APPENDICES

APPENDIX A

Cerium (IV) chemistry and compounds

The tetravalent cerium state Ce(IV) or ceric is the non-trivalent lanthanide ion stable in aqueous solutions. Because of the higher cation charge and smaller ionic size of ceric ion make ceric salt much more hydrolyzed in aqueous solution than other trivalent lanthanides.

$$[CeL_m(H_2O)]^{n+} + H_2O \longrightarrow [CeL_m(OH^-)]^{(n-1)+} + H_3O^+ \qquad (1)$$

According to equation (1), solution of ceric salts is likely to become strongly acidic, and basic salt is also generated from hydrolysis of ceric salt. The orange or red color of ceric salt solution is observed owing to the charge transfer interaction within the molecule. The simple uncoordinated forms of ceric ion can strongly absorb in the ultraviolet region but not in the wavelength of visible region.

The ceric compound with fluorite structure, CeO_2, has large crytal lattice energy and strongly stabilizes in the form of tetravalent cation. Thus, CeO_2 is usually found rather than Ce_2O_3 which is a trivalent cerium compound. $Ce(SO_4)_2$ has the same structure as CeO_2, but it less stable than the complexes of ceric with oxide and fluoride. $Ce(SO_4)_2$ can be produced by dissolving a reactive cerium precursor in the excessive sulfuric acid to prevent basic insoluble salt generated from hydrolysis.

Ceric ammonium nitrate and ceric ammonium sulfate are stable ceric compounds and easily dissolved in water. Both of them are produced by freshly prepared hydrate or oxide of ceric in the excess amount of acid, following by the addition of suitable proportion of ammonium salt. Then, the mixture is evaportated at low temperature to obtain crystals of desirable ceric compound. The ceric complex is presented the anion of these salts. For example, the crystal structure of ceric ammonium nitrate results from the bidentate coordination of six nitrate groups around each ceric ion [50]. However, the complex of these compounds in aqueous solution is quite variable due to the pH and anionic species existing in the solution.

Ce(IV) is oxidizing agent, and can be reduced by oxalic acid, halogen acids, ferrous salts and hydrogen peroxide. The redox potential (E) for conversin of Ce(IV) to Ce(III) is 1.3 V (1 N HCl) and 1.8 V (6 N $HClO_4$). The redox potential is also associated with the electrolyte and the small anionic group complexed with ceric ions. Oxidation based on Ce(IV) is widely used in organic synthesis and employed in quantitative volumetric analysis.

APPENDIX B

The t –Test with multiple samples for the comparison of two methods

The proposed FI-colorimetric method for the quantification of ethanol in alcoholic beverages was validated against gas chromatography, which is a reference method by analyzing several different beverage samples including distilled spirits, wines and beers. In this case, comparison between the proposed method and the reference GC method was made by t-test [51]. A statistical *t* value was calculated from the difference between ethanol contents obtained from two methods on each sample using Excel 2007 [52].

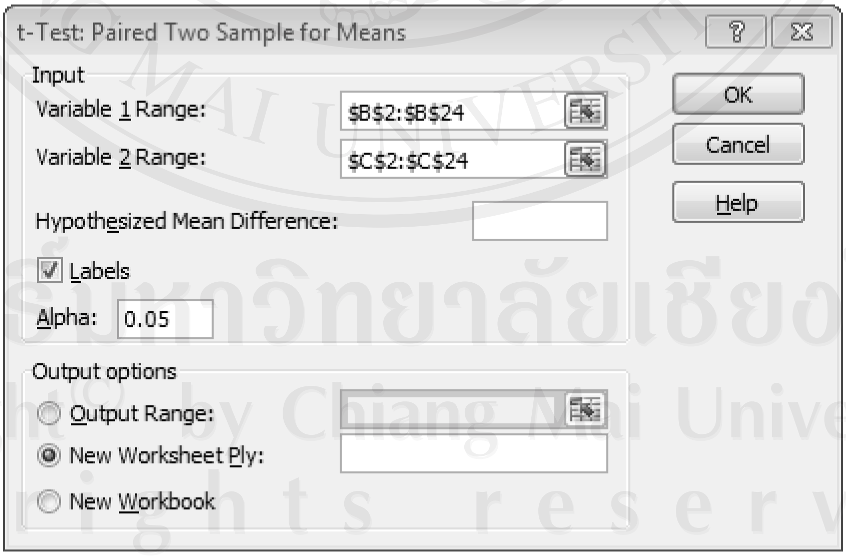

Figure 1 Dependent samples t-test dialog box in Excel 2007

Using the data obtained from two methods as shown in Table 3.17, the hypothesis that there is a significant difference between two methods was decided before computing *t* value. The calculation was performed by selecting Data analysis, t-test: Paired Two Sample for Means. The dialog box is depicted in Figure 1. The values obtained by GC and the proposed method were entered to Variable 1 and Variable 2, respectively. The test at the 95% confidence level was considered, thus an alpha level of 0.05 was selected as shown. The output table for multiple samples t-test is shown in Figure 2. The calculated *t* value of 0.57 which was less than the t critical value (two-tail) of 2.07 indicated that the values obtained from both methods were insignificantly different at the 95% confidence level.

	A	B	C	D
1	t-Test: Paired Two Sample for Means			
2				
3		*FIA*	*GC*	
4	Mean	20.98	20.87	
5	Variance	223.28	210.04	
6	Observations	23	23	
7	Pearson Correlation	0.99856		
8	Hypothesized Mean Difference	0		
9	df	22		
10	t Stat	**0.57**		
11	P(T<=t) one-tail	0.29		
12	t Critical one-tail	1.72		
13	P(T<=t) two-tail	0.57		
14	t Critical two-tail	**2.07**		
15				

Figure 2 Dependent samples t-test output table in Excel 200

THE RELEVANCY OF THE RESEARCH WORK TO THAILAND

Quantification of ethanol becomes important for quality control of products and monitoring processes in many manufactures. Recently, there has been a growing interest in utilization of biomass for ethanol fuel production in Thailand, so the monitoring of fermentation is necessary for evaluating the possibility for large scale production of ethanol. Many commercial analytical methods such as chromatography and biosensor are employed for the analysis of ethanol. However, most of these methods rely on sophisticated and expensive instrument and consumes long analysis time that makes their uses quite limited in specific groups.

This research aims to develop the FI colorimetric method for determination of ethanol and applied the method to the analysis of alcoholic beverage as well as monitoring fermentation process. The proposed method provided high degree of automatic operation and a satisfactory sample throughput. By taking advantages of FI method, not only consumption low amount of reagents and sample but the analysis time also less than those of the commonly used instruments. Moreover, the developed system was on the basis of using cost effective instruments, and the analytical performance was comparable to the traditional method which should be beneficial to apply in small manufactories or even in large industrial sectors in Thailand.

CURRICULUM VITAE

NAME	Miss Piyanut Pinyou
DATE OF BIRTH	September 13, 1986

ACADEMIC STATUS

2008	B.S. (Chemistry), Chiang Mai University
2011	M.S. (Chemistry), Chiang Mai University

SCHOLARSHIPS

2005-2011	Full support from Human Resource Development in Science Project (Science Achievement Scholarship of Thailand, SAST)

EXPERIENCE

2010-2011	Teaching assistant for Analytical Chemistry Laboratory Courses

PUBLICATIONS

1. P. Pinyou, S.K. Hartwell, J. Jakmunee, S. Lapanantnoppakhun, and K. Grudpan. "Flow Injection Determination of Iron Ions with Green Tea Extracts as a Natural Chromogenic Reagent" Analytical Sciences, 26 (2010), 619-623.
2. P. Pinyou, N. Youngvises, and J. Jakmunee. "Flow Injection Colorimetric Method Using Acidic Ceric Nitrate as Reagent for Determination of Ethanol" Talanta, 84 (2011) 745-751.

INTERNATIONAL CONFERENCES

1. P. Pinyou, N. Youngvises, and J. Jakmunee. "Flow Injection Colorimetric Method with Gas Diffusion Separation for the Determination of Ethanol" (Poster Presentation), The 16th International Conference on Flow Injection Analysis Including Related Techniques, Thai Association for Flow-based Analysis, Pattaya, Thailand, 25-30 April 2010.
2. P. Pinyou, N. Youngvises, and J. Jakmunee. "Determination of Ethanol by Flow Injection Colorimetric Method with Gas Diffusion Separation" (Poster Presentation), Pure and Applied Chemistry International Conference 2011, Srinakharinwirot University and Chemical Society of Thailand, Bangkok, Thailand, 5-7 January 2011.

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1. P. Pinyou, S.K. Hartwell, J. Jakmunee, S. Lapanantnoppakhun, and K. Grudpan. "Flow Injection Determination of Iron Using Green Tea Extract as an Alternative Reagent" (Oral Presentation), The 35th Congress on Science and Technology of Thailand, Burapa University, Chonburi, Thailand, 15-17 October 2009.
2. P. Pinyou, N. Youngvises, and J. Jakmunee. "Flow Injection Colorimetric Method with Gas Diffusion Separation for the Determination of Ethanol" (Oral Presentation), The 6th Conference on Science and Technology for Youth 2011, Bangkok International Trade and Exhibition Centre, Thailand, 18-19 March 2011.