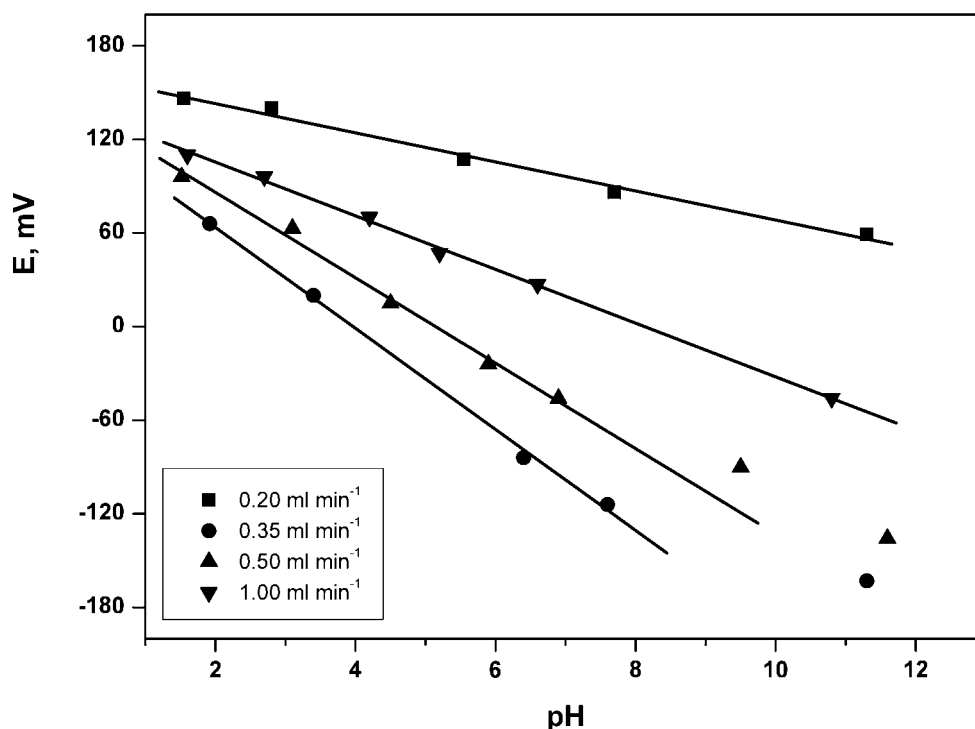
The situation was completely different after introducing a bismuth powder to the carbon paste mixture. Modified electrode responded to varying pH with much higher sensitivity and during consecutive cycling from alkaline to acidic environment and vice versa, the slope reached  $-44$  mV per pH unit and remained practically constant within the pH 3 – 11. Moderate shift of absolute potential can be attributed to surface conditioning after exposing the electrode to both ends of working potential range, where deviations from linearity occurred. Experiments performed in Britton-Robinson buffers (0.04 M phosphoric, boric and acetic acids), adjusted to particular pH with addition of 0.2 M NaOH, showed a shift of linear range to pH 1.9 – 8.5 with a slope  $-42$  mV  $\text{pH}^{-1}$ . Renewing the surface of carbon paste electrode did not have any substantial effect on the potentiometric response (see Fig. 2), which was almost identical also for repetitive measurements at the same electrode surface.



**Figure 2.** Repeatability of pH sensing at Bi-CPE in Britton-Robinson buffers with renewing of electrode surface between sets of measurements.

Bismuth-modified carbon paste was then embedded into groove electrode holder and subsequently used for pH measurements utilizing flow injection analysis. To ascertain the influence of flow rate on the setting of measured potential in time, the series of following experiments were performed. The solutions of  $\text{H}_2\text{SO}_4$  (pH 2) and  $\text{NaOH}$  (pH 11), representing the margins of electrode working range, were continuously pumped with different flow rates through the thin layer cell and the time of first potential change and the time when the potential became stable were recorded. Obtained data were then plotted as dependencies of time upon applied flow rate. Resulting curves (not shown) revealed that the stable potential was achieved nearly twelve times faster when switching from flow rate  $0.1 \text{ ml min}^{-1}$  to  $0.5 \text{ ml min}^{-1}$ . At higher rates up to  $1.5 \text{ ml min}^{-1}$ , the additional time decrease was only half as large. The change in flow rate during abovementioned experiments did not affect much the measured value of potential for both solutions.

In flow injection mode,  $0.001 \text{ M H}_2\text{SO}_4$  was injected into double-distilled water (carrier solution) and resulting peak-shaped potentiometric signals were recorded again for different flow rates (not shown). As it was expected, peak maxima appeared sooner at higher rates indicating faster wash out of the analyte from the thin layer cell.



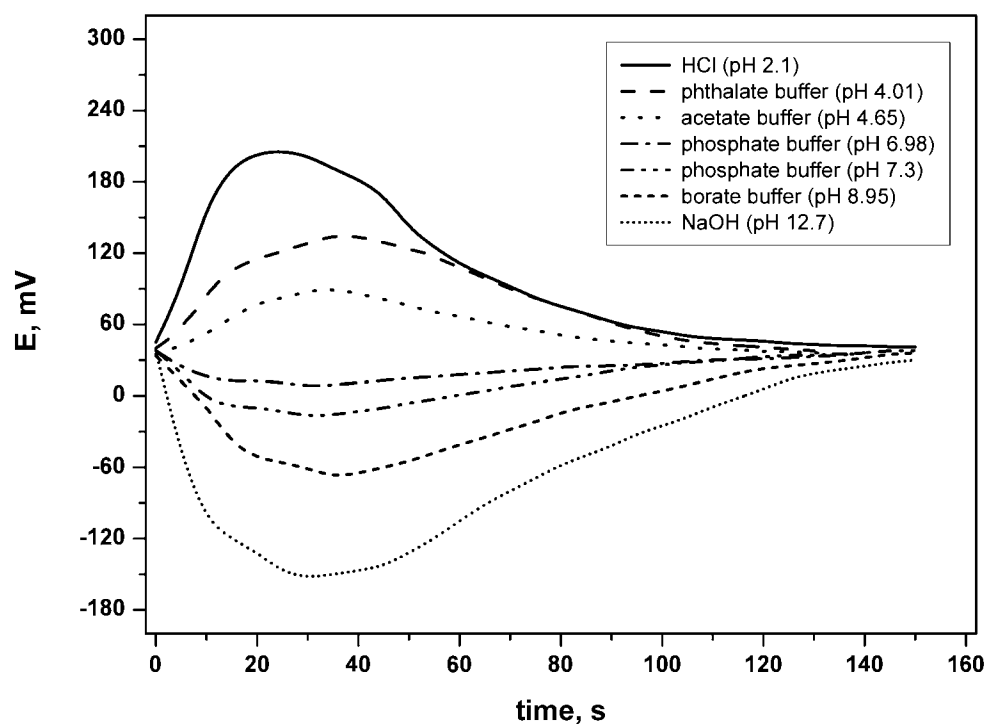
**Figure 3.** pH measurements at Bi-CPE in Britton-Robinson buffers at various flow rates and continuous flow mode.

Furthermore, the influence of flow rate on potentiometric response of carbon paste electrode modified with bismuth powder was also checked in Britton-Robinson buffers using continuous flow mode. After adjusting pH of buffer to particular value with NaOH, the solution was aspirated using peristaltic pump to the thin layer cell at selected flow rate and measured steady potential was registered. Resulting calibration curves are displayed in Fig. 3. Linear calibrations within pH 2 – 12 exhibited rather small slopes ( $-10 \text{ mV pH}^{-1}$ ) at low flow rates, but at higher rates, they became steeper up to  $-32 \text{ mV per pH unit}$ . However, larger deviations from linearity then occur at pH 9 and further. In addition, the time needed for establishing steady potential was much longer (several minutes) in case of low flow rates, whereas only tens of seconds were sufficient for potential equilibrium in faster flows.

Based on abovementioned findings, the flow rate of  $0.5 \text{ ml min}^{-1}$  was chosen as a reasonable compromise between sensitivity, working range of pH and response time for subsequent pH measurements of different solutions using flow injection analysis. To test the potentiometric behavior and performance of Bi-CPE the solutions of 0.01 M HCl (pH 2.1), 0.1 M acetate buffer (pH 4.65), 0.1 M phosphate buffer (pH 7.3), and 0.01 M NaOH (pH 12.7) were prepared and their pH was verified using combined glass electrode. The glass electrode was calibrated against standard phthalate (pH 4.01), phosphate (pH 6.98), and

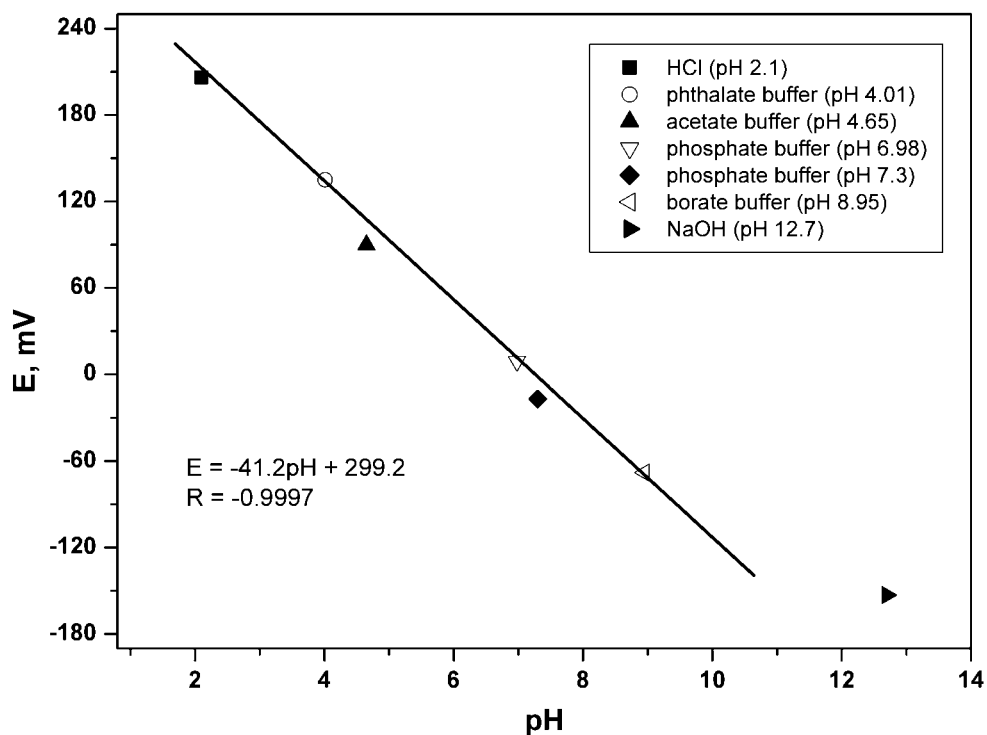
borate (pH 8.95) buffers, which were employed for testing also. The samples were introduced into the double-distilled water as carrier solution via injection valve and sample loop 100  $\mu\text{l}$  and potentiometric response was registered each five seconds. Resulting time based signals are summarized in Fig. 4. It is evident the maximum response is attained within 40 s at given experimental conditions for all the tested solutions injected to the flow.

Peak potential of each response was plotted against the pH of particular solution, which was determined by the glass electrode. Calibration line was then constructed from potentials of phthalate, phosphate, and borate buffers (see Fig. 5). Calculated slope has a value of  $-41.2 \text{ mV pH}^{-1}$ , which is slightly lower than reported for bismuth (film) electrode [32]. Working range was linear up to pH 10 with a strong deviation at higher pH. Evaluated values of potential fitted the calibration well for each tested solution except the 0.01 M NaOH. If all points excluding the last one were included in the regression line, the slope  $-40.7 \text{ mV per pH unit}$  was obtained.



**Figure 4.** Potentiometric response of various solutions at Bi-CPE after injection into double-distilled water. FIA, flow rate  $0.5 \text{ ml min}^{-1}$ , injection loop  $100 \mu\text{l}$ .





**Figure 5.** Calibration for pH measurements at Bi-CPE. Experimental conditions the same as in Fig. 4.

## Conclusions

Although the carbon paste electrode modified with bismuth powder exhibited acceptable sensitivity to change in pH of measured solutions, it will not definitely replace the classical glass electrode for such task; measured slopes were around  $-42 \text{ mV pH}^{-1}$  with limited working pH range. However, it may find its purpose in some special cases, where bismuth-modified electrode is used for electroanalysis of e.g. heavy metals or for continuous monitoring in flow arrangement; acidic to mild alkaline solutions can be potentiometrically checked or verified for their pH before the analytical (voltammetric or amperometric) procedure itself. During such experiments, the electrode works de facto sequentially in two modes of operation, which is rather interesting feature described for an electrochemical sensor.

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