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Forensic Identification of Air Freshener Components from the Toxicological Samples by GC-MS : A Case Report

التحديد الجنائي لمكونات معطر جو في عينات حالة تسمم باستخدام جهاز كروماتوغرافيا الغاز المقترن بمطياف الكتلة : تقرير حالة

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Abstract

Indoor air fresheners are commonly used to deodorize rooms and cars. A case of air freshener intoxication by oral ingestion was forwarded to the forensic laboratory to determine the components and cause of death.

The presumptive tests were conducted for organo-phosphorus and organo-chloro compounds, formaldehyde, carbolic acid, drugs and aromatic compounds. Gas Chromatography–Mass Spectroscopy (GC-MS) was used as a confirmatory test for all these compounds. Presence of toxic substances like dichlorvos (2,2 di-chlorovinyl dimethyl phosphate), phenol, formaldehyde, naphthalene was confirmed in the air freshener that led to the person's death. Laboratory analysis also confirmed the presence of alprazolam in the viscera as per case history.

The methodology used can be utilized as a reference for TLC and GC-MS based analysis of such cases.

Keywords: Forensic Science, Air Fresheners, Toxicology, Mass Spectroscopy, Suicide, Poison

المستخلص

يشاع استخدام معطرات الجو في الأماكن المغلقة لتعطير الغرف والسيارات. وفي هذه الحالة تم إبلاغ المختبر الجنائي عن حالة تسمم نتيجة تعاطي معطر جوي بالفم، وذلك لتحديد مكونات التسمم وسبب الوفاة.

وقد أجريت الاختبارات الافتراضية لمركبات الفوسفور العضوية والكلور العضوية، والفورمالدهيد، وحمض الكربوليك، والمركبات العطرية ومركبات الأدوية باستخدام جهاز كروماتوغرافيا الغاز المقترن بمطياف الكتلة كاختبار تأكيد لجميع هذه المركبات. وقد تم التأكد من وجود مواد سمية مثل ديكلورفوس (2,2 ثنائي كلوروفينيل ثنائي ميثيل فوسفات)، والفينول، والفورمالدهيد، والنفتالين في معطر الجو، ما أدى إلى وفاة الشخص. كما أكد تحليل المختبر وجود البرازولام في الأمعاء وفقاً لتاريخ الحالة.

ويمكن الاستفادة من المنهجية المستخدمة كمرجع للطريقة التحليلية باستخدام تقنية كروماتوغرافيا الطبقة الرقيقة وتقنية كروماتوغرافيا الغاز المقترنة بمطياف الكتلة لمثل هذه الحالات.

الكلمات المفتاحية: علوم الأدلة الجنائية، معطرات الجو، علم السموم، مطياف الكتلة، الانتحار، السم



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1. Introduction

Originally, air fresheners were used by the military to repel insects by dispensing a pressurized spray containing about 1% perfume, 24% alcohol or other solvents, and 75% chlorofluorocarbon (CFC) propellant [1]. Air fresheners are now being extensively used indoors to freshen air and mask odors [2]. Air fresheners are available in a variety of fragrances (lavender, sage, cinnamon, moss, sandalwood, cloves, cedar, etc.) and forms (sprays, oils, gels and beads). Air fresheners can be aerosol, liquid or solid based. There can be solid and passive versions, which use a ceramic material along with water-based ingredients that combine and create a multiphase effect to provide a constantly evolving fragrance [3].

The ingredients vary from brand to brand and may include toxic substances like corrosives [mineral acids (sulphuric acid, hydrochloric acid), organic acids (acetic acid, carboic acid), alkali (sodium bisulphite, sodium hypochlorite, sodium hydroxide and sodium phosphate)], petroleum distillates (paraffinic hydrocarbons, naphthalene, stoddard solvents), aromatic compounds (naphthalene, aerosol propellant), aldehydes (acetaldehydes, formaldehyde), pesticides (dichlorvos or 2,2-dichlorovinyl dimethyl phosphate, parathion), phthalates (di-ethyl, di-n-butyl), essential oils (pine oil, lavender oil, Datura oil) and alcohol (ethyl alcohol, isopropyl alcohol) [4,5].

These components make air fresheners toxic, and the toxicity depends upon the inhalation, ingestion and absorption. Even in lower doses, the components of air fresheners have potentially harmful health impacts (sensory irritation, respiratory symptoms, and dysfunction of the lungs) [6].

It has been reported that nearly 20% of the general population and 34% of asthmatic people had headaches, breathing difficulties, or other health problems when exposed to air fresheners or deodorizers [7,8]. The presence of phthalates, or hormone-disrupting chemicals, in air fresheners may pose a particular health risk to infants and young children [9]. Oral consumption of air freshener may be fatal; and identification of the chemicals responsible for death poses a challenge for forensic experts [10].

2. Case Presentation

This is a case work study involving directed toxicological analysis of air freshener components. The study was carried out on a reported case involving a young lady (25-years-old), who died after consuming bottled liquid from an air freshener along with five tablets of tranquilizer (Alprazolam). The clinical and postmortem manifestation included vomiting, soft abdomen, petechial hemorrhage in the gastrointestinal tract, kerosene like smell from stomach content, enlarged and fibrous liver, enlarged and edematous central nervous system (CNS), congested and hemorrhagic mucosa, edematous, congested, hemorrhagic spots in the respiratory tract, enlarged and edematous heart with 70% blockage in the coronary arteries and edematous, and congested kidneys. The viscera and gastric lavage were sent to the forensic laboratory for toxicological examination as per medico-legal guidelines. The aim of the study was to determine the cause of death and to identify the intoxicants responsible for death.

3. Materials and Methods

The viscera and gastric lavages were subjected to chemical examinations to identify lethal components [11,12]. The samples were analyzed for the presence of pesticides, drug (alprazolam), phthalates, corrosive poisons, naphthalene and aldehydes.

Analysis of viscera for pesticides (organophosphorus and organochloro compound)

Viscera was extracted with hexane: acetone (2:1), by decent overnight, and gastric lavage was used for direct spotting. Pesticides were identified by thin layer chromatography analysis (hexane: acetone (8:2)). Various spraying agents were used for the detection of the spots e.g. triethylene phosphoramidate (TEPA) and 4,4-dinitrobenzyl pyridine (1:1) (for 2,2 di chlorovinyl dimethyl phosphate (DDVP)), palladium chloride (for malathion, parathion), and Tollens' reagent (for carbofuran and carbamates).

Figure-1 shows the TLC analysis of pesticides. Bluish-purple colored petal shaped spots were observed which turned into blackish spots on heating at 110 °C, indicating the presence of DDVP. The above observation was further confirmed with the help of GC-MS, where



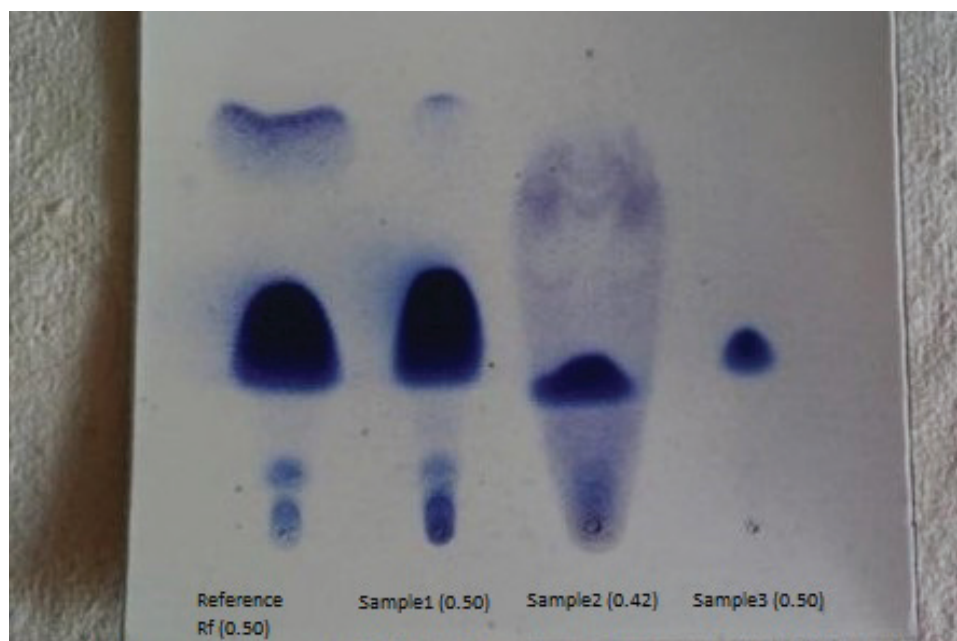


Figure 1- Thin layer chromatography result for 2,2- dichlorovinyl dimethyl phosphate (DDVP).

the peaks were observed (Figure-2).

Analysis of drugs

Viscera was analyzed for the presence of alprazolam, as per case history. The drug was extracted with the basic drug extraction method. Alprazolam was extracted by using a mixture of diethyl ether and chloroform (3:1) in a separating funnel. Thin layer chromatography (TLC) of the extract was done with methanol: ammonia (8:2), as mobile phase, and the spots were developed by Dragon-droff reagent. A pink spot was observed for alprazolam on TLC. Figure-3 shows the presence of alprazolam in gastric lavage, as detected by GC-MS.

4. Results

From the above observations, it was concluded that the components which were present in the samples matched the ingredients of the referenced air freshener. Persistence of purple color in Schiff's reagent test indicated the presence of formaldehyde in the viscera. The appearance of violet color in ferric chloride test that disappeared after adding alcohol indicated the presence of phenol, which was further confirmed by GC-MS as given in figure-4. Appearance of yellow needle shaped crystals of naphthalene picrate indicated the presence of naphthalene. The following compounds were identified in the

viscera and gastric lavages:

- Pesticides: Dichlorvos
- Corrosive poison: Phenol
- Phthalates: Di-butyl phthalates
- Aromatic compound: Naphthalene
- Aldehyde: Formaldehyde

In accordance with the case history, alprazolam was also detected by the viscera examination. After chemical examination, it was concluded that death was caused by ingestion of the air freshener. The toxic effect of these compounds was triggered probably by the synergistic effect of alprazolam.

5. Discussion

With the development of artificial fragrances, the use of air fresheners has increased manifold. It is affecting the physical and mental health of users. Medium level exposure of air fresheners could lead to irritant poisoning (irritation of the eyes, skin, and throat). It has been observed that ingestion of solid and liquid air fresheners having some toxic components may lead to death. Aerosol based air fresheners may cause and sensory and pulmonary irritation. The ASTM-E-981 test was observed

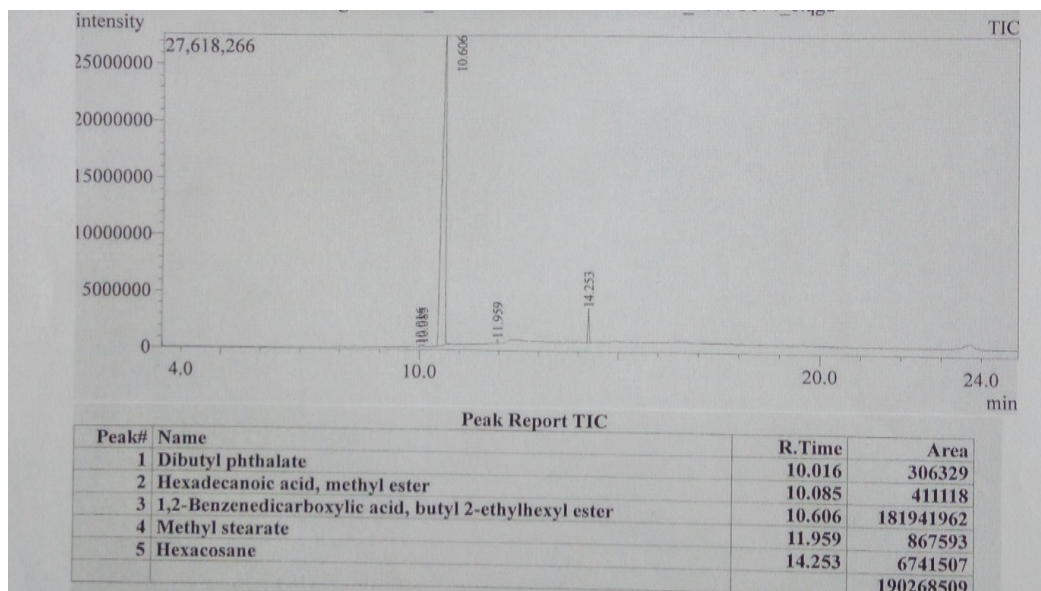


Figure 2- GC-MS analysis for pesticides.

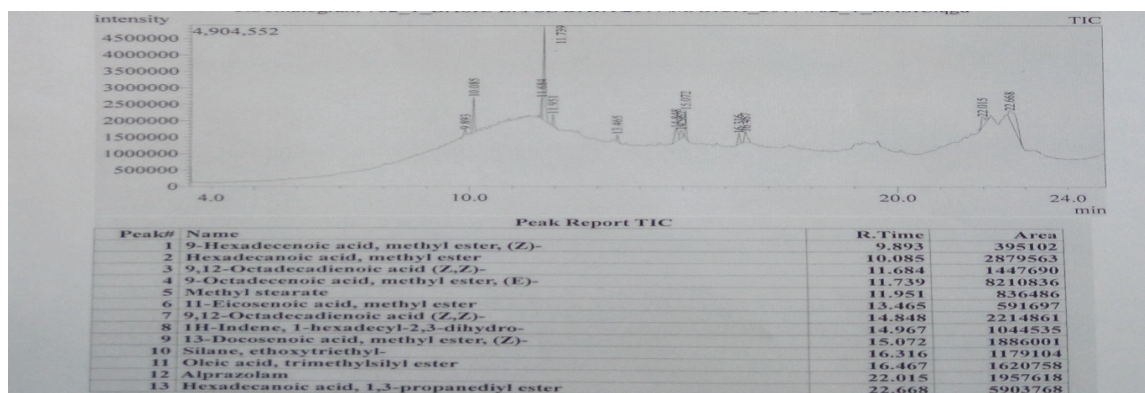


Figure 3- Analysis of Alprazolam by GC-MS.

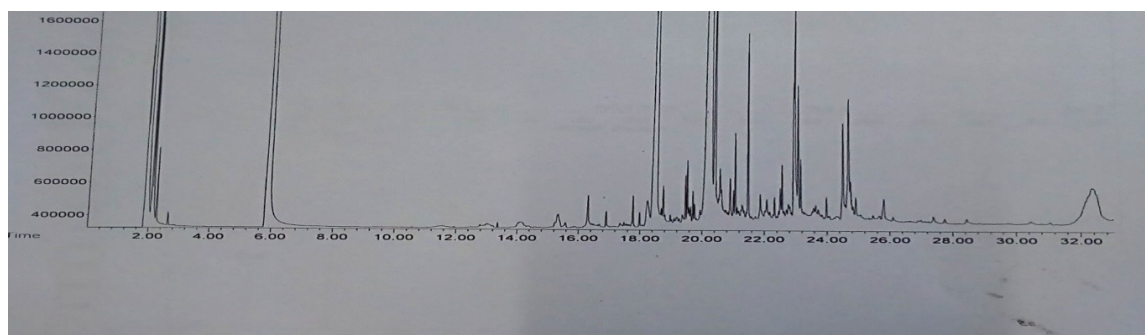


Figure 4- GC-MS analysis for carbolic acid.

in male swiss-webster mice by Anderson [7,8]. Potera (2011) studied 25 branded air fresheners and found the presence of 133 volatile organic compounds in these products. Di-butyl phthalates can be extremely harmful if absorbed through the skin, inhaled, or ingested [13]. It showed mild to severe symptoms like nausea, hallucination, low Glasgow coma scale, depression, headache, dizziness and shock that leads to coma [14].

Formaldehyde, if inhaled, can cause central nervous system depression in the respiratory system, which leads to difficulty in breathing and may lead to an asthmatic attack. Moreover, it can cause irritation to mucous membranes and has carcinogenic properties. In addition to its corrosive effect phenol can cause headaches, dizziness, and liver damage. Some propellants such as butane can lead to drowsiness, narcosis, asphyxia, and cardiac arrhythmia [15]. Earlier studies reported headaches, breathing difficulties, or other health problems in 20.5 % of the population [16,17]. The effects of household chemicals have also been reported in preschool children [9].

In addition to toxicity, cases of burning with air fresheners have also been reported [18]. Air fresheners are highly inflammable because of the presence of alcohol-based substances. According to environmental studies, chronic use of air fresheners by inhalation or ingestion is harmful for all living organisms. These products have endocrine disrupting phthalates (di-cyclohexyl phthalate, di-isobutyl phthalate, and di-n-propyl phthalate) and cytotoxic effects [19, 20]. Environmentalists advise to periodically change the brands and flavors of air fresheners used to avoid chronic exposures [21]. In the case reported above, the ingestion of alprazolam along with the air freshener probably triggered the fatal toxicity level, as phenol and alprazolam have possible synergy effect.

6. Conclusion

In the current study, the cause of death was confirmed as the inhalation of air freshener and the toxic effect was enhanced by alprazolam. Various analytical methods were employed to confirm the presence of various CVC components. Air fresheners manufacturers should only use herbal and natural components; there should be random quality checks on household products. The long-term effects of using them should also be highlighted on

the labels.

Compliance with Ethical Standards

All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and/or National Research Committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards.

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Conflicts of interest

There are no conflicts of interest

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