# CHARACTERIZATION OF THE ESSENTIAL OILS ANTIOXIDANT PROPERTIES BY COULOMETRIC TITRATION

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3rd International Electronic Conference on Applied Sciences

# APPLICATION OF THE ESSENTIAL OILS

Antibacterial, anti-inflammatory, antioxidant and antiviral properties

- **Aromatherapy**
- **Medicine**
- **Food industry**

# ESSENTIAL OILS COMPOSITION

Essential oils are highly concentrated extracts from flowers, leaves, stems, fruits, and roots of plants

- aldehydes
- ketones
- alcohols
- **Major constituents**
- hydrocarbons
- terpenes
- esters
- ethers
- phenols

# METHODS FOR CHARACTERIZATION OF THE ESSENTIAL OILS ANTIOXIDANT PROPERTIES

1. GC-MS

2. Spectrophotometric approaches
   - reaction with 2,2-diphenyl-1-picrylhydrazyl ($DPPH^{\bullet}$) or peroxyl radicals obtained from 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) ($ABTS^{+\bullet}$)
   - the total phenolics assay performed by the Folin-Ciocalteu method
   - ferric reducing-antioxidant power (FRAP)
   - β-carotene bleaching assay

3. Electrochemical approaches
   - reaction of antioxidants with superoxide anion radical

**Applicability of coulometric titration for the evaluation of essential oils antioxidant parameters** ?

# COULOMETRIC TITRATION WITH ELECTROGENERATED TITRANTS

## Bromine

Oxidation reactions

*Phenolic Antioxidants (flavonoids, phenolic acids, guaiacol and its derivatives, curcuminoids, tannin)*

Multiple bond electrophilic addition reactions

*Terpenoids, unsaturated hydrocarbons, eugenol and its derivatives, curcuminoids*

Electrophilic substitution reactions in aromatic systems

*Phenolic antioxidants (flavonoids, phenolic acids, guaiacol and its derivatives, curcuminoids, tannin)*

## Ferricyanide ions

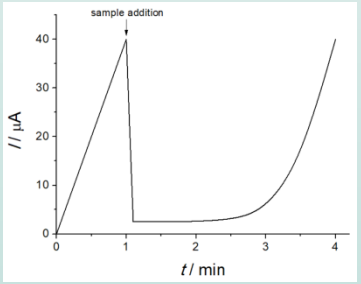
Oxidation reactions

*Phenolic Antioxidants (flavonoids, phenolic acids, guaiacol and its derivatives, curcuminoids, tannin)*

## Total Antioxidant Capacity (TAC)

$2Br^- - 2\bar{e} = Br_2$

$AO_{red} + Br_2 = Products$




## Ferric reducing power (FRP)

$[Fe(CN)_6]^{4-} - \bar{e} = [Fe(CN)_6]^{3-}$

$AO_{red} + [Fe(CN)_6]^{3-} = AO_{ox} + [Fe(CN)_6]^{4-}$

# ESSENTIAL OILS UNDER INVESTIGATION


basil


bergamot


jasmine


lavender


ginger


anise


clove


cinnamon


nutmeg


ylang-ylang


marjoram

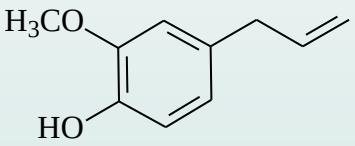

neroli


rosemary

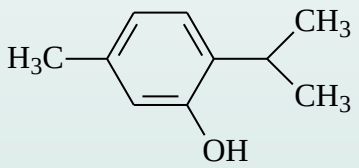

thyme


clary sage

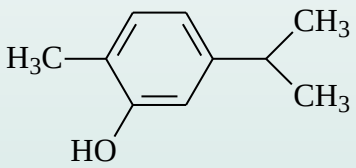
# ESSENTIAL OILS COMPONENTS



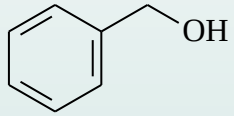

Eugenol



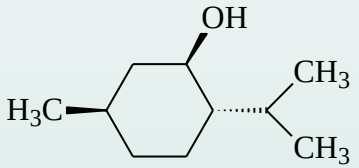

Thymol



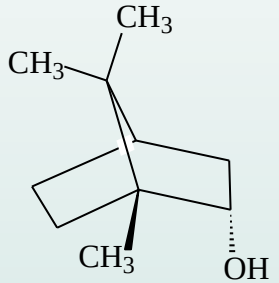

Carvacrol



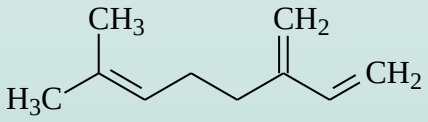

Benzyl alcohol



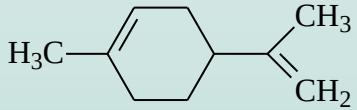

L-menthol



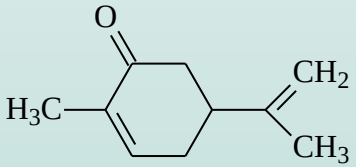

L-borneol



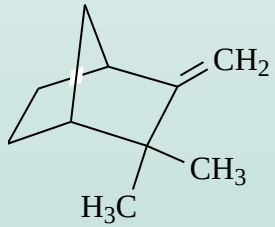

Myrcene



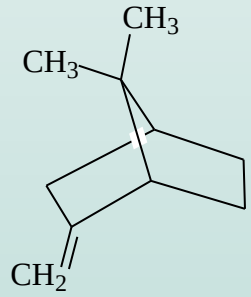

Limonene



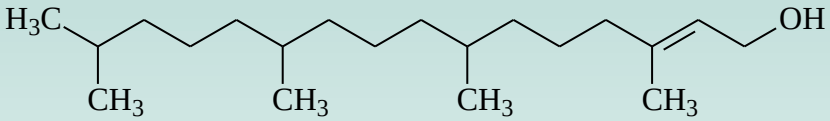

Carvone



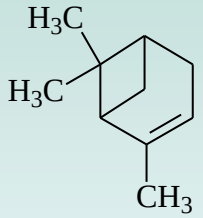

Camphene



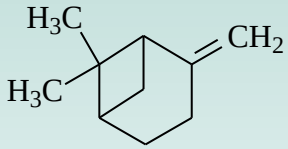

Fenchene




Phytol




α-Pinene

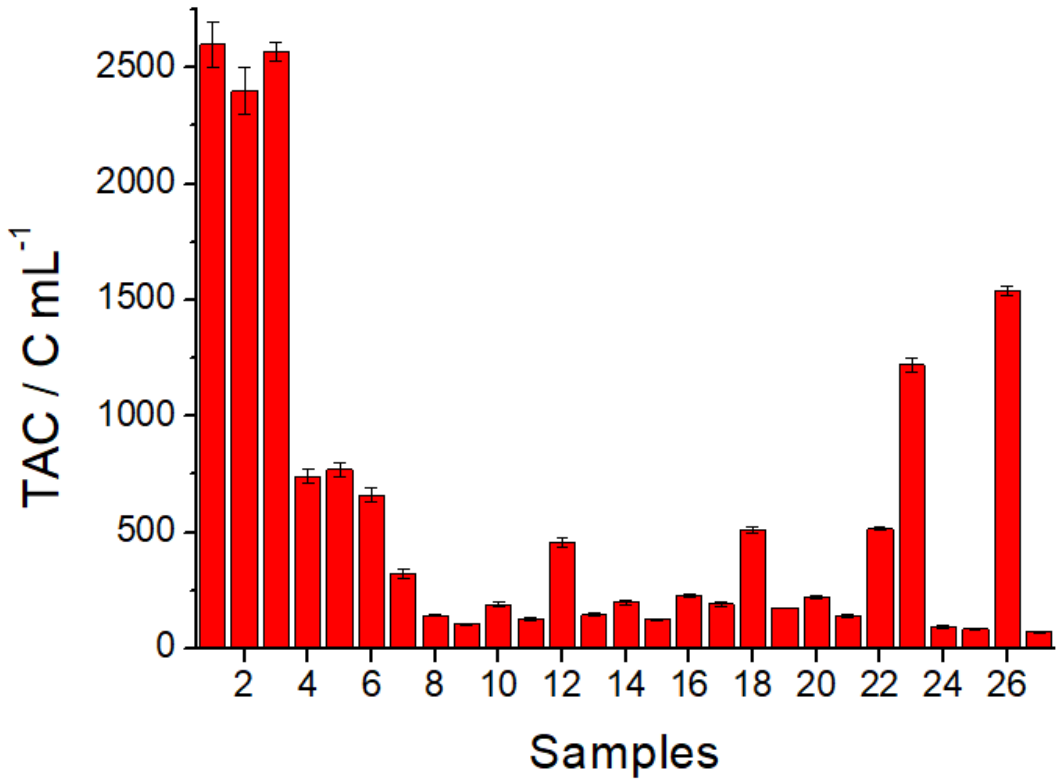


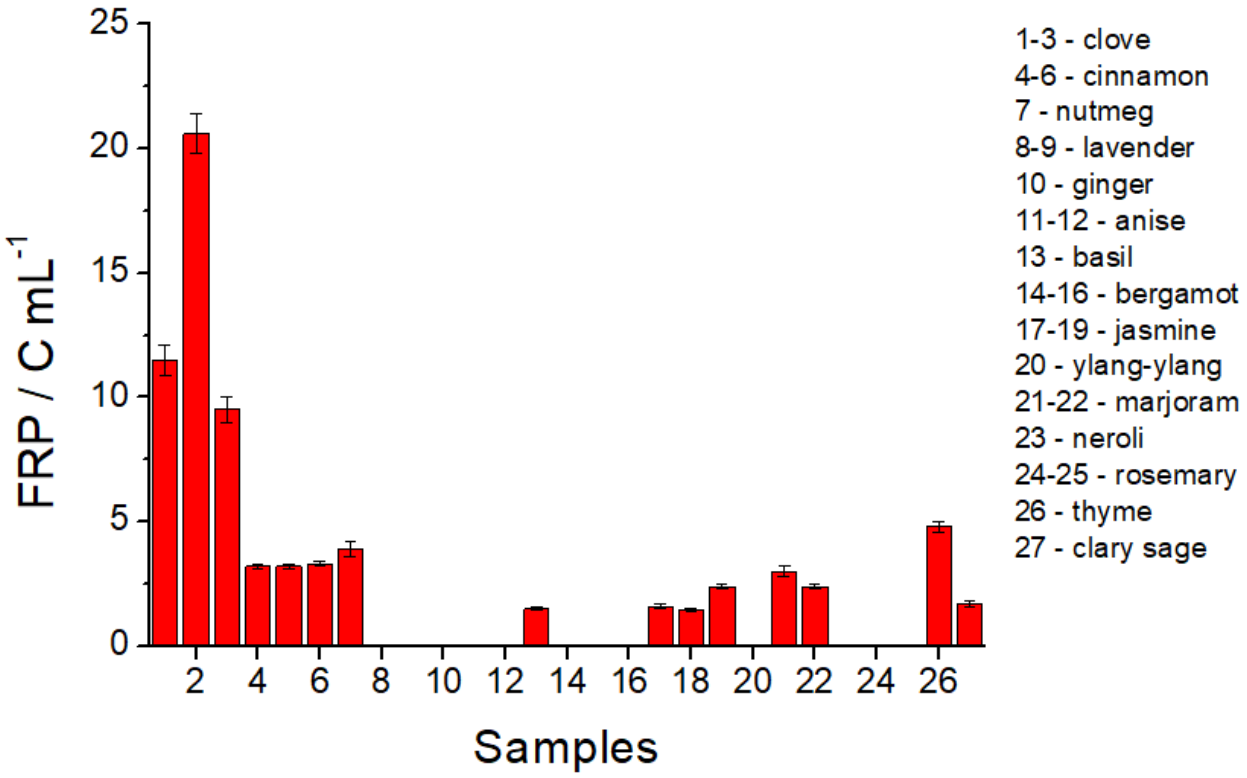

β-Pinene

# NUMBER OF ELECTRONS PARTICIPATING IN THE REACTIONS OF ELECTROGENERATED TITRANTS WITH COMPONENTS OF ESSENTIAL OILS ($n$=5; $P$=0.95)

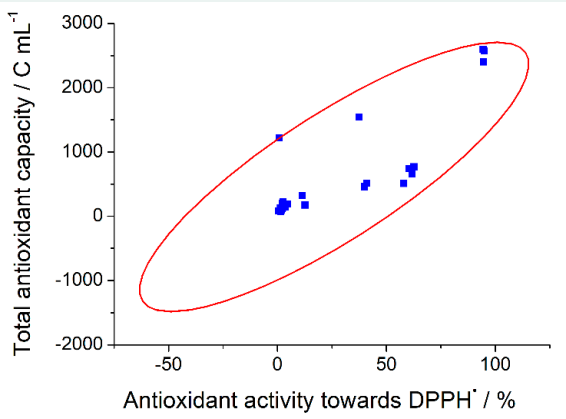
| Titrant | Number of electrons | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Eugenol | Thymol | Carvacrol | Myrcene | Limonen | α-Pinene | β-Pinene | Phytol | Carvone | Camphene | Fenchene | Benzyl alcohol | L-menthol | L-borneol |
| $Br_2$ | 5 | 4 | 5 | 4 | 4 | 2 | 2 | 2 | 2 | 2 | 2 | - | - | - |
| $[Fe(CN)_6]^{3-}$ | 1 | 1 | 1 | - | - | - | - | - | - | - | - | - | - | - |

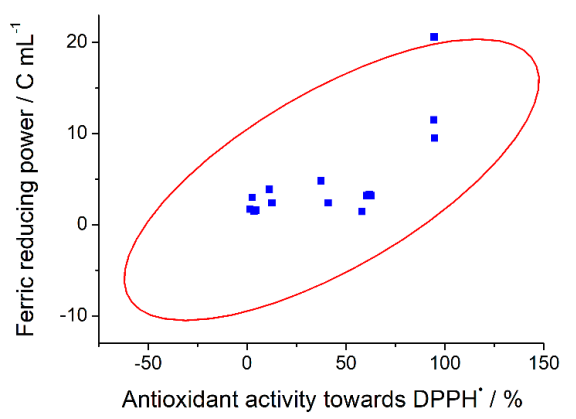
# TOTAL ANTIOXIDANT PARAMETERS OF THE ESSENTIAL OILS ($n$ = 5; $P$ = 0.95)

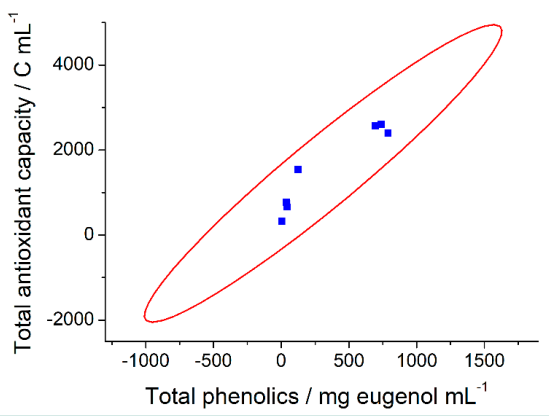


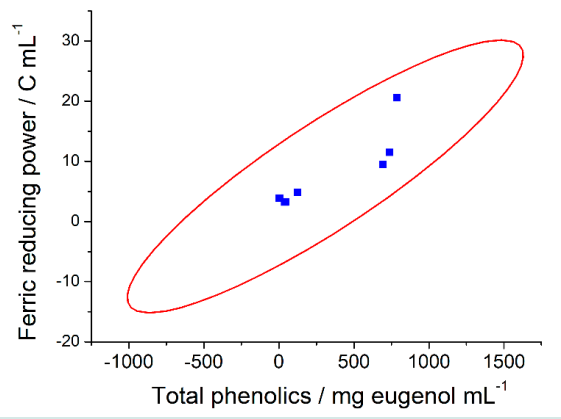



# CORRELATION COEFFICIENTS OF THE ANTIOXIDANT PARAMETERS OF ESSENTIAL OILS




| Antioxidant parameter based on coulometry | Antioxidant activity towards DPPH• (%) | | Total phenolic contents (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 | |

# ADVANTAGES OF COULOMETRIC TITRATION

- The possibility of automation and rapidity make coulometric titration an attractive tool for screening purposes in routine practice;
- No need to prepare a standard solutions of the reagents i.e. standardization stage is excluded;
- Titration is an absolute that excludes usage of calibration plots (an electron acts as a titrant);
- No effect of sample dilution;
- Coverage of almost all types of antioxidants based on the titrants reactivity;
- Ease of calculation and the possibility of using different standard antioxidants;
- High sensitivity, reliability, and reproducibility of the measurements;
- Ferric reducing power reflecting phenolic antioxidant content can be used for all samples of essential oils, while Folin-Ciocalteu method for total phenolic contents is applicable to four types of the essential oils only.

# CONCLUSIONS

Coulometric titration with electrogenerated bromine and ferricyanide ions has been used for the estimation of total antioxidant capacity and ferric reducing power of essential oils for the first time. Data for the reaction of individual antioxidants (volatile phenolics and terpenes) with coulometric titrants confirm applicability of the method for characterization of the essential oils antioxidant properties. Essential oils of clove, cinnamon, nutmeg, lavender, ginger, anise, basil, bergamot, jasmine, ylang-ylang, marjoram, neroli, rosemary, thyme, and clary sage of various trademarks (total 27 samples) have been investigated. The data obtained have been compared to the standard antioxidant parameters (antioxidant activity towards 2,2-diphenyl-1-picrylhydrazyl and total phenolic contents). Positive correlations with coefficients of 0.7051-0.9558 confirm the accuracy of the coulometric approach. Moreover, ferric reducing power reflecting phenolic antioxidant content can be used for all samples of the essential oils, while Folin-Ciocalteu method for total phenolic contents is applicable to four types of essential oils only. Another advantage of the coulometric methods is the possibility of automation and rapidity making it a good alternative to other methods for the essential oils screening in routine practice. TAC and FRP can be considered as quantitative parameters for the essential oils quality control if the standard samples are available for the ranking.