

Introduction

Electrochemistry (EC) in combination with mass spectrometry (MS) creates a powerful platform to simulate various oxidation and reduction processes. Electrochemistry is a complementary technique to traditional *in vivo* or *in vitro* metabolism studies, and delivers the oxidative metabolic fingerprint of a (drug) molecule in a very short time [1].

Recently, the use of EC-MS has been extended towards new applications such as the investigation of the degradation of xenobiotics [2, 3]. Numerous xenobiotics and their derivatives undergo oxidative and reductive degradation and these processes can be mimicked in the electrochemical cell. However, there are substances that remain as persistent organic pollutants in the soil, therefore, on-line EC-MS can be a valuable tool for simulation and prediction of transformation and degradation reactions in environment. Additionally, EC-MS can be used to initiate a chemical reaction between xenobiotic or its metabolite with environmental matrices such as natural organic matter (NOM). Understanding of xenobiotics degradation, their risk assessment and persistence in environment is a field of increasing interest for environmental research.

In this poster, we present a comparison of sulfadiazine (SDZ) metabolites formed in the environment and by chemical oxidation in the electrochemical cell. Sulfadiazine was chosen as a model compound. Sulfadiazine is known as a veterinary antibiotic and its metabolism is well described in the literature [4]. Furthermore, the chemical reaction of sulfadiazine with a model substance for soil organic matter (catechol) is shown to demonstrate a model system for the formation of non-extractable residues.

Methods

A ROXY EC system (Antec, The Netherlands) equipped with a thin-layer cell (ReactorCell™, Antec, The Netherlands) and an infusion pump (Harvard, USA) was used in all experiments. The cell was equipped in working electrode (boron doped diamond or glassy carbon), the reference electrode HyREF™ (Pd/H₂) and an auxiliary electrode. A boron doped diamond (Magic Diamond (MD)) working electrode was used for oxidative degradation of sulfadiazine. Typically, 20 μM solution of xenobiotic in 200 μM ammonium acetate, pH 6.8 / MeOH, 70:30 (v/v) was pumped through the electrochemical (EC) cell at a flow rate of 10 μL/min. Oxidation of catechol in the presence of sulfadiazine was conducted at a glassy carbon (GC) working electrode. MS voltammogram was measured in a flow injection mode while a potential ramp from 0 to 2,500 mV was applied with a step of 10 mV/s.

MS experiments were carried out using an ESI-LTQ-FT Ultra (ThermoFisher Scientific, San Jose, CA, USA) equipped with a 7 T supra-conducting magnet. Mass spectra were recorded in full scan from 90–600 m/z, first with the linear trap, followed by Fourier transform ion cyclotron resonance (FTICR) mass spectra (measured at a resolution of 100,000 at 400 m/z).

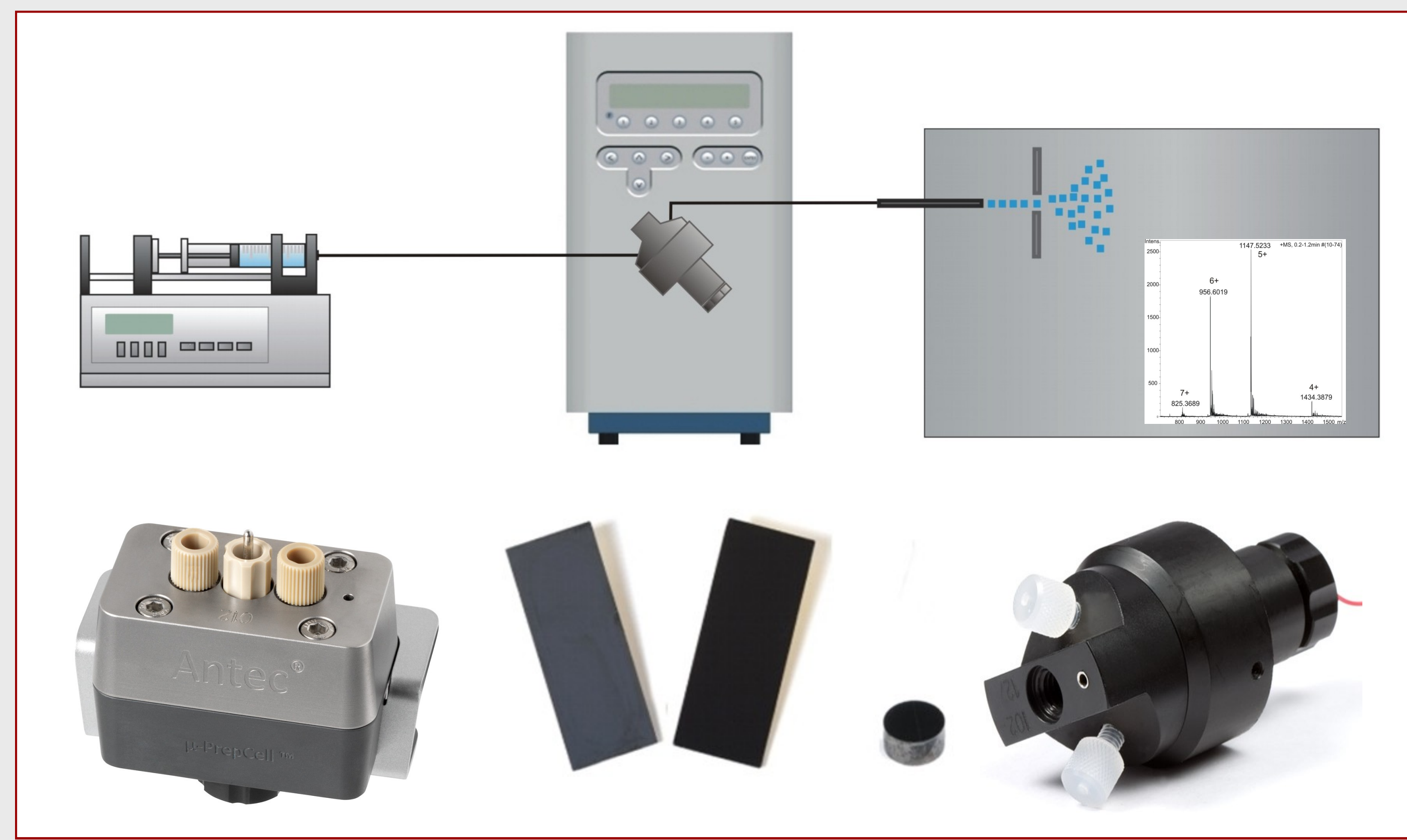


Figure 1: Upper panel: Instrumental set-up of ROXY™ EC system. Bottom panel: μ-PrepCell™ (left) and ReactorCell™ (right). Comparison of working electrodes (μ-PrepCell™ vs. ReactorCell™).

Results

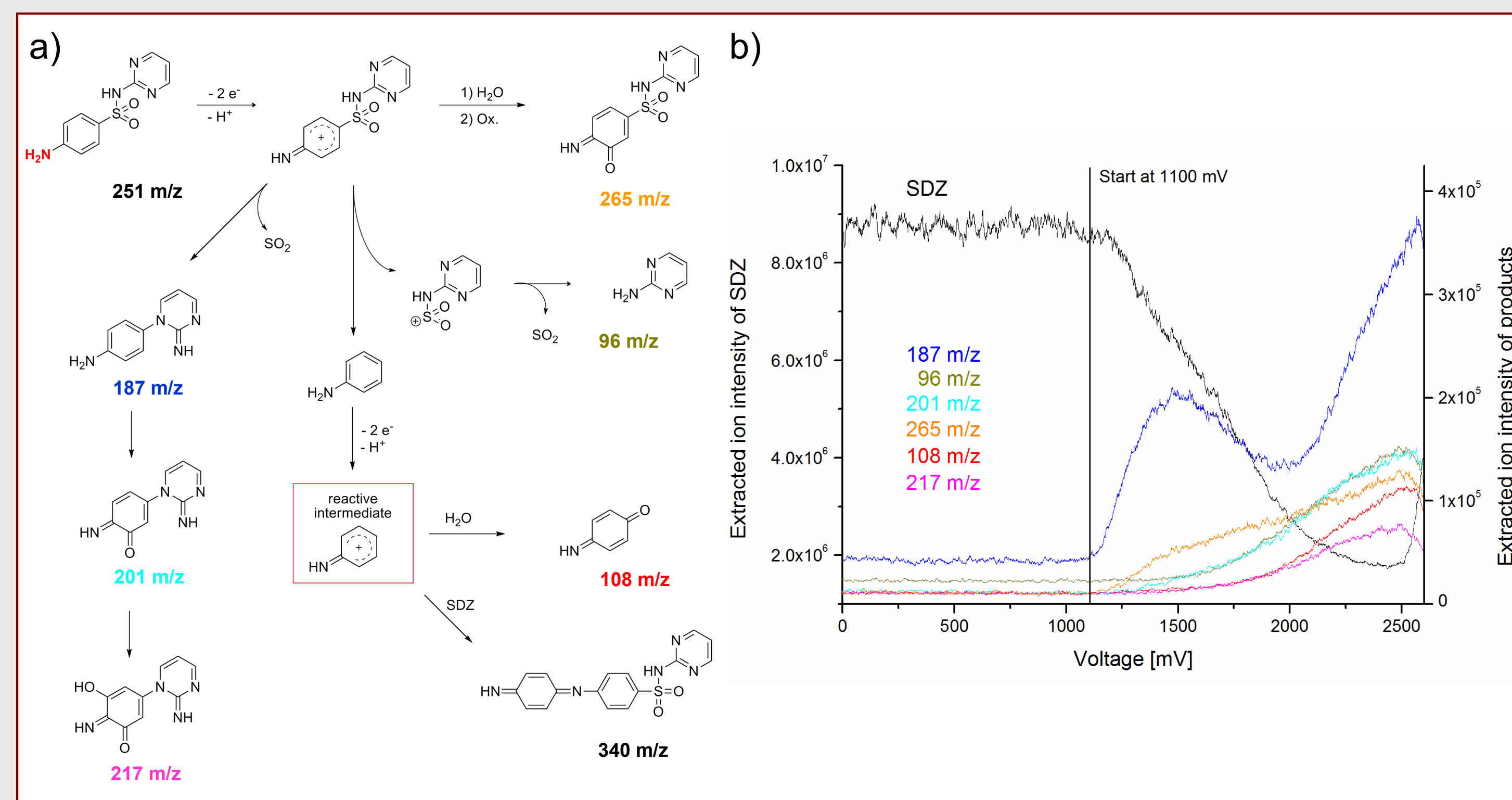


Figure 2 a: Proposed degradation scheme of SDZ. The m/z ratios shown correspond to the protonated species. b: MS voltammogram of SDZ.

Electrochemical degradation of sulfadiazine

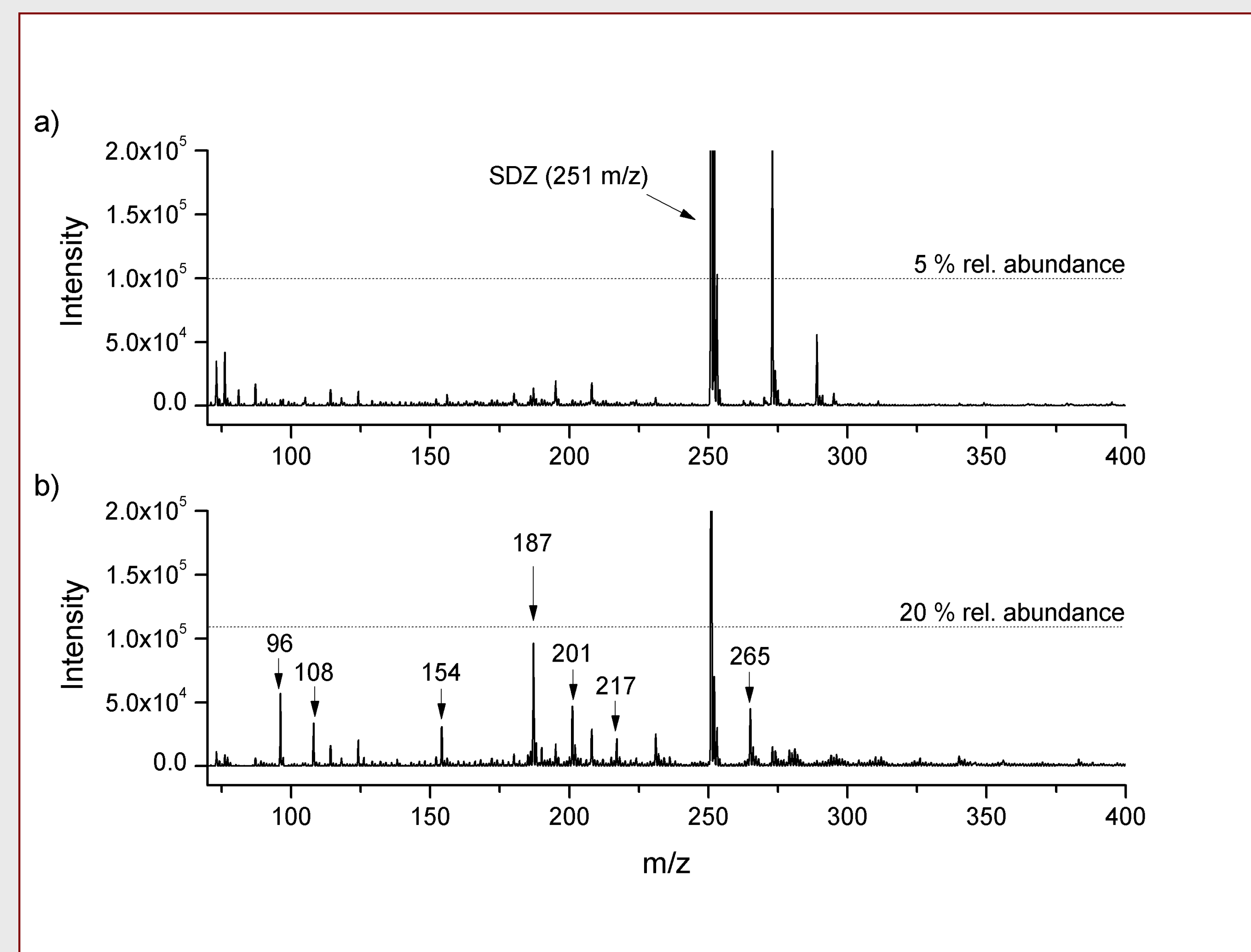


Figure 3 a: Mass spectrum of pure sulfadiazine (SDZ) without voltage applied to the electrochemical cell. b: Mass spectrum of SDZ after electrochemical oxidation.

Chemical binding of sulfadiazine with catechol (SOM)

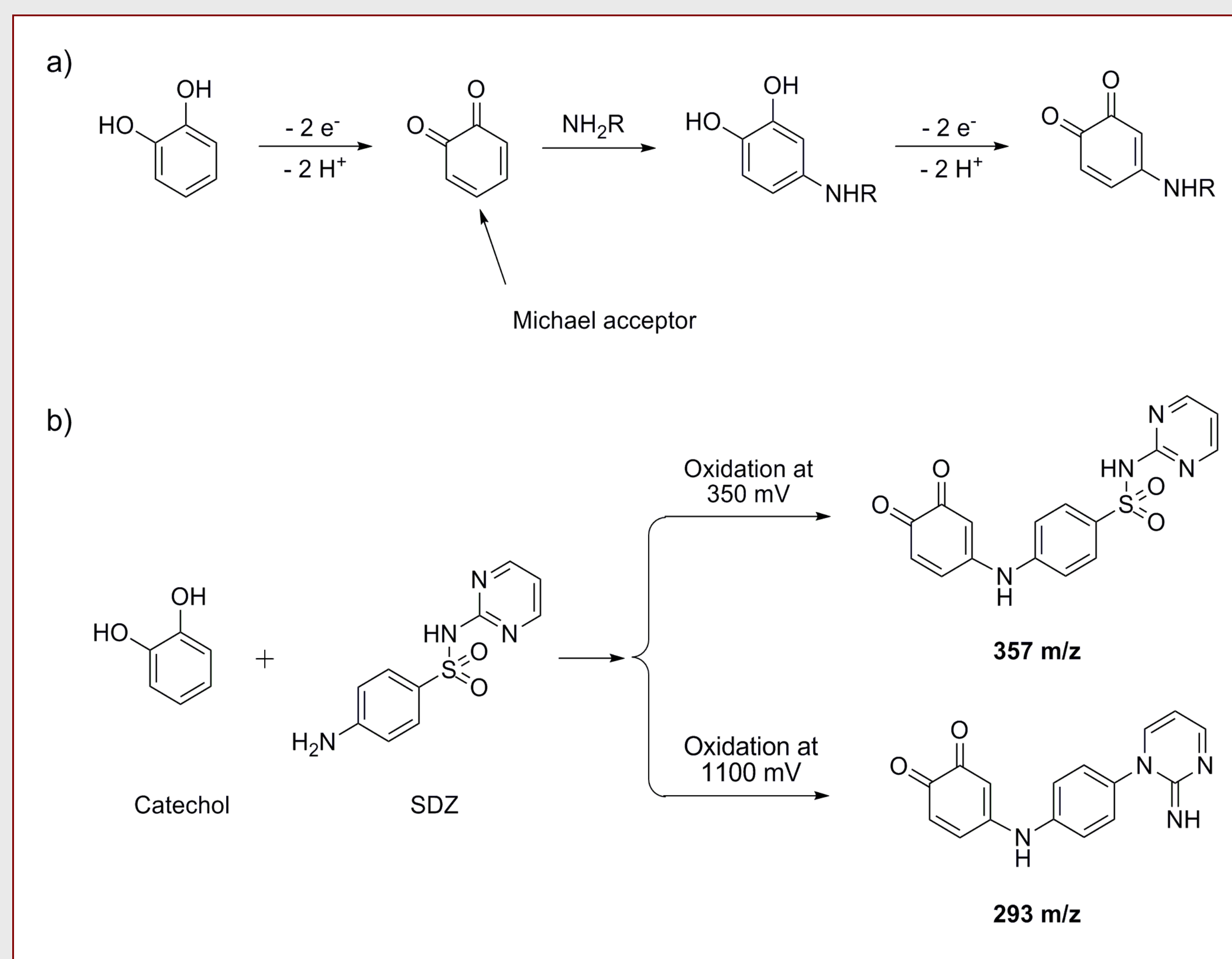


Figure 4: a) Assumed reaction scheme of catechol with a nucleophile under oxidative conditions. b) Products obtained while applying a constant voltage to a solution containing catechol and SDZ. Sample: 10 μM SDZ, 20 μM catechol in 200-μM NH₄OAc, pH 6.8/ MeOH 70:30 (v/v). EC conditions: 10 μl/min flow at a glassy carbon electrode. The m/z ratios shown correspond to the protonated species.

Conclusions

Non-Extractable-Residues (NER) are one of the most difficult research topics in environmental chemistry. With EC-MS it is possible to screen a wide range of possible reactions [3] and understand mechanisms. In addition this approach also gave the opportunity to use a number of different model compounds for possible reactions sites of NOM. Up to now always the extractable part of different chemical compounds was investigated as an indirect measure to the non-extractable part. With EC-MS for the first time a systematic approach to the direct investigation of the non-extractables is possible. A number of different additional approaches are possible for example to predict possible persistence, to understand mechanisms of oxidative wastewater treatment and to compare different approaches of oxidative wastewater treatment.

Acknowledgements

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References

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