# **Disinfection By-products from Water Chlorination Reconfirmed by Electrochemistry-MS**

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- the similarities with dealkylation of secondary/tertiary amines in aqueous chlorination.

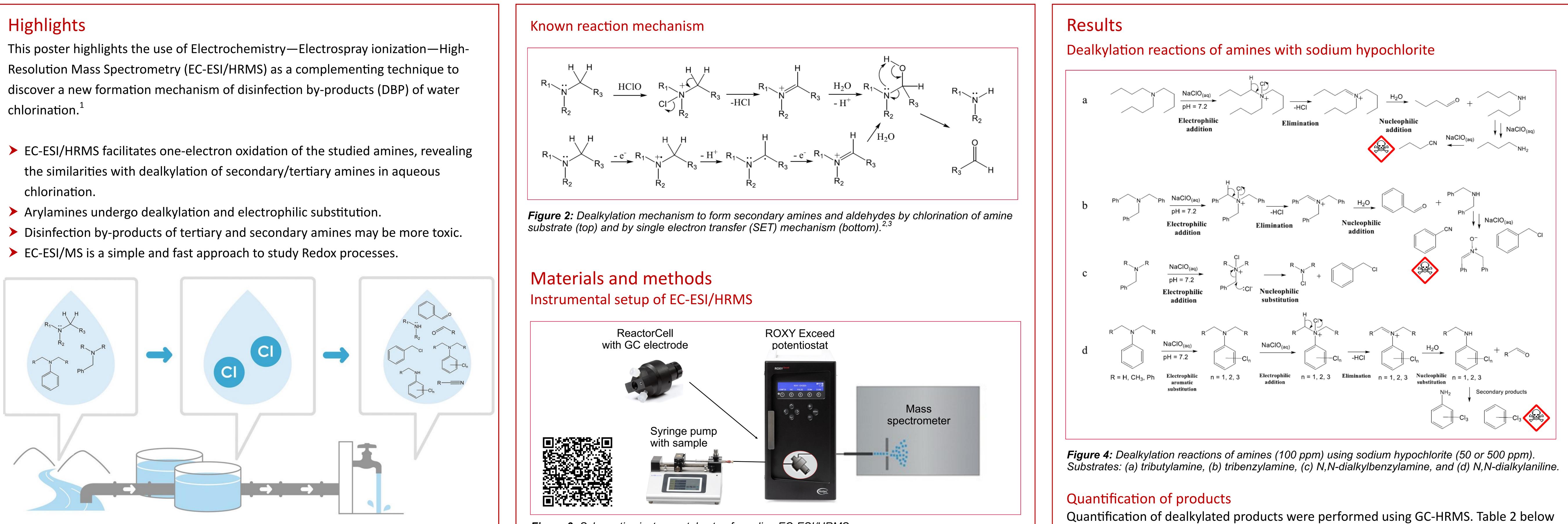


Figure 1: Drinking water preparation from natural source by aqueous chlorination.

## Introduction

Chlorination is the most effective and cheapest method of drinking water preparation. During aqueous chlorination, numerous disinfection by-products (DBP) are formed. Among various DBPs, nitrogen-containing species are of special concern due to their toxicological properties. An interesting reaction involves dealkylation of the substituted amine moiety. In this poster we present the results of the comparative study of one electron oxidation and aqueous chlorination of several aliphatic and aromatic amines. The reaction products were reliably identified with GC-HRMS, HPLC-ESI/HRMS, and electrochemistry-ESI/HRMS). The mechanism of the substituted amines' aqueous chlorination involving one-electron oxidation is proposed and confirmed by the array of the observed reaction.<sup>1</sup>

Figure 3: Schematics instrumental setup for online EC-ESI/HRMS.

Electrochemical reactor	ROXY Exceed potentiostat			
Reactor flowcell	FlexCell with glassy carbon WE, carbon-filled PTFE AE, and HyREF (Pd/H <sub>2</sub> ) RE			
Potential	From 0 to 2.0 V with 0.25 V steps			
MS System	Orbitrap ID-X HRMS			
Ionization mode	Positive			
m/z range	50—500			
Spray voltage	3.5 kV			
Ion source temperature	100 °C			
Sheath, aux, and sweep gas flow rate	10, 3, and 1 arb. units			
Syringe pump flow rate	10 μL/min			
Samples	10 mg/L solutions of amines in 20 mM ammonium formate pH 7 and acetonitrile (1:1)			

shows the amount of identified compounds with different amount of chlorine reagent used. Excess of chlorine (500 ppm) significantly increases the yield of dealkylation products.

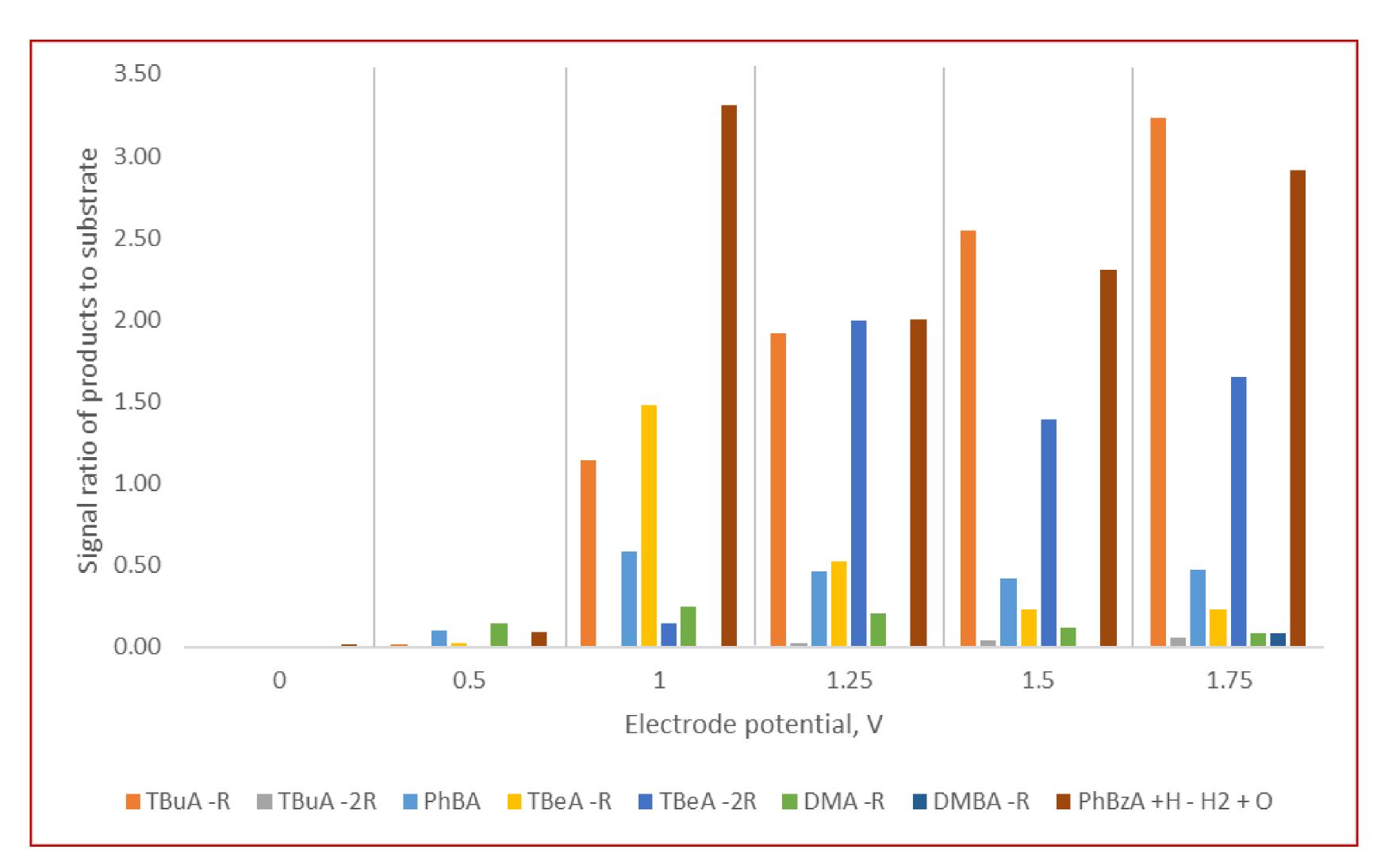
Table 2. Identified compounds in the reactions of amines with sodium hypochlorite						
Compound	RT (s)	Base mass	Relative amount with 50 ppm of chlorine (%)	Relative amount with 500 ppm of chlorine (%)		
N,N-dimethylbenzylamine*	556.7	58.0651	88	9.7		
<u>N-methylbenzylamine</u>	580.7	120.0810	1.9	30		
Benzaldehyde	430.6	105.0336	9.9	61		
Tribenzylamine*	2250.1	210.1281	47	0		
<u>Dibenzylamine</u>	1600.0	91.0541	21	33		
Benzaldehyde	430.6	105.0334	32	67		

\*parent compound; chlorination produces harmful/toxic chemicals (i.e. N-methylbenzylamine and dibenzylamine).



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### Online EC-ESI/HRMS one-electron oxidation reaction of amines



*Figure 5:* Effect of working electrode potential (vs Pd/H<sub>2</sub> reference electrode) on the MS signal ratios of oxidation products and parent alkylamines. TBuA = Tributylamine, PhBA = N-Phenylbenzylamine TBeA= Tribenzylamine, DMA = N,N-dimethylaniline, DMBA = N,N-Dimethylbenzylamine

Using an online EC-ESI/HRMS, we simulated one-electron oxidation reaction of the amines and identified the products. Our findings show:

- > Dealkylated derivatives were detected for all parent compounds.
- Conversion of alkylamines increased significantly at working potential of 1— 1.25 V, except for tributylamine with highest ratio at 1.75 V (Figure 5).
- Imine cations (see Figure 2) were detected for some of the reactions.
- Aqueous chlorination of the amines that results in dealkylation occurred via SET mechanism in Figure 2.

## Conclusion

EC-ESI/HRMS using ROXY enables a deeper understanding of dealkylation of amines by one-electron oxidation, confirming the SET mechanism of dealkylation in aqueous chlorination of amines.

## References

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<sup>4</sup>A. J Ellis, F.G Soper. "Studies of N-halogeno-compounds. Part VI. The kinetics of chlorination of tertiary amines" J. Chem. Soc. (1954): 1750-1755

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