Forensic comparison of unevaporated and evaporated automotive gasoline samples from Australia and New Zealand

by

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Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as acknowledged within the text.

I certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. I certify that all information sources and literature used are indicated in the thesis.

P. Mark L. Sandercock

November, 2002

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I dedicate this research to the One who is the Author of all inspiration. To God be the glory.

"In his heart a man plans his course, but the Lord determines his steps."
Proverbs 16:9 (NIV)

Preface

July, 1994. It was early afternoon on a fine summer day in a small city in Western Canada. The sidewalk cafes were doing a brisk business, and residents were coming and going from the neighbouring apartment buildings. Within this bustling block was a laundromat and drycleaning shop, closed for a lunch break. A natural gas leak was reported by passers-by and the gas company was called in. The leak was traced to the back of the laundromat/drycleaner where it was discovered that the gas mains had been tampered with, filling the shop with natural gas. The area was evacuated, the gas supply shut off and the gas allowed to dissipate. Meanwhile, the Fire Commissioner and the Royal Canadian Mounted Police (RCMP) were called in to investigate the tampering. The investigation led to the discovery of a failed arson attempt at the laundromat. Thirty liquid filled bottles, some stoppered and others with cloth wicks, were found in the crawl space beneath the business. The investigators believed that had the fire not gone out soon after it was lit, the entire city block would have been destroyed by the inevitable gas explosion. The bottles were found to contain automotive gasoline, aviation gasoline, tetrachloroethylene, or combinations of these three liquids. It was likely that the mixtures of tetrachloroethylene and gasoline had caused the fire to go out shortly after it was lit. At the suspect's residence two jerry cans, one with automotive gasoline and one with aviation gasoline, were found. Clearly, it was important to make a comparison between the two types of gasoline found at the suspect's residence and the gasoline present in the bottles. The lack of a scientific method (validated by the RCMP Forensic Laboratory Service) for the comparison of liquid gasoline samples prevented a meaningful comparison being made between the known liquids and those recovered from the scene. Thus began my interest in comparing refined petroleum products, and in particular, comparing automotive gasoline.

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Abbreviations

ADG	Australian Dangerous Goods
AFIRS	Australian Fire Incident Reporting System
ASTM	American Society for Testing and Materials
BP	British Petroleum
bp	boiling point
cf.	Latin: *confer*, "compare"
ci	confidence interval
CSIRO	Commonwealth Scientific and Industrial Research Organisation
e.g.	Latin: *exempli gratia*, "for example"
EIC	extracted ion chromatogram
et al.	Latin: *et alia*, "and others"
FTIR	Fourier transform infrared
g	gram
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
HPLC	high performance liquid chromatography
i.d.	inside diameter
i.e.	Latin: *id est*, "that is"
ISO	International Organisation for Standardisation
km	kilometre
L	litre
LDA	linear discriminant analysis
m	metre
mg	milligram
mL	millilitre
mm	millimetre
MS	mass spectrometry
ms	millisecond
m/z^+	mass to charge ratio
NFIRS	National Fire Incident Reporting System

NIST	National Institute of Standards and Technology
o.d.	outside diameter
PAH	polycyclic aromatic hydrocarbon
PC	principal component
PCA	principal component analysis
ppm	part per million
RON	research octane number
SIM	selected ion monitoring
SIMCA	soft independent model classification analogy
v/v	volume per volume
w/v	weight per volume
w/w	weight per weight
UK	United Kingdom
μL	microlitre
USA	United States of America (also abbreviated as US)

Abstract

The comparison of two or more samples of gasoline (petrol) to establish a common origin is a difficult problem in the forensic investigation of arsons and suspicious fires. The high-boiling fraction of the gasoline was targeted with a view to apply the techniques described herein to evaporated gasoline samples in the future. A novel micro solid phase extraction technique using activated alumina was developed to isolate the polar compounds and the polycyclic aromatic hydrocarbons from a 200 μL sample of gasoline. This technique was applied to 35 randomly collected samples of unevaporated gasoline, covering three different grades (regular unleaded, premium unleaded and lead replacement), collected in Sydney, Australia. The samples were analysed using full-scan GC-MS; potential target compounds identified were the C_0- to C_2-naphthalenes. The samples were then re-analysed directly, without prior treatment, using GC-MS in selected ion monitoring (SIM) mode for target compounds that exhibited variation between gasoline samples. Multivariate statistical analysis (principal component and linear discriminant analysis) was applied to the chromatographic data. The first two principal components described approximately 90% of the variation in the data and showed that the majority of the 35 samples could be differentiated using the method developed. A comparison of unevaporated samples collected in Auckland, New Zealand to those collected in Sydney was also made. Most of the samples could be differentiated based on their country of origin.

The variation of unevaporated regular unleaded and premium unleaded gasoline over time at three different service stations was studied. Ninety-six samples of gasoline were collected over a 16 week period and analysed for their C_0- to C_2-naphthalene content using the GC-MS (SIM) method that was developed. In most cases it was found that the C_0- to C_2-naphthalene profile in gasoline changed from week to week, and from station to station.

Samples of 25%, 50%, 75% and 90% evaporated gasoline (w/w) were generated from the 35 randomly collected samples of unevaporated gasoline. The C_0- to C_2-naphthalene content of all unevaporated and evaporated gasoline samples was determined using the GC-MS (SIM) method. Analysis of the data by principal components followed by linear

discriminant analysis showed that the 35 samples formed 18 unique groups, irrespective of the level of evaporation. The application of the method to forensic casework is discussed.