

## The cathode ray polarography of phenylmercuric nitrate

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**E**XPERIMENTS on the absorption of phenylmercuric nitrate by rubber teats required a simple, rapid and sensitive assay for concentrations of phenylmercuric nitrate from 0.5 to 20.0  $\mu\text{g/ml}$ . Both ultraviolet spectrometry (Eldridge & Sweet, 1956) and chemical methods (British Pharmacopoeia, 1963; Department of Pharmaceutical Sciences Report, 1962) are relatively insensitive, the spectrometric method also being subject to interference by extractive from rubber teats. Ordinary polarographic methods have been used for higher concentrations of phenylmercuric nitrate, two cathodic waves being observed at half-wave potentials of about  $-0.2$  V and  $-0.9$  V respectively. These have been observed in a number of supporting electrolytes, including hydrochloric acid (Page & Waller, 1949), Britton-Robinson buffers (Benesch & Benesch, 1951) and a glycerol-triethanolamine mixture with gelatin (Osborne, 1950).

The cathode ray polarography of phenylmercuric nitrate (0.4–20.0  $\mu\text{g/ml}$ ) was therefore investigated in hydrochloric acid (0.1N), lithium chloride (0.2N) and buffer solutions (Britton-Robinson and Sorensen) in the pH range 1.8 to 12.3. In all cases only one wave of analytical importance was seen, the peak voltage being about  $-0.3$  V. Since good linearity, wave shape and sensitivity were found with both 0.2 N lithium chloride and 0.1 N hydrochloric acid, the latter was chosen as supporting electrolyte.

### EXPERIMENTAL AND RESULTS

*Apparatus.* A Davis differential cathode ray polarograph was used, and peak voltages were recorded with reference to the mercury pool anode.

*Operation.* Trace impurities in the supporting electrolyte became apparent at high instrument sensitivities. Phenylmercuric nitrate concentrations in the range of 0.4–2.0  $\mu\text{g/ml}$  were therefore examined by comparing 50 mS derivative operation with the twin cell subtractive mode. This enabled subsequent adoption of the more rapid and convenient 50 mS derivative working for lower concentrations. Direct operation was used in the concentration range 2.0–20.0  $\mu\text{g/ml}$ . Determinations were made at 25°, all solutions being previously flushed with nitrogen until dissolved oxygen no longer affected wave shape or peak height (5 min).

*Calibration graph.* To solutions (5 ml) containing 0.4–20.0  $\mu\text{g/ml}$  of phenylmercuric nitrate (B.D.H.) in a polarographic cell, 0.6 N hydrochloric acid (1 ml) was added and the solution polarographed (starting potential  $-0.1$  V). A ten point calibration graph was linear ( $r=0.997$ ,  $P>0.999$ ), each point representing the mean of six readings from duplicate determinations on each of three solutions prepared from solid

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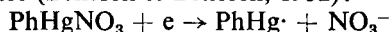
phenylmercuric nitrate. Limits of error at the 1.0  $\mu\text{g/ml}$  level were  $\pm 0.04 \mu\text{g/ml}$ .

*Wave characteristics.* The wave is irreversible since on reverse sweep an altered pattern was obtained. With increase in pH from 1.8 to 12.3 the peak voltage showed little change, but became less negative with increased depolarizer concentration. Peak currents fell by about 30% with increase in pH from 1.8 to 12.3; in hydrochloric acid (0.1N) the peak current temperature coefficient was negative ( $-0.24\%$  per degree) in the range 25–50°.

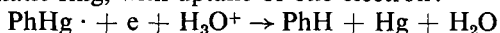
Concentration effects could not be examined above 40  $\mu\text{g/ml}$  in hydrochloric acid due to precipitation of phenylmercuric chloride. Using a support electrolyte of pH 2.0 however (0.1 M sodium acetate, M acetic acid, 0.1 M hydrochloric acid), concentrations of phenylmercuric nitrate (20.0–160.0  $\mu\text{g/ml}$ ) were examined and one wave only observed. The peak current did not increase directly with concentration but reached a maximum, with distortion of the wave peak, at about 120  $\mu\text{g/ml}$ , indicating an adsorption effect. If lead ion (10.0  $\mu\text{g/ml}$ ) and phenylmercuric nitrate (120.0  $\mu\text{g/ml}$ ) were present in the same solution, the more negative lead wave (peak voltage  $-0.5$ ) was unaffected by the presence of phenylmercuric nitrate.

#### DISCUSSION

The electrode reactions suggested by Benesch & Benesch (1951) for the two polarographic waves observed during the reduction of phenylmercuric nitrate are as follows. For the less negative wave, a single electron reduction to the phenylmercury radical, which is adsorbed on the mercury drop surface (Benesch & Benesch, 1952):



The more negative wave corresponds to removal of the mercury atom from the aromatic ring, with uptake of one electron:



The single wave observed during cathode ray polarography is probably produced by the rapid consecutive occurrence of the above reactions. Were it due only to the former reaction, adsorption of the radical at high concentrations would be expected to reduce the effective drop area with consequent distortion or diminution of the wave produced by included lead. At lower depolarizer concentrations (0.4–20.0  $\mu\text{g/ml}$ ), any adsorption effect is slight, as shown by peak current/concentration linearity.

The method described for concentrations of phenylmercuric nitrate from 0.4–20.0  $\mu\text{g/ml}$  is simple and rapid. A single determination takes 6–7 min and a ten point calibration graph 40 min.

#### References

- Benesch, R. & Benesch, R. E. (1951). *J. Am. chem. Soc.*, **73**, 3391–3393.  
 Benesch, R. & Benesch, R. E. (1952). *J. phys. Chem., Ithaca*, **56**, 648–650.  
 Eldridge, A. & Sweet, T. R. (1956). *Analyt. Chem.*, **28**, 1270–1272.  
 Osborne, G. H. (1950). *Analyst, Lond.*, **75**, 671–673.  
 Page, J. E. & Waller, J. G. (1949). *Ibid.*, **74**, 292–294.  
 Report on the work of the Laboratory, January, 1962 to December, 1962, Department of Pharmaceutical Sciences (1963). *Pharm. J.*, **190**, 379–380.