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Editorial Open Access

# Electrochemical Detection versus Ultraviolet Detection

**Hideharu Shintani***

*Chuo University, School of Science, 1-13-27, Kasuga, Bunkyo, Tokyo 112-8551, Japan*

Electrochemical detection (ED) is used for the sensitive detection and measurement of electro-active analytes in many areas of analytical chemistry and biochemistry. These applications range from electrode sensor devices *via* flow injection analyses to direct measurements of neurochemicals in brain tissue using *in vivo* cyclic voltammetry. In separation science, ED is used to detect and measure responsive analytes in flowing streams following analysis by high-performance liquid chromatography (HPLC) or capillary electrophoresis (CE). The use of ED with HPLC is by far and away the most important application of ED in flowing systems. The use of HPLC-ED grew by 5 times between the 1980s and the 1990s. However, its popularity should be compared to HPLC with fluorescence detection and HPLC with MS detection. Most published HPLC methods use UV/VIS detection without fail.

Unlike UV or fluorescence detectors, ED does not exploit a physical property of an analyte, but an induced chemical change that results from an electrochemical reaction. ED must, therefore, be considered to be a type of post-column chemical reaction detector. ED differs, however, from other post-column reactors used in HPLC in that no reagents or reaction devices are normally required to effect the chemical change in the analyte. In addition, the reaction kinetics are usually fast leading to minimal extra-column effects. With UV detectors, selectivity is adjusted by varying the detection wavelength, lower wavelengths often giving enhanced sensitivity and a response from a wider range of analytes. A modest degree of selectivity is achieved by using UV detection in the aromatic region (240-270 nm) and traditionally 254 nm has proved popular. However, at lower wavelengths (200-210 nm), the absorption of the eluent, of other eluent constituents or of oxygen become limiting. Relatively few compounds show useful absorption at wavelengths higher than 340 nm (the lower limit of the deuterium lamp emission). Generally, responses are usually independent of eluent conditions. In ED detection both sensitivity and selectivity are adjusted by varying the potential maintained between the working and reference electrodes, higher potentials, up to a local maximum, giving increased sensitivity. However, higher potentials usually induce a response from more compounds and therefore compromise selectivity. In oxidative mode, oxidation of eluent constituents becomes limiting at higher applied potentials, whilst in reductive mode, interference from dissolved oxygen can prove difficult to exclude. The response at the electrode is also very dependent on the eluent composition, especially its pH. Thus, as in all analytical methods, it is the signal-to-noise (S/N) ratio that is important and the detection conditions eventually adopted for a separation are a compromise between the electrochemical response of the analyte, the optimum eluent for both detection and elution, and interference from the sample matrix or from noise or drift from electronic or other sources.

In HPLC-ED the column elute flows over the surface of an 'inert' electrode maintained at an appropriate positive or negative potential relative to a reference electrode. At the electrode surface analytes possessing electro active functional groups undergo oxidation or reduction. The electrons released travel *via* the electrode and the change in current can be measured and related to the concentration of the analyte. Modem electronics allow the applied (working) potential to be held within very tight limits while at the same time measuring and amplifying the very small currents created. Hence ED can be very sensitive. Both ED and fluorescence detectors can be at least 100 times more sensitive towards responsive compounds than a standard UV detector and are much more selective. Unfortunately, with time electrochemical reaction products tend to accumulate at the electrode surface leading to loss of activity and hence loss of detector response - this is the major reason ED remains a relatively specialized field compared with UV detection, which is much popular even though less sensitive and selective due to an easy handling.

The readers can choose which detectors may be the most appropriate detector for your purpose from the characteristics of the compound(s) of interest to determine in your study.

***Corresponding author:** Hideharu Shintani, Faculty of Science and Engineering, Chuo University, 1-13-27, Kasuga, Bunkyo, 112-8551, Tokyo, Japan, Tel: +81425922336; Fax +81425922336; E-mail: shintani@mail.hinocatv.ne.jp

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