Electrocoagulation in two phase separation for manipulation of volatile compound profiles in perfumes

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งานวิจัยนี้ได้ทำการประยุกต์ใช้เทคนิคการตกตะกอนด้วยไฟฟ้าเคมีโดยใช้ขั้ว2แผ่นซึ่งวัสดุทำมาจากอลูมิเนียมร่วมกับสารละลายตัวกลาง2เฟส คือ สารละลายน้ำเกลือ และ ตัวทำละลายเฮกเซน เพื่อใช้เป็นระบบ2เฟสการตกตะกอนด้วยไฟฟ้าเคมี โดยกระบวนการไฟฟ้าเคมีใช้เป็นดารปรับปรุงระบบสารประกอบให้กลิ่นในน้ำหอมสกัด ตัวอย่างน้ำหอมก่อนและหลังกระบวนการ2เฟสตกตะกอนด้วยไฟฟ้าเคมี ที่บริเวณขั้วcathode, anode และ บริเวณระหว่างทั้ง2ขั้วหลังปฏิกิริยาไฟฟ้าเคมีได้ทิ้งไว้เพื่อให้เกิดสมดุลทางเคมี ได้ทำการวิเคราะห์โดยใช้เทคนิคการสกัดด้วยตัวดูดซับของแข็งปริมาณน้อย (SPME) และ แก๊สโครมาโทรกราฟีแมสเสปคโตมีทรี (GC-MS) กระบวนการเทคนิคดังกล่าวได้นำมาใช้เพื่อการระบุสารประกอบระเหยง่ายในแต่ละตัวอย่างโดยขึ้นอยู่กับการเปรียบเทียบกับแมสเสปค และ ฐานข้อมูล retention index หลังปฏิกิริยาการตกตะกอนด้วยไฟฟ้าเคมีกลิ่นน้ำหอมได้เกดการเปลี่ยนแปลงซึ่งขึ้นอยู่กับชนิดและปริมาณของสารประกอบให้กลิ่นต่างๆ เช่น การเพิ่มกลิ่นสดชื่น, หวาน และ กลิ่นดอกไม้ โดยกลิ่นสารประกอบหลักที่ได้รับหลังจากกระบวนการปฏิกิริยา2เฟสไฟฟ้าเคมีของผลิตภัณฑ์ที่ขั้วanode ได้แก่ 2-phenylethanol และ benzyl acetate และผลิตภัณฑ์ที่ขั้วcathode ได้แก่ phenylmethanol โดยเปรียบเทียบจากการสังเกตตัวอย่างโปรไฟล์ของน้ำหอมได้เกิดการตกแต่งกลิ่นของสารประกอบหลายอย่างที่บริเวณแต่ละขั้วอลูมิเนียมโดยไม่ได้ทำปฏิกิริยาทางไฟฟ้าเคมี โปรไฟล์สารตั้งต้น และผลิตภัณฑ์หลักได้ทำการตรวจสอบด้วยเครื่อง gas analyzer ได้เกิดการลดอัตราการลดลงของสารตั้งต้นและผลิตภัณฑ์ระหว่างการเกิด2เฟสตกตะกอนด้วยไฟฟ้าเคมี วิธีการตกตะกอนทางไฟฟ้าเคมีและการวิเคราะห์นี้ได้สร้างศักยภาพ และการประยุกต์ทางด้านการเกิดปฏิกิริยาทางไฟฟ้าเคมีในตัวกลางอินทรีย์ต่อไปในอนาคต

สาขาวิชา	เคมี	ลายมือชื่อนิสิต	....
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Electrocoagulation (EC) approach employing two aluminium electrodes and a two phase medium of aqueous solution of NaCl and hexane (2-phase-EC) was developed. The approach enabled electrochemical treatment of odor active compounds in perfume extract. The samples before and after 2-phase-EC at cathode, anode and between the two electrodes left for equilibrium after the treatment were analyzed by using solid phase micro extraction (SPME) and gas chromatography hyphenated with mass spectrometry (GC-MS). This allowed identification of volatile compounds in each sample based on comparison with MS and retention index database. After the treatment, the perfume smells were fresher, sweeter and more floral corresponding to their different types and amounts of the odor active compounds. The major odor active products mainly obtained at the anode of the 2-phase-EC system were methyl benzoate, 2-phenylethanol and benzyl acetate. The corresponding product at the cathode was phenylmethanol. Comparison of the investigated sample profiles further reveals enrichment of several compounds at each electrode without undergoing electrochemical reaction. The major reactant and product profiles were further investigated with Gas Analyzer revealing slower rate of decrease in the amounts of the characteristic *m/z* of the products during the 2-phase EC. The 2-phase-EC and analytical approach have a potential for application in the area of electrochemical reaction in organic media in the future.

Field of Study:	Chemistry	Student's Signature ....
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Isaya Thaveesangsakulthai

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CHAPTER I

INTRODUCTION

1.1 Problem Definition

Electrochemical techniques are recognized in the aspects of reliable and economical approaches for treatment of environmental samples since the techniques can be effectively applied to cope with ecological systems. The treatment system can also be recycled and monitored [1]. Among different approach, electrocoagulation (EC) has been applied to effectively remove several ion species in wastewater samples [2] by removals of organic wastes, metal ions and the other species such as PO_4^{3-}, NO_3^- or NH_4^+. The technique relies on either electrochemical reaction at the electrodes maintaining continuous flow of current to the electrodes or generation of adsorbents as a result of electrode corrosion and complexation. This method is considerably auto-coagulation or electro-catalytic method even without addition of chemicals, thus producing small amount of sludge. An electrocoagulation system consists of two conducting electrodes immersed in a container filled with electrolytes. When significantly high voltage is applied to the electrodes, the electrocoagulation occurs with the rate governed by the polarities of the two electrodes [3]. The wastewater treatment involves several processes including electrochemical reactions of chemicals at the electrodes resulting in the solid or gas products, corrosion of the electrodes which results in solid complexes (sludge) as a result of complexation between metal ions from the corroded electrode and hydroxides [4], coagulation and adsorption of chemical wastes onto the sludge and removal of the solid species. Since the mechanism relies on electrode corrosion, relatively low-cost materials (such as stainless-steel electrodes) can be applied facilitating a large scale synthesis.

Apart from the environmental applications, electrochemical approach is also applied for synthesis of a wide range of organic compounds [5]. With the focus on the EC synthesis in organic media, addition of organic salt into the electrolyte is generally performed in order to enhance conductivity and maintain current in an electrical circuit [6]. In addition, a two-phase system of aqueous/organic electrolyte can be performed allowing a complete electrical circuit via the conductive aqueous phase, and the reactants in the nonconductive organic phase could undergo partitioning into the aqueous phase prior to electrochemical reactions. Beside oxidation and reduction, this system has been reported for a wide range of chemical reactions including epoxidation, halogenation, hydrodimerization and ozonolyze [7]. Recently, two-phase EC method has been applied for improved overall quality of a perfume sample with the capability to perform a large scale and cost-effective synthesis using aluminium electrodes and $NaCl_{(aq)}$ electrolyte. This is related to adjustment of odor active compound profile in the sample [8],[9],[10]. With this approach, the EC reaction occurred inside the $NaCl_{(aq)}$ phase with the reactants continuously supplied from the organic phase. The products then underwent partitioning into the organic phase and were collected. Their yields were enhanced by using small volume of water minimizing the mass loss inside the water phase. Their chemical profile of the organic phase after EC can then be analyzed using suitable analytical technique. A challenge is to further investigate the capability of the 2-phase EC for a wider range of perfume samples and establish the data analysis criteria in order to propose chemical reaction mechanisms for the change of odor active compounds. For perfume analysis, headspace solid phase microextraction (HS-SPME) can be effectively applied as a simple and fast sample preparation approach where a wide range of volatile compounds in the sample headspace can be extracted onto the SPME materials [11] prior to analysis with gas chromatography hyphenated with mass spectrometry (GC-MS) [12]. These techniques allow precise identification of volatile compounds according to MS library match and retention index data.

In this study, a cost effective EC system with aluminium electrodes and two-phase electrolyte system of $NaCl_{(aq)}$ and hexane (2-phase EC) was applied to adjust the odors of personal care products with the focus on two perfume extracts containing different sets of volatile organic compounds. Volatile profiles of the samples before and after the 2-phase EC synthesis were analyzed by SPME-GC/MS.

Possible synthesis mechanisms were proposed and discussed based on the potential reactants and products in the investigated samples.

1.2 Literature review

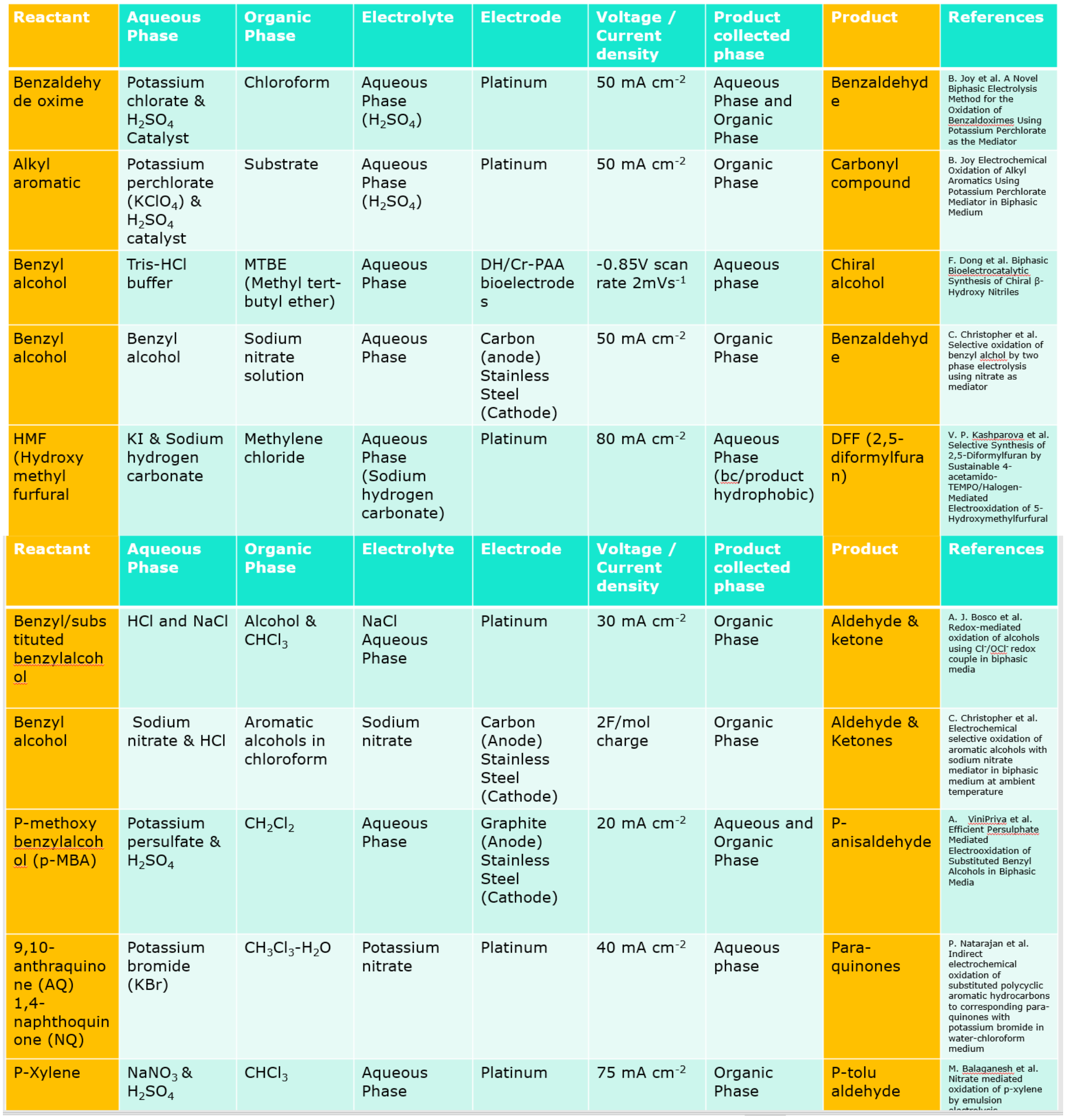
Electrochemical synthesis in organic media is widely recognized as reliable and cost-effective approach with the recycling and monitoring capabilities [13],[14],[15]. The technique has been applied to produce a wide range of organic compounds [16]. Since usable electrochemical system requires conductive media throughout an electrical circuit, addition of salt, such as tetra-ammonium salts with long chain alkyl groups that are soluble in organic solvents, is required to promote conductivity and maintain current in the system. Due to the fact that resistance of the organic media can be reduced by reducing distance between the two electrodes and increasing the electrode surface area, the analytical scale Platinum (Pt) microelectrodes can be applied without addition of salt [17], [18] . Alternatively, two-phase system of aqueous electrolyte and organic solvent has been reported. This approach allows maintenance of electrical current by the aqueous phase; whilst, the reactants were continuously supplied from the hexane phase, *e.g.* to undergo partitioning into the aqueous phase prior to electrochemical reactions [19]. This system has been effectively applied to perform a wide range of chemical reactions such as oxidations, epoxidations, ozonolyze, halogenation processes, reductions or hydrodimerizations [20]. A challenge is to apply this 2-phase technique to improve quality of industrial products and the capability to perform larger scale synthesis with low-cost electrode and electrolyte system, *e.g.* use of stainless steel electrodes and NaCl salt.

There are several instruments applied along the wastewater treatment process. However, a great challenge is to remove the ion contents in these samples. Several approaches can be applied to remove the ions contents in wastewater [21],[22],[23],[24] samples such as chemical precipitation by addition of counter-ions into samples increasing solid formation, filtration by using membranes[25],[26] reverse osmosis (RO) applying high-pressure forcing solution through the membrane, electrodialysis (ED) with the application of the polyelectrolyte membrane or physical/chemical adsorption onto the surface of solid phase materials [31,32]. Apart from these approaches, electrocoagulation (EC) has been generally applied to wastewater treatment, *e.g.* by removals of organic wastes, metal ions and the others such as phosphate (PO_4^{3-}), nitrate (NO_3^-) or ammonium (NH_4^+). A simple platform of EC system consists of two conducting electrodes connected with a power supply and immersed in a container filled with electrolytes. When significantly high voltage is applied to the electrodes, EC occurs with the rate governed by the polarities of the two electrodes [27]. The system relies on either electrochemical conversion of chemical wastes into the solid forms at the electrodes or corrosion of the applied electrodes resulting in formation of the solid complexes (sludge), *e.g.* formed as a result of complexation between metal species from the corroded electrode and hydroxides [28] with the subsequent adsorption of the wastes onto the sludge and their removal. The system performance depends on several factors such as system design, material, shape and arrangement of electrodes and sample components.

Since corrosion occurs in EC, relatively low-cost electrode materials such as aluminum or stainless steel can be applied.

The two-phase electrolysis has been developed for synthesis of specific chemicals such as fragrance or food additives through low-cost electrochemical reaction, increasing values of redox agents, small amount of redox reagent with large amounts of product generation [4], such as benzaldehyde and *p*-anisaldehyde (with the other examples provided in **Table 1.1**).

Table 1.1 Experimental approach and application of two-phase electrolysis for synthesis of volatile organic compounds.



Reactant	Aqueous Phase	Organic Phase	Electrolyte	Electrode	Voltage / Current density	Product collected phase	Product	References
Benzaldehyde oxime	Potassium chlorate & H_2SO_4 Catalyst	Chloroform	Aqueous Phase (H_2SO_4)	Platinum	50 mA cm^{-2}	Aqueous Phase and Organic Phase	Benzaldehyde	B. Joy et al. A Novel Biphasic Electrolysis Method for the Oxidation of Benzaldoximes Using Potassium Perchlorate as the Mediator
Alkyl aromatic	Potassium perchlorate ($KClO_4$) & H_2SO_4 catalyst	Substrate	Aqueous Phase (H_2SO_4)	Platinum	50 mA cm^{-2}	Organic Phase	Carbonyl compound	B. Joy Electrochemical Oxidation of Alkyl Aromatics Using Potassium Perchlorate Mediator in Biphasic Medium
Benzyl alcohol	Tris-HCl buffer	MTBE (Methyl tert-butyl ether)	Aqueous Phase	DH/Cr-PAA bioelectrodes	-0.85V scan rate 2mVs^{-1}	Aqueous phase	Chiral alcohol	F. Dong et al. Biphasic Bioelectrocatalytic Synthesis of Chiral β-Hydroxy Nitriles
Benzyl alcohol	Benzyl alcohol	Sodium nitrate solution	Aqueous Phase	Carbon (anode) Stainless Steel (Cathode)	50 mA cm^{-2}	Organic Phase	Benzaldehyde	C. Christopher et al. Selective oxidation of benzyl alchol by two phase electrolysis using nitrate as mediator
HMF (Hydroxy methyl furfural	KI & Sodium hydrogen carbonate	Methylene chloride	Aqueous Phase (Sodium hydrogen carbonate)	Platinum	80 mA cm^{-2}	Aqueous Phase (bc/product hydrophobic)	DFF (2,5-diformylfuran)	V. P. Kashparova et al. Selective Synthesis of 2,5-Diformylfuran by Sustainable 4-acetamido-TEMPO/Halogen-Mediated Electrooxidation of 5-Hydroxymethylfurfural
Benzyl/substituted benzylalcohol	HCl and NaCl	Alcohol & $CHCl_3$	NaCl Aqueous Phase	Platinum	30 mA cm^{-2}	Organic Phase	Aldehyde & ketone	A. J. Bosco et al. Redox-mediated oxidation of alcohols using Cl^-/OCl^- redox couple in biphasic media
Benzyl alcohol	Sodium nitrate & HCl	Aromatic alcohols in chloroform	Sodium nitrate	Carbon (Anode) Stainless Steel (Cathode)	2F/mol charge	Organic Phase	Aldehyde & Ketones	C. Christopher et al. Electrochemical selective oxidation of aromatic alcohols with sodium nitrate mediator in biphasic medium at ambient temperature
P-methoxy benzylalcohol (p-MBA)	Potassium persulfate & H_2SO_4	CH_2Cl_2	Aqueous Phase	Graphite (Anode) Stainless Steel (Cathode)	20 mA cm^{-2}	Aqueous and Organic Phase	P-anisaldehyde	A. ViniPriya et al. Efficient Persulphate Mediated Electrooxidation of Substituted Benzyl Alcohols in Biphasic Media
9,10-anthraquinone (AQ) 1,4-naphthoquinone (NQ)	Potassium bromide (KBr)	CH_3Cl_3-H_2O	Potassium nitrate	Platinum	40 mA cm^{-2}	Aqueous phase	Para-quinones	P. Natarajan et al. Indirect electrochemical oxidation of substituted polycyclic aromatic hydrocarbons to corresponding para-quinones with potassium bromide in water-chloroform medium
P-Xylene	$NaNO_3$ & H_2SO_4	$CHCl_3$	Aqueous Phase	Platinum	75 mA cm^{-2}	Organic Phase	P-tolu aldehyde	M. Balaganesh et al. Nitrate mediated oxidation of p-xylene by emulsion

The procedure applies two electrolytic cells with direct power supply (DC) with mediated aqueous (act as supporting electrolyte) and organic phases. The electrodes were placed in the aqueous phase close to interphasial region with the organic phase stirred with magnetic stirrer. After the completion of electrolysis, the organic phase or aqueous phase was separated to remove solvent by distillation. The amount of product residue indicated the final product obtained from the reaction [5]. In addition, two-phase electrolysis has advantage over conventional homogeneous and emulsion electrolysis in electroorganic synthesis. In homogeneous system, the over-oxidation of the substrate occurred on the electrode surface. In emulsion electrolysis, electrode passivation led to high energy consumption and high current density in the system. In two-phase electrolysis systems, the reactive species formed with electrolytic oxidation-reduction of mediator in aqueous phase electrolyte reacted with substrate to form the final products [6].

1.3 Aim, scope and expected benefits of this work

In this study, new 2-phase EC approach with electrodes will developed and applied for treatment of odor active compounds. Two-phase system of $NaCl_{(aq)}$ and hexane was applied. For the example application, a perfume sample extracted in hexane was used providing a set of volatile reactants for the 2-phase EC synthesis. Samples were prepared by solid phase microextraction (SPME) which offers a simple and fast extraction process where volatile compounds in the sample headspace can be adsorbed onto the SPME fiber [29]. The extracted samples were further analyzed by GC─qMS [12]. The results were discussed, and possible treatment mechanisms were proposed according to different volatile compound profiles in different samples.

CHAPTER II

THEORY

2.1 Electrocoagulation

Electrocoagulation technique has several instruments applied along the wastewater treatment process. The presence of ions such as phosphate (PO_4^{3-}), nitrate (NO_3^-) or ammonium (NH_4^+) in either inoculum or percolate samples can cause potential damage to the instruments. For example, the continuous reduction of fine solids based on anaerobic hydrolysis can increase viscosity of the sample which affects the pumping and piping system in the recirculation. The increase in total ions of the sample can lead to a higher potential for a controlled and external precipitation of NH_4MgPO_4 and $CaCO_3$ [41]. Thus, a great challenge in waste treatment process is to remove the ions contents in these samples. Several approaches can be applied to remove ions from wastewater samples [42] such as chemical precipitation by addition of counter-ions into samples increasing solid formation [43]. The ions can also be filtered out by using membranes, the performances of which depend on the pore size and chemical functionalities of the membranes [24], [25]. For example, Microfiltration (MIF) is applied to remove microorganisms from water. Ultrafiltration (UF) approach provided higher selectivity due to selective binding mechanisms of the membranes [26], [27], [28]. Nano-filtration (NF) is used for removal of toxic metal from wastewater [29]. Reverse osmosis (RO) can be performed by application of high-pressure forcing solution through the membrane. The performance of this method depends on several factors such as ion concentration, magnitude of pressure or rate of water flow through the membrane [30]. Electrodialysis (ED) approach is applied with the application of polyelectrolyte membrane which is inserted between anode and cathode [31], [32], [33]. Ions are also removed based on physical/chemical adsorption onto the surface of solid phase materials [34], [35].

Apart from the methods above, electrochemical techniques are recognized in the aspects of more reliable and economical approaches since the techniques can be effectively applied to cope with ecological systems with recycling and monitoring capabilities [36], [37]. An example includes electroflocculation separating solid/liquid mixture by floating of contaminants to the surface of wastewater assisted gas bubble products generated at the electrodes according to electrolysis [38]. Advantages and disadvantages of the approaches above are summarized in **Table 2.1**.

Table 2.1 Advantages and disadvantages of conventional approaches to remove ions from wastewater [39,40].

Treatment approach	Advantages	Disadvantages
Chemical precipitation	● Simple ● Low cost	● Additional step required to remove sludge
Adsorption	● Simple ● Applicable to a wide range of pH	● Low selectivity ● Generation of waste products
Membrane filtration	● Small operation space ● High selectivity	● High cost due to membrane fouling
Electroflocculation	● Capture coagulated pollutants floating to the surface	● Large amount of sludge

Alternatively, electrocoagulation can be applied to effectively remove several ion species in wastewater samples [41-44]. The technique relies on generation of adsorbents as a result of redox reactions maintaining continuous flow of current to the electrodes. This method is considerably auto-coagulation or electro-catalytic method even without addition of chemicals, thus producing less amount of sludge compared with other conventional techniques [45], [46]. An electrocoagulation system consists of 2 conducting electrodes immersed in a container filled with electrolytes. When significantly high voltage is applied to the electrodes, the electrocoagulation occurs with the rate governed by the polarities of the two electrodes [47-49]. The system performance depends on several factors such as system design, shape and arrangement of electrodes and sample components.

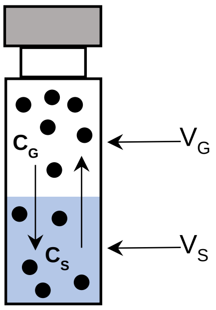
2.2 Headspace

Headspace sampling is applicable with the qualitative or quantitative analysis of volatile species in samples where the volatiles evaporate into gas volume of the sample headspace from either a liquid or solid matrix. It is a good technique for injection of analytes into GC instrument without being in contact with the entire sample. Nonvolatile contaminants remain behind in the headspace vial and do not accumulate in the inlet or the column. Volatiles may be extracted from heavy or more polar sample matrices [50]. Many kinds of samples can be prepared in HS vial and extraction in the headspace of the samples isolated from non-volatile components in the sample vials, and the volatile components can then be transferred into a GC system for analysis. HS sampling is also particularly amenable to the trace analysis. This technique is considerably easy and fast.

The theory of HS sampling can be explained with the example of liquid sample in a closed vial as shown in **Figure 2.1** the volatile components diffused from the solid sample into the gas phase. In equilibrium, the concentrations in both phases remain constant. The ratio of analyte concentration in each phase is captured by a partition coefficient (K value). This parameter is the product of two terms including mass ratio of analyte in the solid to that in gas phase (k) and phase ratio of the solid to the gas volume (ß value) [50]. The K value directly affects the efficiency of headspace analysis. Lower the K value by increasing sample temperature or by adding inorganic salts to the sample matrix increases the volatile amount in HS leading to improved sensitivity of the analysis. The sample volume can also be increased which increase the analyte yield in HS [51].

$$K = \frac{C_S}{C_M}$$

$$\beta = \frac{V_S}{V_g}$$



C_s = Analyte concentration in solid phase

C_g = Gas phase concentration

V_s = Solid phase volume

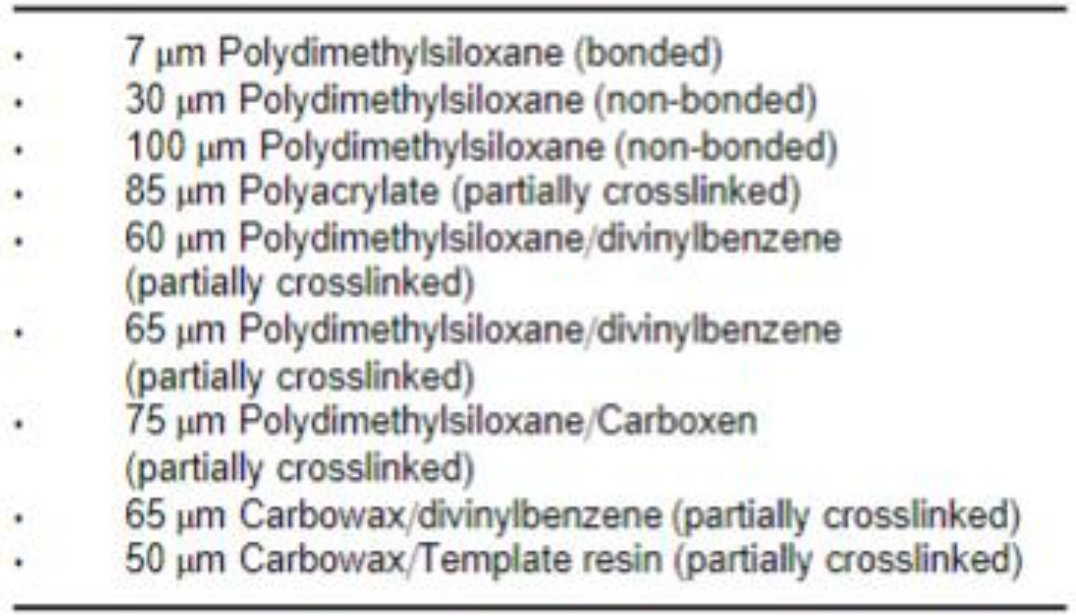
V_g = Gas phase volume

Figure 2.1 Volatile compound in the headspace vial containing liquid sample [51].

2.2.1 Head-space solid phase microextraction (HS-SPME)

Solid phase microextraction (SPME) has been applied to various conjunction with other chromatographic analysis techniques, such as UV, IR and mass spectrometry. In this research, SPME has commonly coupled with technique gas chromatography-mass spectrometry. Overview of SPME device consisting of a stationary phase fiber coated with fused silica **(Table 2.2)** within a syringe-type holder **(Figure 2.2)** to protect fiber before the insertion of needle fiber into the hot condition of GC-MS injection port [52]

This technique is used to clarifies the extraction technique by extract and concentrate compounds from headspace vapor sample. The head space will adsorb the analyte from the atmosphere achieved by fiber insertion into the headspace phase inside the glass vial [53]. The needle syringe fiber made of fused silica fiber coated with immobilized stationary phase film was inserted into the headspace vial which accommodating above the sample and the coated fiber would expose into the headspace vial continuously adsorb volatile compounds analytes in the sample **(Figure 2.3)** [54]. After SPME fiber was accumulated the analyte vapor phase sample, the fiber will be transferred back to the plunge syringe needle and inserted into the hot injector GC injection port [55]. The thermal desorption of fiber containing analytes sample was introduced at the GC-MS injector liner and the carrier gas to transfer analyte to the GC column for analysis as shown in **Figure 2.4**. and performed the signal responses chromatogram. The advantages of this technique is provided successfully eliminate effects of solvent trap which may interfering the column and wide range of analyte pre-concentration [56].



- 7 µm Polydimethylsiloxane (bonded)
- 30 µm Polydimethylsiloxane (non-bonded)
- 100 µm Polydimethylsiloxane (non-bonded)
- 85 µm Polyacrylate (partially crosslinked)
- 60 µm Polydimethylsiloxane/divinylbenzene (partially crosslinked)
- 65 µm Polydimethylsiloxane/divinylbenzene (partially crosslinked)
- 75 µm Polydimethylsiloxane/Carboxen (partially crosslinked)
- 65 µm Carbowax/divinylbenzene (partially crosslinked)
- 50 µm Carbowax/Template resin (partially crosslinked)

Table 2.2 Overview commercially SPME device consisting of stationary phase fiber coatings [57]

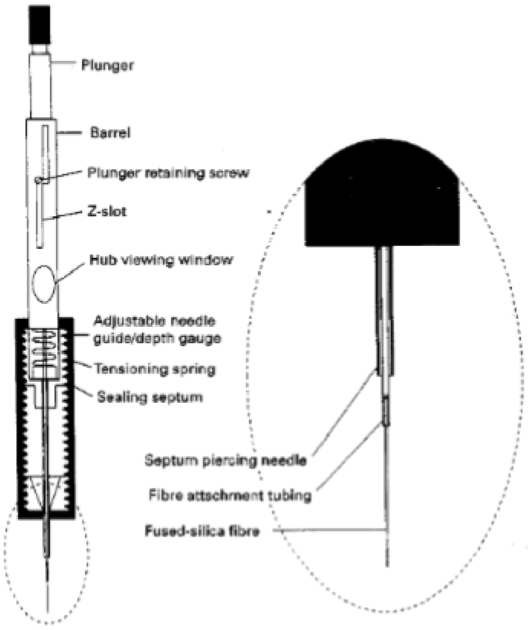


Figure 2.2 Solid phase microextraction device [57]

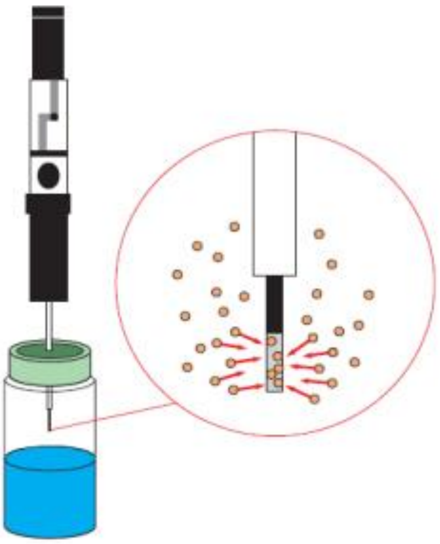


Figure 2.3 Schematic view of extraction by headspace-solid phase microextraction (HS-SPME) [58]

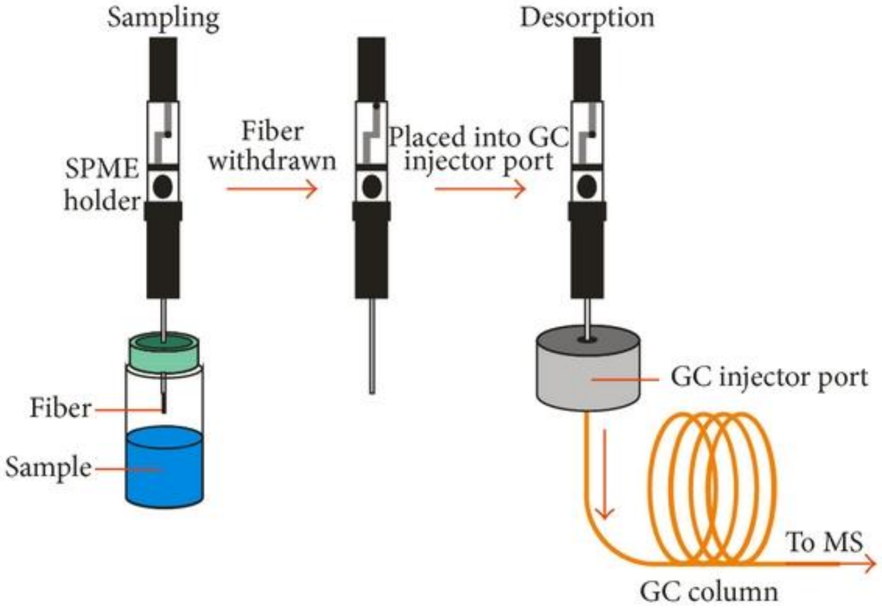


Figure 2.4 Schematic view of manual SPME approach [57]

2.2.2 Sorbent

The SPME device consists of a fused-silica fiber rod coated with thin layer polymeric coating or on the internal capillary tube surface as sorbent. The silica fiber core of polydimethylsiloxane coating with 7 mm thickness is applied. The availability of variety commercial adsorbent phase, including [polydimethylsiloxane (PDMS), polyacrylate (PA), and Carbowax (CW)] and mixed-phase sorbents [e.g., Carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and Carbopack Z/PDMS [59]. To improve stability in SPME, the PDMS/DVB is a bipolar sorbent coating with multiple components. DVB/CAR/PDMS is a bipolar phase with multiple-component that contains DVB-PDMS (50 mm) layered over CAR-PDMS (30 mm) combination [60]. The bipolar sorbent arrangement enhanced the molecular weight range of analyte, since larger analytes are retained in the meso- and macropores of the outer DVB layer, while the micropores in the inner layer of Carboxen retain smaller [61]. The dual-layered phase, DVB/CAR/PDMS is used for odor compounds, volatile and semi-volatile compounds extraction prior to GC analysis [62].

2.3 Gas chromatography-Mass Spectrometry

Gas chromatography mass spectrometry (GC-MS) is referred to as a hyphenated method, combining the benefits of two distinct analytical techniques: GC to separate volatile organic compounds in a complex sample, and MS to detect, identification and/or quantification [63]. This technique is in dispensable in the field of environmental science, forensic, health care, medical and biological research, flavor and fragrance industry, food safety, packaging, and many others [64]. In order to be analyzed by GC-MS, a compound must be sufficiently volatile and thermally stable. This technique provides separation of components in a complex mixture which results in mass spectra of individual compounds. This is useful for qualitative and quantitative proposes [65]. The sample solution is injected into the GC inlet where it is vaporized and swept onto a chromatographic column by the carrier gas. The sample flows through the column and the compounds comprising the mixture of interest are separated according to their relative interaction with the stationary phase of the column and the carrier gas [66,67]. The latter part of the column passes through a heated transfer line and ends at the entrance to an ion source as shown in **Figure 2.5** where compounds eluting from the column are converted to ions.

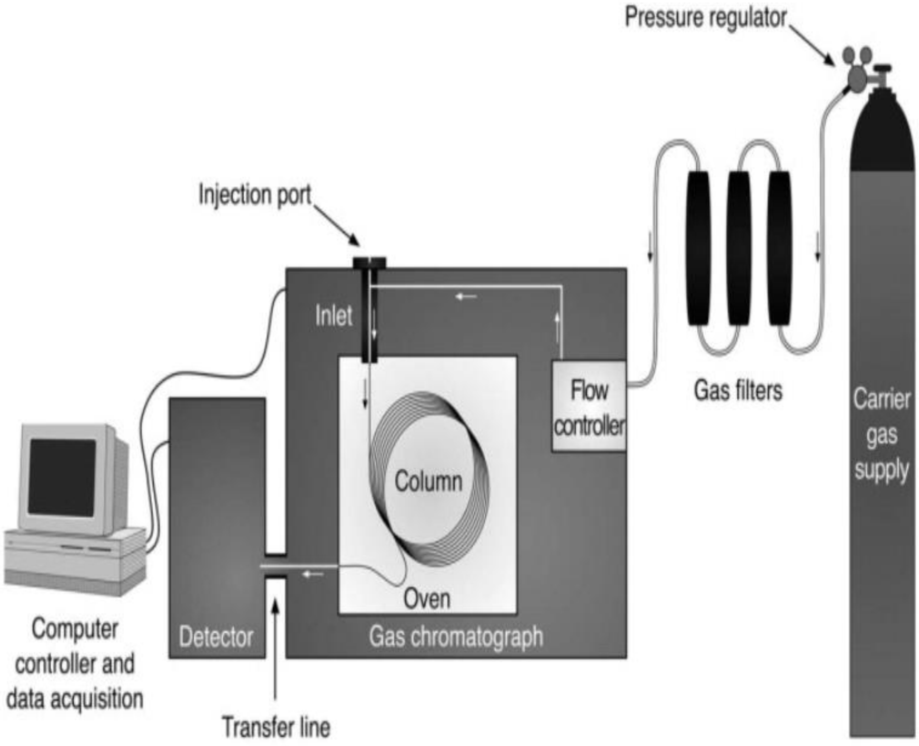


Figure 2.5 The gas chromatography and its main components [67]

Chapter III

Experimental

3.1 Instruments and apparatus

3.1.1 Gas chromatography-mass spectrometer (GC-MS), Agilent technologies with 7890A equipped with a mass spectrometer Agilent 7000 scan mode Triple Quadrupole, GC consists of autosampler and column oven, electron ionization (EI) interface and MassHunter software processing

3.1.2 Capillary column HP-5MS (30m x 0.25 mm i.d., 0.25 µm film thickness), J&W Scientific, USA

3.1.3 SPME 50/30 µm DVB/CAR/PDMS fiber, Supelco (sigma-Aldrich, Bellefonte, PA)

3.1.4 SPME holder, Supelco (Sigma-Aldrich, Bellefonte, PA)

3.1.5 Ultra-high purity helium (99.999%), Linde

3.1.7 Balance (4 digits), Satorius Model AC2115-00MS (Germany)

3.1.8 Screw cap and vial HS 20 mL, Agilent technologies

3.1.9 DC Power Supply, KORAD KA3005D (Korea)

3.1.10 Rectangular Aluminium electrode sheet 8x2 cm

3.2 Chemicals

3.2.1 Series of *n*-alkanes

A mixture of *n*-alkanes (C_8-C_{20}), sigma Aldrich (St. Louis, MO) was used as a reference to calculate retention index (*I*) of the compounds

3.2.2 Hexane, Sigma Aldrich (St. Louis, MO).

3.2.3 $NaCl_{(s)}$, Sigma Aldrich (St. Louis, MO).

3.2.4 Liquid Perfume samples were purchased from local supermarket, Thailand

3.3 Liquid Phase Extraction

15 mL perfume sample was transferred into 15 mL of hexane. The perfume and hexane mixture were shaken then left at 25 °C at room temperature for 5 min

until phase separation occurred. The hexane phase derived from hexane extract was then collected for analysis with SPME/GC-MS.

3.4 2-phase electrocoagulation

15 mL of the hexane extract containing perfume volatile organic compounds was transferred into a 25 mL beaker used as the 2-phase EC sample. 2 mL of water and 2.5 g NaCl were then added into the beaker to perform a 2-phase electrolyte system. Two aluminium electrodes sheets with 8 cm x 2 cm each were submerged into the EC system with the electrodes ends reaching the aqueous phase located at the bottom of the system. The electrodes were connected with a power supply and applied constant voltage of 2 V for 1 h reaction time enabling EC treatment of the sample. The samples before (Control) and after 2-phase EC at three different regions (Figure 1B) were then analyzed with SPME/GC-MS. The sample collected at the cathode and anode after 1 h of EC were called as “Samp Cat” and “Samp An”, respectively. In addition, the sample region between the cathode and the anode after 2 h of EC followed by 5 min equilibrium time was also collected and called as “Samp All”. This represents the region containing all the 2-phase EC products and the remaining reactants. The 5 min equilibrium time was performed in order to reach the equilibrium concentration of all the species in the system. All the samples were collected and analyzed in triplicate.

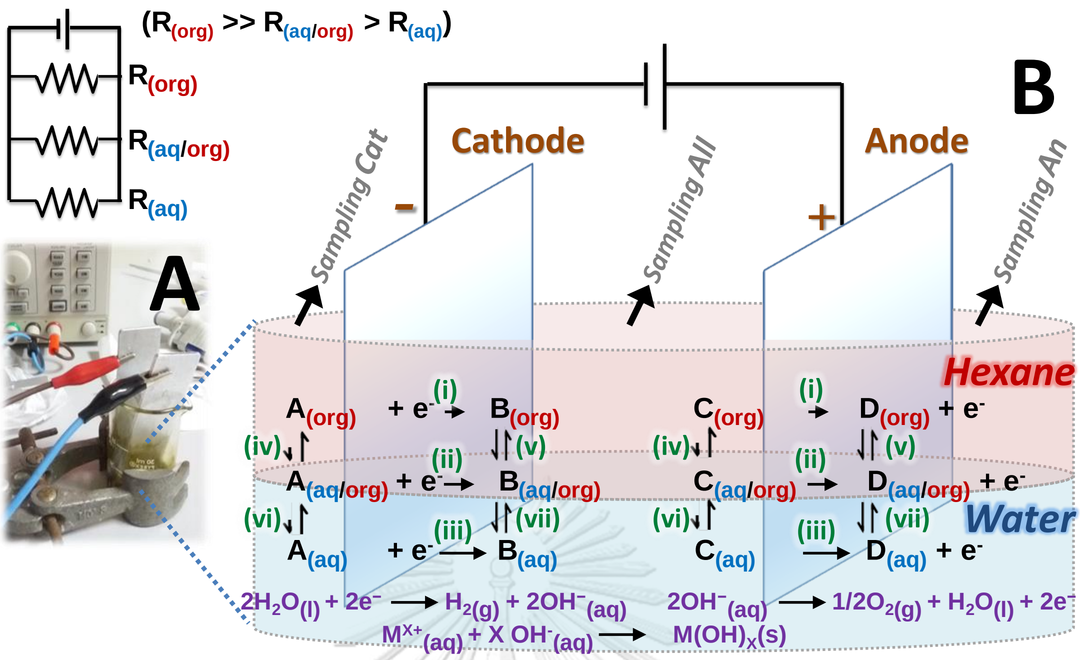


Figure 3.1 (A) Experimental set up of the 2-phase electrocoagulation system, and (B) diagram illustrating phase separation and electrochemical reaction for conversion of compounds A and C into compounds B and D, respectively, according to the reduction and oxidation reactions at different positions (i) in hexane, (ii) at the interface and (iii) in water with partitioning of the related compounds between these phases (iv)-(vii). The reactions at the bottom indicate formation of $H_{2(g)}$ and $O_{2(g)}$ and sludge.

3.5 Analysis of volatile compounds

The SPME fiber was conditioned for 1 h inside a GC injection port at 270 °C. The blank fiber was injected to check the background signal for GC-MS analysis. Each 200 µL sample was transferred into a 20 mL glass vial enclosed with an aluminum cap and left at 25 °C room temperature for 5 min period. The sample with headspace was extracted with the SPME fiber using 10 min extraction time at 25 °C room temperature and injected into the GC injection port under splitless mode at 220 °C using the desorption time of 5 min. The volatile compounds were then separated and analyzed by using GC hyphenated with triple quadrupole MS (GC-QqQMS, 7890A-7000, Agilent technologies Inc.) which was applied under single Q scan mode with the other quadrupoles operated with total transfer of ion mode.

A HP-5 MS capillary column (30 m x 0.25 mm i.d., 0.25 µm film thickness; J&W Scientific, USA) was applied with ultra-high purity helium (99.999%) as the carrier gas at a flow rate of 1 mL min^{-1}. The GC oven temperature increased from 40 to 240 °C (4 °C min^{-1}). For MS conditions, the ion source temperature, electron ionization voltage, mass range and scan time were 230 °C, -70 eV, 30–300 Da and 100 ms, respectively.

3.6 Data processing

Data presentation and peak integration were carried out using Agilent MassHunter Software. A peak was tentatively identified by comparison of the MS spectrum with that from the NIST library 2017 version with the MS match score of >650. The compound identity was confirmed by comparison between the experimental retention index (I) and the literature I for the same (or a similar) stationary phase within the difference of 20 units. *I* of a peak of interest was identified relative to the retention time of a homologous series of alkanes C8 to C20 (Sigma Aldrich, St. Louis, MO) which was obtained by injection of an alkane mixture under the same experimental conditions used for separation of the sample. The experimental I was calculated based on the retention time of the alkane references under the same experimental conditions according to the van den Dool and Kratz relationship as shown **(1)** [67]. For the calculation, data processing alignment and further data processing were performed by using Microsoft Excel.

$$I = 100n + 100\left(\frac{t_r(i) - t_r(n)}{t_r(n+1) - t_r(n)}\right) \tag{1}$$

where

$t_{r(i)}$ is the retention time of a compound of interest

$t_{r(n)}$ is the alkane eluting immediately before the unknown compound with the carbon number of *n*

$t_{r(n+1)}$ is the alkane eluting immediately after the compound with the carbon number of *n*+1[15].

The odor descriptors of compounds were obtained from the olfactometry database from literatures.

Chapter IV

Results & Discussions

EC system containing water/hexane phases was developed and used to modify perfume compounds. The reactants for the EC were obtained from liquid/liquid phase extraction of a perfume in hexane. This was used as the control to be compared with the same sample after the EC treatment. Volatile compounds in the EC treated sample were sampled at different positions and analyzed by HS-SPME/GC-MS. The results were compared, and possible reactants and products were proposed according to volatile compound profiles of the samples before and after the treatment. The 2-phase EC synthesis mechanisms were then proposed.

4.1 Two-phase electrocoagulation system

The EC system consists of two aluminium electrodes located in 2-phase of hexane and $NaCl_{(aq)}$ as the electrolyte system, shown in the **Figure 3.1A**. To complete the overall electrical circuit, the hexane phase and electrode ends were in contact with the $NaCl_{(aq)}$ conductive phase to reach the beaker bottom.

Several phenomena could occur during the EC treatment. Oxidation and reduction reaction phenomena mainly produced $O_{2(g)}$ at the anode and $H_{2(g)}$ at the cathode which can be observed by the presence of gas bubbles at the electrodes around the hexane/water interface during the EC. The oxidation and reduction also enabled organic compounds and sludge formation resulting from electrode corrosion (*e.g.* resulting in Fe^{2+}, Fe^{3+}, Cr^{3+}, or Al^{3+}) and the following complexation between the ions and hydroxides. The sludge was isolated into the water phase and can be simply removed from the system after the EC. Note that polar compounds such as alcohols or esters in the hexane extract undergo partitioning into the aqueous. This decreased the product amount in the hexane phase. This problem was solved by reducing water volume in the system because the product concentrations at the equilibrium are approximately constant. 2.0 mL of water was thus applied, compared with 15.0

mL of hexane. The operated system was constructed under constant voltage mode at 2 V the current ranges of which were from 0.01-0.05 A during the EC reactions. The 2-phase-EC system was separated into three main regions as anode, cathode and in between the two cathode and anode electrodes according to the two electrode sizes fit with the beaker as shown in **Figure 3.1B**.

This research mainly aims to analyze possible volatile compound products and reactants in the hexane phase of the 2-phase EC system. The analysis of the samples can be performed by collecting the top layer of hexane at different regions (*e.g.* before EC, after 2 h EC at cathode and after 2 h EC at anode) by HS-SPME technique. There are four main parts of before and after the EC treatment which were namely "*Control*" sample (before EC treatment), "*Samp Cat*" derived via directly collecting 200 μL of the sample solution at the cathode position (illustrated by the position in **Figure 3.1B**) after 1 h EC reaction transferred into the 20 mL HS-SPME vial. The volatiles compounds in the headspace of "*Samp Cat*" were extracted using SPME technique and then analyzed with GC-MS technique. The third sampling section namely "*Samp An*" was gathered at the anode position of EC system. The final sampling section called "*Samp All*" was gathered between the cathode and anode after 2 h EC reaction. However, to reach equilibrium concentrations of overall volatiles in the sample solution, the system was left for 5 min after EC treatment without applied voltage.

The system was operated under 2 V constant voltage mode with 0.01-0.08 A of the current values. In order to enable the electrode corrosion, organic reactions, gases production (H_2 and O_2) and sludge formation, the sufficiently high voltage value was required. The well-ventilated space is recommended for the experiment to be performed due to the explosive H_2 gas production. The further EC conditions optimization would be enhanced to improve the 2-phase EC performance via adjustment of voltage, current and electrode materials. For example, different electrode materials such as platinum electrodes can be applied to enable synthesis of various ranges of organic compounds with improve corrosion resistance at higher standard electrode potential. In addition, the EC treatment process can be fastened by applying higher current or voltage potential. In this research, the condition was to minimize voltage as much as possible to enable the most effective EC treatment with lower amount of sludge formation.

4.2 Proposed reaction mechanisms

To explain electrochemical treatment with the developed 2-phase EC system, the possible pathway is proposed in **Figure 3.1A**. Due to very high resistance of the hexane medium without electrolyte or micro-electrodes, volatile compounds could not undergo electrochemical reaction (as shown in (i) pathway in **Figure 3.1B**). In contrast, the water phase containing saturated NaCl with significantly lower resistance can enhance EC reaction to occur as illustrated by pathway (iii)-(vi) in **Figure 3.1B**. The hydrolysis of water as the major EC reaction was bringing on $H_{2(g)}$ and $O_{2(g)}$, (pathways (iv) and (v) in **Figure 3.1B**). The existence of bubbles gases at two electrodes with higher amount of H_2 than O_2 indicates water electrolysis, according to the 2:1 stoichiometric ratio. The electrode corrosion took place via ionization of the electrode into metal ions (mainly $Al^{3+}_{(aq)}$) with the succeeding sludge formation illustrated by the pathway (vi), **Figure 3.1B**, *e.g.* $M(OH)_{x(s)}$ and the (iv) pathway shown in **Figure 3.1B**). In this research, the aluminium complexes from sludge formation were precipitated and settled down into the water phase. The sludge would be removed from the EC system clearly segregated into aqueous phase. The two phases partitioning between reactants and products also occurred, (shown in the pathway (ii) in **Figure 3.1B**). The polar oxygenated compounds in the EC system experienced partitioning into the water phase. The analysis of perfume extract before the EC reaction in hexane and water fractions indicated the significant peak areas in both hexane and water phase. The presence of volatile compounds is shown in **Figure 4.1**). This certifies the partitioning mechanism during the 2-phase EC treatment.

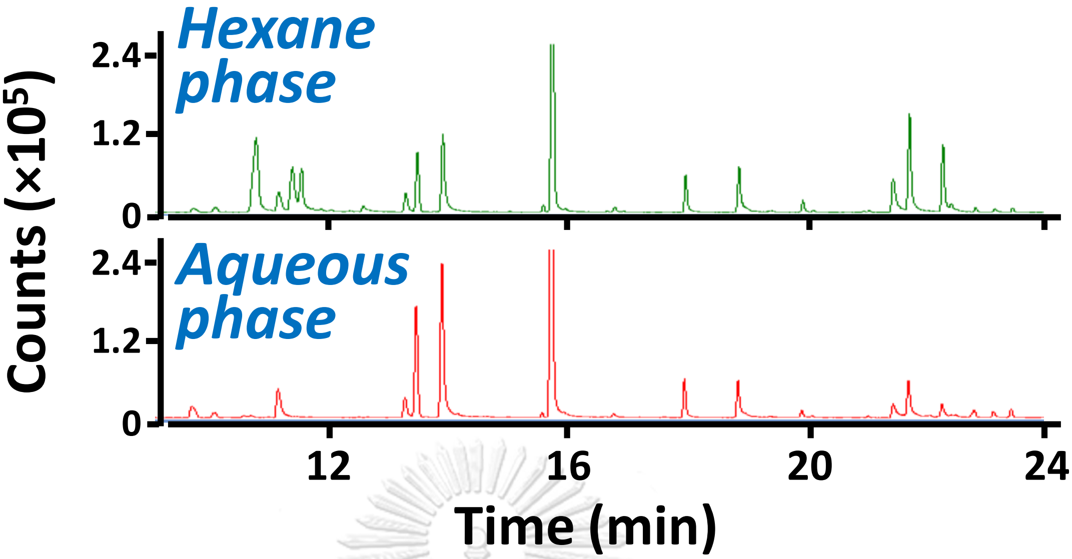


Figure 4.1 HS-SPME/GC-MS chromatograms of the perfume extract showing volatile organic compounds in (A) hexane and (B) water phase in equilibrium condition before 2-phase EC

4.3 Identification of volatile compounds in the perfume extract

The volatile compounds in the hexane samples were determined via HS-SPME technique prior to analysis with GC-MS. The volatile compounds profiles in the hexane extract of perfume before the 2-phase-EC-treatment and the total ion chromatogram (TIC) were provided in **Table 4.1, Table 4.2,** and **Figure 4.2**. The "Control" result indicated the crucial volatile compounds as methyl anthranilate, linalool, propylene glycol, and benzyl acetate with fruity/musty/floral, woody/sweet/floral/citrus, inactive odor, and fruity/floral/fresh/sweet odor descriptions. This contributed to the overall smell of this perfume extract as fruity, floral and fresh smell.

Table 4.1 The reactant profiles with logarithmic partitioning coefficient (log p), odor description, peak area and literature retention indices after two-phase electrocoagulation (2-phase EC) of the perfume extract sample at 2 V with different sampling positions: after 1 h EC at cathode (Samp Cat), after 1 h EC (Samp An) at anode, between the cathode and anode electrodes after 2 h EC with 5 min equilibrium (Samp All) and before EC treatment (Control). The experiments were performed three times.

Compound name	Literature *I*	Odor description	Average %area ± S.D.				
			Control	Samp An	Samp Cat	Samp All	log *p*
Propane-1,2-diol *(R1)*	740	Odorless	8.7±3.8	3±2.6	4.2±3.7	1.8±1.5	-1.0
2,6,6-Trimethylbicyclo[3,1,1]hept-2-en /α-Pinene	929	Woody green herbal	0.4±0.4	1.6±1.1	0±0	0±0	4.4
2-(2-hydroxypropoxy)-1-propanol *(R2)*	1046	Nearly odorless	6.8±4.8	0±0	0.2±0.2	0±0	-0.2
Methyl salicylate	1192	Wintergreen mint	0.7±0.4	0.2±0.1	0±0	0.1±0.1	2.6
(R)-(+)-β-Citronellol	1220	Citronella rose leafy oily petal	1.4±0.7	0±0	0.6±0.5	1±0.9	3.6
Citronellol	1228	Floral leathery waxy rose citrus	1.2±0.9	1.5±0.7	0.5±0.4	0±0	3.3
Geraniol	1255	Sweet floral fruity rose waxy citrus	1.3±1.1	1.1±0.6	1.3±0.6	1.1±1	2.7
Benzyl propionate	1262	Sweet fruity floral banana jasmine balsamic	0.3±0.2	0.1±0.1	0.3±0.2	0±0	2.4
Ethyl salicylate / Salotan	1269	Sweet wintergreen minty floral spicy balsamic	0.2±0.1	0.1±0.1	0.1±0	0.1±0.1	2.8
Piperonal	1330	Heliotrope sweet powdery coconut vanilla	4±2.4	1.2±0.8	2±1.7	2±1.1	1.3
Methyl anthranilate (*R3*)	1343	Fruity grape orange flower powdery	6.8±2.8	4.5±2.2	6.2±1.3	3±2.6	2.0
α-Terpinyl acetate	1350	Herbal bergamot lavender lime citrus	0.1±0.1	0.1±0	0±0	0±0	4.0
Eugenol	1357	Sweet spicy clove woody	1.9±0.9	0±0	0±0	0.2±0.2	2.4
α-Damascone	1384	Floral rose apple fruity current black currant	0.2±0.1	0.1±0.1	0.2±0.1	0±0	3.9
Benzyl dimethylcarbinyl butyrate	1493	Floral green herbal fruity plum prune	0.1±0.1	0±0	0±0	0±0	4.1
Caparratriene	1493	Pleasant / floral odor	0.1±0.1	0±0	0.1±0.1	0±0	5.3
Lilial	1533	Floral muguet watery green powdery cumin	0.1±0	0±0	0.1±0	0±0	4.1
Anozol / Diethyl Phthalate	1594	Without significant odor	0.4±0.3	0.1±0.1	0.4±0.2	0±0	2.4

Table 4.2 The product profiles with logarithmic partitioning coefficient (log p), odor description, peak area and literature retention indices after two-phase electrocoagulation (2-phase EC) of the perfume extract sample at 2 V with different sampling positions: after 1 h EC at cathode (Samp Cat), after 1 h EC (Samp An) at anode, between the cathode and anode electrodes after 2 h EC with 5 min equilibrium (Samp All) and before EC treatment (Control). The experiments were performed three times.

	Compound name	Literature *I*	Odor description	Average %area ± S.D.			
				Control	Samp An	Samp Cat	Samp All
Potential products at the Anode	Benzaldehyde	962	Strong sharp, sweet, bitter almond cherry, spicy	0.2±0.1	0.2±0.1	0.1±0.1	0.3±0.1
	Methyl benzoate (*A1*)	1094	Phenolic wintergreen almond floral canaga	2.6±0.5	4±1.7	1.8±1	4.1±1.3
	2-Phenylethanol (*A2*)	1116	Sweet, floral rose	2.4±2	11.3±5.3	9.9±4.2	22.6±6.6
	Benzyl acetate (*A3*)	1164	Sweet floral jasmine fresh, fruity	32±6.5	56.8±2.4	25.9±7.1	48.5±9.8
	Linalyl acetate	1257	Sweet citrus bergamot-lavender woody fresh floral	0.2±0.2	0.1±0.1	0±0	2.3±1.5
Potential products at the Cathode	Limonene	1030	Citrus orange fresh sweet	0±0	0.2±0.2	0.3±0.3	0.2±0.1
	Phenylmethanol (*C1*)	1036	Floral rose phenolic balsamic	1.3±0.6	4.3±2	29±18	8.3±4.2
	Terpin	1279	Oily woody terpene lemon	0.3±0.3	0.5±0.4	0.8±0.4	0.6±0.5
Enriched compounds	4-Methylanisole	1021	Naphthyl, phenolic, camphoraceous, minty, powdery and nutty	0±0	2.1±1.9	1.4±1	0±0
	γ-Terpinene	1060	Oily woody terpenic lemon tropical herbal	0±0	0.1±0.1	0±0	0±0
	Sabinene hydrate	1070	Cooling minty eucalyptus green terpenic spicy	0±0	0±0	0.9±0.8	0±0
	Linalool	1099	Citrus orange floral terpenic waxy rose	7.2±1.9	9.4±1.5	2.7±1.2	7.2±3.8
	Ethyl benzoate	1171	Fruity dry musty sweet wintergreen	0.4±0.4	0.5±0.4	0.5±0.4	0.2±0.2
	Estragole	1196	Sweet phenolic anise spicy green herbal minty	0.3±0.3	0.5±0.5	0.2±0.2	0.3±0.1
	Caryophyllene	1419	Sweet woody spicy clove dry terpenic	0±0	0.1±0.1	0.1±0.1	0±0

4.4 Identification of potential reactants and products obtained from the 2-phase EC synthesis

The GC-MS regions indicate the products forming after 2-phase EC at cathode, anode, and between cathode and anode region. The samples with different sampling regions (shown in **Figure 3.1B**, Samp Cat, Samp An and Samp All) after the 2-phase EC reaction at constant voltage for 2 V, 1 h were analyzed via HS-SPME prior to GC-MS technique. The 2-phase EC system was separated into three main regions managed to fit with the dimension of EC beaker system. The GC-MS results were indicated in **Figure 4.2A-D** compared with that before the EC treatment (Control), **Figure 4.2A**. The data from **Table 4.1** and **Table 4.2** show the average compound peak area percentages in different samples after the EC treatment.

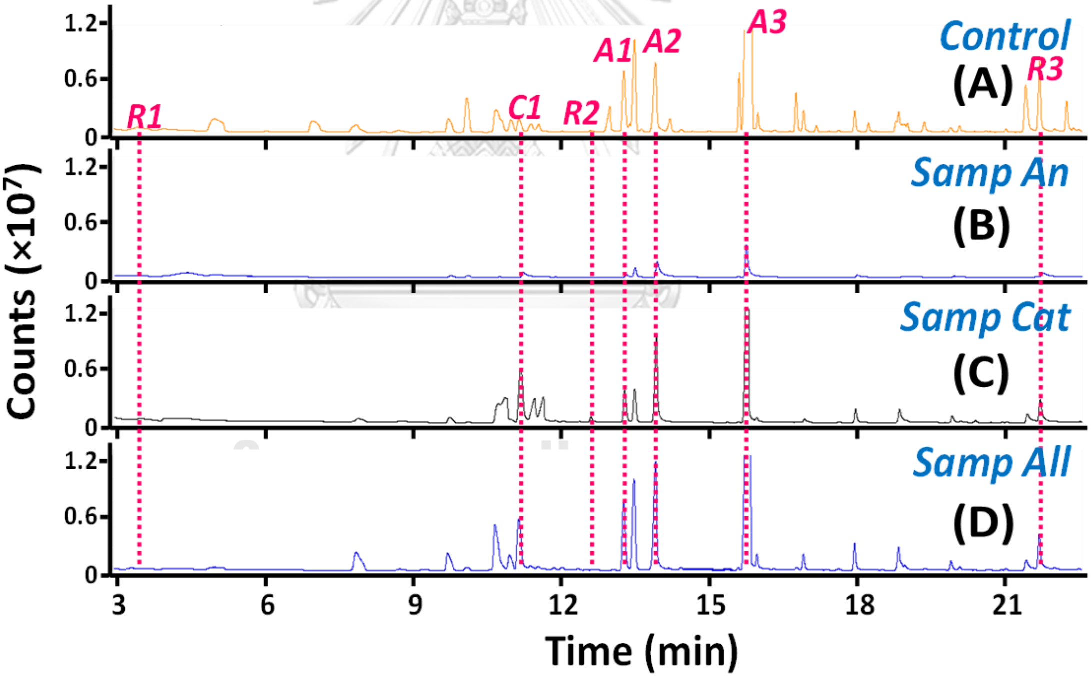


Figure 4. 2 HS-SPME/GC-MS chromatograms of hexane perfume extracted before 2-phase EC (Control) and the samples after the EC obtained from three different regions: at the anode region (Samp An), at the cathode region (Samp Cat), and between the cathode and anode electrodes region after 5 min equilibrium (Samp

All). Table 4.1 and 4.2 showed the reactants (R1-R3), products at the anode region (A1-A3) and products at the cathode region (C1).

The existence of the possible products in the 2-phase EC is indicated by the enlarging amounts of the compounds in Samp All in **Table 4.2** as "*Potential products at the Cathode*" and "*Potential products at the Anode*". The product samples obtained products from each electrode in both anode and cathode were remarked.

The crucial product at the cathode was phenylmethanol with the phenolic/floral/rose odor description, compare peak of Samp Cat (***C1***) in **Figure 4.2C** with the Control in **Figure 4.2A.** In addition, the potential products at the anode were benzyl acetate (peak ***A3***), 2-phenylethanol (peak ***A2***) and methyl benzoate (peak ***A1***) with the odor descriptions of fruity/fresh/floral/sweet, fresh/rose/sweet and phenolic odors, respectively, compare **Figure 4.2B** with the control in **Figure 4.2A.**

Possible reaction mechanisms can be suggested according to the profiles of possible EC reactants and products above in **Table 4.1** and **4.2**. The significant reaction mechanism would be the oxidation of ethanol as the considerable solvent in the perfume. This is anticipated to results in acetic acid to further encounter esterification reaction with various alcohols in **Table 4.1** leading to various -acetate products in **Table 4.2**. In contrast, hydrolysis of esters to produced acetic acid and alcohol could be significantly indicated via benzyl acetate (***A3***) in **Table 4.2**, hydrolyzed into phenylmethanol (***C1***) in **Table 4.2**.

It could be highlighted that enrichment of the compound concentrations under the influence of electric field at the electrode positions would influence the inspection rather than the electrochemical reaction. For example, amounts of charge or polarizable species can be promoted according to their adsorption onto the electrode surface. **Table 4.2** indicates the potential compounds as "*Enriched compounds*" revealed the same area percentages of the compounds in Control, Samp All and the increasing percentages in Samp Cat or Samp An.

4.5 Online analysis of target *m/z* profile during 2-phase EC of the perfume extract with gas analyzer

The changes in the amounts of the major compounds (***A1***, ***A2***, ***A3***, ***C1***, ***R1*** and ***R2***) in the perfume extract during the 2-phase EC treatment were analyzed using gas analyzer. This was performed according to their distinctive *m/z* in electron ionization mass spectra (EI MS) observed in HS-SPME/GC-MS analysis.

The volatiles in the open headspace of the EC system were directly sampled via a heated transfer line (at 150 °C) into the Gas Analyzer vacuum chamber as illustrated in **Figure 4.3A**. The intensity profiles of *m/z* 59, 77, 79, 91, 103, 105, 108, 122, 136 and 150 indicated remarkably high signal. During the EC treatment, the voltage application started at 5 V and the m/z signal above the headspace sample was collected for 5 min prior to the applied voltage. Evolution and evaporation of various volatile compounds can be represented by the different m/z value profiles. **Figure 4.3B** indicates the 2-phase EC with 2 h treatment of the perfume compounds with the normalized intensity profiles.

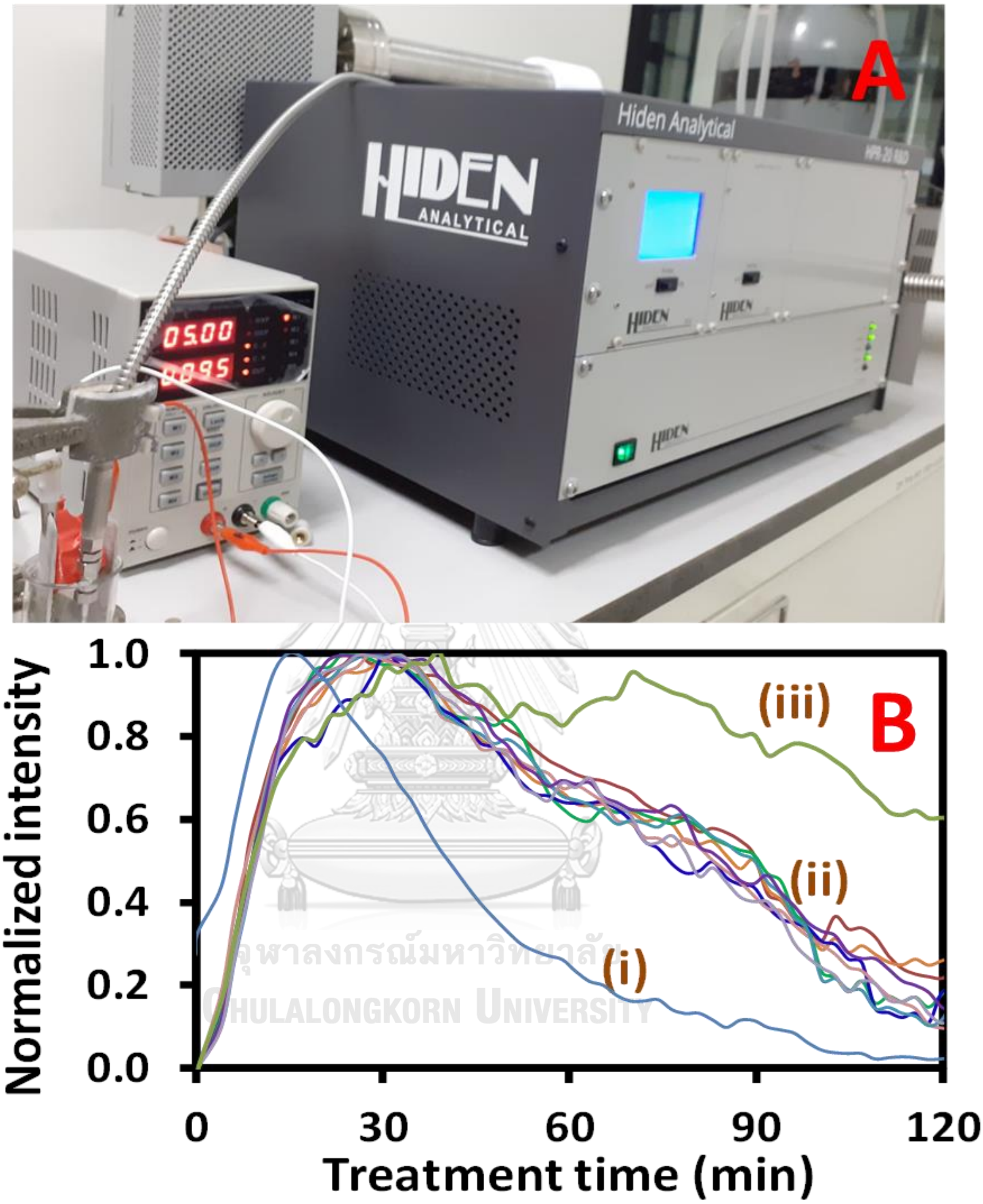


Figure 4.3 (A) Gas Analyzer system and (B) the resulting relative intensity of different m/z; (i) 59, (ii) 77, 91, 103, 105, 108, 122, 136 and 150 and (iii) 79, during 2-phase EC of the perfume sample at 5 V for 2 h.

The increasing evaporation rate could be influenced by higher amount of H_2 evolution at the cathode electrode (**Figure 4.4**) within the EC treatment interval as shown in **Figure 4.3B** with all the *m/z* signals increased within 15 min of the EC. After the longer EC treatment time, conversion of the volatile compounds to the non-volatiles or adsorption of compounds onto the EC sludge may occur resulting in the lower the signal detection. Whilst most of the *m/z* values decreased similarly as illustrated by (ii) in **Figure 4.3B**, *m/z* 59 signal dropped with the fastest rate, see (i) in **Figure 4.3B**. This can be the fragment *m/z* of 2-(2-hydroxypropoxy)-1-propanol (***R2***). Emphasize that other compounds (such as 2,6-dimethyl-6-hepten-2-ol which is the product at the anode) also have this *m/z* 59 albeit with the lower abundances contributing to the *m/z* 59 profile with much less extent. This is confirmed by their lower area percentages (**Table 4.2**) compared with that of ***R2*** in **Table 4.1**.

On the other hand, *m/z* 79 signal slowly decreased with the EC time, see (iii) in **Figure 4.3B**. This is *m/z* of the products of benzyl acetate (***A3***) and phenylmethanol (***C1***) resulting in the slow signal decrease. This *m/z* 79 also belongs to benzyl propionate (reactant) and caryophyllene (enriched compound) with less abundance. Other related species such as O_2, H_2, H_2O and hexane gases produced during the 2-phase EC treatment of the perfume extract were also detected with their relative intensity profiles provided in **Figure 4.4**.

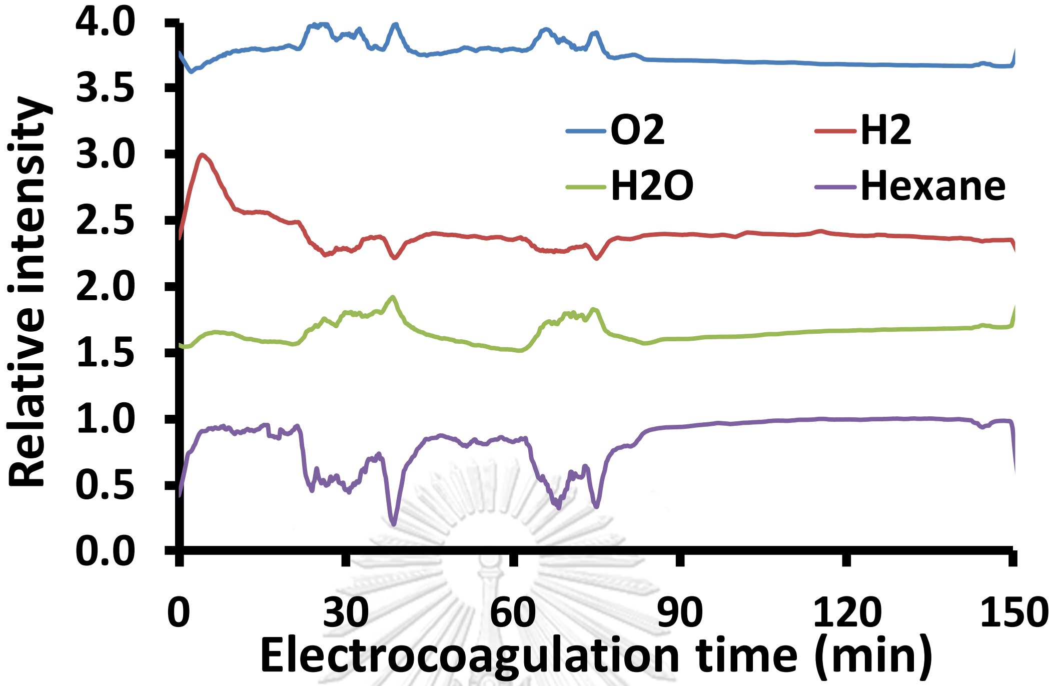


Figure 4.4 Relative intensity profiles of different gases: O2, H2, H2O and hexane; generated during 2-phase EC of the perfume sample at 5 V for 2 h obtained from Gas Analyzer.

4.6 Proposed reaction mechanisms

Based on the investigation above, several phenomena could occur during the EC treatment. During the EC treatment, the major reactions were $H_{2(g)}$ and $O_{2(g)}$ evolutions which can be clearly observed by the presence of gas bubbles at the electrodes around the hexane/water interface during the EC treatment. In addition, under the investigated voltage, corrosion of the aluminium electrode also occurred which leads to metal ions (e.g. Al^{3+}) with the subsequent formation of sludge, see Figure 1B, according to the reaction between the metal ions and hydroxides in the solution. It should be emphasized that although the sludge level was significant in this study, it was isolated into the water phase (where the reactions occurred) and can be easily removed from the system after the EC synthesis. In addition, volatiles in hexane phase are not expected to continuously undergo redox reaction due to very low conductance of hexane. On the other hand, electrochemical reaction could easily occur in the conductive $NaCl_{(aq)}$ phase. However, the volatiles in the hexane phase could undergo partitioning into the aqueous phase, especially the polar oxygenated compounds in the sample.

According to the profiles of possible EC reactants and products of Perfume1 and Perfume2 (Table 1 and 2), the reaction mechanisms can be proposed as summarized in **Figure 4.5**.

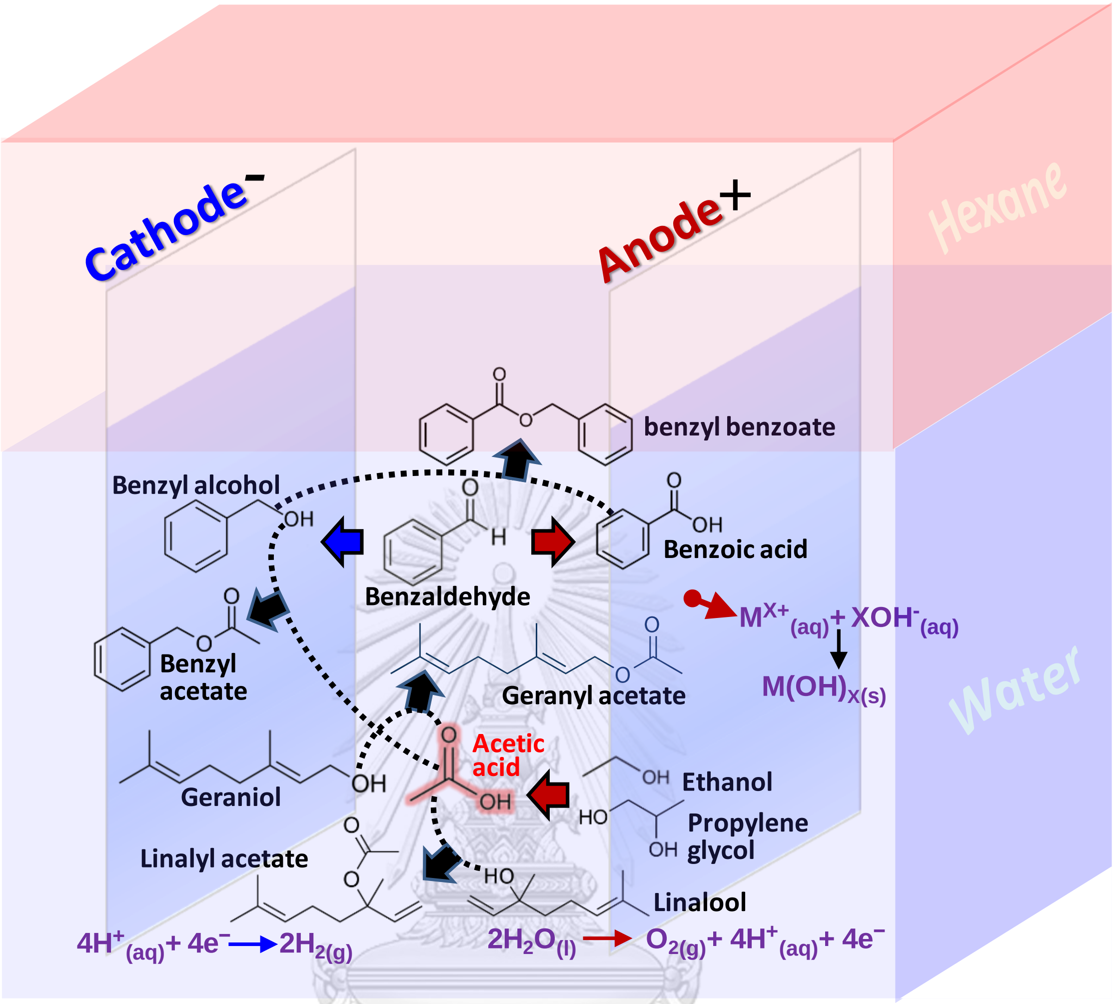


Figure 4.5 Diagram indicating the proposed chemical reactions for the 2-phase electrocoagulation of perfumes. The red, blue and black arrows show oxidation, reduction and esterification, respectively.

An important mechanism can be the oxidation of ethanol applied as the major solvent in both perfumes. This is expected to mainly result in acetic acid [68] which can further undergo esterification with several alcohols (e.g. linalool already existing in the perfume profiles, see **Enriched compounds** in **Table 4.2**) to result in several -acetate products in perfume products (e.g. benzyl acetate and linalyl acetate, **A3** in **Table 4.2**). Apart from electrochemical esterification/hydrolysis and oxidation/reduction, isomerization may also be responsible for the different products in each perfume sample. [69]

CHAPTER V

CONCLUSION

Electrocoagulation system with two-phase electrolyte has been developed with the demonstration for adjustment of the perfume smells according to change in volatile compound profile of the treated samples. Volatile compounds before and after the 2-phase EC of the samples were successfully analyzed by SPME/GC-MS. The analysis shows different odor active compound types and contents leading to modification of the overall smell of the perfume samples. The EC system was designed to allow separate regions of the sample at the anode, at the cathode and in bulk which provides the insight into the possible 2-phase EC mechanisms. This is related to electrode corrosion, electrochemical reaction of the potential reactants to result in different products based on oxidation or reduction reaction, the compound concentration enrichment and their hexane/water partitioning. The potential contaminants from the electrode corrosion were clearly isolated into the aqueous phase which can be easily removed from the products and the remaining reactants in the hexane phase. Since the developed system applied two aluminium electrodes with hexane and saturated $NaCl_{(aq)}$, this is considerably simple, cost effective and expected to be applicable with the large-scale synthesis of organic compounds in the future.

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