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# Complex electrochemical assessment of the antioxidant properties of essential oils

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## INTRODUCTION & AIM

Essential oils are one of the sources of natural antioxidants in food industry. Their major representatives are phenolic compounds, whose composition is strongly dependent on the type of plant material, the geographical conditions of its growth, the vegetation stage, and the processing method. Therefore, the characterization of the antioxidant properties of essential oils is in demand today. The total antioxidant parameters obtained by electrochemical methods were shown as an effective approach for the sample characterization. Commercial essential oils of basil, ylang-ylang, bergamot, marjoram, clove, jasmine, neroli, cinnamon, lavender, rosemary, ginger, nutmeg, thyme, anise, and clary sage were studied.

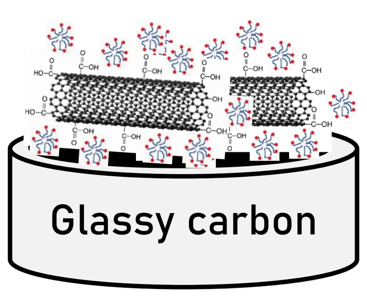
## METHODS

### Galvanostatic coulometry with electrogenerated titrants

| | | |
|---|---|---|
| $Br_2$ | Total antioxidant capacity (TAC) assay | |
| | Electrochemical reaction | $2Br^- - 2\bar{e} = Br_2$ |
| | Chemical reaction in solution | $AO_{red} + Br_2 =$ Products |
| | TAC reflects the impact of both phenolic antioxidants and terpenes | |
| $[Fe(CN)_6]^{3-}$ | Ferric reducing power (FRP) assay | |
| | Electrochemical reaction | $[Fe(CN)_6]^{4-} - \bar{e} = [Fe(CN)_6]^{3-}$ |
| | Chemical reaction in solution | $AO_{red} + [Fe(CN)_6]^{3-} = AO_{ox} + [Fe(CN)_6]^{4-}$ |
| | FRP indicates the content of phenolic antioxidants only | |

### Chronoamperometry

Chronoamperometry at modified glassy carbon electrode makes it possible to differentiate the impact of phenolic compounds and terpenes applying various potentials, i.e., 0.8 and 1.4 V, respectively. The antioxidant capacity has been expressed as a current at 0.8 V reflecting the contents of phenolics ($AOC_{0.8}$) and the total current at 1.4 V ($AOC_{total}$). The sufficient electrolysis time was 75 s on each step.




**Electrode surface modification**

Carboxylated multi-walled carbon nanotubes (Aldrich, Germany) ($D$ = 9.5 nm, $l$ = 1.5 µm, carboxylation degree >8%)
$c$ = 1 mg mL$^{-1}$ in 1% sodium dodecyl sulfate, sonication for 30 min,
2 µL of suspension was drop-casted on the electrode surface

### Spectrophotometry

Standard spectrophotometric approaches for antioxidant parameters evaluation using Folin-Ciocalteu reagent and 2,2-diphenyl-1-pycrilhydrazil (DPPH) has been applied. Total phenolic contents has been expressed in eugenol equivalents per 1 mL of essential oil.

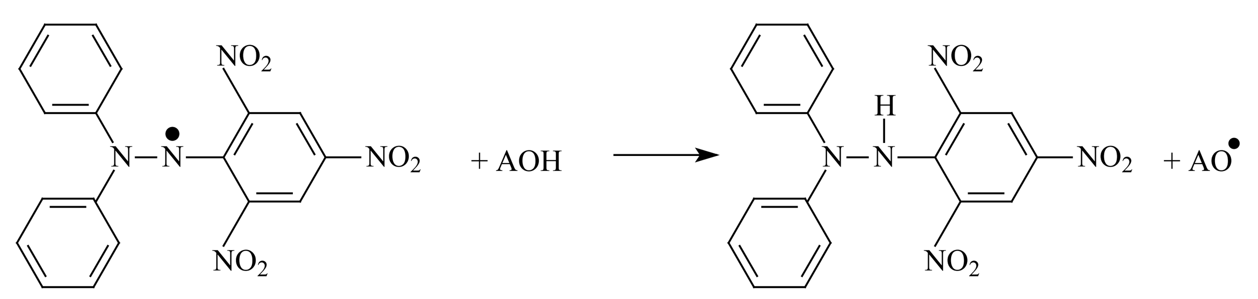
Folin-Ciocalteu reagent

$H_3PW_{12}O_{40} + H_3PMo_{12}O_{40}$ → ($Ph_{red}$ → $Ph_{ox}$) $W_8O_{23} + Mo_8O_{23}$

Blue, λ = 765 nm

The total phenolic contents by Folin–Ciocalteu method was applicable to clove, cinnamon, nutmeg, and thyme essential oils only. The turbid systems were obtained for other oils after the addition of photometric reagents.

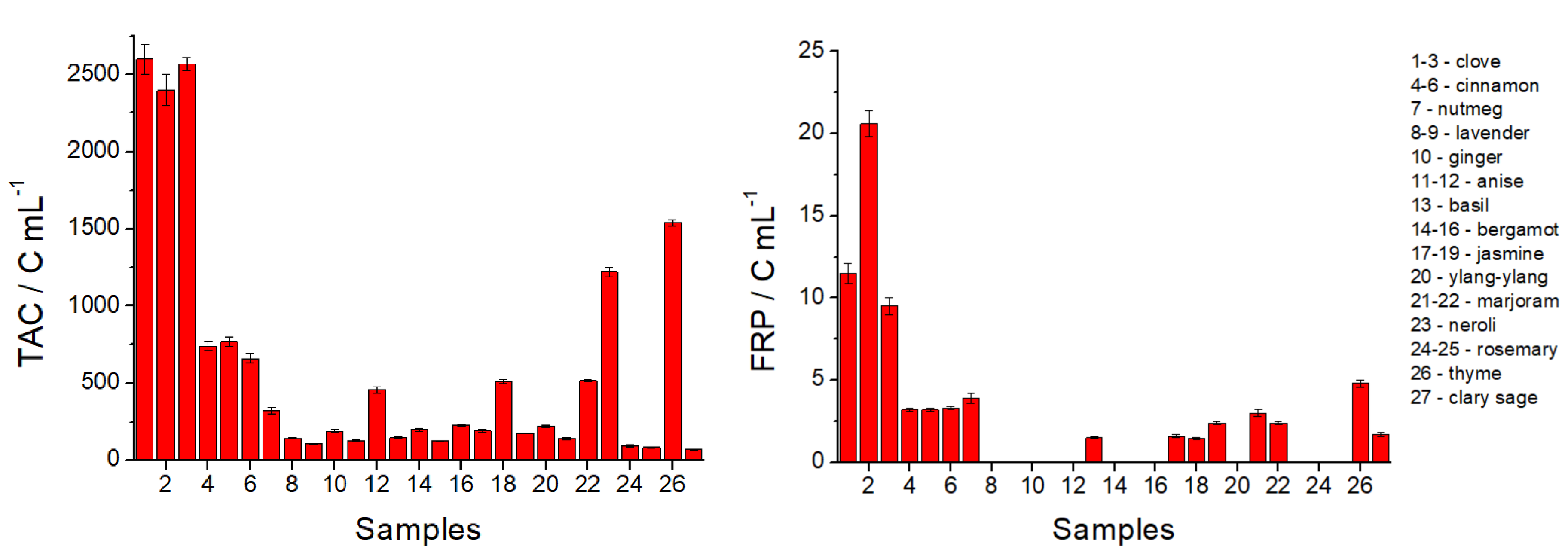
Antioxidant capacity towards DPPH has been expressed as inhibition percentage obtained for 4 µL of 10-fold diluted with ethanol essential oil.



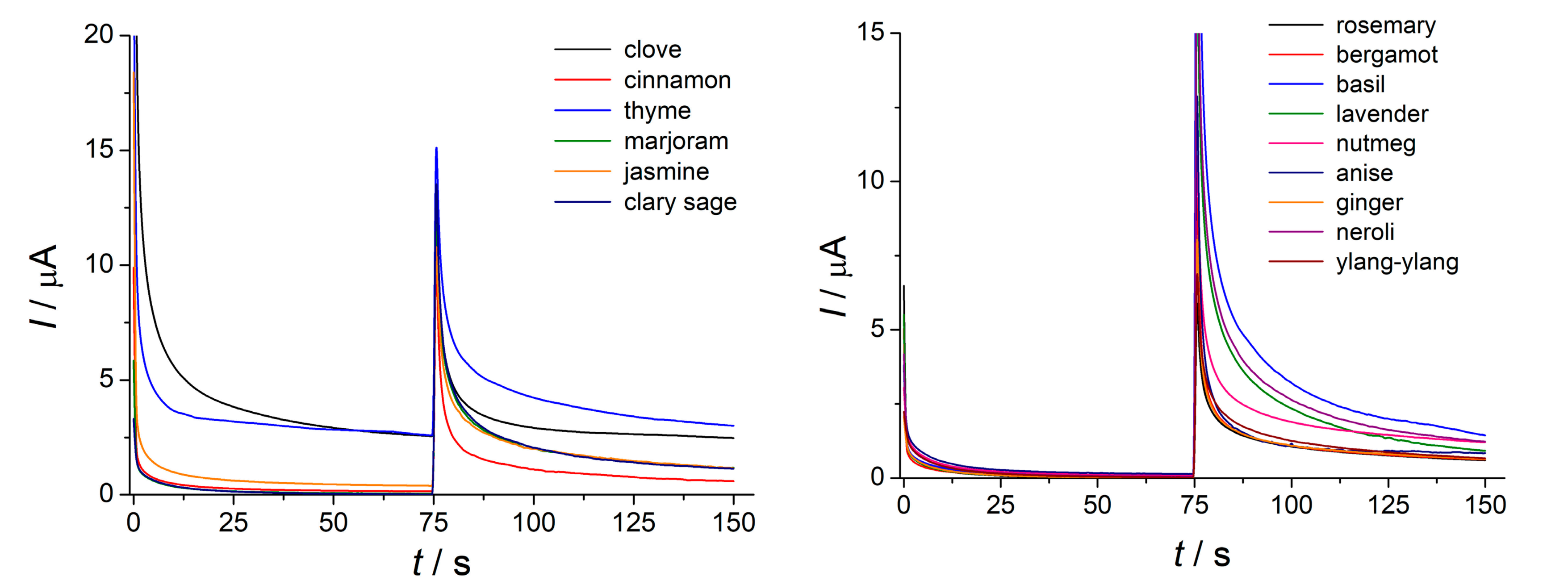

Violet, λ = 515 nm — Transparent

## RESULTS & DISCUSSION

### TAC and FRP of essential oils based on coulometry data

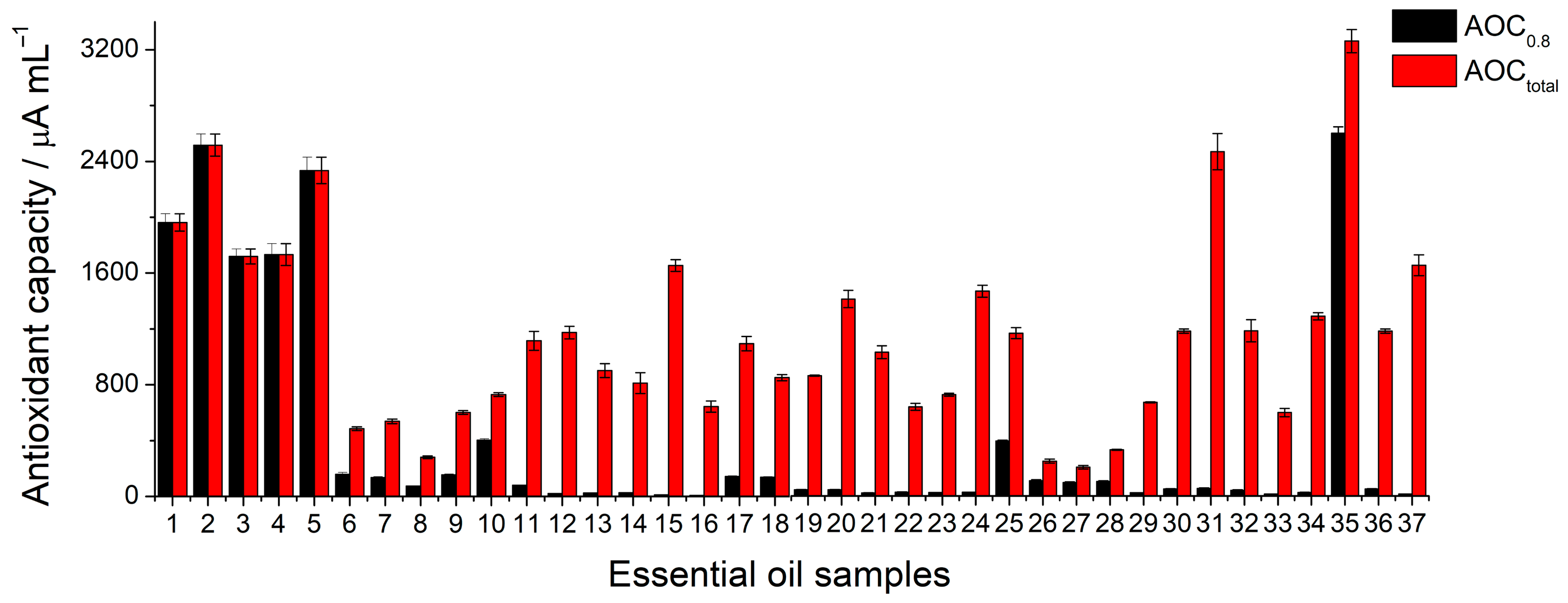



### AOC of essential oils by two-step chronoamperometry




$E_1$ = 0.80 V $E_2$ = 1.40 V $t_{step}$ = 75 s

Blank –phosphate buffer with pH 7.0




### Correlation of the antioxidant parameters of essential oils ($P$ = 0.95)

| Parameter | Antioxidant activity (DPPH-test), % | | Total phenolics, mg eugenol mL$^{-1}$ | |
|---|---|---|---|---|
| | $r$ | $r_{critical}$ | $r$ | $r_{critical}$ |
| TAC / C mL$^{-1}$ | 0.8379 | 0.3809 | 0.9558 | 0.7067 |
| FRP / C mL$^{-1}$ | 0.7051 | 0.5140 | 0.8886 | |
| $AOC_{0.8}$ / µA mL$^{-1}$ | — | — | 0.7969 | 0.5760 |
| $AOC_{total}$ / µA mL$^{-1}$ | 0.4458 | 0.3245 | — | — |

## CONCLUSION

The total antioxidant parameters screening was performed, and positive correlations with the standard spectrophotometric methods (Folin-Ciocalteu for clove, cinnamon, nutmeg, and thyme essential oils only and DPPH test for all samples) were found. Electrochemical approaches are express, cost-effective, simple, reliable, and have no limitations typical for spectrophotometry. Therefore, electrochemical assessment of the antioxidant properties of essential oils is a perspective for practice.