

SHORT COMMUNICATION

Voltammetric Determination of Cocaine in Confiscated Samples

María Teresa Fernández Abedul, José Ramón Barreira Rodríguez, Agustín Costa García, and Paulino Tuñón Blanco¹

Department of Physical and Analytical Chemistry, University of Oviedo, 33071 Oviedo, Asturias, Spain

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ABSTRACT

The electrochemical behavior of the abuse drug cocaine has been studied. Cocaine undergoes an irreversible oxidation process on carbon paste electrodes. It was calculated that 2 electrons were involved, and the value obtained for the charge transfer coefficient was 0.362 ± 0.006 . Comparative voltammetric experiments yielded an estimated diffusion coefficient value for cocaine of $0.27 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. A linear calibration plot from 1.0×10^{-6} to $1.0 \times 10^{-4} \text{ M}$ was obtained by using a scan rate of 50 mV s^{-1} . A simple and reproducible procedure is proposed for the determination of cocaine in illegal dosage forms confiscated by police authorities; the results agree with those of a HPLC-UV method.

INTRODUCTION

The large increase in the consumption of drugs of abuse (among them cocaine) in recent years, and the necessity to control its purity in the batches, seized by both health and police authorities, have prompted analytical chemists to provide a means of carrying out such determinations.

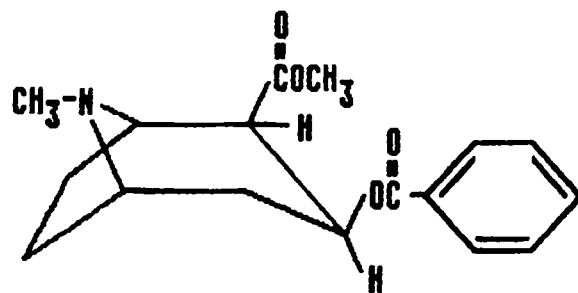
Gas chromatography (GC) [1–4] and liquid chromatography (LC) [5–7] have both been used in the analysis of cocaine and its metabolites in several matrices. Although these techniques are very powerful, they are time-consuming, and this poses a serious problem when dealing with a large number of samples.

Other techniques currently used include EMIT (enzyme-multiplied immunoassay techniques) [8] and RIA (radioimmunoassay) [9]. In spite of the good sensitivity shown by these immunoassay techniques, they lack the desired selectivity (as obtainable by liquid chromatography–mass spectrometry). The use of radioactive materials, the high cost of enzymes and/or specific antibodies, the long incubation periods required, and the interference arising from cross-reactivity are but a few of the disadvantages of the immunoassay techniques.

The advance in experimental electrochemical techniques in the field of analysis of drugs of abuse [10] is due to their simplicity, low cost, and relatively short analysis time when compared with the above-mentioned techniques.

The study of electrooxidizable species on solid electrodes allows the development of rapid procedures of analysis in relatively simple matrices because a deaeration

step is not required. Besides, these techniques possess adequate sensitivity to analyze cocaine seized by authorities without any preseparation step. Sample preparation is as simple as dissolving the material in a suitable medium (aqueous or nonaqueous) and carrying out the analysis in one aliquot of the resulting solution.



Cocaine

The electrooxidation of the tertiary amine present in the structure of cocaine has been used for the amperometric detection of the drug after a chromatographic separation [11, 12], that seems to offer better perspectives than the spectrophotometric detection.

To the best of our knowledge, there has not been a report in the literature on the electrochemical behavior of cocaine. This induced us to carry out a comprehensive study of the oxidation process this drug undergoes on carbon paste electrodes, as well as to set up an analytical procedure to determine by means of voltammetric techniques samples of the drug obtained in seizures.

¹ To whom correspondence should be addressed.

EXPERIMENTAL

Apparatus and Reagents

Linear sweep voltammetric experiments were carried out by coupling a Metrohm VA-612 scanner to a Metrohm VA-611 potentiostat, and by using the traditional three-electrode potentiostatic system. A home-made carbon paste electrode having a 0.071 cm^2 surface area was used as the working electrode, while a platinum wire served as auxiliary electrode. Potentials were measured versus an Ag/AgCl reference electrode. Voltammograms were recorded on a Graphtech WX 4221 X-Y recorder. A Metrohm E-506 polarograph was used for the coulometric experiments. Britton–Robinson buffers covering the whole range of pH values were used, as well as 0.1 M $\text{NH}_3/\text{NH}_4\text{Cl}$ solutions of pH 9.0. Stock solutions of cocaine (Sigma) were prepared in methanol from the respective hydrochloride. Its concentration was periodically checked by high performance liquid chromatography–ultraviolet spectroscopy (HPLC-UV).

Electrode Activation

The following procedure was used to obtain reproducible voltammetric signals:

The electrode was kept in a stirred solution for 30 seconds with electrolysis at potential higher values than $+1.25 \text{ V}$. Electrolysis was then switched off and the solution was stirred for 10 seconds. Finally, the starting potential was maintained for 10 seconds in quiescent solution before the potential scan was started.

Using this procedure and ignoring the first scan, reproducible voltammetric responses were obtained for five scans with a relative standard deviation less than 0.9%.

Analytical Procedure

First 10 mg of sample, accurately weighed, is dissolved in methanol and made up to 10 mL of methanol. An aliquot of $100 \mu\text{L}$ of the resulting solution is transferred to a polarographic cell containing 10 mL of a pH 9.0 buffer. The voltammogram is then recorded in the linear sweep voltammetric (LSV) mode from an initial potential of $+0.5 \text{ V}$ at a scan rate of 50 mV s^{-1} . Quantitation of the drug is achieved by the standard addition method.

RESULTS AND DISCUSSION

On carbon paste electrodes, cocaine was observed to give rise to a single oxidation process that is irreversible in nature. This process is observable only at pH values higher than 6.5, and the pH of the assay solution possesses a marked effect on its half-peak potential ($E_{p/2}$).

A plot of $E_{p/2}$ versus pH yields two straight lines, from which intercept point a $\text{p}K_a$ value of 8.5 can be deduced (Figure 1) in good accordance with the literature [13]. On the other side, the effect of pH on peak magnitude is almost negligible up to pH 8; a small increase in peak current was observed at more alkaline pH values, reaching a plateau at pH 9. Since at pH 9 the drug presents a well-

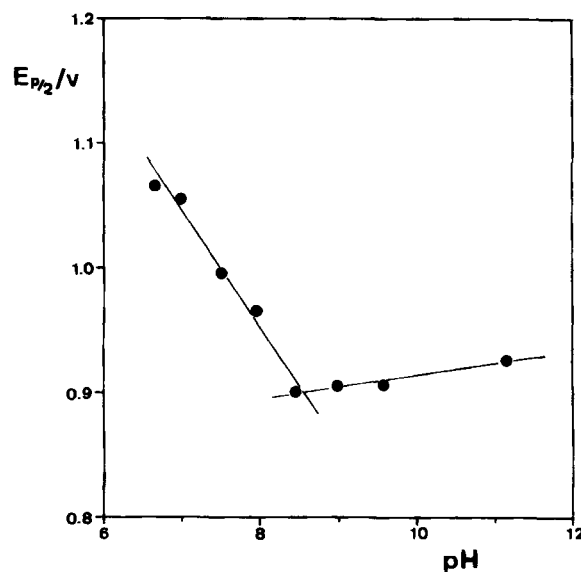


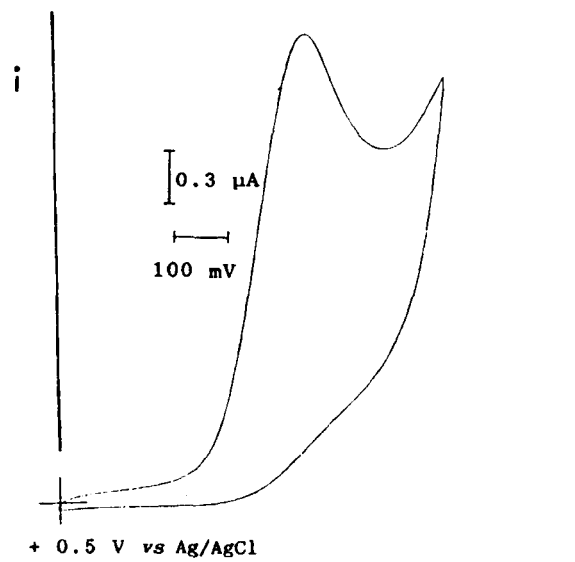
FIGURE 1. Influence of pH on the half-peak potential of cocaine. Concentration, $5.0 \times 10^{-5} \text{ M}$; scan rate, 100 mV s^{-1} .

defined peak that is easily measurable (Figure 2), pH 9 was chosen for the remainder of the work.

Voltammograms obtained for a $6.0 \times 10^{-5} \text{ M}$ solution of cocaine for increasing scan rates showed that a linear relationship exists between the peak intensity i_p and the square root of the scan rate $v^{1/2}$ in the range 2–100 mV s^{-1} according to the following equation:

$$i_p = 18.977 v^{1/2} - 0.402, \quad r = 0.9992, n = 9$$

FIGURE 2. Cyclic voltammogram obtained for a $2.0 \times 10^{-5} \text{ M}$ solution of cocaine at pH 9.0. Scan rate, 50 mV s^{-1} .



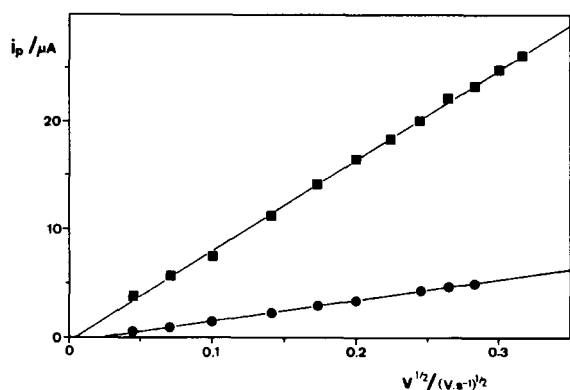


FIGURE 3. Variation of peak current with the square root of the scan rate for solutions of hexacyanoferrate(II) (4.76×10^{-4} M, ■) and cocaine (5.96×10^{-5} M ●), at pH 9.0.

where i_p is in microamperes and $v^{1/2}$ in (volts per second) $^{1/2}$.

The use of a scan rate of 50 mV s^{-1} has allowed the attainment of a wide range of linearity that covers 2 orders of magnitude, from 1.0×10^{-6} to 1.0×10^{-4} M, as expressed by the following equation:

$$i_p = 1.19 \times 10^5 c + 0.069 \quad r = 0.999, n = 9$$

where concentration is in molar units and peak intensity again in microamperes.

Potentiostatic coulometric experiments have been carried out to calculate the number of electrons involved in the oxidation process. For this purpose, successive exhaustive electrolysis runs were done for solutions containing $0.10 \mu\text{mol}$ of the drug by applying a potential of $+0.950 \text{ V}$ and using a carbon paste macroelectrode having an area of 4.52 cm^2 . An average value of 1.93 ± 0.09 was found, and we have concluded that two electrons are involved in the mechanism.

The charge transfer coefficient was calculated from nine voltammograms of a 9.10×10^{-6} M cocaine solution in pH 9.0 buffer using a scan rate of 50 mV s^{-1} with the well-known equation for irreversible processes [14]:

$$\beta = \frac{0.048}{n(E_p - E_{p/2})}$$

where potentials are measured in volts units. The value obtained for β was 0.362 ± 0.006 .

The diffusion coefficient of the drug was calculated at 25°C from the Randles-Sevcik equation by comparing the slopes of the lines obtained by plotting i_p versus $v^{1/2}$ for a 5.96×10^{-5} M solution of cocaine and a 9.1×10^{-4} M solution of hexacyanoferrate(II), respectively.

The experimental data are shown in Figure 3, and by assuming a value of $0.65 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficient of hexacyanoferrate(II) [15], it was possible to establish the corresponding diffusion coefficient for cocaine:

$$D_0 = 0.27 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

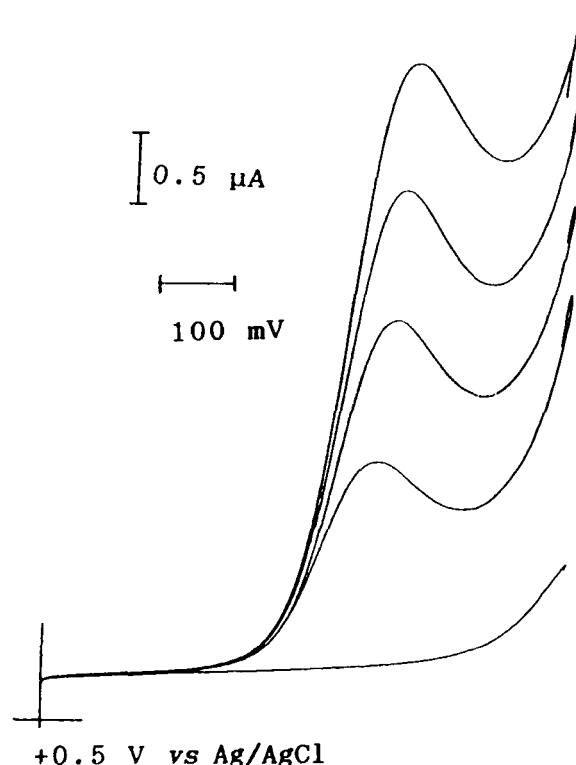


FIGURE 4. Standard addition method for cocaine determination in a real sample. Voltammograms corresponding to the blank, the sample, and successive additions of $44.9 \mu\text{g}$ of cocaine at pH 9.0. Scan rate, 50 mV s^{-1} .

ANALYTICAL APPLICATION

The above-described process for the oxidation of cocaine has been used to determine the drug in illegal dosage samples seized by police authorities, and the results have been compared with those obtained by HPLC with UV detection.

Following the procedure described under Experimental, three samples were analyzed in triplicate. The standard addition method was used to quantitate the contents of the samples (Figure 4), and the results are given in Table 1.

The results obtained show that the proposed method could be a good tool for rapid and inexpensive screening of cocaine or for the determination of the drug in street cocaine samples.

TABLE 1 Comparative Analyses Carried Out for Three Samples Acquired from a Police Seizure

Sample	Results ($\mu\text{g mL}^{-1}$)	Techniques from Analytical
1	281	296 ± 5
2	277	284 ± 4
3	42	44 ± 1

ACKNOWLEDGMENTS

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REFERENCES

1. D. M. Chinn, D. J. Crouch, M. A. Peat, B. S. Finkle, and T. A. Jennison, *J. Anal. Toxicol.* 4 (1980) 37.
2. C. A. Amon, L. G. Tate, R. K. Wright, and W. Matusiak, *J. Anal. Toxicol.* 10 (1986) 217.
3. M. J. Prager, S. M. Harrington, and T. F. Governo, *J. Assoc. Off. Anal. Chem.* 62 (1979) 304.
4. P. Jacob, B. A. Elias-Baker, R. T. Jones, and N. L. Benowitz, *J. Chromatogr. Biomed. Appl.* 61 (1987) 277.
5. I. R. Tebbett and Q. W. McCartney, *Forensic Sci. Int.* 39 (1989) 287.
6. R. Gill, R. W. Abbott, and A. C. Moffat, *J. Chromatogr.* 301 (1984) 155.
7. W. A. Trinler and D. J. Reuland, *J. Forensic Sci. Soc.* 15 (1975) 153.
8. W. M. Asselin, J. M. Leslie, and B. McKinley, *J. Anal. Toxicol.* 12 (1988) 207.
9. R. D. Budd, *Clin. Toxicol.* 18 (1981) 773.
10. J. R. Barreira, V. Cabal, A. Costa, and P. Tuñón, *Analyst*, 115 (1990) 209.
11. C. M. Selavka, I. S. Krull, and I. S. Lurie, *Forensic Sci. Int.* 31 (1986) 103.
12. R. S. Schwartz and K. O. David, *Anal. Chem.* 57 (1985) 1362.
13. D. D. Perrin, *Dissociation Constants of Organic Basis in Aqueous Solution*, London, Butterworths, 1965; supplement, 1972.
14. R. N. Adams, *Electrochemistry at Solid Electrodes*, Dekker, New York, 1969, p. 126.
15. M. Von Stackelberg, M. Pilgram, and V. Toone, *Electrochemistry*, 57 (1953) 342.