Razi University

Faculty of Chemistry
Department of Analytical Chemistry

Ph.D. Thesis

Title of the Thesis

Development of Analytical Methods in Trace Determination of Furaldehydes and Methyl *tert*-Butyl Ether as Pollutants Emitted from Petroleum Industry

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March 2010

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ACKNOWLEDGEMENTS

research. Without their encouragement and understanding it would have been impossible for me to finish this work.

My deepest gratitude goes to my parent, mother and father. They worked hard to support the family and spare no effort to provide the best possible environment for me to grow up and attend school. My special gratitude is due to my wife's parents and my brothers, a constant source of support during this thesis, and the work would certainly not have existed without them.

This thesis is the result of five years of work during which I have been accompanied and supported by many people. It is now my great pleasure to take this opportunity to thank them. I believe that I would not be able to name everyone separately and to thank for everything that they did for me. However I would like to take the opportunity and express a few words of thanks to my best colleagues and friends.

Tehran, Iran, March 2010

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Abstract

Sensitive and precise voltammetric methods for the determination of trace amounts of furaldehydes, mainly as furfural (F) and 5-hydroxymethyl-2-furaldehyde (HMF), in waste waters and other matrices is described. Determination of total furaldehyde at $< \mu g \ g^{-1}$ levels in alkaline buffered aqueous media was individually investigated. By the use of ordinary SWV and adsorptive square wave stripping voltammetry (Ad-SWSV), the detection limits for determination of F and HMF found to be 400 and 10 ng g^{-1}, respectively. At a 1.0 $\mu g \ g^{-1}$ level of furfural in sample, the relative standard deviation (n = 4) was 2.79%. The use of Ad-SWSV of F and HMF, after their in situ derivatization with trimethylaminoacetohydrazide chloride (Girard's reagent T) at a static mercury drop electrode (SMDE) in NH_3-NH_4Cl buffer of pH 9.5, resulted in a limit of detection of 10 ng g^{-1} for the resolved peaks of HMF and F. The results obtained by the proposed method for the real samples were compared with the corresponding results from UV-spectrophotometry and HPLC experiments in various matrices.

A 2-furaldehyde-selective PVC-membrane electrode was designed based on the host-guest interaction between tetrabenzyl ether Calix[4]arene, as an ionophore, and a lipophilic hydrazone derivative generated in situ from reaction of 2-furaldehyde and Girard's reagent T. At a pH of 9.2, the electrode exhibited a Nernstian response over the 2-furaldehyde concentration range of (5.0×10^{-5}) - (1.0×10^{-1}) M. The electrode found to be chemically inert and of adequate stability with a response time of 15 s with a good reproducibility ($\pm$ 0.2 mV), and could be used for a long working lifetime. In order to improve the minimum detectable concentration of 2-furaldehyde, further studies have been performed using a coated graphite electrode and coated platinum and gold disks. Some analytical aspects of adsorptive square wave voltammetry have also been presented in order to elucidate the adduct formation between 2-furaldehyde and Girard's reagent T. The interfering effects of some Na^+, K^+, NH_4^+, formaldehyde, 5-hydroxymethyl 2-furaldehyde (HMF), excess of Girard's reagent T and organic solvents such as isopropyl alcohol and N,N-dimethylformamide on the sensor's response have been studied. The viability of using the electrode for the trace determination of 2-furaldehyde in several Iranian oil refinery wastewater samples was also demonstrated. The results obtained from the developed method for real samples were compared with those from UV-spectrophotometric and high-performance liquid chromatographic experiments.

Three types of ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF$_4$]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][OTf]), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPyrr][NTf$_2$]) were prepared and a variety of their fundamental properties such as kinematic (ν) and dynamic (η) viscosities, thermal stability, surface tension (σ), refractive index (n$_D$), pH and density (ρ) were investigated as a function of temperature. The coefficients of thermal expansion (α_p) of the ionic liquids were also calculated from the experimental values of the density in different temperatures. Electrochemical stability of the ionic liquids (as electrolytes for voltammetric aspects) was also studied at glassy carbon electrode (GCE). The measurements were performed in a double wall three electrode cell, applying Pt wire as a quasi-reference electrode. The results showed an ideal wide range of potential windows for studies of electrochemical behavior of some species such as furaldehydes in the lipophilic and hydrophilic ionic liquids.

In one another work, the three selected ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF$_4$], 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][OTf], and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [bmpyrr][NTf$_2$] were studied as electrolytes in electroanalytical quantification of 2-furaldehyde using square wave and differential pulse voltammetries. On applying a cathodic scan, a well-defined 2-electron wave was observed corresponding to the reduction of 2-furaldehyde to furfuryl alcohol. The electrochemical stability of the ionic liquids as electrolytes for analytical aspects and electrokinetic studies were investigated using a glassy carbon electrode (GCE). The measurements were carried out in a designed double wall three-electrode cell, using two platinum wires as the quasi-reference and counter electrodes. Differential pulse voltammetry was found to be the most sensitive method at GCE. The detection limits of 1.4, 19.0 and 2.5 μg g^{-1} were obtained for the determination of 2-furaldehyde in [EMIM][BF$_4$], [BMIM][OTf] and [BMPyrr][NTf$_2$], respectively. At a concentration of 50 μg g^{-1}, the maximum relative standard deviation (n = 3) was 4.9%. The effect of water on the potential window and waveforms was also investigated in the ionic liquids studied. The proposed method was ideally suited for trace determination of 2-furaldehyde, especially in oil matrices.

Chemometric methods were also used in simultaneous determination of some petroleum pollutants with nearly similar chemical structures. Ant colony optimization (ACO) is a population-based metaheuristic that can be used to find approximate solutions

to difficult optimization problems. The solution process is stochastic and is biased by a pheromone model, which is used to probabilistically sample the search space. ACO is a relatively novel technique for solving hard combinatorial optimization problems. The inspiring source of ACO is the foraging behavior of real ants. Since wavelength selection is a strategy used for improving the quality of calibration methods, we investigated simultaneous spectrophotometric determination of two furaldehydes, namely, 2-furaldehyde (F) and 5-hydroxymethyl-2-furaldehyde (HMF), using ant colony optimization-partial least squares (ACO-PLS) regression. Predictive abilities of ACO in wavelength selection process was examined for spectrophotometric analysis of these species, and was compared with other regression methods, such as CLS, PCR, PLS, and GA-PLS. The ACO-PLS showed superiority over other methods regarding to the prediction ability of the resulted model and providing useful information about the chemical system. The proposed method was also successful when applied to the determination of furaldehydes in oil refinery waste waters.

A sensitive and reliable method based on static headspace-extraction (HS) followed by GC/MS was developed for the qualitative and quantitative analysis of methyl tert-butylether (MTBE) and formaldehyde in water matrices. To enhance the extraction capability of the HS, the extraction parameters such as extraction temperature, extraction time, the ratio of headspace volume to sample volume and sodium chloride concentration were optimized. Good linearity was verified in a range of 5-10000 μg/L for MTBE (r=0.9998), while that for HCHO was 5-500 μg/L (r=0.9996). Detection limits for MTBE and HCHO were 0.2 μg/L and 0.3 μg/L, respectively. Best results were obtained when the analyzed water samples were heated to 70 $^{\circ}$C for 20 min, with a sample volume 10 mL, in a 20 mL vial, while 30% (w/v) NaCl was used to saturate the samples. The proposed analytical method was successfully used for the quantification of selected analytes in environmental water samples.

MTBE is widely used as an gasoline oxygenate and octane number enhancer for more complete combustion in order to reduce the air pollution caused by motor vehicle exhaust. The possible adverse effects of MTBE on human health are a major public concern. However, information on the metabolism of MTBE in human tissues is lacking. The present study demonstrates that human liver is active in metabolizing MTBE to tert-butyl alcohol (TBA) and formaldehyde, major circulating metabolites and markers for exposure to MTBE. CYP2A6 is known to be constitutively expressed in human livers and

metabolism of gasoline ethers is catalyzed by this enzyme. The present study used CYP2A6 to assess the contribution of 2A6 to the metabolism of MTBE. In comparison with literature, our results clearly demonstrate that 2A6 plays a significant role in the metabolism of MTBE.

When a degradation process is performed, the use of analytical techniques to identify and quantify the degradation products is an aspect of interest. Subsequently, analytical techniques which give structural information of intermediates have special interest when a pathway is required. Although instrumental techniques used in previous works like HS GC-FID and P&T GC-MS, were not sufficient for proposing a mechanism, this work is a proof to previous probable pathways by using HPLC (for monitoring aldehydes and ketons) and HS-GC-MS (for TBA, alcohols and other intermediates).

چکیده

ــ روشهای ولتامتری حساس و دقیقی برای تعیین مقادیر جزئی فورالدهیدها (عمدتاً بصورت فورفورال و 5ـهیدروکسی متیل 2ـفورفورال) در پسابهای نفتی، مایعات دارویی و محصولات غذایی تشریح گردیده است. تعیین فورالدهیدها در ترازهای زیر ¹⁻µgg بویژه در محیطهای آبی بافری شده در pH های قلیایی مورد مطالعه قرار گرفته است. با استفاده از تکنیکهای ولتامتری موج مربعی (SWV) و ولتامتری جذبی موج مربعی (Ad-SWSV)، حدود تشخیص برای تعیین F ، HMF به ترتیب ¹⁻µgg 400 و ¹⁻µgg 10 بدست آمدند. در تراز ¹⁻µgg 1 انحراف استاندارد نسبی برای چهار اندازهگیری (n=4) ، 2/79% بود. استفاده از تکنیک Ad-SWSV بعد از مشتق سازی فورالدهیدها توسط معرف جرارد T (Girards reagent T) در سطح الکترود قطره جیوه ایستا امکان دسترسی به حد تشخیص ¹⁻µgg 10 را فراهم نموده است. علاوه بر آن سبب جداسازی کامل پیکهای احیاء فورفورال (F) و هیدروکسی متیل فورفورال (HMF) در pH 9.5 (استفاده از بافر NH₃-NH₄Cl) گردیده است. روش پیشنهادی روی برخی از نمونههای حقیقی اجرا گردیده و نتایج آن با نتایج حاصله از تکنیکهای HPLC و اسپکتروفتومتری مقایسه گردیده است.

ــ یک حسگر انتخابی پتانسیومتری برای 2ـفورالدهید بر اساس مکانیسم مهمانــ میزبان با استفاده از کالیکس (4) آرن تترابنزیل اتر (بعنوان یونوفور) طراحی گردیده است. در این رابطه مشتق هیدرازون 2ـفورالدهید (فورفورال) با معرف جـرارد T بعنـوان یـک زوج یـون بـا کاتیون بالکی فورازونیوم¹ تاثیرات متقابل ضعیف و تعادلی با یونوفور مورد نظر برقرار می کنـد. در pH 9.2 ،الکترود سنتزی یک رفتار نرنستی در محدوده غلظتی⁻⁵10×5.0- ⁻¹10×1.0 از 2ـفورالدهیـد بـه نمایش میگذارد. الکترود مذکور از نظر شیمیایی خنثی، دارای پایداری خوب با زمـان پاسـخ دهـی 15

1- furazonium