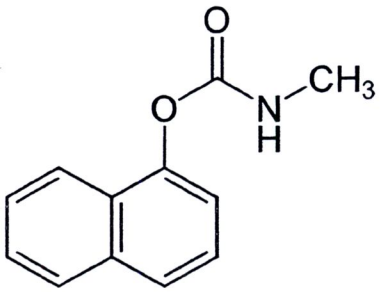
CHAPTER I
INTRODUCTION

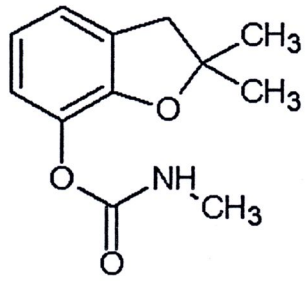
1.1 Rational and problems

Pesticide is a generic term of compounds used for control, prevention and elimination of plagues that attack plantations and vectors of disease in human. Pesticides can be classified based on either functional groups in their molecular structures (e.g. organic, inorganic, organonitrogen, organosulfur compounds), or their specific biological activities on target species (e.g. insecticides, fungicides, herbicides, acaricides, etc.) (Van der Hoff, Van Zoonen, 1999; Ahmed, 2001). Among the type later classified, herbicides are most commonly used pesticides followed by insecticides, fungicides and others. For organic pesticides, the most widely employed group, present pronounced physiological activity, are constituted mostly by organochlorine, organophosphorous, carbamate and triazine. However, organochlorine pesticides have been banned for applying in agriculture because of their high persistence in the environment and also high toxicity to animal and human. Nowadays, organophosphorous and carbamate are instead used.

Carbamate compounds were introduced as pesticides in the early 1950s and are still used extensively as pesticides (Cheng et al., 2007). Carbamates are compounds with chemical structure R-O-C(O)-N(CH_3)-R′, where R is an alcohol, an oxime or a phenol and R′ is a hydrogen or a methyl group. There are approximately 30 commercially available carbamate pesticides in the market, some of the most common ones being carbaryl (1-naphthyl-N-methylcarbamate, CBR) and carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate, CBF). The structures of carbaryl and carbofuran are shown in Figure 1.1. CBR and CBF are widely used in agricultural fields including stored grain, ornamentals, lawns, fruits and vegetables (Santalad et al., 2008). The toxicity of carbamates arises from the inhibition of acetylchlorinesterase (Bateman, 2003). Due to their widespread usage in agriculture, they can contaminate in environment and crops. Among the crops, vegetables and fruits are the main source of contamination from pesticides.



CBR



CBF

Figure 1.1 Structures of carbaryl (CBR) and carbofuran (CBF)

In order to investigate the contamination of pesticides in food, it needs sensitive analytical methods as well as effective methods for sample preparation. The widely used techniques for the analysis of carbamates are high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) (Yang et al., 1996; Cheng et al., 2007). HPLC and CE provide simultaneous analysis and able to eliminate some interferences. The common detector for both techniques is UV-detector. While, mass spectrometer (MS) is used to improve sensitivity. However, the mentioned instruments are expensive and sophisticated. While, the sample preparation for the analysis of pesticides from vegetables and fruits are consisted of (i) extraction and (ii) clean up and/or preconcentration of the extracts. Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are among the popular methods (Diez et al., 2006).

Recently, cloud-point extraction (CPE) has been introduced as an alternative technique to LLE and SPE (Chen et al., 2009). CPE uses surfactant to extract the target analytes from aqueous phase. None toxic organic solvents are required in CPE. Quick Easy Cheap Effective Rugged and Safe (QuEChERS) method is another sample preparation technique, it has been recognized as an effective sample preparation for various food matrices (Koesukwiwata et al., 2008).

The present work was aimed at the development of a simple method using Vis-spectrophotometry for the simultaneous determination of carbaryl and carbofuran in vegetable samples. CPE and QuEChERS was chosen as the sample preparation methods. This thesis emphasizes on optimization of conditions for both sample

preparation and spectrophotometry to improve the sensitivity for the detection of CBR and CBF.

1.2 Objectives of the research

1.2.1 To develop a spectrophotometric method for the determination of carbaryl using 2,4-dimethoxyaniline as the derivatizing agent.

1.2.2 To develop a spectrophotometric method for the simultaneous determination of carbaryl and carbofuran using 4-aminoantipyrine as the derivatizing agent.

1.2.3 To apply QuEChERS and CPE as sample preparation methods for the analysis of carbaryl and carbofuran in vegetable samples by spectrophotometry.

1.3 Scope and limitation of the research

1.3.1 The carbamates studied were carbaryl and carbofuran.

1.3.2 The derivatizing agents investigated were 2,4-dimethoxyaniline and 4-aminoantypyrine.

1.3.3 The sample preparation methods were QuEChERS and CPE, which the optimum conditions for both methods were investigated.

1.3.4 The validation of the proposed method was studied in terms of linearity, limit of detection (LOD), limit of quantitation (LOQ), selectivity, precision and accuracy.

1.3.5 HPLC was used for comparison.

1.4 Anticipated outcomes

1.4.1 A simple method based on spectrophotometry will be obtained for the simultaneous determination of CBR and CBF.

1.4.2 An effective sample preparation method using QuEChERS and CPE for the analysis of CBR and CBF from vegetable samples will be obtained.