ANALYSIS OF INORGANIC CATIONS IN LOW EXPLOSIVE RESIDUE USING SOLID PHASE EXTRACTION AS A PRE-CONCENTRATION TECHNIQUE

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To my family, friends and nation

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LIST OF ABBREVIATIONS

CE	–	Capillary Electrophoresis
DDDW	–	Double Distilled Deionized Water
FTIR	–	Fourier Transform Infrared
GC	–	Gas Chromatography
HPLC	–	High Performance Liquid Chromatography
IC	–	Ion Chromatography
IED	–	Improvised Explosive Device
MCAX	–	Mixed Cation Acidic Exchange
ND	–	Not detected
RSD	–	Relative Standard Deviation
RMP	–	Royal Malaysia Police
SPE	–	Solid Phase Extraction
SPME	–	Solid Phase Microextraction

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ABSTRACT

Solid Phase Extraction (SPE) is a very powerful technique for clean-up and pre-concentration of the sample. Even though there is no universal method for SPE, there have been an increasing demand for a reliable and accurate forensic trace analysis. Samples received by a forensic laboratory are often in small amounts and there is a need to develop methods that are capable to detect lower concentration. The objectives of this study were to develop, evaluate and compare an SPE procedure as a pre-concentration step with conventional cotton swabbing method for analysis of ions in explosive residue. Four samples of pyrotechnics were analysed in this study. The samples were Mercun Bola (MB), Mercun Ketupat (MK), Happy Bomb (HB) and Monster Bomb (MS). The results of this study showed that all six standard cations (lithium, sodium, ammonium, potassium, magnesium and calcium) were successfully separated within 45 minutes using Metrosep C4 column (250 x 4 mm i.d) with 5 µm particle size. The eluent used were 0.7 mmol/L dipicolinic acid and 1.7 mmol/L nitric acid with a flow rate of 1.0 mL/min and pressure of 9.5 MPa. The calibration graph gave a good linearity with $r^2 \geq 0.992$. The detection limits were 0.32 µg/L to 1.32 µg/L and quantitation limits in the range of 1.26 µg/L to 4.4 µg/L. The SPE method was optimized using several parameters before the method was applied to post-blast residues. The SPE cartridge used was Supelco MCAX with 500 mg sorbent bed packed with sulfonilic functional group. The SPE parameters that have been chosen were sample flow rate, type of eluents and volume of eluent. The results indicated that SPE procedure gave good pre-concentration of the analytes of interest with the pre-concentration factor in the range of 7 to 74.

ABSTRAK

Pengestrakan fasa pepejal (SPE) adalah suatu teknik pembersihan dan prapemekatan yang baik. Walaupun tiada kaedah yang universal untuk SPE, keperluan untuk menghasilkan keputusan analisis forensik yang baik dan tepat sentiasa diperlukan. Sampel yang diterima oleh makmal forensik kebiasaannya adalah pada kepekatan yang rendah dan adanya keperluan untuk membina kaedah yang dapat mengenalpasti kepekatan sisa bahan letupan pada kepekatan yang rendah. Objektif kajian ini adalah untuk membentuk, menilai dan membuat perbandingan antara SPE sebagai kaedah prapemekatan terhadap kaedah konvensional sapuan kapas bagi analisis sisa bahan letupan. Empat sampel piroteknik dianalisis di dalam kajian ini iaitu Mercun Bola (MB), Mercun Ketupat (MK), Happy Bomb (HB) dan Monster Bomb (MS). Hasil kajian ini mendapati kesemua enam piawai kation (litium, natrium, amonium, kalium, magnesium dan kalsium) berjaya dipisahkan dalam masa 45 minit menggunakan turus Metrosep C4 (250 x 4 mm i.d) dengan saiz zarah 5 µm. Eluen yang digunakan adalah 0.7 mmol/L asid dipikolinik dan 1.7 mmol/L asid nitrik dengan kadar aliran 1.0 mL/min dan tekanan 9.5 MPa. Graf penentukuran menunjukkan garis lurus yang bagus dengan $r^2 \geq 0.992$. Had pengesanan adalah 0.32 µg/L hingga 1.32 µg/L dan had kuantitasi adalah antara 1.26 µg/L hingga 4.4 µg/L. Kaedah SPE dioptimumkan dengan beberapa parameter terlebih dahulu sebelum diaplikasikan kepada residu bahan letupan. Kartrij SPE menggunakan Supelco MCAX dengan 500 mg penjerapan dan kumpulan berfungsi asid sulfonilik. Parameter yang dipilih adalah kadar aliran sampel, jenis eluen dan isipadu eluen. Keputusan menunjukkan prosedur SPE memberikan analisis yng bagus dengan faktor prapemekatan antara 7 hingga 74.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Identification of ions in post-blast residues at crime scenes generally helps the investigator to know the type and source of explosives used by the criminals. There are two types of explosives, which are high and low explosives. Low explosives are usually modified by using improvised explosive device (IED) to give explosion of high impact.

There are several techniques of ion determination in ion chromatography (IC); ion-exchange chromatography, ion-exclusion chromatography, and ion-pair chromatography. A number of selected cations and anions can be determined by using ion-exchange chromatography with high sensitivity. For explosives, determining the type of ions is very valuable in forensic science since it can help the crime scene investigator to detect the source of the explosives

Cotton swabbing is the most universal method commonly used for sample extraction in explosives analysis. There are two types of cotton swabbing, which are dry and wet swab. Water is a good extraction solvent for inorganic substances. There has been much research that focuses on different kind of solvents for extraction of organic and inorganic substances rather than finding another method for pre-concentration of samples. Normally after cotton swabbing, the sample is analysed directly by using ion chromatography. Detection of explosives types becomes more

challenging with the advent of more IEDs by the criminals. This makes the quest for the details of the crime more difficult. Hence, more research is needed to solve this problem.

In most cases, sample preparation steps take up most of the required analysis time, contributing substantially to the analysis costs (Weiss, 1995). Manipulation of the sample can falsify the analytical result. Therefore, sample preparation can directly affect the quality of the results. Pre-concentration of samples by using solid phase extraction (SPE) has been proven to help in the development of better methods for analysis of explosives due to its selectivity and sensitivity.

1.2 Problem Statement

The conventional cotton swabbing has several weaknesses in samples preparation. Sometimes, the amount of samples, such as the real field samples, is not enough for analysis purpose. Therefore, forensic laboratory needs to develop methods with low limit of detection (LOD). They are needed to improve detection method for explosives to get the most accurate results. Currently, there is a lack of analytical method for inorganic analytes since most research focuses more towards the organic substances.

Cotton swabbing is still a commonly used method for extraction of inorganic explosives. However, this method does not clean up the sample and causes the sample to be not pure. The interferences and unknown peaks may appear in the chromatogram during analysis, making the data interpretation and peaks identification to become harder. Hence, a new method that can clean up and remove interferences may be useful to solve this problem.

1.3 Research Objectives

The objectives of this study are:

i. To develop an SPE procedure as a pre-concentration step for analysis of cations in explosive residues.
ii. To evaluate the SPE procedure by comparison with the current cotton swab method.
iii. To apply the developed SPE procedure for post-blast pyrotechnic residues.

1.4 Scope of Study

This study focused on the inorganic components of hand-made low explosives. Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} were detected by using IC. The accuracy of SPE was tested and compared with the conventional method of cotton swab extraction protocols.

1.5 Significance of Study

Identification of explosives becomes crucial due to the need of the investigators to determine its source every time the crimes occur. There are several high and low explosives that are usually used by the criminals. The SPE method provides fast and reliable result in determination of various samples including forensic sample. It is necessary to develop a sample preparation method that enables determination of the targeted ions at lower concentration level.

This study can be used by Royal Malaysia Police (RMP) to improve the accuracy of explosive types detection. This is useful for the RMP in tracking the criminal by getting the accurate data regarding the explosives. Furthermore, profiling and database are really crucial for RMP due to the increasing number of criminal cases using low

explosives in this country. Further method development is always needed in order to keep up with the advanced technology and well-educated criminals.

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