C1_019_OF: TRACE ELEMENT ANALYSIS FOR DISTINGUISHING BETWEEN LEGAL AND COUNTERFEIT CIGARETTES BY USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract: A tobacco plant (*Nicotiana tabaccum*) is naturally absorbing and accumulating trace elements from soil in its leaves at uncommonly high concentrations. Some of trace elements found in tobacco leaves could be distinguished between legal and counterfeit cigarettes and also related to geographical origins. In this work, 5 legal and 4 counterfeit cigarette samples originated from Thailand and Cambodia were analyzed. For each sample, the amounts of Be, Ga, Se, Cs, Tl, Bi, and U were determined by an inductively coupled plasma-mass spectrometry (ICP-MS). Statistical analysis, principal component analysis (PCA) and discriminant analysis (DA) were applied for data analysis. The results from DA revealed that legal cigarette and counterfeit cigarette could be distinguished completely.

Introduction: A tobacco plant (*Nicotiana tabaccum*) is naturally absorbing and accumulating trace elements from soil in its leaves at uncommonly high concentrations [1]. Trace elements have significantly toxicity to humans, even at very low levels of intake. The dried tobacco leaf is an important material for cigarette industries. Various types of tobacco has similar chemical components but different concentrations, so cigarette manufacturers have to mix different types of tobacco leaves in appropriate proportion to get the flavor and sense for consumer satisfaction.

Legal cigarettes are manufactured with authorization from government and to legitimate paying duty. In contrast, counterfeit cigarettes are illegally manufactured tobacco products which are produced from inferior materials without authorization of the rightful owners, with intention to deceive consumers and to avoid paying duty. The counterfeit cigarette has smuggled continuously come to Thailand, especially, the Thai-Cambodian border in Aranyaprathet, Sa Kaeo province and others places such as the eastern provinces of the Gulf of Thailand (Chonburi, Rayong, and Trat) and also the southern provinces (Satun). The Thai army was quoted as the counterfeit cigarettes produced in Cambodia and there are a lot of illegal factories. Selling price of counterfeit cigarette is lower than legal cigarette 2-4 times. Besides counterfeit cigarettes, Cambodia is also a transit point for smuggled genuine or legal cigarettes from other countries. The counterfeit cigarette was transferred to Bangkok and other big cities where there are a lot of smokers. Demand of consumers is always high around April and December, due to long vacations and celebrations of the traditional and New Year festivals. The problem would never end as long as there was demand and supply. Normally, legal and counterfeit cigarette have classified by security feature or label of package such as thermochromic ink printing, UV active point under barcode, tobacco stamp, and printing system. However, this method cannot classify geographical origins of cigarette.

There are many researches about trace metal analysis in cigarette samples but most of them focused on quantification of trace metal [1-3]. Therefore, this work is proposed to find the method to distinguish between legal and counterfeit cigarette and moreover classification of their origin by using trace element analysis.

Methodology:

Sample: Four legal cigarette samples were originated from Thailand under controlling of Thailand Tobacco Monopoly and 4 counterfeit cigarette samples produced from illicit factory in Cambodia. These samples were obtained from Office of Illicit Cigarettes Prevention, Thailand Tobacco Monopoly. One legal cigarette sample originated from Cambodia was purchased from supermarket in Cambodia.

Preparation of sample: Each brand of the cigarette was chosen randomly from the pack. The filters were removed, and the wrappers were ripped open to disclose the tobacco. The tobacco samples were manually ground in an agate mortar, ground samples were placed in crucible and let dry in an oven (Heraeus, B5042E) at 45 °C for 3 hours, following which, 0.2 g. of powdered samples was placed in a 50

mL of beaker. 5 mL of concentrated nitric acid (HNO_3, 65%, AR grade, RCI Labscan) were added and heated at 90 °C on a hot plate. 2 mL of concentrated nitric acid were added again until the clear solution was obtained, and then 10 mL of deionized water (18.3 MΩ cm^{-1}) and 0.25 mL of hydrogen peroxide (H_2O_2, 30%, Merck, Hohenbrunn, Germany) were added. Heat was applied to the solution until it reached to 2 mL, and then the beaker was lifted off from hot plate. After cooling, the solution was transferred into 25 mL volumetric flask and the volume was adjusted with deionized water. The stock of sample solution was kept in a refrigerator at 2 °C.

Preparation of sample solutions: 4 mL of all sample solutions were added with 2% (v/v) sub-boiled nitric acid in 10.00 mL volumetric flask before ICP-MS analysis. Calibration standards were prepared by diluting multi-element standard solutions (AccuTrace™ Reference standard, ICP-MS Multi-Element Standard, New Heaven, CT, USA).

Instrumentation: All sample solutions were analyzed by using 8800 Triple Quadrupole ICP-MS at National Institute of Metrology (Thailand), Pathum Thani.

Table 1 Parameters of ICP-MS

Operating parameters	Setting
RF power (W)	1550
RF matching (V)	1.80
Sample depth (mm)	8.0
Plasma gas (L/min)	1.25
Nebulizer pump (rps)	0.10
Spray chamber temperature (°C)	2
Gas switch	Makeup gas
Isotope monitored (m/z)	^{9}Be, ^{71}Ga, ^{78}Se, ^{133}Cs, ^{203}Tl, ^{209}Bi, ^{238}U

Results and Discussions: Analysis of seven trace elements comprising Be, Ga, Se, Cs, Tl, Bi, and U in cigarette samples is shown in Fig. 1. The legal and counterfeit cigarette samples (sample 1-3) under Thai local brands, the results show that the counterfeit cigarette samples shown higher concentration of trace elements than legal cigarette samples. But the counterfeit cigarette sample 4, Se and Bi were higher than in legal cigarette (Fig. 1d).

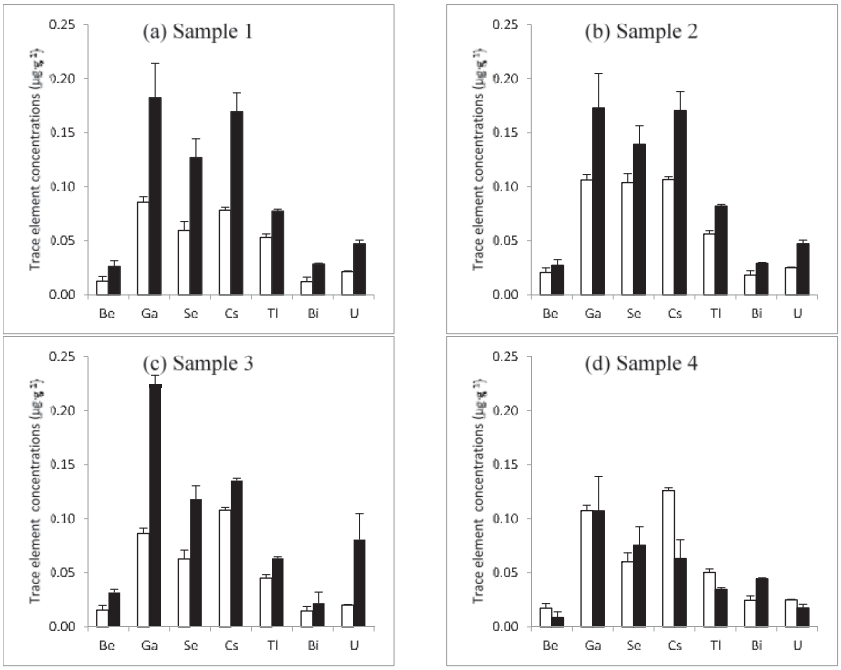

Fig.1 Trace element concentrations (µg·g^{-1} dry weight) in (a) Sample 1, (b) Sample 2, (c) Sample 3, and (d) Sample 4. The white bar is legal cigarette and the black bar is counterfeit cigarette.

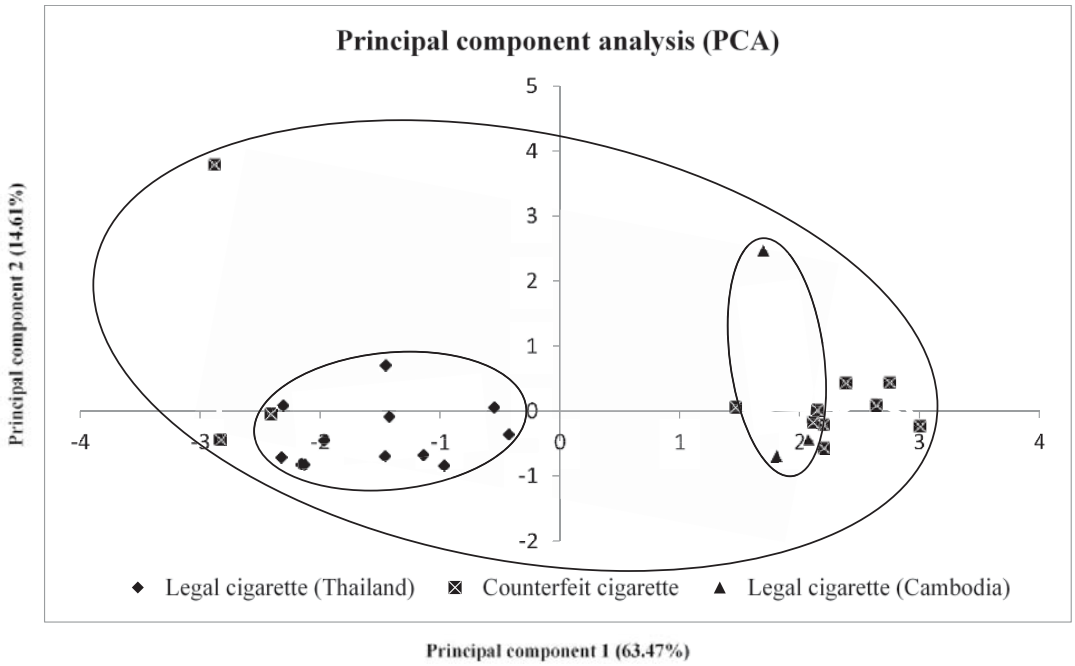

Fig. 2 Principal component analysis (PCA) on trace element concentration based on 9 cigarettes (4 legal cigarettes originated from Thailand, 4 counterfeit cigarette come from Cambodia, and 1 legal cigarette originated from Cambodia). Grouping according to geographical origin is shown by principal component 1, and 2.

The concentrations of 7 trace elements comprising Be, Ga, Se, Cs, Tl, Bi, and U were evaluated by statistical analysis as a principal component analysis (PCA) to distinguish legal cigarette and counterfeit cigarette and geographical origin. According to PCA result (Fig. 2) legal cigarette (Thailand) could be differentiated from legal cigarette (Cambodia) but cannot classify between legal cigarette and counterfeit cigarette. Discriminant analysis (DA) is another alternative statistical technique to be tested. The result is revealed in Fig. 3. The legal cigarette (Thailand), counterfeit cigarette come from Cambodia and legal cigarette (Cambodia) could be differentiated completely. Therefore, DA shows more potential than PCA for classification between legal and counterfeit cigarettes.

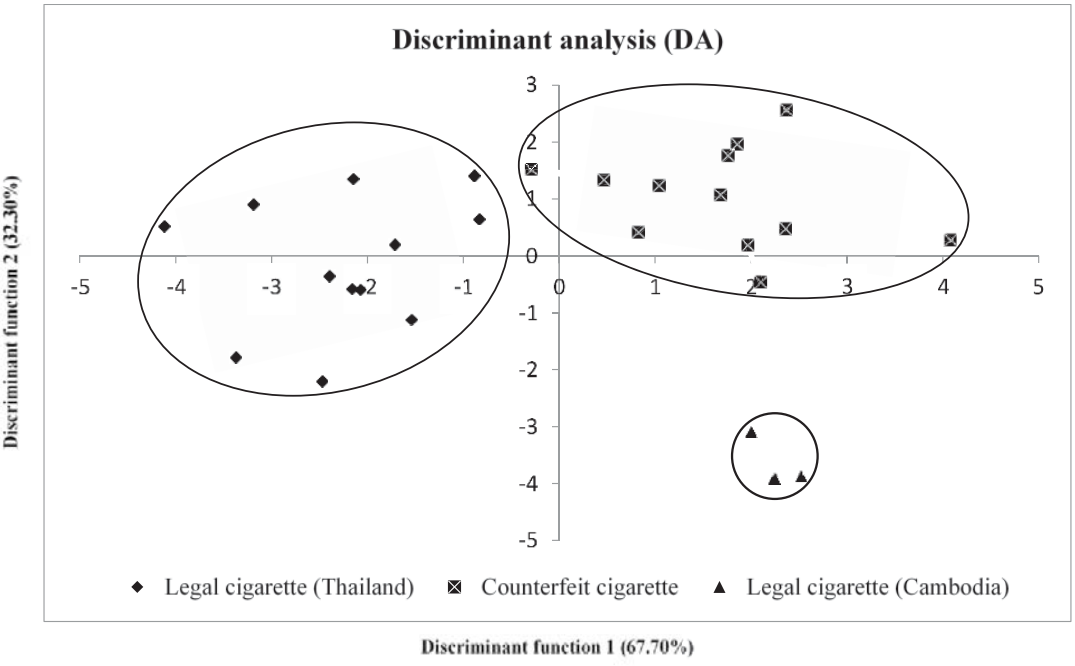

Fig. 3 Discriminant analysis (DA) on trace element concentration based on 9 cigarettes (4 legal cigarettes originated from Thailand, 4 counterfeit cigarette come from Cambodia, and 1 legal cigarette originated from Cambodia). Grouping according to geographical origin is shown by principal component 1, and 2.

Conclusion: The results revealed that the set of trace elements comprising Be, Ga, Se, Cs, Tl, Bi, and U can be distinguished between legal and counterfeit cigarettes based on discriminant analysis (DA) statistical technique. Trace element profiling combined with multivariate statistical analysis has been demonstrated to be an assuring analytical tool which can be useful for differentiation between various brands of cigarette and also geographical origin classification.

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