Zachar Martin – Mitterová Iveta – Majlingová Andrea

ÉGÉSGYORSÍTÓ ANYAGOK KIMUTATÁSA A TŰZESET HELSZÍNÉN

Absztrakt

A cikk tűzvizsgálati tevékenységekkel foglalkozik, különös tekintettel az égésgyorsító anyagok használatával történt szándékos gyújtogatás eseteire fókuszálva. A szerzők ezen kívül áttekintést nyújtanak az égésgyorsító anyagok kimutatásának módjairól a tűzeset helyszínén, valamint bemutatják a szlovákiai Egységes Mentési Rendszer (Integrated Rescue System) különböző segélyszolgálatai által használt kimutatási technikákat. Gyakorlati tapasztalatok alapján Szlovákiában a rendőrség keresőkutyáinak bevetése tűnik a legelőnyösebb lehetőségnek, melyet a modern kimutatási módszerek használata és a helyszínen vett minták laboratóriumi elemzése követ. A cikk eredményeként újszerű megközelítésből láthatjuk a tűzvizsgálati tevékenységet.
Kulcsszavak: tűzvizsgálat, égésgyorsító anyagok, keresőkutyák, detektor

USAGE OF THE ANALYSERS FOR DETECTING THE PRESENCE OF FIRE ACCELERANTS AT THE FIRE SITE

Abstract

The paper deals with fire investigation in connection with intentionally started fires using the fire accelerators. It provides an overview of the available ways to detect the fire accelerants at the fire site and describes the process and the detection technique used by various emergency services of the Integrated Rescue System in Slovakia. In terms of practical use, in Slovakia the police sniffer dog seems to be the most advantageous variant of fire accelerators detection at the fire site, followed by the use of modern detection techniques and subsequent laboratory testing of samples taken.
Key words: fire investigation, fire accelerators, accelerant detection dog, detector

1. INTRODUCTION

Intentionally started fire, respectively an arson, it is one of the leading causes of fires from a statistical point of view. Under the term intentional fire we can understand the intentional crime, which results in a fire or explosion. Intentional fire is most easily to commit, but the hardest to solve. The role of the Fire and Rescue Service members, in co-operation with the members of the Police Force, is to investigate the fires, to track down responsible persons and to establish criminal liability to persons who should be responsible for their own actions. In order to explain the causes of fire, it is necessary to have knowledge of its course, and about production of combustion products, what is influenced mostly by the particular material that is burning. The particular importance is given to the so-called fire accelerator, wherever their occurrence is believed. Their detection and subsequent sampling at the fire site plays a key role.

The issue of fire investigation has engaged in a number of authors, e.g. Makovická-Osvaldová et al in their work dealt with the tasks and procedures in fire investigation and with the graphical records of the evidence. There are photographically captured also such things, objects and items that may have special meaning, such as the existence of intact web, glass fragments, dust and other circumstances. [1]

Martinka dealt with the analysis of the assessment of a short circuit as the cause of the fire. He dealt with the temporal correlation between the occurrence of a short circuit and the fire. The short circuit occurring before a fire and subsequently was a cause of fire initiation, he knows as the primary short-circuit and the short circuit, which is caused by the fire as a secondary short circuit. [2]

Nicdaeid defined, that the fire accelerant is highly inflammable fuel used to accelerate the intensity of a fire or facilitate its spread. Usually it is a flammable liquid, but it may be also a chemical mixture. [3]

As Corry stated, among the most frequently used liquid fire accelerators belong: acetone, carbon disulfide, ethanol, ether, aviation fuel, diesel, gasoline, isopropanol, methanol, methyl ethyl ketone, toluene, turpentine and xylene. [4]

In terms of fire protection, the hazardous substances can be divided into oxidizing, flammable, highly flammable and extremely flammable. By Opekar, the oxidising substances

in contact with other substances particularly flammable, produce highly exothermic reactions, it means, that the heat is released. [5]

As stated in his work Gažo, a fire accelerator (catalyst) plays an important role in chemistry. The catalysts convert the chemical attraction, speed up the chemical process. In the fire protection sphere the term catalyst includes any substance or mixture that accelerates the propagation of a fire. Many accelerators are hydrocarbon-based fuels, e.g. gasoline, kerosene and various other flammable solvents. They are also known as the flammable liquids. In case of fire, they leave irregular patterns on the surface, suggesting their presence in a fire and requiring increased attention of the fire investigator. [6]

Some work demonstrates some dangers at the fire sites and more options to increase the safety. [7] [8] Flammable liquids all over the world can be characterized on the basis of the same classification. It is set based on the standards proposed for testing the fire parameters, e.g. ASTM E1387 and ASTM E1618. In the current version, which has been in force since 2001, the classification system has nine classes of flammable liquids. [9] [10]

2. PROBLEM

In the process of fire investigation, first, it is determined the place of fire, and then is determined the fire cause. In many cases it is not easy immediately after the fire because it requires a very carefully study however during supressing fires require total different way of thinking or making decision. [11] Often, the fire place is determined with some precision, but the fire cause remains unknown. To the fire investigators, in the process of fire investigation, greatly facilitate the interviews with persons, who were the witnesses of the early stages of fire propagation, as well as the persons, who are closely familiar with the situation of structures, furniture and material stored, and who can help to determine the exact location of materials and structures with high absorption. These places are the key places, from which the samples are taken in case of finding the traces of fire accelerators. The aim of all fire investigators is to find the exact location of the causes, routes of fire spread and to determine the responsibility for the incident. Improper documentation of the fire site can prevent the other interested parties to have an opportunity to gain the valuable information value from this

data in terms of probative value. Elaboration of a comprehensive documentation of the crime scene and collecting the data is extremely important. [12]

As stated in the work of Svetlik, an important factor is the early recognition of the commander of the fire intervention, that there is the right time to call the fire investigator. His quick appearance at the fire site enables secure an important evidence that could be in further fire propagation, respectively the activity of the fire units, destroyed. [13]

According to the statements of Čahojová, to clarify the causes of fire and its determination, it is required to examine and evaluate the three groups of questions:

- Ascertaining the situation at the fire site before the fire initiation,
- Detection and determination of the place of fire initiation,
- Compiling and reviewing the versions of the cause of fire initiation. [14]

In case of suspicion of intentionally set fire, through the operations centre, the fire investigator may apply for calling the handler with a dog trained to locate the traces of flammable liquids at the fire site. The usage of trained dogs is directly related to their ability to detect the minute amounts of potential fire accelerators (flammable liquids) in the complex of sample matrix. The ability of dogs to determine the likely location of the residual flammable liquids at the fire site with a high accuracy, can significantly reduce the number of samples of fire debris that the fire investigator must take, and this way reduce the burden of the laboratory. [15]

3. OBJECTIVE

The aim of the paper is to describe the selected methods of detecting the fire accelerants at the fire site. A commonplace is a combination of practical experience of a fire investigator and a dog trained to detect the hydrocarbon fire accelerators or the usage of the electronic measuring devices (detection equipment), followed by laboratory testing.

4. RESULTS AND DISCUSSION

4.1. Specially trained dog for detection of fire accelerators

Based on the valid legislation in the Slovak Republic, the fire cause is investigated in every fire (Order of the President of the Fire and Rescue Service no. 60/2002). [16] In more severe fires or in case of an arson, there are used several methods in fire investigation. Among those methods belongs also the usage of specially trained dog for detection of fire accelerators (Figure1). [17] The role of the dog at the fire site is to find the traces of the catalysts, which have contributed to fire initiation and accelerated its propagation. From the published statistics results the fact, that the dogs have a higher percentage of fruitfulness than the electronic measuring instruments. [18]

Figure1: Usage of a dog by the detection of fire accelerators occurrence [17]

The great advantage of the usage of a dog is that it can capture the amount of fire accelerators at the fire site in the order of 0.1 ηm, that the measuring instruments can no longer capture. [19]

4.2. Advantages of specially trained dog usage:

- Detection of very small quantities of fire accelerators,
- Ignoring the conventional pyrolysis products resulting from the fire,

- Capabilities of the dog‘s performance in all climate conditions,
- Detection capabilities of the dog on a large area in a short time,
- Possibilities to deploy the dog:
    - Verification of the sample taken,
    - Checking the tools used for sampling (to avoid possible contamination among samples),
    - Other related activities, e.g. "screening" the persons occurring at the fire site in the incriminating time, exploring the area around the fire place to take the tracks and material evidence. [20]

5. DETECTION DEVICES FOR FLAMMABLE LIQUIDS

The electronic measuring devices, called hydrocarbon detectors, are sensitive to gasoline component in an amount of 1 ppm (one millionth). The detectors operate on the principle of suction of vapours, and then they detect a moderate or severe flammable liquid. But they cannot determine whether the substance was situated there before the fire. [18]

In terms of evaluating the response of the device and type of output signal, the equipment used for chemical research are divided into:

- Simple detection equipment (detector tube)
- Universal detectors.
- Analysers. [21]

An ideal method of detecting the fire accelerators at the fire place is a combination of dogs and measuring equipment. The dog shall specify the place where technicians should then to collect the samples to send them for laboratory testing and evaluation.

6. SIMPLE DETECTION EQUIPMENT

The simple detection equipment issued mostly for fast and easy measurement in the field. The principle of this equipment is based on the coloured chemical reaction of the substance with a suitable agent that is applied to a particular carrier. The coloured reaction product is evaluated visually. The contact with contaminated air with a sorbent is provided by an induction of nozzle air intake after opening the tube. [22]

7. UNIVERSAL DETECTORS

These detectors were first developed for chemical analyses of potentially emergency situations, but they found the application in exploring the fire site in time. Today their use is primarily in supplementing the visual indicators of fire accelerators traces. The principle of the universal detection is that the air components do not provide a positive detection and the devices are usually "reset" to the non-contaminated air.

These detectors are based on the physical or physic-chemical processes that are subjected to certain group of substances. It may be possible to use a number of principles, but in the practice dominate the following types of detectors: combustible gas-indicator (cathetometer), photoionization detectors and flame detectors. [22]

All these detectors work almost the same way. The detectors consist of four main parts: a sensor, pump, detector and recording or audio device. The sensors may differ in size in particular. Preferred are especially the long sensors that allow easy inspection of the fire place. The pump is usually driven by a battery and it may suck the air up to several litres per minute. The detector varies depending on the type. Some devices have an integrated recording device that prints the results on paper, but most of them have an output device such as an LCD display, which shows the indicated concentration of analyses. Many systems are also equipped with loudspeakers that sound for a certain level of concentration. [22]

8. CATALYTIC COMBUSTION DETECTOR (COMBUSTIBLE GAS-INDICATOR)

Catalytic combustion detector is the cheapest type of detector used. The gas measured is catalytically combusted on the incandescent body made of semiconductor ceramics, which changes its resistance this way. The electronic part of the detector evaluates the current intensity changes due to changes in the resistance of incandescent body. The results are expressed in units of volume concentration, usually ppm. These detectors usually have a long life, but are also very sensitive to changes in humidity.

A drawback of these devices is their low selectivity, because they respond to all types of hydrocarbons, as well as to gas, such as ammonia, alcohols, carbon monoxide, carbon dioxide, and even water vapour. Therefore, if they are to be used effectively, the fire investigator must be familiar enough with them and aware of its shortcomings. The main advantage of using those detectors is their price and dimensions. In Slovakia, the widespread is the use of detectors PD-5, PD-6 (Fig. 2) and PD-81. [21]

Figure 2: Detector for combustible gases and vapours PD-6

8.1. Flame ionization detector (FID)

Flame ionization detector is a common detector used in gas chromatography. FID is very suitable for the analysis of hydrocarbons, but also of almost all organic substances in a wide range of concentrations. The measured gas is burned by a flame incurred by burning the hydrogen in synthetic air. In the flame, there are formed the ions and free electrons. The mechanism of the ions production can be explained as the process, where the cracking and hydrogenation of the carbonaceous material take place in the flame, resulting in production of the radical and energy rich ions and fragments. Among the carbonaceous radicals and oxygen fragments occurs the exothermic reaction during the combustion, resulting in formation of

additional radicals. This energy released causes their ionization, producing the action and electron. The charged particles in the carrier gas creates a measurable current flow in the space between the two electrodes of the detector. The resulting current flow is greater than the intensity of the resulting current flow at a rate of only pure carrier gas and hydrogen. The difference of the measured signal gives accurate information on the sample, because the current is proportional to the ionization which depends on the composition of the sample. This type of detector is sensitive to almost all compounds. There are some compounds to which the detector has very small, respectively no sensitivity. These include: O_2, N_2, CS_2, H_2S, SO_2, NO, N_2O, NO_2, NH_3, CO, CO_2 and H_2O. This feature is very useful in investigation the fire place. [23]

A representative of the universal flame detectors is the MicroFID device (Fig. 3). It features the application possibilities and properties identical with modern photo-ionization detectors.

Figure 3: MicroFid detector

8.2. Photo-ionization detectors

Among the other examples belong the HC51-LCD flame hydrocarbon analyser and Thermo-FID. There are also detectors which combine various principles, such as the TVA 1000 dual detector (Fig. 4), that uses as a photo-ionization as a flame principle in the measurement. [23]

Figure 4: TVA 1000 detector

A sample of the air with a hazardous substance is sucked into the pump through the filter into the ionization chamber, where occurs the ionization of molecules of the substance by the means of emitted photons from the UV lamp, resulting in an electric charge. Custom sensors detect the resultant charge of ionized gas that is converted into electricity. The current is amplified and converted to a concentration in ppm or ppb. The gas ionization is nevertheless conditioned by the fact that the ionization potential of the studied mixture is less than the energy of photons emitted by the UV lamp. [22]

This group includes the DL-101 detector. In the Slovak Republic, it has been progressively replaced by more modern types, among which is the especially popular MiniRAE 2000 photo-ionization detector (Fig. 5), which is characterized by minimum dimensions and weight, and built-in calibrations for more than 100 organic compounds, high sensitivity and extremely easy to use outsourced by three buttons. The similar user features and capabilities have also 2020 photo-ionization detector, MultiRAE and ModuRAE devices. [21]

Figure 5: MiniRAE 2000 photoionization detector

8.3. Analysers

These detectors represent the fully automated devices for determining and sometimes identification of the hazardous substances. Those devices are usually distributed into two groups:

- **Selective analysers**, which selectively measure the concentration of a particular hazardous substance, which has been set ahead, including also mixtures with other gases and vapours (as opposed to universal detectors). The condition for the selective detection of a particular substance is set such characteristic or property of the substance which is different to the other. This is a measurement of the electrochemical potential, absorption in the infrared or UV spectrum region, or the colouring the layer of absorbent in the visible region of the spectrum.
- **Multi-component analysers**, which, in addition to determination of the concentration, allow also the identification of substances of unknown composition. These devices belong to the leaders in the mobile instrumental techniques. They are mostly the high-quality analytical devices that work outside the laboratory.

In this category of devices the three types of analysers dominate currently:

- Portable gas chromatographs (Figure 6),
- Infrared gas analysers,
- Mobile gas chromatography with mass detector (Fig. 7).

The main advantages of the use of analysers is the measuring comfort, the possibility of continuous monitoring, storing the measured data in the memory, their evaluation in the PC, the possibility of involving sound and light signal at a fixed concentration, high selectivity, etc. The disadvantages are very high procurement costs, higher requirements for maintenance and servicing, the need for a skilled operator. [21]

Figure 6: Voyager portable digital gas chromatograph

Figure 7: Gasmet DX-4000 multicomponent gas FTIR analyzer

A significant part of processes involved in the fire investigation is a sampling of traces at the fire site and selection of analytical methods for the subsequent identification of the sample taken. Sampling at the fire site is necessary to implement with a knowledgeable member of the Fire and Rescue Service, who knows the sampling methodology, creation of a sufficient description and allocation of samples, their packaging, storage and treatment before the laboratory testing itself. Sample containers used for the storage of the samples must be air-tight and clean, to prevent loss of the analyse and the sample was not contaminated. The packaging bags and envelopes made of polyethylene cannot be used, because they may contaminate the sample with the volatile hydrocarbons. The best and most commonly used are airtight metal containers. The procedure for sampling, handling of sampling techniques, sample handling, etc., all these activities must be carried out according to standard operating procedures. [24]

After the sample was collected, the next step is the choice of the appropriate method of sample preparation for chemical expertise. The pitfall of sample preparation is the number of physical and chemical properties of flammable liquids, so there is no one optimal sampling method from the rubble of fire place.

Although the first attempts at chemical analysis of materials from the fire sites have been made already in 1940, and in addition, we now have much better analytical instruments, the identification of traces of fire accelerators is still a very difficult task. [22]

There are two main factors that significantly complicate the chemical analyses:

- Material matrices pyrolysis produces a significant amount of volatile substances which can mask the fire accelerators or interfere with them,
- The flammable material itself may undergo changes due to exposure to extreme temperatures.

Current methods of chemical analysis of samples taken from the fire place consist of three steps:

- First, there is implemented a process of extracting the flammable liquid from the materials occurring at the fire place,
- In the second step, there is the extract of the sample analysed by instrumental methods, such as the gas chromatography combined with mass spectrometry,
- In the last step, there are the drawn data interpreted (identification of the substance).

The techniques used for the isolation and concentration of fire accelerator were developed gradually. Initially, (during the fifties and sixties of the 20th century), there were the vacuum distillation, steam distillation and liquid extraction used mainly. [25] [26] Later, among the most commonly used techniques belonged the analysis of the equilibrium gas phase referred to as the head-space method. [27] Initial expertise, used in the fire investigation, tested the chemical and physical properties of flammable liquids, such as refractive index, density or boiling point. Towards the end of the fifties of the 20th century, there has been introduced a gas chromatography, and since this times, this technique is the most used method for determining the presence of accelerants at the fire site.

9. CONCLUSIONS

This paper briefly summarizes and provides the overview of the different methods used in fire investigation, applicable especially when searching for the liquid fire accelerators at the fire site. An ideal method of detecting the fire accelerators at the fire site is a combination of special dogs trained to detect the fire accelerators and portable detection technology. Deploying the detectors and gas analysers at the fire site significantly reduces the number of samples specified for laboratory testing. This combination is suitably applied in the fire investigation in the Slovak Republic.

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Dr. Martin Zachar,
Technical University in Zvolen, Department of Fire Protection, Masaryka 24, 960 53 Zvolen, Slovak Republic
zachar@tuzvo.sk
Orcid: 0000-0001-9698-6254

Dr. Iveta Mitterová
Technical University in Zvolen, Department of Fire Protection, Masaryka 24, 960 53 Zvolen, Slovak Republic
mitterova@tuzvo.sk
Orcid: 0000-0002-1242-8093

Dr. Andrea Majlingová
Technical University in Zvolen, Department of Fire Protection, Masaryka 24, 960 53 Zvolen, Slovak Republic
majlingova@tuzvo.sk
Orcid: 0000-0002-7450-4004

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Lektorálta:
Dr. Kerekes Zsuzsa
Szent István Egyetem, Ybl Miklós Építéstudományi Kar, Tűz és Katasztrófavédelmi Intézet